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REMOVAL OF DIRECT DYES FROM WASTEWATER BY SORPTION ONTO SMECTITE-CLAY

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Keywords: Direct dyes, smectite-clay, sorption isotherms, kinetics.

Abstract: Dyes and pigments are an important class of organic pollutants of the water environment. Dyes may be removed from wastewater by using one of the most efficient methods for wastewater treatment—adsorption onto porous (natural and waste) minerals or organogenic substances. Feasibility of using smectite-clay, co-occurring in brown coal deposits, for removal of direct dyes was investigated. The Freundlich linear regression model was better in modeling of sorption direct dyes onto smectite-clay; it yielded better fit of the theoretical isotherm to the experimental data. The electrostatic interactions and hydrogen bonds were shown to play the most important role in adsorption of direct dyes onto smectite-clay.

INTRODUCTION

Surface and ground waters are subject to the European Union legislation mainly due to their role as a source of high quality drinking water. Restrictive regulations concerning contamination of the aquatic environment in the EU Directives as well as increasing demands for high quality water require more efficient and environmentally sound methods for water and wastewater treatment.

Dyes and pigments are an important class of organic pollutants.

Synthetic dyes are used and released with wastewater by several industries e.g. textile and leather dyeing, cosmetics and paper production. Even low concentration of a dye causes coloring of a large body of water. In water, dyes adversely affect the aquatic ecosystem by reducing availability of sunlight to aquatic plants. Dyes exhibit considerable structural diversity and are classified in several ways. By their water-solubility, they may be divided into soluble (acid, mordant, metal complex, direct, basic and reactive dyes) and insoluble (azoic, sulphur, vat and disperse dyes). Direct dyes play an important role in the textile industry. They are water-soluble and have good color persistence. They are
used for dyeing of cellulosic fibers (cotton, viscose, linen), natural silk and polyamide. In water, molecules of these dyes dissociate into cations or anions giving colorful solutions. Moreover, direct dyes contain azo groups.

Dye-containing wastewater may be treated by means of adsorption, oxidation, coagulation and flocculation, membrane processes and biological methods [3]. Adsorption onto porous (natural or waste) minerals and organogenic substances is one of the most efficient methods of wastewater treatment. The most often used minerals are bentonite, clay, zeolites, sepiolite, diatomite, fuller’s earth, and peat [3, 4, 10]. They are very efficient, low cost, and may be an alternative to activated carbon. The rich in smectites clays have high specific surface and porosity and negative surface layer charge. Moreover, they are plentiful and occur in coal deposits. Minerals of smectite family (montmorillonite and beidelite) are 2:1 clay minerals, with both interlayer and ionisable hydroxyl sites on the external surface; they have permanent negative charge in their structural framework. The negative surface layer charge, resulting from the isomorphous substitution of Mg$^{2+}$ or Fe$^{2+}$ for octahedral Al$^{3+}$ or Fe$^{3+}$ and Al$^{3+}$ for tetrahedral Si$^{4+}$, causes binding of exchangeable cations to the interlayer sites. The cation exchange capacity (CEC) of these minerals is due to the substitution within the structure (pH independent) and to the charges at the edge of the sheets (pH dependent). The point of the zero charge (pH$_{PZC}$ – the pH value at which a solid submerged in an electrolyte has zero net electrical charge on the surface) lies about 2.5.

The principal method for describing the sorption process is an equation that expresses the relation between the concentration in water and the corresponding concentration in solid phase at equilibrium conditions, i.e. the sorption isotherm. The sorption parameters can be determined by using mathematical models, laboratory experiments or in situ. Data from experiments are interpreted by using linear or non-linear isotherms. The isotherm is selected by fitting a theoretical curve to empirical data; the coefficient of determination ($R^2$) is a measure of goodness of the fit [6, 14].

The paper presents application of the batch method in investigations of adsorption of direct yellow 142, direct red 81, and direct blue 74 from a single-dye solution onto smectite-clays from brown coal deposit. Isotherms and kinetics of sorption of the dyes were also studied.

**MATERIALS AND METHODS**

Three direct dyes were examined: direct yellow 142 (DY 142), direct red 81 (DR 81) and direct blue 74 (DB 74). They are produced by Boruta Zachem-Kolor sp. z o.o. (Poland), the leading Polish producer of synthetic organic dyes. Main functional groups of these dyes are azo, nitro, amine, sulfo, carbonyl and hydroxyl groups.

The key features of the used dyes are given in Table 1. The CAS registry numbers of the dyes from the ChemIDplus Lite database are also provided. They help to identify such chemical compounds as dyes that may have different common names.
Table 1. Characteristics of the investigated direct dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>CAS</th>
<th>Systematic name</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Structural formula</th>
<th>pH of 1 g/dm³ water solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct yellow 142</td>
<td>71902-08-4</td>
<td>[8-(4-amino-3-nitrophenyl)azo-7-hydroxy-2-naphthyl]-trimethylammonium chloride</td>
<td>C19-H20-N5-O3-Cl</td>
<td>401.5</td>
<td><img src="image" alt="Structure of Direct yellow" /></td>
<td>6.95</td>
</tr>
<tr>
<td>Direct red 81</td>
<td>2610-11-9</td>
<td>2-naphthalenesulfonic acid, 7-(benzoylamino)-4-hydroxy-3-((4-(4-sulfophenyl)azo)azo), disodium salt</td>
<td>C29-H19-N5-O8-S2.2Na</td>
<td>677.6</td>
<td><img src="image" alt="Structure of Direct red" /></td>
<td>8.22</td>
</tr>
<tr>
<td>Direct blue 74</td>
<td>33540-94-2</td>
<td>2-naphthalenesulfonic acid, 5(or 8)-(2-(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)diazenyl)-8(or 5)-(2-(6(or 7)-sulfo-4-(2-(3-sulfophenyl)diazenyl)-1-naphthalenyl)diazenyl)-, sodium salt (1:4)</td>
<td>C36-H25-N7-O13-S4.4Na</td>
<td>983.8</td>
<td><img src="image" alt="Structure of Direct blue" /></td>
<td>8.03</td>
</tr>
</tbody>
</table>
The smectite-containing neogene clay from the brown coal deposit in Belchatów (Belchatów Brown Coal Mine, Central Poland) was used as an adsorbent. It is mainly composed of smectite, and it also contains quartz, calcite kaolinite and iron(III) oxide-hydroxide (FeOOH) (Fig. 1a). Bands of H-O-H, Si-O, Al₂-O-H, Al-Fe-O-H, Al-O-Si and Si-O-Si are characteristic of this clay, therefore O-H, Si-O, Al₂-O-H, Al-Fe-O-H groups are the main sorption centers of reaction in it (Fig. 1b). The hydroxyl groups on the surface can, depending on pH, gain or lose a proton. At low pH, the surface sites are protonated and the surface becomes positively charged:

$$\text{H}^+ + \text{MOH} \rightarrow \text{MOH}^+_2$$  \hspace{1cm} (1)

At high pH, the surface minerals lose their protons and surface becomes anionic:

$$\text{MOH} \rightarrow \text{H}^+ + \text{MO}^-$$  \hspace{1cm} (2)

Fig. 1a. X-ray diffractogram of the smectite-clay

Fig. 1b. FTIR spectra of smectite-clay
The air-dried and homogenized samples of the clay were sieved through a 0.5 mm sieve. The physicochemical properties of the samples are shown in Table 2 [8, 9].

<table>
<thead>
<tr>
<th>Bulk density</th>
<th>Specific gravity</th>
<th>Porosity</th>
<th>Specific surface area</th>
<th>CEC</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>[kg/m³]</td>
<td>[kg/m³]</td>
<td>[%]</td>
<td>[m²/g]</td>
<td>[mol(+) / kg]</td>
<td></td>
</tr>
<tr>
<td>1943</td>
<td>2557</td>
<td>6.82</td>
<td>41.38</td>
<td>141.83</td>
<td>82.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>chemical composition [%]</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64.70</td>
<td>13.65</td>
<td>4.37</td>
<td>0.99</td>
<td>1.373</td>
<td>0.109</td>
<td>1.499</td>
</tr>
</tbody>
</table>

The sorption capacity was determined in static conditions by using the batch method. The initial concentrations \(C_0\) of the dye solutions were within the range 1–1000 mg/dm³, the ratio solid phase (m)/solution (V) was 1:20 and shaking time was 24 h. The clay suspensions were centrifuged at 4000 rpm for 20 min. \(C_0\) and equilibrium metal concentrations \(C_{eq}\) in solutions were determined by means of UV/VIS spectrometry (Varian Cary 50 Scan spectrophotometer, 1 cm long cell). The wavelengths \(λ_{max}\) used were: 392 nm for direct yellow 142, 510 nm for direct red 81, and 582 nm for direct blue 74. The amount of adsorbed dyes (S) was calculated from:

\[
S = (C_0 - C_{eq}) \times V / m \text{ [mg/kg]}.
\]  

Additionally, pH was determined in the equilibrium solutions.

To determine whether growth of the concentration causes polymerization of the dye molecules in the solution, the absorbance spectra of dye solution at concentrations 1, 5, 10, 25 mg/dm³ were recorded every one nanometer in the range of 400–700 nm. Sorption parameters were estimated by using linear forms of the Freundlich and the Langmuir equations [13, 14]. Moreover, non-linear regression (STATISTICA ver. 8.0) was used to estimate the constants in these equations. For each system, \(R^2\) expressed goodness of the fit of a theoretical curve to experimental data. In addition, the Lagergren’s pseudo-first order rate equation and the pseudo-second order rate equation were used to describe the mechanism of dye sorption onto the smectite-clays. The initial concentration of dyes in the kinetic experiments was 250 mg/dm³. The clay suspensions with dyes were shaken from 5 to 1440 min. For each shaking time, after centrifugation, the concentrations of dyes in the solutions were measured.

RESULTS AND DISCUSSION

Sorption of the direct dyes onto smectite-clay

The dye sorption isotherms were determined by using smectite-clay samples in \(S = f(C_{eq})\) system (Fig. 2a).
According to the Gilles classification [2], direct yellow 142 and direct red 81 had the H-type sorption isotherms what means their very high affinity for smectite-clay. The maximum sorption capacities of smectite-clay for DY 142 and DR 81 were 18378 mg/kg and 16932 mg/kg, respectively. The high affinity of direct yellow 142 for the clay may be explained by the dye cationic structure (Tab. 1). The clay contained mainly smectite (difractogram in Fig. 1), which was beidellite [7]. Therefore, the clay had high internal and external surfaces, porosity and permanent negative charge, and also high affinity for cationic dyes. High affinity of cation dyes for sorption centers in fuller’s earth (rich in Ca-montmorillonite) and the H-type adsorption isotherms were also observed by Atum et al. [1]. In the spectrum of DR 81 solution, at the concentrations 10 and 25 mg/dm$^3$, beside the maximum at $\lambda = 510$ nm, a peak at $\lambda = 380$ nm appeared (Fig. 3). It means that, at higher concentrations, DR 81 occurred in dimmer forms and in such forms it was bound. Instead, for all initial concentrations, direct blue 74 was bound by the clay in smaller than other dyes amounts. It had the L-type sorption isotherm and maximum sorption capacity of smectite-clay for this dye was 4700 mg/kg. The slighter than for other dyes slope of the DB 81 isotherm means its weaker affinity for the sorption centers of the clay. This dye
has anionic character and has high affinity for positively charged surfaces. In equilibrium solution at pH between 8.0 and 8.4, smectite surface is negatively charged and has low ability to bind anionic dyes. The only positively charged component of the clays at pH lower than 9.0 is Fe(III) oxide-hydroxides (FeOOH). Their point of zero charge (pH_{PZC}) is 8.5. However, the iron present in smectite-clay is mainly bound in the smectite structure (96.04% of Fe), and only 634.5 mg/kg (1.41 of Fe) occurs in nonevy stalline forms [8]. Dyes uptake depends on the dye structure and different dyes have different molecular structures. Sorption capacity of smectite-clay for the studied direct dyes increased in the order: DY142 > DR81 > DB74. Similar order of maximum sorption capacities of montmorillonite for direct dyes was reported by Yavuz and Aydin [15].

The pH values of the equilibrium solutions are presented in Figure 2b, where a semi-logarithmic scale is used to make the charts more understandable. The sorption of dyes by smectite-clay occurred practically at constant pH due to high buffering capacity of the equilibrium solutions. It demonstrates high efficiency of cationic dye removal and rather low sorption capacity for anionic dyes that increases with decreasing pH of the dye solution [11].

The surface functional groups and chemical properties of the direct dyes were the cause of electrostatic (coulombic) attraction between DY$^+$ and negative charge on surface of smectite, and between DB$^-$ and positive charge on surface of oxide-hydroxide (FeOOH) at high pH (6–8). Moreover, there occurred surface hydrogen bonds between the Si-O, FeAl-O and Al-O surface groups of smectite, and the -NH, -NH$_2$ and -OH dye groups.

**Adsorption isotherms**

**Linear adsorption isotherms**

Two isotherm equations non-linearly model adsorption equilibrium in solution:

\[
S = K_f C_{eq}^n
\]  \hspace{1cm} \text{Freundlich equation, (4)}

\[
S = \frac{K_L Q C_{eq}}{1 + K_L C_{eq}}
\]  \hspace{1cm} \text{Langmuir equation, (5)}
where:
S – amount of dye adsorbed per unit mass of clay [mg/kg],
C_{eq} – equilibrium concentration of dye [mg/dm³],
n – Freundlich constant related to surface affinity for the solute,
K_F – constant,
Q – maximum sorption capacity of clay for dye [mg/kg],
K_L – adsorption equilibrium constant [dm³/kg].

In this paper, to estimate the sorption parameters, the linear forms of them were used:

\[ \log S = \log K_F + n \log C_{eq}, \]  

\[ \frac{C_{eq}}{S} = \frac{C_{eq}}{Q} + \frac{1}{K_L Q}. \]  

The experimental linear relationship was obtained between \( \log S \) and \( \log C_{eq} \) (Freundlich) and \( \frac{C_{eq}}{S} \) and \( C_{eq} \) (Langmuir) (Fig. 4a, b). The values of constants were calculated, and are presented in Table 3.

![Fig. 4a. Freundlich plots corresponding to the sorption of studied direct dyes onto the smectite-clay](image1)

![Fig. 4b. Langmuir plots corresponding to the sorption of studied direct dyes onto the smectite-clay](image2)

The sorption parameters calculated from (6) fitted the experimental data best; the determination coefficient \( (R^2) \) for Freundlich isotherms was close to 1.0. The Langmuir equation (7) was not applied to the results for direct yellow 142. The best performance of
the Freundlich model in the case of adsorption of the direct dyes indicates the heterogeneous surface binding (Tab. 3).

**Non-linear adsorption isotherms**

Application of linear regression is burdened with an error since, depending on the selected isotherm, the determined regression line does not minimize the total of:

\[ \sum_i [S_i - K_F C_{eq}^n]^2 \quad \text{or} \quad \sum_i [S_i - \frac{Q K_L C_{eq}}{1 + K_L C_{eq}}]^2 \]

The best-fitting isotherm parameters for the data were received by using the non-linear regression based on the classical least-squares method. The sorption parameters and \( R^2 \) values are given in Table 4. Higher \( R^2 \) values indicate that application of non-linear regression provided better fit of the curves to the experimental data. Both the Freundlich and the Langmuir isotherms satisfactorily fitted the experimental data (Tab. 4). However, for all dyes, the Langmuir isotherms were better. Shen *et al*. [12] report similar findings in their studies on sorption of anionic dyes onto bentonite.

**Adsorption kinetics**

Two models were used to describe the mechanism of dye sorption onto smectite-clay. In order to investigate the mechanism of sorption, characteristic constants of sorption were estimated by using the pseudo-first order Lagergren equation and the pseudo-second order equation based on the solid phase sorption. The kinetic parameters for studied dyes were determined for the initial concentration 250 mg/dm\(^3\).

The pseudo-first order rate kinetic equation is of the form:

\[ \frac{dq_t}{dt} = k_1(q_e - q_t). \]  

Equation (9) may be transformed for linear data plotting into:
\[ \ln (q_{e1} - q_t) = \ln (q_{e1}) - k_1 t, \]  
(10)

where:

- \( k_1 \) – rate constant of first order sorption [1/min],
- \( q_{e1} \) – amount of dye sorbed at equilibrium [mg/kg],
- \( q_t \) – amount of dye sorbed onto clay at time \( t \) [mg/kg].

A linearity of \( \ln(q_{e1} - q_t) \) versus \( t \) confirms the applicability of this kinetic model. From the slopes and intercepts, the rate constant (\( k_1 \)) and \( q_{eq} \) value were determined. The pseudo-second order rate equation can be written as:

\[ \frac{dq_t}{dt} = k_2 (q_{e2} - q_t)^2, \]  
(11)

and after transformation, integrating for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_{e2} \), it gives the following linear equation:

\[ \frac{t}{q_t} = \frac{1}{k_2 (q_{e2})^2} + \frac{t}{q_{e2}}, \]  
(12)

where:

- \( k_2 \) – rate constant of sorption [kg/(mg•min)],
- \( q_{e2} \) – amount of dye sorbed at equilibrium [mg/kg],
- \( q_t \) – amount of dye sorbed onto clay at time \( t \) [mg/kg].

If the experimental data fits the plot of \( t/q_t \) versus \( t \), the pseudo-second order kinetic model is valid [4, 5]. The calculated values of the rate constant \( k \) and \( q_{eq} \), experimental \( S \) at equilibrium sorption capacity, and the determination coefficient \( R^2 \) are presented in Table 5. Figures 5a and 5b illustrate the correlation of \( \ln(q_{e1} - q_t) \) versus \( t \) and \( t/q_t \) versus \( t \), respectively.

**Table 5. The pseudo-first and pseudo-second order rates**

<table>
<thead>
<tr>
<th>Dyes</th>
<th>S [mg/kg]</th>
<th>Pseudo-first order model</th>
<th>Pseudo-second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e1} ) [mg/kg]</td>
<td>( k_1 ) [1/min]</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>DY142</td>
<td>4762</td>
<td>6.33</td>
<td>0.00196</td>
</tr>
<tr>
<td>DR81</td>
<td>4482</td>
<td>173.2</td>
<td>0.0057</td>
</tr>
<tr>
<td>DB74</td>
<td>2632</td>
<td>1569</td>
<td>0.0028</td>
</tr>
</tbody>
</table>

Fig. 5. Pseudo-first order (A) and pseudo-second order (B) sorption kinetic of direct dyes onto smectite-clay
The correlation coefficients in the pseudo-first order model for adsorption of dyes from a single-dye solution changed in the range of 0.2704–0.8154 for the direct dyes. The experimental data did not agree with the pseudo-first order kinetic model. The correlation coefficients in pseudo-second order model were greater than 0.9945. Confrontation of the computed time dependencies with the experimental data assures that the pseudo-second order kinetic equation describes the dye adsorption processes more accurately, especially for the longer period [12]. A similar observation was made for the adsorption of different acid dyes onto bentonite and sepiolite [10].

The kinetic data were fitted very well by the pseudo-second order kinetic model that assumes the chemical sorption or chemisorption, involving valency forces through sharing or exchange of electrons between sorbent and sorbate, as the rate-limiting step [5]. Moreover, the theoretical \( q_e \) values from this model were almost equal to the experimental value of \( S_{\text{max}} \).

CONCLUSION

The raw smectite-clay was effective in removal of direct dyes from aqueous solution in the range of the investigated concentrations. Being plentiful and inexpensive, smectite-clay may serve as an adsorbent in removal of direct dyes from textile wastewater.

High affinity of smectite-clay for direct yellow 142 and direct red 81 is confirmed by the H-type isotherm curves, whereas the L-type curve indicate that direct blue 74 adsorption on smectite-clay is not so good.

Within the studied concentration range of investigated direct dyes, the Freundlich adsorption isotherm model fitted equilibrium data much better than the Langmuir one.

The pseudo-second order kinetic model fitted the kinetic data very well, much better than the pseudo-first kinetic model.

Concluding, the smectite-clay from overburden of a brown coal deposit can be used as a cost effective sorbent in removal of dyes from wastewater produced by textile industries.

Acknowledgments

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USUWANIE BARWNIKÓW BEZPOŚREDNICH ZE ŚCIEKÓW METODĄ SORPCJI NA IŁACH SMEKTYTOWYCH

Barwniki i pigmenty stanowią ważną grupę zanieczyszczeń organicznych środowiska wodnego. Jedną ze skutecznych metod usuwania barwników z wód i ścieków jest ich adsorpcja na porowatych substancjach zarówno naturalnych, jak i odpadowych. Przeprowadzono badania nad możliwością wykorzystania iłów smektytowych towarzyszących pokładom złóż węgli brunatnych do usuwania barwników bezpośrednich. Przy oszacowywaniu parametrów sorpcji tych barwników na cząsteczkach ilu smektytowego lepsze dopasowanie izotermy teoretycznej do danych doświadczalnych uzyskano wykorzystując model regresji liniowe Freundlicha. Uzyskane wyniki badań pokazują, że największą rolę w wiązaniu barwników bezpośrednich przez il smektytowy odgrywały oddziaływania elektrostatyczne oraz wiązania wodorowe.
BIOMASS YIELD IN POROUS CERAMIC CARRIERS
FOR MUNICIPAL WASTEWATER TREATMENT

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Keywords: Immobilization of activated sludge, wastewater treatment, biomass yield.

Abstract: Two different porous ceramic carriers with immobilized activated sludge comprised a stationary filling of the reactors. Municipal wastewater was treated at hydraulic retention times from 15 to 70 min and internal circulation capacity of 20, 40 and 60 dm$^3$·h$^{-1}$. Depending on hydraulic retention time, the sludge yield ranged from 0.138 to 0.066 g TSS·g COD$^{-1}$ in reactor I and from 0.175 to 0.107 g TSS·g COD$^{-1}$ in reactor II. An increase in volumetric loading rate and internal circulation capacity caused a reduction in sludge yield. A decrease in the sludge yield corresponded to an increase in the ratio of endogenous to substrate respiration by the immobilized biomass.

INTRODUCTION

In aerobic wastewater treatment systems, large amounts of excess sewage sludge are formed, and their treatment and disposal involves significant investment and operating costs. For this reason the minimization of sludge production has become important and technological solutions to sludge reduction are therefore needed. In the case of single-stage activated sludge systems, it is known that reduced sludge yield is obtained when the plant is operated at increased solids retention time (SRT) [13]. Such a strategy requires high aeration volumes and results in increased costs. Other methods of lowering sludge yield include promotion of bacterial predation implying the elongation of food chains [27], increasing process temperature or the introduction of chemical uncoupling [22].

One method of minimizing the sludge yield is the use of reactors with immobilized biomass; these can be operated at increased sludge concentrations, resulting in reduced sludge loading rates without the need of additional aeration volume. The immobilization of activated sludge permits a high concentration of biomass in the reactor and long solids retention time (SRT) [8], which can limit sludge production [6]. According to Gander et al. [12] and Chiemchaisri, Yamamoto [7], the higher the biomass concentration the lower the Food/Microorganisms ratio (F/M). For this reason wastewater can be treated with reduced sludge production. For a conventional activated sludge system, F/M is in the range of 0.05–1.5 kg BOD·kg MLSS$^{-1}$·d$^{-1}$ [1]. For systems with a biomass concentration from 5 to 20 kg MLSS·m$^{-3}$, F/M usually equals 0.1 kg BOD·kg MLSS$^{-1}$·d$^{-1}$. A low F/M ratio means little substrate per unit of biomass, which leads to a competition among the
microorganisms and results in reduction of the net sludge production [24]. Under conditions of high biomass concentration, low F/M and long SRT, the processes of pollution removal function according to the maintenance concept. This reflects insufficient food entering the biomass to allow cell growth [16]. Based on RNA research, Witzig et al. [29] have indicated that bacteria present in the highly concentrated biomass of the membrane reactor used the energy supplied for their maintenance metabolism and were not in a physiological state characteristic for growth. Only if energy is supplied in excess, are bacteria able to grow.

Numerous researches on immobilization biotechnology involve mainly the exploitation of reactors with different kinds of moving carriers. However, the examination of wastewater treatment effectiveness and sludge production in stationary ceramic carriers (advantageous in terms of mechanical durability) and at different hydraulic loadings is not widespread. In this work the exploitation of bioreactors filled with static macroporous ceramic carrier with immobilized biomass was the leading objective. The impact of hydraulic retention time (HRT) and capacity of internal circulation (q) on biomass yield was investigated. The composition of wastewater also influences sludge production. For this reason the determination of the chemical characteristics of wastewater has been found to have great theoretical and practical significance. Assessment of the concentration of readily biodegradable COD is particularly important, since this parameter is the only substrate component directly related to microbial growth.

In order to determine the physiological state and metabolic activity of bacteria present in the reactor with immobilized biomass, the oxygen uptake rates in substrate (exogenous) and endogenous respiration were examined.

**MATERIALS AND METHODS**

*Characteristics of carriers*

Activated sludge was immobilized in two porous cylindrical carriers. The carriers differed in internal structure, number of internal channels, size of internal surface and total volume (Tab. 1). The carrier volume was calculated as the total volume with the volume of channels. The pore diameters of both carriers ranged from 4 to 6 μm and the material porosity was 35–40%. These characteristics were provided by the carrier producer, TAMI Industries, Germany. Both carriers were made as a structured bed from a mixture of aluminum oxide (Al₂O₃), titanium oxide (TiO₂) and zirconium oxide (ZrO₂). From this powdered mixture a paste was made and formed in the shape of multi-channeled tubes. The tubes were then sintered at > 1000°C.

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Cross-section</th>
<th>External diameter [mm]</th>
<th>Hydraulic diameter [mm]</th>
<th>Internal surface [m²]</th>
<th>Total volume [dm³]</th>
<th>Length [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>10</td>
<td>3.6</td>
<td>0.04</td>
<td>0.1</td>
<td>1178</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>25</td>
<td>6.0</td>
<td>0.20</td>
<td>0.6</td>
<td>1178</td>
</tr>
</tbody>
</table>
**Reactor characteristics**

Each carrier with immobilized biomass comprised the stationary filling of the reactor with internal circulation. Carrier I was placed into reactor I, carrier II – into reactor II. The total volume of the reactors I and II was 0.7 dm$^3$ and 1.2 dm$^3$, respectively. In both reactors free space outside the carrier equaled to 0.6 dm$^3$.

The bioreactors were continuously aerated. Air was supplied at 50 dm$^3\cdot$h$^{-1}$ to reactor I and 120 dm$^3\cdot$h$^{-1}$ to reactor II, in order to maintain dissolved oxygen (DO) concentration in the effluent of about 2 mg O$_2$·dm$^{-3}$. The general reactor scheme and dimensions of reactor II (in millimeters) are shown in Figure 1.

![Fig. 1. Scheme of the reactor](image)

The carrier was fixed into the bioreactor using O-rings. Two spaces were created inside the bioreactor: the internal channels and the external space. Raw wastewater flux and the circulating stream were mixed before they flowed into the reactor. The influent was divided into two streams flowing parallel through the external space and internal channels. This allowed the pressure on the internal and external surfaces to be kept equal.

**Colonization procedure**

Activated sludge, derived from a full scale wastewater treatment plant with nitrification, was the source of inoculum. This was thickened to a concentration of about 23 g TSS·dm$^3$. 
Immobilization was carried out by circulating the activated sludge in the reactors for 24 h. The circulation was conducted in such a way that it allowed the biomass to flow through the internal channels of the carriers and not through the space outside the carriers. As a result, the biomass was immobilized both inside the pores and on the internal surfaces of the carriers. The initial carrier loading amounted to 24.5 g TSS·dm\(^{-3}\)·d\(^{-1}\) (carrier I) and 18.2 g TSS·dm\(^{-3}\)·d\(^{-1}\) (carrier II). The carrier loading was calculated from the total volume of a carrier.

**Wastewater characteristics**

Municipal wastewater taken each day directly from a sewer pipe inspection chamber was introduced to the reactors. Average concentration of total chemical oxygen demand (COD) was 373.6 ± 280.4 mg·dm\(^{-3}\), soluble COD (after filtration) 121.9 ± 47.8 mg·dm\(^{-3}\), Kjeldahl nitrogen 48.4 ± 14.2 mg·dm\(^{-3}\), ammonium nitrogen 27.8 ± 8.8 mg·dm\(^{-3}\) and total suspended solids 228.0 ± 212.2 mg·dm\(^{-3}\).

**Experimental set-up**

The studies were carried out for hydraulic retention times (HRT) of 70, 60 and 30 min for both reactors. Additionally, a HRT of 15 min was carried out for reactor I due to continued high efficiency of COD removal (over 90%). In Table 2 the carrier surface loading rates (SLR) and volumetric loading rates (VLR) for both reactors are shown. HRT was altered by changing the wastewater feed rate. The volumetric loading rate was calculated per total volume of the carrier according to German ATV directions concerning dimensioning of biological beds. Total carrier volumes are given in Table 1. For reactor I at a HRT of 60 min and for reactor II at a HRT of 70, 60 and 30 min, a variable internal circulation capacity (q) was used: 20, 40 and 60 dm\(^3\)·h\(^{-1}\). In the remaining series, internal circulation capacity was maintained at 40 dm\(^3\)·h\(^{-1}\).

<table>
<thead>
<tr>
<th>HRT [min]</th>
<th>Reactor I</th>
<th>Reactor II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>SLR [g COD·m(^{-2})·d(^{-1})]</td>
<td>15.3</td>
<td>18.8</td>
</tr>
<tr>
<td>VLR [g COD·dm(^{-3})·d(^{-1})]</td>
<td>6.5</td>
<td>8.0</td>
</tr>
</tbody>
</table>

All experimental series were carried out consecutively in the same reactor. Before the start of the first experimental series inoculum was immobilized in the carriers and used throughout the whole experiment. The adaptation period before each series lasted about 30 days and was considered complete when the range of changes of particular parameters of the effluent (COD, TKN, N\(_{\text{NH}_4}\)) within 7 days did not exceed 5–10%. At each hydraulic retention time, after biomass adaptation for the experimental conditions, the research was carried out for about 3 weeks. During the experiment, samples were collected twice a day. The data presented are the arithmetic mean of the experimental results.

**Analytical methods**

The wastewater was assayed for the concentration of organic compounds, expressed as COD and soluble COD (measured after filtration), volatile acids, Kjeldahl nitrogen, ammonium nitrogen and total suspended solids, according to Polish Standards [23].
The respirometric activity of the immobilized biomass was measured in an OxiTop device. In order to determine the substrate respiration, a sample of the biomass collected from the carriers, raw wastewater and allylthiourea as a nitrification inhibitor were put into measuring vessels. To determine the oxygen uptake for endogenous respiration, the measuring vessels included a sample of biomass (centrifuged at 4000 rpm for 3 min) and distilled water. The organic loading rate was maintained at 0.25 g COD·g TSS⁻¹·d⁻¹ (similar to that used by van Benthum et al. [5]).

**Calculation methods**

The sludge yield (Y) was calculated with the use of equation (1). It was assumed that the total excessive biomass was washed out of the reactor and all TSS from the influent were solubilised and hence it was not included in the calculation of the sludge yield [13]:

\[
Y = \frac{\text{TSS}_1 - \text{TSS}_0}{\text{COD}_i - \text{COD}_e}, \quad [\text{g TSS} \cdot \text{g COD}^{-1}]
\]  

\( \text{TSS}_1 \) – total suspended solids in effluent at time \( t_{n+1} \) [mg TSS·dm⁻³]
\( \text{TSS}_0 \) – total suspended solids in effluent at time \( t_n \) [mg TSS·dm⁻³]
\( \text{COD}_i \) – organic compounds in influent [mg COD·dm⁻³]
\( \text{COD}_e \) – organic compounds in effluent [mg COD·dm⁻³]
\( n \) – day of sampling

In the composition of raw wastewater, the organic compounds expressed as COD were divided into soluble and particulate. The concentration of particulate COD was calculated as the difference between total COD and soluble COD. Particulate organic compounds were divided into biodegradable and non-biodegradable or slowly biodegradable. Soluble organic compounds included very readily biodegradable, readily biodegradable and non-biodegradable or slowly biodegradable components. The fractions of organic compounds were calculated using coefficients given by Barnard [4]. It was assumed that non-biodegradable or slowly biodegradable particulate compounds account for 5% of total COD, and non-biodegradable or slowly biodegradable soluble compounds account for 3% of total COD.

The oxygen uptake rates (\( r \)) for substrate and endogenous respiration were described by first-order kinetic and defined by the following equation (2):

\[
r = k \cdot C_t
\]  

\( k \) – constant of reaction rate [h⁻¹]
\( C_t \) – concentration of oxygen used after time \( t \) [mg O₂·dm⁻³]

The solution for this could be fitted to the experimental data according to the equation (3):

\[
C_t = C_0 \cdot (1 - e^{-k \cdot t})
\]  

\( C_0 \) – initial oxygen concentration [mg O₂·dm⁻³]
\( t \) – time [h]

Constants of reaction rates were determined based on the experimental data by non-linear regression with the use of Statistica 7.
RESULTS AND DISCUSSION

Reactor I was operated at hydraulic retention times (HRT) from 70 to 15 min, and at volumetric loading rate (VLR) from 6.5 to 48.8 g COD·dm⁻³·d⁻¹. In reactor II, HRT was maintained from 70 to 30 min, and VLR from 5.4 to 16.6 g COD·dm⁻³·d⁻¹. Under these technological conditions, low values of sludge yield were obtained: for reactor I from 0.138 to 0.066 g TSS·g COD⁻¹, for reactor II from 0.175 to 0.107 g TSS·g COD⁻¹ (Tab. 3). Other authors have observed similar biomass growth. Performance of a sequencing batch reactor using a membrane for effluent filtration was investigated by Choo, Stensel [8]. During operation at a 1400-day calculated SRT, the average observed biomass yield was approximately 0.03 g MLVSS·g COD⁻¹ at the organic loading rate of 0.3 g COD·m⁻²·d⁻¹. In a membrane reactor the excess sludge production was 0.094 g MLSS·g COD⁻¹ at 5400 g BOD₅·m⁻³·d⁻¹ [17]. In a membrane bioreactor Cicek et al. [9] the obtained sludge production was 0.29 g TSS·g COD⁻¹ at the organic loading rate of 650 g COD·m⁻²·d⁻¹. A sludge yield of 0.2–0.3 g TSS·g COD⁻¹ was noticed in the reactor with biomass immobilized on cylindrical carriers [2]. Zhan et al. [30] calculated the biomass yield coefficient at a level of 0.18 g VSS·g COD⁻¹ in a sequencing batch biofilm reactor treating synthetic dairy wastewater at a volumetric loading rate of 487 g COD·m⁻³·d⁻¹ and an areal loading rate of 5.4 g COD·m⁻²·d⁻¹. In a moving bed biofilm reactor, Aygun et al. [3] obtained the biomass yield of 0.12 kg TSS·kg COD⁻¹ at the organic loading rate of 6 g COD·m⁻²·d⁻¹.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>HRT [min]</th>
<th>Sludge yield (Y) [g TSS·g COD⁻¹]</th>
<th>Load of COD removed [g COD·d⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.138</td>
<td>0.50</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>0.117</td>
<td>0.50</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>0.074</td>
<td>1.68</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.066</td>
<td>3.92</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.175</td>
<td>1.85</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>0.149</td>
<td>2.74</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>0.107</td>
<td>3.73</td>
</tr>
</tbody>
</table>

In the present study the sludge yield was calculated with the assumption that the total excess biomass was washed out of the reactors. As shown in Table 3, the sludge yield (Y) decreased with the shortening of HRT and increase in VLR. In reactor I, a 7.5-fold increase in VLR caused a decrease in Y of 52%. In the case of reactor II, a decline in Y of 39% resulted from a 3.1-fold increase in VLR. The load of COD removed increased along with the shortening of HRT from 0.5 to 3.92 g COD·d⁻¹ in reactor I, and from 1.85 to 3.73 g COD·d⁻¹ in reactor II. The phenomenon of a decrease in sludge yield following an increase in VLR may be caused by a change of aerobic and anaerobic growth conditions, which has not been documented and requires further research. At high VLR and short HRT anoxic or anaerobic zones could have formed in the reactors. Aerobic yield is higher than the corresponding anoxic yield [10], therefore in our investigations the reduction of sludge yield by an increase in VLR was observed.
Additionally, the hydrodynamic conditions in the reactor and biofilm structure may explain the experimental results given above. At higher substrate loading a denser biofilm with lower porosities is formed [28]. According to Zhan et al. [30], increasing substrate loading favors an increase in the thickness of the active biofilm. The thicker the biofilm, the greater the amount of extracellular polymeric substances (EPS) produced [31]. The traditional view is that organic compounds are either shunted to the electron acceptor to generate energy or are converted to biomass. However, when a significant part of them is shunted to EPS (extracellular polymeric substances) or SMP (soluble microbial products) formation, the amount of organic compounds available for synthesizing active biomass is reduced, and active biomass yield and specific growth rate decline. Therefore, ignoring EPS and/or SMP can lead to a general overestimation of cellular growth rates [18].

The capacity of internal circulation in reactors with biomass immobilized in stationary carriers can be used to control biomass production. Our studies indicate that a change of internal circulation from 20 to 60 dm$^3 \cdot h^{-1}$ affects the sludge yield (Y) (Fig. 2). In reactor I, at a HRT of 60 min Y decreased by 71.4%. Similarly, in reactor II, at a HRT of 70 min Y decreased by 44.4%, at a HRT of 60 min by 20.8%, and at a HRT of 30 min by 36.8%. The circulation causes the dilution of the influent, so the higher the wastewater dilution the lower the sludge yield (Y). The decrease in biomass yield was probably the result of an increase in hydraulic loadings of carriers because of circulation. In order to explain the low amount of biomass washed out of the reactors following the increase in wastewater flow, the Laspidou, Rittmann [19] hypothesis can be used. They stated that the continual exposure to physical forces from the flowing water causes the biofilm solids to consolidate or pack more densely as water is squeezed out. Additionally, according to Vieira et al. [26], the bacteria reinforce the EPS matrix to protect themselves against the more aggressive forces from the surrounding liquid.

![Fig. 2. Sludge yield (Y) for reactors I and II at different internal circulation capacity (q)](image)

The changeable contribution of particular fractions of organic compounds in wastewater can be one of the factors affecting the values of the sludge yield (Y). The values of Y in reactor II were higher compared to the values obtained in reactor I. In the influent to
reactor I, soluble organic compounds accounted for 27.4% of total COD, the remaining being particulate. The influent to reactor II was characterized by the amount of soluble COD, which increased to 55.3% compared to the influent to reactor I. The contribution of particular fractions of soluble and particulate compounds was also different (Fig. 3). The differences in the composition of raw wastewater flowing into both reactors are due to the fact that municipal wastewater was taken directly from a sewer pipe inspection chamber each day, and its composition changed during the experimental period. In Guellil et al. [14], the wastewater composition was similar to that flowing into reactor I. Particulate, colloidal and soluble proportions were found to be 45, 31 and 24% of total COD, respectively. According to Çokgör et al. [11], the average total soluble fraction was determined as 30%, and the average readily biodegradable fraction as 9% of the total COD content of domestic sewage. In our research, the higher biodegradable soluble fraction and lower particulate fraction in the influent to reactor II were probably the reasons for direct assimilation of organic compounds, omitting hydrolysis. Therefore, a higher biomass production was obtained in reactor II in comparison to reactor I at equivalent HRTs (Tab. 3). A major part of the organic matter in municipal wastewater is suspended and is partly hydrolyzed during the biological treatment processes. The products of hydrolysis supply organic matter for the microbial metabolism [15].

![Fig. 3. Contribution of organic compound fractions in the influent (A – very readily biodegradable, B – readily biodegradable, C – non-biodegradable or slowly biodegradable, D – biodegradable, E – non-biodegradable or slowly biodegradable)](image)

The internal carrier structure could have been a further factor affecting the higher values of sludge yield in reactor II. In the three-channeled carrier I the internal channels occupied about 50% of the total volume, whereas in the eight-channeled carrier II the internal channels accounted for about 44% of the total volume. According to Matsumura et al. [21], the proper balance between the active surface of a carrier and open space is very important, since it influences the rate of mass transport.

In our study, the increase in VLR in reactor I from 6.5 to 48.8 g COD·dm⁻³·d⁻¹ caused a change in oxygen uptake rate by the immobilized biomass for substrate respiration. The rate decreased from 0.116 to 0.045 mg O₂·mg TSS⁻¹·h⁻¹. In reactor II, despite an increase in VLR from 5.4 to 16.6 g COD·dm⁻³·d⁻¹, the rates of substrate respiration were similar in
the range from 0.043 to 0.054 mg O₂·mg TSS⁻¹·h⁻¹ (Tab. 4). In investigations by Witzig et al. [29], sludge samples taken from the membrane reactor consumed the dissolved oxygen at the rates of 0.032–0.036 mg O₂·g MLVSS⁻¹·min⁻¹. Rostron et al. [25] determined the respiration activity of biomass immobilized in polyurethane foam. The respiration rate increased by about 400% when the HRT of the reactor was reduced from 1.5 to 1 d. The rate decreased almost three-fold when the HRT was lowered to 0.5 d, possibly due to an increase in shear forces at the greater flow rate.

Table 4. Oxygen uptake rate for substrate and endogenous respiration at different HRTs and VLRs

<table>
<thead>
<tr>
<th>Reactor</th>
<th>HRT [min]</th>
<th>VLR [g COD·dm⁻³·d⁻¹]</th>
<th>Rate of substrate respiration [mg O₂·mg TSS⁻¹·h⁻¹]</th>
<th>Rate of endogenous respiration [mg O₂·mg TSS⁻¹·h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>70</td>
<td>6.5</td>
<td>0.116</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>8.0</td>
<td>0.100</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>20.8</td>
<td>0.079</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>48.8</td>
<td>0.045</td>
<td>0.057</td>
</tr>
<tr>
<td>II</td>
<td>70</td>
<td>5.4</td>
<td>0.051</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.8</td>
<td>0.054</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>16.6</td>
<td>0.043</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Total respiration activity includes the oxygen uptake for substrate respiration, endogenous respiration and for ammonia oxidation. In reactor I, at a HRT of 70 and 60 min, endogenous activity of the immobilized biomass accounted for 13–15% of total respiration activity (Table 4; the oxygen consumption for nitrification is not shown). A shortening of a HRT to 30 and 15 min caused an increase in the participation of endogenous respiration to over 30%. In reactor II, the participation of endogenous respiration in total oxygen uptake increased from 14 to 39% following a shortening of HRT from 70 to 30 min. Van Loosdrecht, Henze [20] stated that the endogenous respiration in many cases accounted for more than 50% of the total oxygen consumption.

CONCLUSIONS

In reactors with biomass immobilized in a stationary filling, the values of the sludge yield decreased by increasing the volumetric loading rate. This may have been connected with the change of aerobic conditions in the immobilized biomass. The values of the sludge yield depended on wastewater composition (COD fractions) and the internal structures of the carriers (percentage of free space in the total volume of each carrier).

In reactors with biomass immobilized in a stationary filling, an increase in the capacity of internal circulation from 20 to 60 dm³·h⁻¹ reduced the sludge yield from 20 to 70%.

An increase in the ratio of endogenous respiration to substrate respiration by immobilized biomass corresponded to a decrease in the sludge yield.
NOMENCLATURE

q – capacity of internal circulation [dm$^3$·h$^{-1}$],
HRT – hydraulic retention time [min],
SLR – carrier surface loading rate [g COD·m$^{-2}$·d$^{-1}$],
VLR – volumetric loading rate [g COD·dm$^{-3}$·d$^{-1}$],
DO – concentration of dissolved oxygen [mg O$_2$·dm$^{-3}$],
Y – sludge yield [g TSS·g COD$^{-1}$],
TSS – total suspended solids [g·m$^{-3}$],
VSS – volatile suspended solids [g·m$^{-3}$],
MLSS – mixed liquor suspended solids [g·m$^{-3}$],
MLVSS – mixed liquor volatile suspended solids [g·m$^{-3}$].

REFERENCES


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PRZYROST BIOMASY W POROWATYCH NOŚNIKACH CERAMICZNYCH PODCZAS Oczyszczania Ścieków Komunalnych

Dwa porowate nośniki ceramiczne z unieruchomionym osadem czynnym stanowiły stacjonarne wypełnienie bioreaktorów, w których oczyszczaniu poddawano ścieki komunalne przy hydraulicznym czasie zatrzymania od 15 do 70 min i cyrkulacji wewnętrznej równej 20, 40 i 60 dm$^3$·h$^{-1}$. W zależności od hydraulicznego czasu zatrzymania, współczynnik przyrostu biomasy zmieniał się z 0,138 do 0,066 g TSS·g COD$^{-1}$ w reaktorze I oraz z 0,175 do 0,107 g TSS·g COD$^{-1}$ w reaktorze II. Zwiększenie obciążenia objętości reaktorów ładunkiem zanieczyszczeń oraz wydajności cyrkulacji wewnętrznej powodowało zmniejszenie przyrostu biomasy. Spadek przyrostu biomasy odpowiadał wzrostowi stosunku oddychania endogennego i substratowego unieruchomionej biomasy.
KINETICS OF DAIRY WASTEWATER TREATMENT IN THE SBR SYSTEM

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Keywords: Industrial wastewaters, SBR system, dairy industry.

Abstract: There are two kinds of wastewater that may originate at a dairy plant: post-production and non-production waste. Dairy wastewater treatment is a process consisting of several stages. In the pre-treatment stage, fat and sand is removed from wastewater. The second stage treatment consists mainly in aerobic treatment with activated sludge, advanced oxidation methods and an anaerobic treatment. In recent years, more and more plants have been treating their wastewater in SBR type reactors, because they are flexible at work and enable the user to change conditions to suit the variable quality of raw wastewater. The research on the kinetics of the wastewater treatment process in an SBR reactor has been conducted. The removal of several factors such as nitrogen compounds, TOC, phosphorus and the kinetics of oxygen concentration and redox potential have been analyzed. The experiment was carried out in two 12 dm³ volume SBR reactors in a lab-scale. The SBR reactors were operated with a cycle time of 12 hours with three hours of filling, seven hours of aeration, an hour of sedimentation, half an hour of decantation and half an hour of technical break. In presented research average parameters of raw wastewater were: TOC 329 mg C/dm³, ammonium nitrogen 11.15 mg N NH₄/dm³, and total phosphorus 15.42 mg P/dm³.

INTRODUCTION

There are two kinds of wastewater that may originate at a dairy plant: post-production and non-production waste. Post-production waste is mainly produced during floor and equipment washing, but it also includes milk leakage and loss, as well as brine and casein washing wastewater. Post-production waste contains remnants of milk and dairy products, manufactured at the site, as well as washing agents. In some dairy plants whey is also channeled off into the drain, thereby increasing the impurity load considerably [3]. Non-production, i.e. sanitary, post-cold-storage and rainstorm wastewater may account for a large portion of wastewater, but it contains low concentrations of organic matter. It is produced when washing vehicles, in boiler rooms or in cooling systems (unless water circulates in a closed system).

Dairy wastewater treatment is a process consisting of several stages. In the pre-treatment stage, fat and sand are removed from wastewater. The wastewater is subsequently averaged out. Colloidal impurities are removed by floatation, coagulation and precipitation with calcium at pH > 10 [2]. The amount of wastewater and impurity load
may be reduced by recovering milk – separating the first fraction of slops that contain it in considerable quantities – and selling it as fodder [12]. Recovering brine, which is used in hard cheese production, may be regarded as the first step of wastewater treatment [10]. Application of microfiltration in brine purification ensures the almost total removal of microorganisms; it does not significantly alter the chemical composition of brine, it removes all physical contaminations and does not bring about a large loss of salt (0.5–1.0%). After the microfiltration process brine may be returned to the process. The second stage treatment consists mainly in aerobic treatment with activated sludge, which includes rotating biological contractors, trickling filters, classical method of activated bed, the SBR system [2] and other modifications of aerobic methods. Interest has also been growing in advanced oxidation methods, which mainly employ the use of ozone, dihydrogen dioxide, photolysis and radiolysis. Researchers [11] have attempted to determine whether it is possible to apply the methods of advanced oxidation in dairy wastewater treatment. The method chosen for the study involved the use of Fenton’s reagent, in which dihydrogen dioxide is activated by iron(II). In its modified version, a magnetic field is applied as the factor generating hydroxyl radicals. The analysis of different samples of synthetic wastewater has shown that a better effect of treatment is achieved for the wastewater containing powdered milk. The COD level in those samples was reduced by 79%, whereas the COD level for the synthetic wastewater prepared from dried and powdered whey was reduced by 52%. Additional magnetic field wastewater treatment made it possible to reduce the amounts of reagents with no negative effect on the result of purification.

Secondary treatment is also an anaerobic process involving a flow-through anaerobic reactor with sludge bed and mixed fermentation [9, 16]. Secondary treatment may also include agricultural use and membrane methods [14], as well as dairy wastewater treatment in hydrobotanic systems [15]. Generally, agricultural industrial waste, including dairy waste, is treated effectively in hydrophytic treatment plants. With high variability of the impurity load, waste pre-treatment should be considered, e.g. in lagoons [6]. Such a system could also be applied in a less favorable (cool) climate [6, 13]. Many dairy plants in Poland channel their post-production waste to municipal wastewater treatment plants. Such wastewater contains proteins supporting the purification of waste that is poor in organic matter. Dairy waste can also be a source of volatile fatty acids (VFA), which can be used as an external source of carbon. Research conducted so far [8] has shown that application of an anaerobic process results in increasing the amount of VFA in wastewater, regardless of the amount of sludge in reactors. Raw wastewater itself does not contain large amounts of such substances: from ca. 50 mg/dm³ in raw milk wastewater to 800 mg/dm³ in whey, which is a by-product of cottage cheese manufacture. VFA production is considerably affected by acidification of wastewater [4], which increases with the added impurity load, easily undergoing acidic fermentation. Some heavy metals have also been found to inhibit the process of acidogenesis [5]. Research conducted to evaluate the effect of zinc and copper, which are the most commonly found in heavy industry wastewater, has revealed that zinc concentrations of ≥ 10 mg/dm³ inhibit the process of acidogenesis, whereas zinc at concentrations below that level significantly improves the process. Copper has been found to inhibit the process of acidogenesis in the entire range of concentrations under study, from 5 to 400 mg/dm³.

In recent years, more and more plants have been treating their wastewater in SBR type reactors, as these are flexible and enable the user to change conditions to suit the
variable quality of raw wastewater. All the stages of purification in SBR reactors are carried out in one tank. They work alternately under aerobic and anaerobic conditions, which enable the removal of nitrogen and phosphorus. Unfortunately, SBR reactors often work with incorrectly selected process phases, with an excessive impurities load, which makes pre-treatment possible and the treatment proper impossible. Lack of pre-neutralization of wastewater may result in degradation of the activated sludge [1]. Therefore, the study presented in this paper sought to explore the possibility of treatment of dairy wastewater in the SBR system.

MATERIALS AND METHODS

The experiment was conducted using the set-up as shown in Figure 1. The system consisted of two SBR reactors working in a parallel arrangement. The total capacity of a single reactor was 16 dm³, whereas the active volume was 12 dm³. Synthetic wastewater was fed to the system with a 4-channel type ISM 828 peristaltic pump, manufactured by Ismatec Reglo; purified wastewater was decanted through a U-shape decanter with a 2-channel PumpDrive 5001 pump manufactured by Heidolph. Using such a decanter shape meant that wastewater could be channeled off without any improperly settling sludge being carried away with it. The depth of the decanter fixing ensured the amount of decantation of ca. 33% of the reactor’s active volume. Wastewater was stirred with HEIDOLPH RZR 2051 agitators at a speed that ensured its proper mixing. Stirring was effected with the
VISCO JET stirring tips, whose shape ensured the flow without destroying the flocculate structure of the activated sludge. Air was fed into the reactors with HIBLOW AIR PUMP H810, type SPP-15GA blowers through aerating curtains of small air bubbles, the curtains being 90 cm long and situated at the bottom around the container’s perimeter. The duration of individual process phases was controlled by a PCm.08 3k digital programmer, manufactured by METRON. Only excessive sludge was removed manually. The values of the basic system indicators were monitored with the computer connected to the experimental set-up; the indicators included oxygen concentration, pH, redox potential, and monitoring was effected by MultiLab® pilot communication software and the appropriate electrodes. The characteristic of synthetic wastewater has been presented in Table 1. The work cycle lasted 12 hours and consisted of the basic process phases – Table 2.

Table 1. Quality characteristics of the basic composition of synthetic dairy wastewater

<table>
<thead>
<tr>
<th>Sample number</th>
<th>pH</th>
<th>Ammonium nitrogen</th>
<th>Nitrate nitrogen</th>
<th>Total phosphorus</th>
<th>Phosphates</th>
<th>BOD₅</th>
<th>TOC</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Unit</td>
<td>[mg N₉H₄/dm³]</td>
<td>[mg N₉O₃/dm³]</td>
<td>[mg P/dm³]</td>
<td>[mg P₉O₄/dm³]</td>
<td>[mg O₂/dm³]</td>
<td>[mg C/dm³]</td>
</tr>
<tr>
<td>1</td>
<td>7.41</td>
<td>12.6</td>
<td>0.24</td>
<td>16.5</td>
<td>28.8</td>
<td>680</td>
<td>357.6</td>
</tr>
<tr>
<td>2</td>
<td>7.46</td>
<td>8.75</td>
<td>0.31</td>
<td>15.9</td>
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<td>–</td>
<td>348.8</td>
</tr>
<tr>
<td>3</td>
<td>7.25</td>
<td>9.5</td>
<td>0.39</td>
<td>13.3</td>
<td>28.4</td>
<td>680</td>
<td>332.8</td>
</tr>
<tr>
<td>4</td>
<td>7.49</td>
<td>11.6</td>
<td>0.26</td>
<td>14.6</td>
<td>24.4</td>
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<td>355.9</td>
</tr>
<tr>
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<td>9.15</td>
<td>0.48</td>
<td>15.2</td>
<td>24.2</td>
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<td>15.0</td>
<td>0.08</td>
<td>16.7</td>
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<tr>
<td>7</td>
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<td>13.7</td>
<td>0.26</td>
<td>18.3</td>
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<td>11.1</td>
<td>22.4</td>
<td>640</td>
<td>356.6</td>
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<tr>
<td>9</td>
<td>7.11</td>
<td>11.6</td>
<td>0.23</td>
<td>15.4</td>
<td>28</td>
<td>–</td>
<td>359.4</td>
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<tr>
<td>10</td>
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<td>10.5</td>
<td>0.24</td>
<td>13.5</td>
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<td>720</td>
<td>332.1</td>
</tr>
<tr>
<td>11</td>
<td>7.20</td>
<td>10.8</td>
<td>0.24</td>
<td>15.2</td>
<td>29.6</td>
<td>–</td>
<td>310.4</td>
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<tr>
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<td>11.3</td>
<td>0.22</td>
<td>14.4</td>
<td>29</td>
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<tr>
<td>13</td>
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<td>11.5</td>
<td>0.21</td>
<td>17.25</td>
<td>28.6</td>
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<td>294</td>
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<tr>
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<td>10.3</td>
<td>0.21</td>
<td>13.99</td>
<td>33</td>
<td>–</td>
<td>292.2</td>
</tr>
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<td>16</td>
<td>7.11</td>
<td>11.5</td>
<td>0.28</td>
<td>15.2</td>
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<tr>
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<td>0.3</td>
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<td>700</td>
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<tr>
<td>18</td>
<td>7.15</td>
<td>11.0</td>
<td>0.42</td>
<td>18.2</td>
<td>33.2</td>
<td>–</td>
<td>303.3</td>
</tr>
<tr>
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<td>17.6</td>
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<td>680</td>
<td>315.2</td>
</tr>
<tr>
<td>Mean</td>
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<td>11.15</td>
<td>0.27</td>
<td>15.42</td>
<td>29.0</td>
<td>689</td>
<td>329.0</td>
</tr>
</tbody>
</table>

Table 2. The process phase system in the SBR system, adopted for treating synthetic dairy wastewater

<table>
<thead>
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<td>Stirring</td>
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<td>Decantation</td>
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<tr>
<td>Break</td>
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</tbody>
</table>
RESULTS AND DISCUSSION

Nitrogen compounds removal
The analysis of the wastewater quality characteristics during different process phases revealed an increase in nitrate(V) nitrogen during the static filling phase – Figure 2. The increase was caused by introducing to the reactor raw wastewater, containing 0.27 mg/dm$^3$ of silver nitrate(V). The concentration of dissolved oxygen decreased nearly to zero during the dynamic filling phase. The post-nitrification concentration of nitrate(V) nitrogen decreased to the value of 0.52 mg/dm$^3$ as a result of its reduction by heterotrophic denitrificators. With the beginning of the aeration phase, the concentration of nitrate(V) nitrogen increased as a result of nitrification, reaching the value of 12 mg/dm$^3$ before the settling phase. Before the decantation phase the concentration of nitrate(V) nitrogen decreased to the value of 9.6 mg/dm$^3$, which may result from denitrification effected by denitrificators which contain organic matter in their cells. When the accumulated organic matter was exhausted, the nitrification process took place until the end of the decantation process, in the presence of oxygen.

Fig. 2. Concentration of nitrate(V) nitrogen during individual phases of the SBR system operation

The kinetics of ammonium nitrogen concentration during different phases of the SBR operation is presented in Figure 3. As a result of nitrification, ammonium nitrogen was oxidized to nitrates(III) and nitrates(V). A considerable decrease in the concentration of ammonium nitrogen and the concurrent increase in the concentration of nitrate(V) nitrogen were observed during the first three hours of the aeration phase (III) – Figure 2. After about 3 hours of aeration, the concentration of ammonium nitrogen reached its minimum value of ca. 2 mg/dm$^3$ and remained so until the end of the decantation phase. Concentration of ammonium nitrogen in the reactor increased during the phase of static (I) and dynamic (II) filling as a result of the introduction to the reactor of raw wastewater containing a larger load of nitrogen compounds.
Removal of total organic carbon

Figure 4 shows the kinetics of total organic carbon concentration in the wastewater under treatment during different phases of the SBR operation. During the anoxic phase (I + II) as a result of the reactor filling up with raw wastewater at a concentration of 329 mg C/dm$^3$, TOC concentration in reactor slowly increased to reach 19 mg C/dm$^3$ during the final stage of the anoxic phase. Such a slight increase in concentration (despite a considerable difference in the concentration of raw and purified wastewater) was caused by carbon assimilation by heterotrophic organisms – Figure 2. Organic matter can also be precipitated and adsorbed in activated sludge. At the beginning of the aeration phase (III) organic carbon concentration was recorded to have decreased to the level of 8–9 mg C/dm$^3$. The denitrification process was still going on – anoxic conditions still prevail inside the flocules. As aeration continued, the concentration of dissolved oxygen increased; it got inside the flocules and full nitrification occurred, and the TOC concentration remained at 8–9 mg C/dm$^3$ since the nitrification organisms in a majority are autotrophs. They do not need organic carbon – they can assimilate carbon from inorganic compounds (carbonates, CO$_2$). The concentration of TOC decreased to the value of 7.5 mg C/dm$^3$ during the settling and decantation phase, which may have been caused by carbon consumption by denitrificators – Figure 2.

Phosphorus compounds removal

The kinetics of phosphate removal is presented in Figure 5; for total phosphorus – in Figure 6. The mechanism is the same in both cases. In order to remove phosphorus biologically, alternate aerobic and anaerobic conditions have to be ensured. During the anoxic phase, phosphate concentration in the wastewater under treatment increased from 8 mg/dm$^3$ to 54 mg/dm$^3$ (to 17 mg/dm$^3$ for total phosphorus) as a result of introducing raw wastewater with a concentration of 28.98 mg P$_{PO4}$/dm$^3$ (15.42 mg/dm$^3$ for total phospho-
and as a result of secondary phosphorus release to the liquid under anaerobic conditions. As the time of aeration increased, the phosphorus and phosphate concentration decreased, as they were assimilated by certain bacteria strains (e.g., *Acinetobacter* sp., *Arthrobacter globiformis*) in as much as 25% of dry cell weight [7]. The concentration of phosphates at the end of the reactor work cycle was 5 mg/dm³ and that of total phosphorus – 3 mg/dm³. During the decantation phase the concentration of total phosphorus was recorded to increase by ca. 1 mg/dm³ as a result of the phosphorus being released to the liquid from the precipitate.

Fig. 4. TOC concentration during different phases of the SBR operation

Fig. 5. Phosphate concentration during different phases of the SBR operation
The changes in the concentration of dissolved oxygen during different process phases in the reactor are shown in Figure 7. During the stage of static filling, the oxygen that was introduced into the system during the aeration phase was consumed by autotrophic nitrification organisms. No air was introduced into the system during the dynamic filling phase and the concentration of dissolved oxygen was close to zero (0.03 mg O$_2$/dm$^3$ on average). As has already been said, the denitrification took place and the process of secondary phosphorus release to the liquid at that time. Wastewater was aerated during phase III and the concentration of dissolved oxygen steadily increased up to the level of
8 mg O₂/dm³. At this time, nitrification and biological dephosphatation took place. During phase IV and V the remaining oxygen, dissolved during the nitrification phase, was gradually consumed down to the concentration of 4 mg/dm³ at the end of the decantation process (V).

Dissolved oxygen concentration is directly related to the redox potential, whose kinetics during the SBR system operation is presented in Figure 8. During the initial phase of static filling, the redox potential rapidly decreased from 11.7 mV to -211.6 mV, reaching the value of -332.2 mV at the end of the anoxic phase. The rapid decrease in the redox potential at the beginning of the anoxic phase was probably caused by denitrification. Raw wastewater introduced to the reactor has provided the necessary organic carbon to the system. The denitrification process, which requires reducing conditions, lasted until the end of the anoxic phase (during which time the concentration of nitrate(V) nitrogen and total organic carbon in the purified wastewater decreased – Figure 2 and Figure 4). With the beginning of the aeration phase, the redox potential began to increase steadily, reaching its maximum value (20 mV) at the end of decantation. When the redox potential increased during the aeration process, oxidation conditions prevailed and nitrification occurred – Figure 3.

Fig. 8. The value of redox potential during different phases of the SBR system operation

Changes to the wastewater pH in the SBR reactor are shown in Figure 9. During the anoxic phase, pH of wastewater decreased due to the mixing of wastewater in the reactor (pH = 7.66) with neutral (pH = 7.25) raw wastewater. Further decrease in wastewater pH (to 6.85) was caused by increasing the amount of carbon dioxide, which was produced by decomposition of organic compounds in the denitrification process. Hydrolysis of organic substances and fermentation in phase I produced carbon dioxide and other acidic products, such as volatile fatty acids (VFA) that affected phosphorus compounds removal during phase III. After stirring was switched on, a slight pH increase to 7.2 was observed; when the wastewater in the reactor was thoroughly mixed, pH decreased to 6.85. The
pH value increased during the oxidation phase and reaches a value of 7.97 at its end. An increase in the pH value during the oxidation phase resulted from consumption of carbon dioxide (carbonates) by nitrification organisms and removal of VFA.

Fig. 9. Changes to wastewater pH during different phases of the SBR operation

SUMMARY

The 12-hour work cycle of the SBR reactor has ensured high effectiveness of contaminants removal from modeled dairy wastewater. Earlier research [17] indicated that a sludge age of 15 days was the optimum age for removal of most contaminants. The effectiveness of ammonium nitrogen removal was about 82%, which is similar to that of phosphorus (81.5% on average); TOC removal ratio was high – 97.75%. Only the concentration of nitrate(V) nitrogen increased, being higher after than before the purification process. Exploring the kinetics of the wastewater treatment process in an SBR reactor reveals characteristic changes in ammonium and nitrate(V) nitrogen concentrations for the nitrification and denitrification processes. Moreover, changes typical of phosphorus removal by phosphate microorganisms are also observable; during the anoxic phase the process of secondary phosphorus release to the liquid takes place.

REFERENCES


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KINETYKA PROCESU OCZYSZCZANIA ŚCIEKÓW PRZEMYSŁU MLECZARSKIEGO W SYSTEMIE SBR

Na terenie zakładów mleczarskich powstają dwa rodzaje ścieków: poprodukcyjne i nieprodukcyjne. Oczyszczanie ścieków przemysłu mleczarskiego przebiega kilkuetapowo. W oczyszczaniu wstępnym ze ścieków usuwane są min. tłuszcze i piasek. Oczyszczanie drugiego stopnia to głównie oczyszczanie tlenowe metodą osadowego utlenienia, a także oczyszczanie beztlenowe. W ostatnich latach coraz więcej zakładów decyduje się na oczyszczanie ścieków w sekwencyjnych reaktorach biologicznych (SBR), ponieważ wykazują wysokim stopniem elastyczności w działaniu, pozwalając użytkownikowi zmieniać warunki, tak, aby dopasować je do zmieniającej się jakości ścieków surowych. W przeprowadzonych badaniach prześledzono kinetykę oczyszczania syntetycznych ścieków przemysłu mleczarskiego w systemie SBR. Analizowano usunięcie związków azotu, fosforu, węgla organicznego a także kinetykę stężenia tlenu rozpuszczonemu i potencjału redoks. Badania przeprowadzono w skali laboratoryjnej w dwóch reaktorach o pojemności 12 dm$^3$ każdy. Reaktory pracowały w cyklu 12-godzinnym, z czego napelnianie trwało 3 godziny, napowietrzanie 7 godzin, następnie była godzina sedymentacji, półgodzinną dekantację i półgodzinną przerwę techniczną. W prezentowanych badaniach średnie stężenie zanieczyszczeń w ściekach surowych wynosiło: OWO 329 mg C/dm$^3$, azotu amonowego 11,15 mg N$_{NH_4}$/dm$^3$, a fosforu ogólnego 15,42 mg P/dm$^3$. 

KINETICS OF DAIRY WASTEWATER TREATMENT IN THE SBR SYSTEM
DISINFECTION BYPRODUCTS PRECURSORS REMOVAL FROM DAM RESERVOIR WATER

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Keywords: DBPs, enhanced coagulation, hydrolyzing coagulant, pre-hydrolyzed coagulant.

Abstract: The water of the Wisła-Czarne reservoir is of very low hardness and alkalinity. In spite of high SUVA values it is not susceptible to enhanced coagulation. In order to achieve the assumed results, coagulation with ALS (aluminium sulphate) should be conducted in two optional technological systems – in a conventional system and in “in-bed” coagulation dependently of water quality and its temperature. Effective treatment with ALS is possible, even at low temperature of the water, but at strict technological parameters. However, because of significant variations of water quality, especially after rainstorms, it is very difficult to meet such requirements. Application of pre-hydrolyzed Flokor 1,2A instead of ALS enables to eliminate reagents to the pH adjustment and to apply “in-bed” coagulation when water supplied to the WTP is of low turbidity. To assure stable technological system operation, in aspect of raw water quality changes, some activities were also undertaken, i.e. modernization of rapid filters, which involved a drainage system and exchange of sand bed for anthracite-sand bed. Treatment based on direct filtration results in decrease of reagents usage and, what is especially important, effective DBPs precursors removal.

INTRODUCTION

Organic matter in natural waters contains both hydrophobic and hydrophilic fractions of NOM. The hydrophobic fractions are generally composed of higher molecular weight NOM with activated aromatic rings, phenolic hydroxyl groups and conjugated double bonds, while the hydrophilic fractions are typically composed of the lower molecular weight NOM with aliphatic ketones and alcohols [9, 20]. The hydrophobic fractions of NOM exhibit higher ultraviolet absorbance (UV254) and higher SUVA (Specific UV Absorbance) while the hydrophilic fractions of NOM exhibit lower UV254 and lower SUVA. The SUVA is an operational indicator which, on the one hand allows to determine the characteristics of NOM, and on the other hand, the effectiveness of coagulation in removal of NOM, TOC and DBPs (Disinfection By-Products) precursors [12]. For waters with low SUVA ≤ 2.0 dm³/mgC·m organics are mainly of non-humic nature and they are not susceptible to “enhanced” coagulation.
Pretreatments prior to chlorination can partially remove NOM and this removal can be enhanced by using GAC or enhanced coagulation. Introducing alternative disinfectants or a combination of disinfectants (chloramine, ozone, chlorine dioxide and ultraviolet radiation followed by post chlorination) can also reduce formation of DBPs. However, the use of these alternative disinfectants can still lead to the formation of more toxic DBPs. More than 118 models to predict DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and haloketones (HKs) formations in drinking waters have been reported. The parameters frequently incorporated in the development of DBP predictive models include total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm ($\text{UV}_{254}$), specific ultraviolet absorbance (SUVA), pH, temperature, bromide ion concentrations, chlorine dose and reaction time. It was stated that the longer reaction time (the higher consumption of residual disinfectant) the more DBPs are produced. However, some research indicate that chlorinated DBPs such as HAAs may degrade in endings of distribution systems [6, 25, 26]. The effect of the pH is variable for different by-products. THM concentration increases with the increase of the pH. For HAA the effect is opposite. The higher pH the lower concentration of HAA is observed [28]. It has been also proved that higher temperature increases the rate of DBP formation. Singer and Chang [27] stated linear relationship between TOX (Total Organic Halogens), THM, $\text{UV}_{254}$ and TOC. There have been many other investigations which developed the relationships between precursors and operational indicators and DBPs [1, 6, 14, 15, 28]. Korshin, Li and Benjamin [19] stated that there is a linear correlation between the decrease of absorbance UV at 272 nm and TOX formation. This relationship was confirmed for waters of variable quality with wide range of DOC (dissolved organic carbon), at various chlorine doses, various duration of chlorination and at wide range of pH = 5–11. The equation is as follows:

$$\text{TOX} = 10834 \Delta \text{UV}_{272}$$  

Enhanced coagulation is an effective method for DBPs precursors removal, especially for high MW organic compounds (> 30 kDa) [11, 18, 24, 32]. Aluminium chloride ($\text{AlCl}_3$) and polyaluminum chloride (PACl) are common used coagulants for DBPs precursors removal. Many researchers believe that PACl is more effective in removing turbidity, dissolved organic carbon (DOC), and $\text{UV}_{254}$ absorbance than traditional aluminium coagulants. PACl is characterized by high positive charge and strong binding ability. Preformed Keggin-$\text{Al}_{13}$ compounds are regarded to be the most active species responsible for coagulation. Some research proved that traditional aluminium salts ($\text{AlCl}_3$) generated this type of aluminium polymeric species at pH 5.0–6.0 in situ. $\text{AlCl}_3$ with a high content of in situ transformed polymeric species was more effective than PACl in removing DOC and $\text{UV}_{254}$ [5, 6, 7, 29].

It was also found that a combination of flocculant and coagulant enhanced the coagulation-flocculation process and humic acid removal. The optimum conditions of coagulation-flocculation were established in reference to the ratio of humic acid and coagulant. The ratio of E4/E6 (the ratio of absorbance at 465 nm and 665 nm) shows the molecular size variations using different coagulants and flocculants [8, 33].
CHEMICAL CHARACTERISTICS OF THE BIAŁA AND THE CZARNA WISEŁKA

The literature data present classification of natural waters on the basis of mineralization, concentration of total solids and dissolved substances. Waters of low mineralization consist of up to 3 g/dm$^3$ of total solids. The maximal concentration of dissolved substances in these waters is 200 mg/dm$^3$. Such waters are met in mountainous areas. In the years 1993–1995 the Institute of Nature of the Polish Academy of Sciences in Cracow made the chemical research of both Wiselka rivers. The results indicate that the waters of the Czarna Wiselka are acidified, of low pH, sometimes they lack alkalinity and they are also characterized by very low concentration of calcium. High concentrations of aluminium were also noted there. The highest acidification, the highest aluminium and organic matter concentration were observed in the period of snow melting and after rainstorms. With the course of the Czarna Wiselka its chemical characteristic changed. Concentration of calcium and magnesium acid carbonate increased, so did pH, but aluminium concentration decreased. The Biała Wiselka waters distinctly differed from the Czarna Wiselka ones. The pH was over 6.0, alkalinity always exceeded 0.25 mval/dm$^3$. Taking into consideration the basin of both Wiselkas, ionic composition of water in the reservoir was influenced by the waters of the Biała Wiselka.

The reservoir drainage area mainly consists (88%) of forests. The soil testing showed that the Czarna Wiselka basin is covered mainly by podsol produced on poor calcium and magnesium sandstone of the Istebnian stratum. In the Biała Wiselka basin there is more brown soil produced from sandstones and mudstones. The Czarna Wiselka basin soil is more acidic and of higher exchangeable aluminium concentration. The Biała Wiselka basin soil reveals higher concentration of exchangeable cations, so a higher calcium concentration in water flowing from this area is noted [21, 22]. Last century spruce monoculture replaced mixed stand resulting in acceleration of soil podzolization [10]. The intensive rainfalls were also the additional agent which enhanced that process. The rainfalls washed the shallow soil and caused soil leaching from alkalies [16]. It was the reason of higher soil sensitivity to inflow of acidic compounds originated from the atmosphere contamination.

In 1981–1983 Pająk [23] conducted long-term investigations on both net and sedimentsed phytoplankton samples collected in the Wisła-Czarne Dam Reservoir and its bays at the Biała Wiselka and at the Czarna Wiselka (Western Carpathians). Wróbel [31] emphasized that the occurrence of “water bloom” above the reservoir was observed periodically with the inflow of acidified water (mainly after snow melting and heavy rainfall). It suggested that acidification did not prevent eutrophication. “Water bloom” in the reservoir was associated with increased acidification, which caused a decrease in biodiversity [2, 3, 4, 23].

WATER CHARACTERISTICS IN THE WISŁA-CZARNE RESERVOIR

The Wisła-Czarne dam reservoir was built on the Vistula River in the area where the Biała and the Czarna Wiselka connect. It is the highest located dam reservoir in Poland [30]. The reservoir plays a significant role in supplying water to some cities of great recreation importance. The dam of the maximal height of 36 m and the length of 280 m is situated about 300 m beneath the place where both Wiselka rivers meet. The basic role of the res-
reservoir is compensation of strongly changing water flow. The total capacity of reservoir is 5.06 mln m$^3$, of maximal area 40 ha. The retention time of the Wisła-Czarne reservoir at the typical water level (544.4 m npm) and corresponding capacity 2.1 mln m$^3$ and average flow of the both rivers 0.825 m$^3$/s is 29 days. Water is taken from three levels dependently of its quality. Water recirculation in the reservoir strongly depends on the bottom outlet. In 1995 the reservoir was emptied because of the repair work of its construction. The work lasted for some years until the beginning of 1999. Since then for some months the level of water in the reservoir had been changing till autumn 1999 [17]. Temperature measurements and dissolved oxygen concentration at the close-to-dam part of the reservoir show the lack of typical for lakes thermal stratification. When the reservoir was under modernization the pH of the water was much higher (pH = 6.9–7.1) than in the following year after its filling (pH = 5.5–6.3). In 2001 pH significantly increased and was changing in the range of 6.5–7.35. Such pH variations probably result from the fact that the reservoir started its new operation as a biological system. In the first period after the filling, the reservoir was a typical oligosaprobic reservoir and some time was needed to increase its fertility. At that time the compounds, that leached from the bottom and from the reservoir construction during its filling, strongly influenced the pH values. The results indicate that these compounds must have had alkaline properties. After completing the process of the reservoir filling, when the amount of water in the reservoir was stable, the pH value decreased, because it was only dependent on the quality of the Wisełka waters. Later phytoplankton developed, microorganisms became more and more significant in carbon dioxide circulation. Because of low buffer capacity of the water, the changes of carbon dioxide concentration were of great importance for the pH values. Therefore, it could be assumed that in the reservoir there was a group of microorganisms which was able to absorb CO$_2$ and stabilize its concentration at the level lower than it resulted from that gas concentration in the water supplying the reservoir.

The water of the reservoir is qualified as low mineralized. Its conductivity is in the range of 45–90 µS/cm. Maximal hardness is 60 mg CaCO$_3$/dm$^3$, alkalinity is noted at very low level 0.4–0.7 mval/dm$^3$. It means that the water is of low buffer capacity, which is especially important in conventional coagulation with hydrolyzing coagulants, because it is very difficult to maintain proper technological parameters of a treatment process. In the analyzed research period the highest POD (Permanganate Oxygen Demand) value was 7.4 mg O$_2$/dm$^3$ with corresponding turbidity 16.8 NTU and colour 55 mg/dm$^3$. The highest turbidity (120 NTU) in the water of the reservoir after its filling was noted in August 2006. Very high values of turbidity were incidentally noted after rainstorms. However, the average values did not exceed 6 NTU. The highest colour was 82 mg/dm$^3$ and average annual values were 30 mg/dm$^3$. Figure 1 presents the characteristics of the water in the reservoir.

The analysis of UV$_{254}$ absorbance in filtered (0.45 µm) and unfiltered samples, measurements of TOC (Total Organic Carbon), DOC (Dissolved Organic Carbon) showed that from the moment of the reservoir filling organic matter in water was mainly in a dissolved form. The highest amount of THMs precursors in raw water collected from the reservoir was measured in autumn. Chloroform concentration after 30-min-chlorination was 113 µg/dm$^3$, after 24 hour-chlorination time – 210 µg/dm$^3$. The lowest precursors concentration was in a winter-spring season. In summer time maximal chloroform concentration was 75 µg/dm$^3$. Chlorine doses applied in the testing were the same as the disinfectant
doses used at the Wisła-Czarne WTP (Water Treatment Plant). The results showed that 80% of chloroform was produced within the first 2 hours, the process was completed within 6 hours. Hence, it might be concluded that in water the distribution system, when water is transported for long distances, the amount of THMs should not distinctly increase. However, no correlation was found between TOC and chloroform concentration (Fig. 2).

SUVA values were noted in the range of 2.0–4.9 dm$^3$/mg C·m which confirmed that the water was rich in DBPs precursors. It also indicated the water susceptibility to “enhanced” coagulation. The research proved that in waters where SUVA was higher than 3.0
dm$^3$/mg C⋅m humic fractions were predominant compounds, because they easier reacted with chlorine than fulvic acids [13]. Fig. 3 presents changes of chloroform concentration in the water of the Wisła-Czarne reservoir vs SUVA.

![Graph](image)

**Fig. 3.** SUVA and chloroform concentration (after chlorination) in the water of the Wisła-Czarne reservoir

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THE ANALYSIS OF OPERATIONAL PROBLEMS AT THE WISŁA-CZARNE WTP

The treatment system at the Wisła-Czarne WTP was designed as a conventional treatment system (a hydraulic tank of rapid-mixing, vertical sedimentation tanks combined with rotational flocculators and rapid filters). Disinfection is run with the usage of low-pressure UV lamps and sodium hypochloride (NaOCl). Taking into consideration high aggressiveness of treated water corrosion inhibitors are also applied. Inhibitors are added to minimize the risk of secondary contamination by corrosion products. Requirements for coagulation effectiveness in the analyzed technological system are very high, because of high values of THMFP (Trihalomethans Formation Potential) and lack of ozonation and active carbon filtration. So that to estimate treatment effectiveness the research in two technological systems was made (conventional treatment and direct filtration). The system of conventional coagulation consisted of a rotational flocculation chamber, a vertical sedimentation tank and a pressure rapid filter. The system of direct filtration involved a pressure rapid filter. The dual media filter were applied in both systems (sand – 0.8–1.2 mm and anthracite – 0.6–2.0 mm). Each layer was 55 cm high. Both systems were supplied with the source water directly from the water intake. Operating parameters of the system tested in a pilot scale are presented in Table 1.

The water quality was evaluated on the basis of the pH, colour, turbidity, POD (Permanganate Oxygen Demand) and $\text{UV}_{254}$ absorbance and chloroform concentration. The results of the research showed that the effectiveness of coagulation depended mainly on a proper choice of technological parameters of the process [17]. Taking into consideration
the variations of raw water quality, the optimum dose was stated just before the beginning of each testing series. Because of low mineralization and lack of buffer capacity of treated water, a very precise pH adjustment was required during a hydrolyzing coagulant (aluminium sulphate) dosing. It was stated that the optimum pH for conventional treatment was 6.0–6.5. When only ALS was applied (at the effective dose) pH dropped from 6.5 to 3.5. The optimum pH for direct filtration was in the narrow range of 6.0–6.2. Figures 4 and 5 present the effect of pH on residual aluminium concentration after treatment in the conventional system and in “in-bed” coagulation.

To optimize the technological process it was necessary to use both hydrolyzing coagulant and alkalies or to change the type of coagulant. Characteristics of water supplied to the distribution system at the Wisła-Czarne WTP confirm that at the optimum technological parameters of coagulation, the removal of THMs precursors was effective (Fig. 6). The acceptable level of THMs for drinking water was exceeded only in the first year after the reservoir modernization had been finished. In the later period maximal chloroform...
concentration in water supplied to the distribution system was 15 µg/dm³. However, no correlation between color or POD values and chloroform concentration could be stated (Figs 7 and 8).

Because of significant variation of water quality, especially during rainstorms, treatment with aluminium sulphate caused a lot of technological problems. The effective coagulant dose was stated in a very narrow range, so it was extremely difficult to maintain it during exploitation. Due to low hydraulic efficiency of the sediment tanks, unfavourable flocculation conditions in the combined flocculation tank and low water temperature,
improper coagulant dose (in aspect of water quality changes) caused delay in its hydrolysis. As a consequence, a decision was made to apply a new coagulant type. In laboratory research many hydrolyzing and pre-hydrolyzed coagulants were tested, in aspect of their effectiveness and the possibility of treatment without necessity of the pH adjustment. The crucial criterion of a reagent choice was its effectiveness in treatment of water of variable quality. Initially, a coagulant type and its dose was stated in jar testing. Then, a new coagulant was tested in the technical system. On the basis of those results Flokor 1,2 was chosen as the most effective coagulant and it was introduced in the plant without further pilot tests.
In the technical system dosing of Flokor 1,2A started in February 2007. In comparison to ALS treatment, “in-bed” coagulation with Flokor 1,2A was possible without the pH adjustment when water supplied to the WTP was of low turbidity. The average doses of pre-hydrolyzed reagent were ca. 2.0 mg Al/dm$^3$ in conventional coagulation and 0.7–1.3 mg Al/dm$^3$ in “in-bed” coagulation. The doses of pre-hydrolyzed coagulant were twice lower than ALS.

So that to assure stable technological system operation in aspect of raw water quality variations, some activities were undertaken, i.e. modernization of the rapid filters which involved a drainage system and exchange of sand bed for anthracite-sand bed. Treatment based on direct filtration resulted in decrease of reagents use and, what is especially important, effective DBPs precursors removal.

**CONCLUSIONS**

The water of the Wisła-Czarne reservoir is of very low hardness and low-mineralized. In spite of high SUVA values it is not susceptible to coagulation. The reason is probably lack of buffer capacity what requires the pH adjustment during coagulation. Another factor is low temperature of the water for many months in the year which inhibits the processes of coagulant hydrolysis and its precipitation.

The water requires treatment in “enhanced” coagulation because of the presence of dissolved organic matter which in disinfection with chlorine becomes a source of carcinogenic THMs in the amount exceeding even many times the level acceptable for drinking water.

To achieve the assumed results, the coagulation should be run in two optional technological systems – in conventional treatment and in direct filtration dependently of water quality and its temperature.

Effective treatment with ALS was possible, even at low temperature of the water, but at strict technological parameters (very low range of effective ALS dose and pH ~ 6). However, because of significant variations of water quality, it was very difficult to meet such strict requirements.

The application of pre-hydrolyzed Flokor 1,2A instead of ALS enabled to eliminate reagents to the pH adjustment and to apply “in-bed” coagulation when water supplied to the WTP was of low turbidity.

Treatment based on direct filtration with Flokor 1,2A and exchange of sand bed for anthracite-sand one ensured effective DBPs precursors removal.

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USUWANIE PREKURSORÓW UBOCZNYCH PRODUKTÓW DEZYNFEKCJI Z WÓD ZBIORNika ZAPOROWEGO

Wody ujmowane ze zbiornika zaporowego Wisła-Czarne należą do wód miękkich o niskiej zasadowości. Pomiędzy wysokich wartości SUVA należą do wód trudnopodatnych na oczyszczanie metodą koagulacji. W celu uzyskania założonych efektów uzdatniania proces koagulacji musi być prowadzony w różnych układach technologicznych (koagulacji objętościowej lub powierzchniowej), których wybór zależy od jakości oraz temperatury wody surowej. Skuteczne uzdatnianie badanych wód siarczanem glinu, nawet w okresach bardzo niskich temperatur wody było możliwe przy zachowaniu ścisłe ustalonych parametrów technologicznych. Jednak z uwagi na dużą zmienność jakości ujmowanej wody, zwłaszcza w okresie intensywnych opadów atmosferycznych były one trudne do utrzymania. Zmiana rodzaju koagulantu na wstępnie zhydrolizowany koagulant glinowy Flokor 1.2A pozwoliła nie tylko na eliminację środków do korekty pH, ale także umożliwiła zastosowanie koagulacji powierzchniowej w okresach niskiej mętności wody surowej. Dzięki wprowadzeniu koagulacji powierzchniowej w połączeniu z modernizacją filtrów pospiesznych w zakresie konstrukcji drenażu oraz wymiany złoża z piaskowego na antracytowo – piaskowe uzyskano stabilniejszą pracę układu uzdatniania w aspekcie zmian jakości wody surowej, mniejsze zużycie reagentów oraz zapewniono pełne usuwanie prekursorów ubocznych produktów dezynfekcji.
LANDFILL LEACHATE TREATMENT USING CONSTRUCTED WETLAND WITH SHORT DETENTION TIME

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Keywords: Constructed wetland, landfill leachate, leachate treatment, reed, cattail, willow, detention time.

Abstract: The paper presents results obtained during experiments with constructed wetlands that were built and monitored on the site of a municipal landfill in Southern Poland. The wetland was filled with gravel and rock in which reeds, cattails and willow were planted. A control plot without vegetation was also constructed. Each wetland was loaded with a portion of the leachate generated by the landfill. Measurements of the leachate quality showed very high concentrations of several pollutants. Particularly high concentrations of BOD, COD, nitrogen, and heavy metals were measured. High pollutant levels were probably responsible for the demise of the willows, which were dead within several months of planting. The efficiency of pollution removal with detention time up to 24 h ranged from 0 to 87% based on decreasing concentration of selected parameters. However, the removal efficiency of the control plot was typically only several percent lower than the removal efficiencies of the plots with vegetation.

INTRODUCTION

The leachates are one of the main environmental concerns in the landfills. They can occur as uncontrolled runoff or be collected with engineering facilities [5, 12]. However, when collected, they are difficult and expensive to treat because they are usually high in toxicity and because of wide variations in both quality and quantity [5, 8, 10, 12]. For these reasons, in Poland, more than 50% of landfills send their leachates to municipal wastewater treatment plants using mainly trucks (equipped with containers). Discharge into municipal sewer systems occurs at about 6% of Polish landfills. An alternative and potentially less expensive method of leachate management is available using a constructed wetland.

In this paper, research on this topic undertaken in Southern Poland is described. Main goal was to study the possibility of leachate treatment through application of a constructed wetland in which the water table is maintained under ground level. Experimental plots constructed next to a landfill allowed for the study of several phenomena including the changes of efficiency of the contaminant removal correlated with time of flow through the wetland.
LEACHATE QUALITY AND QUANTITY

Municipal landfill leachate quantity and quality vary substantially depending primarily on meteorological conditions, age of the landfill, and technology of landfilling [1, 8, 12, 16].

Biochemical oxygen demand can vary from 10 ppm to as high as 7000 ppm, COD from 10 ppm to up to 10000 ppm, phenol from 0.17 ppm to 112 ppm, pH from 1.5 to 9.5, toluene from 280 ppb to 1680 ppb [2, 8, 10, 12, 16]. Also important is considerably high concentration of chloride, which in some cases excides 5000 ppm. A high concentration of heavy metals is another factor that limits options for biological wastewater treatment. Cited in the literature are concentrations of cadmium from 0 to 2 ppm, zinc from 0.2 to 3 ppm, lead from 0 to 6.6 ppm, and cooper from 0.186 to 5.09 ppm.

WETLANDS FOR WASTEWATER TREATMENT

Interest in non-conventional ecologically sound methods of wastewater treatment is not new, but is increasing recently all over the World [2–4, 6–9, 12, 14]. The main advantages of such systems are low cost of construction and low energy and labor for operation. Additionally, there are possibilities of resources recovery in some cases as well as support of wildlife. Wetlands applied to wastewater treatment can be classified in various ways but most commonly can be split into two major categories [3, 4, 7]:

– Free Water Surface Wetlands (FWS),
– Subsurface Flow Wetlands (SFW).

FWS systems can be similar to stabilization ponds, consisting of basins or channels with the vegetation either floating or rooted in the bottom sediments. The treatment processes occur in the water column as well as on parts of the plants submerged in the water [7, 9, 13]. The most common plants used in these systems are duckweed, hyacinth, pennyworth, cattail, bulrush, and reed.

In SFW systems purification processes take place underground where wastewater flows laterally through the medium (soil or artificial substrate such as gravel, for example) and the root zone of vegetation. In Europe these systems are sometimes called Root-Zone Method.

Biochemical processes in the bed of such wetlands are the same as in trickling filters or soil filters with same additional support from vegetation. The roles of the vegetation are considered to be following:

– transportation of oxygen to the root zone to create aerobic conditions that are favorable for biochemical organic matter degradation,
– release of enzymes that participate in biochemical processes in the root zone,
– roots provide additional support for the microbes including symbiotic bacteria,
– direct uptake of the contaminants.

The most common plants used in subsurface systems are reed, cattail, rush, bulrush, and sedge [4, 7]. SFW are found to be very resistant to changes in quality and quantity of wastewater and even to the presence of toxic substances such as heavy metals, does not decrease efficiency of treatment substantially [4, 9]. However, the price we usually have to pay for these benefits is in the form of a significant requirement for land on which the wetland is to be constructed.
EXPERIMENTAL SITE DESCRIPTION

The studied landfill is located in Southern Poland, about 20 km South of Cracow. Ground elevation is about 215 m above sea level. The site is in a valley of the Vistula River with an interesting microclimate characterized by large differences in ambient temperature between night and day. Also high variations of the humidity are monitored. Average rainfall is 665 mm, 60–70% of which occurs during the vegetation (growing) season.

About 300,000 Mg of municipal wastes were stored during the 20 years of the landfill operation. The wastes were not segregated before disposal, and some toxic wastes were present, such as batteries, pesticides or their containers, containers of automobile oil, light bulbs, home appliances and many other household wastes. There is a possibility that some industrial wastes from small businesses were also damped illegally from time to time. The area of the landfill is 6 ha at the bottom and about 4 ha at the top. No special compactor was used except for a caterpillar tractor for moving and burying waste. The landfill had no leachate management facilities.

The experimental plots are located on the north side of the landfill, just between the landfill and a pond created by uncontrolled outflow of leachates from the landfill. They consist of three channels made of wooden board lined by the two-geomembrane layers (Fig. 1).

![Experimental plots at Skawina](image-url)
Each channel was 20 m long, 0.53 m width, and 0.5 m deep. The slope was 1.5%. The plastic pipe at the inflow allows for directing the leachates to the experimental plots.

The experimental plots were filled up with porous media dominated by rocks and gravel of about 25 mm (see the sieve curve of this material in the Figure 2).

Experimentation began with planting of about 500 seedlings of willow (*Salix viminalis*) on one plot and about 600 seedlings of reed (*Phragmites communis*) on another plot. One control plot was left without vegetation. After a year all of the willows and about 50% of the reeds died. An additional 450 seedlings of reed were planted to reach 75 plants/m\(^2\). Also it was decided to replace the willows with cattails, about 400 seedlings of which were planted. Unfortunately, after a year many of the cattail plants died as well, and during the testing and monitoring phases described in this paper, the density of cattail was only about 3 plants/m\(^2\).

Reeds and other vegetation grow near the plots, so a lot of effort was required to keep the plots free of other vegetation, which came to the plot as a natural migration process.

**TESTING AND MONITORING METHODS**

Three different flow rates through the experimental plots were obtained by adjusting the inflow manipulations to obtain detention times of 8 h, 12 h, and 24 h. For each detention time the samples were taken from the influent and effluent in accordance with this time so as to capture the same volume of leachate on inflow and on outflow. The samples were
analyzed in a certified laboratory according to the Polish Standards. Since cattail density during the experiments was very low, also this plot could be considered as control plot.

RESULTS

The pH during the experiments did not change significantly (Fig. 3a), with the exception for a decrease in the cattail plot for the 24 h detention time (which was most probably due to experimental error).

The COD of the influent during the experiments was high and varied from 599 ppm to 897 ppm. Increase of detention time caused increase efficiency of COD of the effluent (Fig. 3b). For the detention times of 8 h, 12 h, 24 h, the COD reduction was 20%, 23%, and 41%, respectively. It is important to notice that for 8 h and 12 h there is a difference in efficiency of treatment between reeds and the control plot as well as the plot with some cattails. However for 24 h detention time this deference was much smaller.

Similar effects were obtained for reduction of BOD (Fig. 3c). For 24 h detention time, the reduction in BOD was very good for all plots. BOD of influent varied from 80 ppm to 186 ppm.

Increases in detention time resulted in improved total nitrogen removal for all plots (Fig. 3d). For this parameter there were significant differences of efficiencies between the plot with reed and control plot for all detention times. The plot with reeds experienced significantly more nitrogen removal which reached 35% for the 24 h detention time. Total nitrogen of the influent varied from 80 ppm to 180 ppm.

Very high removal efficiency of zinc, lead and other heavy metals was observed (Figs 3e and 3f). However, there were variations with detention time that cannot be explained, and more data are required to find relationships between the vegetated and control plots for various detention times. Concentrations of zinc and lead at the influent were up to 0.5 ppm and 0.12 ppm, respectively.

The influent had a very high salinity resulting in high conductivity which reached 17 mS/cm during the course of research.

CONCLUSIONS

Constructed wetlands are shown to have a good ability to remove contaminants from landfill leachates, even with a short detention time not exceeding 24 h. Efficiency of removal of nitrogen and metals was significantly higher on the plot with reeds than on control plots with little or no vegetation. However, removal of BOD and COD was just as effective in the control plots as it was in the vegetated plots, probably due to microbial growth in the control plots.

As it was expected, increasing the detention time strongly increases the treatment effect.
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Fig. 3. Efficiency or removal of selected leachate contaminants by constructed wetland
ENSURING PERMEABLE REACTIVE BARRIER EFFICACY
AND LONGEVITY

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Keywords: Remediation, precipitate formation in zero-valent iron, safety factor in PRB Technology.

Abstract: PRB technology is a technique of groundwater remediation where contaminants are removed from an aquifer by the flow through a permeable reactive barrier (PRB) filled with a special material called a “reactive material”. In this paper problems connected with precipitate formation in zero-valent iron Fe⁰ used as a reactive material were described – the precipitate may finally reduce the reactivity of this material and its hydraulic conductivity. Then, on the basis of the laboratory test changes of pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) concentration which accompany precipitate formation were demonstrated. Moreover, on the basis of hydrologic modeling the following rule was presented and proved: in order to increase PRB efficacy (in Funnel-and-Gate System) by increasing the hydraulic capture zone width, the ratio of the gate hydraulic conductivity (“gate” includes the reactive material in Funnel-and-Gate System of PRB Technology) to the aquifer hydraulic conductivity (k_gate/k_aq) should take the value of six. The precipitate formatted in zero-valent iron may reduce the hydraulic conductivity of the reactive gate. Therefore, it was assumed that the ratio of k_gate/k_aq should amount to 10. This value gives certainty that reduction in gate hydraulic conductivity due to precipitate formation will not impact the hydraulic capture zone width. The above mentioned solution can ensure effective and long-lasting treatment process in reactive barrier.

INTRODUCTION

Permeable reactive barrier (PRB) technology is a technique of groundwater remediation. Many toxic contaminants may be removed from groundwater by applying this technology. This technique is a passive one where contaminants are removed from an aquifer by the flow through a permeable barrier filled with a reactive material [2, 3, 5, 6, 9]. Many reactive materials may be used as a filler in PRB, but up to now zero-valent iron Fe⁰ is the most common reactive material in the majority of field scale and commercial implementations [5, 8, 11]. The processes applied in it are [12]: chemical detoxification of halogenated hydrocarbons and precipitation of heavy metals.

Halogenated hydrocarbons, often present in groundwater, are very toxic whereas most hydrocarbons are non-toxic or slightly toxic. So, in the reactive material consisting of zero-valent iron Fe⁰, a reaction which can change these chemicals into non-toxic hydrocarbons is created [12]. The zero-valent iron can act as reducing agent and generate a ferrous ion. The resulting electron activity is believed to reduce the halogenated
compounds to potentially non-toxic products. The overall reaction for detoxification of halogenated hydrocarbons (RCl) can be presented as [2]:

\[
\text{Fe}^0 + \text{H}_{2}\text{O} + \text{RCl} \rightarrow \text{RH} + \text{Fe}^{2+} + \text{OH}^- + \text{Cl}^-
\]  

(1)

The reduction is primarily proceeded by the removal of the halogen atom and its replacement by hydrogen.

In the case of groundwater flowing through the industrial disposal sites it may bear positively charged inorganic cations such as Cd\(^{2+}\), Co\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\). All these cations are characterized by standard electrode potential higher than zero-valent iron. So it displaces hazard cations from groundwater, according to following reaction:

\[
\text{Fe}^0 + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}^0
\]  

(2)

This reaction proceeds on condition that:

\[
U_{\text{Fe/Fe}^{2+}} < U_{\text{Cu/Cu}^{2+}}
\]  

(3)

where:

\(U_{\text{Fe/Fe}^{2+}}\) – standard electrode potential (also known as standard redox potential, standard oxidation/reduction potential or ORP) [V].

The PRB is a technology that has the potential to effectively remediate subsurface contamination at many types of sites with significant cost savings compared to other ones. The economics of a PRB application depend largely on the useful life (longevity) of the reactive media.

PRB has several advantages over other methods of groundwater remediation. Reactive barrier can degrade or immobilize contaminants \textit{in situ} without bringing them up to the surface. It also usually does not require continuous input of energy. PRB is currently built in two basic configurations: Continuous Reactive Barrier and Funnel-and-Gate System [5, 9] divided into: Funnel-and-Gate Open System and Funnel-and-Gate Closed System (Fig. 1) [7]. Both configurations require some degree of excavation and are limited to fairly shallow depths of aquitard, about 15 m [12]. The contaminant plume must not pass over, under or around the PRB and the reactive zone must reduce the contaminant to concentration goal without rapidly plugging with precipitates or becoming passivated. The Funnel-and-Gate System uses impermeable walls (sheet piles, slurry walls, etc.) to direct the contaminant plume to a “gate” containing the reactive material, whereas the Continuous Reactive Barrier is completely filled with the reactive material and is rather

Fig. 1. Main types of PRB [7]
homogeneous. Due to the impermeable walls, the Funnel-and-Gate System has a greater impact on altering the groundwater flow than Continuous Reactive Barrier.

The two primary interdependent parameters of concern when designing a PRB are **hydraulic capture zone width** and **residence time**. Capture zone width refers to the width of the zone of groundwater that will pass through the reactive cell (in the case of Continuous Reactive Barrier) or gate (in the case of Funnel-and-Gate System) rather than pass around the ends of the barrier or beneath it. Capture zone width can be maximized by maximizing the discharge (groundwater flow volume) through the reactive cell or gate. Residence time refers to the amount of time during which contaminated groundwater is in contact with the reactive medium within the gate or reactive cell. Residence times can be maximized either by minimizing the discharge through the reactive barrier or by increasing the flow through thickness of the reactive barrier. Thus, the design of PRBs must often balance the need to maximize capture zone width (and discharge) against the desire to increase the residence time. Contamination occurring outside the capture zone will not pass through the reactive barrier. Similarly, if the residence time in the reactive barrier is too short, contaminant levels may not be reduced sufficiently to meet regulatory requirements [2].

The two primary goals of this study were:

- presenting (on the basis of laboratory measurement and literature survey) the precipitate formation possibility in zero-valent iron, which can coat the surface of it or occupy the available pore space and eventually reduce the reactivity and the hydraulic conductivity of this material. This effect could shorten the useful life of the reactive media causing necessity to replace it and thus make PRB more expensive. It was finally suggested to use some solution to prevent such a problem;
- presenting (on the basis of hydrologic modeling) the following rule: in order to increase PRB efficacy (in Funnel-and-Gate System) by increasing hydraulic capture zone width the gate hydraulic conductivity should be several times higher than aquifer hydraulic conductivity.

In the highly reducing environment produced by zero-valent iron, dissolved species, including oxygen, carbonate, sulphate, calcium, magnesium, iron, and silica can potentially interact to form precipitates that could deposit on the iron or within the pore spaces [3]. In this way the reactivity of this material and its hydraulic conductivity can be reduced which then leads to the failure of the whole system. The same effect may arise when in treated groundwater the pH is increasing as a result of reactions which occur in the reactive material.

In case when dissolved oxygen (DO) is present in groundwater as it enters the reactive iron material, iron is oxidized and hydroxyl ions are generated [2]:

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$$  \(4\)

The importance of this reaction is that DO can quickly corrode the first few centimeters of iron layer in the reactive barrier [13].

Under oxygen conditions, Fe\(^{2+}\) (formed in reaction 4) oxidizes to Fe\(^{3+}\), which can be written as:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$  \(5\)

Fe\(^{3+}\) may then precipitate out as Fe(III) oxyhydroxide – FeO(OH) or Fe(III) hydrox-
ide – Fe(OH)$_3$ (reaction 6) at the elevated pH condition, in which case the permeability and reactivity as well could potentially become considerably lower in the first few centimeters of the reactive barrier at the influent end. So, the aerobic condition in groundwater is unfavorable to that material [13].

$$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3(s)$$  (6)

Fe(III) (oxy)hydroxides formed in the reactive material are converted over time to magnetite.

According to the reactions 1, 4 and 7 (reaction 7 proceeds slowly) the oxidation of Fe$^0$ to Fe$^{2+}$ causes increase in pH (in weakly buffered system), which may next cause precipitation of Fe(III) hydroxide in aerobic condition (reaction 6) and Fe(II) hydroxide in anaerobic condition (reaction 8), and also precipitation of other compounds [13]. In accordance with Figure 2, Fe(OH)$_2$ is relatively insoluble and Fe(OH)$_3$ is extremely insoluble.

$$\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$$  (7)

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2(s)$$  (8)

In strongly buffered system the presence of bicarbonate (alkalinity) can limit pH increase, which can be written as:

$$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$  (9)

Fig. 2. The effect of pH and ORP on iron speciation (iron concentration: 0.01–100 g Fe/m$^3$) [4]
The effect of pH on the mobility and precipitation of many inorganic hydroxides is shown in Figure 3 [15]. According to this Figure the increase in pH would be positive (for the condition when toxic cations are presented in the groundwater) if it was the main factor generating groundwater treatment process and if these cations did not precipitate out using reaction 2.

![Fig. 3. Metals hydroxide solubility as a function of their concentration and pH [15]](image)

The precipitate formation in zero-valent iron through pH increasing causes decrease in permeability of the reactive material and its reactivity. So it is unfavorable to the reactive material as well [13].

So, once contaminated groundwater passes through zero-valent iron the geochemical parameters like pH and oxidation-reduction potential (ORP) are changing radically. The pH is increasing while, at the same time, the ORP is decreasing. In that condition the bicarbonate (HCO$_3^-$) ions are converted to carbonate ions (CO$_3^{2-}$) (reaction 9). The CO$_3^{2-}$ ion can then combine with the cations present in solution (Ca$^{2+}$, Fe$^{2+}$) to form carbonate mineral precipitates such as calcite (CaCO$_3$) and siderite (FeCO$_3$). At some sites, Mg$^{2+}$ may precipitate in solid solution with CaCO$_3$. The potential for precipitation of calcite, magnesite and siderite minerals can be evaluated by monitoring the changes (losses) in alkalinity, ferrous ion, calcium and magnesium [3, 9].

Moreover, reducing conditions lead to reduction of sulphate to a lower oxidation state of sulphur, such as sulphide, which then can precipitate with inorganic constituents
like Fe, Cu, Zn, Pb, V, Mn. The “Green rust,” a compound of ferrous or ferric ion containing hydroxide, chloride, and sulphate, is another precipitate that may be created in those conditions [2].

Dissolved silica is inorganic constituent present in groundwater that is of potential concern to the longevity of a barrier as well. Monomeric silicic acid, $\text{H}_4\text{SiO}_4$, is known to form polymers that may coat iron grains, producing a passivating film. It is unknown whether or to what extent dissolved silica acts as a corrosion inhibitor for granular iron [2].

Although, the effect of precipitate mass on reactivity is rather unclear, the amount of inorganic species lost as the groundwater moves through the reactive medium may be an important indicator of the type and degree of precipitation that is occurring [2, 3, 14].

**METHODOLOGY OF THE RESEARCHES AND USED MATERIAL**

The pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) are inorganic parameters that are easily monitored during column tests and are good indicators of conditions created in reactive barrier. For these reasons they were used in the laboratory test presented in the paper for determining whether conditions are favorable to formation of inorganic precipitates. The effect of pH, DO and ORP changing was observed in the laboratory test carried out in the measuring set shown in Figure 4. This test was conducted in the glass column packed with scrap iron taken from industrial waste lagoon “HK.

![Fig. 4. Installation for simulation of flow and treatment processes of contaminated groundwater in reactive barrier; 1, 2, 3, 4, 5, 6, 7 – sampling points [13]](image-url)
Table 1. Grain-size distribution of zero-valent iron used in the column test

<table>
<thead>
<tr>
<th>Size grade [mm]</th>
<th>&gt; 1.6</th>
<th>1.6–1.0</th>
<th>1.0–0.8</th>
<th>0.8–0.5</th>
<th>0.5–0.1</th>
<th>&lt; 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction [%]</td>
<td>1.01</td>
<td>9.73</td>
<td>38.26</td>
<td>32.88</td>
<td>8.39</td>
<td>9.73</td>
</tr>
</tbody>
</table>

Table 2. Parameters of zero-valent iron Fe⁰

<table>
<thead>
<tr>
<th>Reactive material parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity [m/s]</td>
<td>2.1 \times 10^{-2}</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>7.61</td>
</tr>
<tr>
<td>Bulk density [g/cm³]</td>
<td>2.52</td>
</tr>
<tr>
<td>Effective porosity [-]</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Both sand and iron were cleaned before filling column with them. Sand was cleaned with the use of distilled water whereas iron was first cleaned with spirit and then with distilled water. Both materials were next dried and carefully packed into column.

Wastewater was prepared by mixing distilled water (5 dm³) and CuSO₄·5H₂O (71 mg). It was circulated in the column from bottom to the top (Fig. 4) and during that time redox processes were proceeded in it. The wastewater Darcian velocity amounted to 25.26 cm/h while the initial concentration of Cu²⁺ in wastewater amounted to 3.51 mg/dm³. There were five sampling points along the column in order to draw wastewater out and to take measurements. The conditions in the column corresponded to the aquifer. The measurements were just begun after achieving steady state in the column i.e. after wastewater located in the column was changed five times.

As for any decontamination technology, it is important also to fully understand the factors that determine their efficiency. This section describes methodology for creation of theoretical models used to evaluate dependence between the gate hydraulic conductivity and aquifer hydraulic conductivity in a Funnel-and-Gate System of PRB Technology.

There are many kinds of programs for modeling groundwater and contaminants diluted in it, for example: FEFLOW, FLONET/TRANS, FLOWPATH II, FRAC3DVS, FRACTRAN, PRINCE, RBCA TIER 2 ANALYZER, VISUAL MODFLOW. The Visual MODFLOW program and its modules were chosen for PRB hydrologic designing because they allow [10]:

- to model the hydrodynamic field in the area of groundwater,
- to model the chemical distribution of contaminants,
- to calculate the quantity of water which flows through the specific area (Zone Budget module),
- to specify the direction of groundwater (Modpath module),
- to use in the model cut-off wall, which is characterized by different thickness and different hydraulic conductivity.

The theoretical model (Fig. 5) used for hydrologic modeling has the shape a of square (400/400 m). The surficial geology at the model consists of an upper sand aquifer and a clay aquitard which insulate the aquifer. The thickness of the aquifer is of depth up
to 12 m. Both the gate and cut-off wall were keyed into the underlying confining layer. The hydrologic modeling was carried out for:

- Funnel-and-Gate System – total Funnel-and-Gate width in the model amounted to 220 m, whereas the thickness of the gate equaled to 5 m. The Funnel-and-Gate System was made of cut-off wall with a permeability of $1 \times 10^{-12}$ m/s and a thickness of 0.07 m. The system was orientated perpendicular to groundwater flow direction,
- different site parameters, i.e.:
  - aquifer hydraulic conductivity – the model was simulated with aquifer hydraulic conductivity from $1 \times 10^{-6}$ m/s to $5 \times 10^{-4}$ m/s. Moreover, the aquifer was set up as a homogeneous and hence the hydraulic capture zone in every model was symmetrical;
  - hydraulic gradient – the model was simulated with an aquifer gradient from 0.01% to 0.5%;
  - different gate width – the model was simulated with gate width from 5 m to 30 m,
  - different gate hydraulic conductivity – the model was simulated with gate hydraulic conductivity from $1 \times 10^{-6}$ m/s to $5 \times 10^{-3}$ m/s,
  - different distance between the PRB and the source of contaminants – the model was simulated with distance between the PRB and the source of contaminants from 30 m to 120 m.

By the use of such a model, the combined effect of several critical parameters can be incorporated simultaneously into one model.

In order to facilitate the analysis, it was assumed that the aquifer is isotropic and the source of contaminants (dumping site) has a shape of a rectangle (100/50 m). Specified head nodes were set along the first row (top row) and the last row (bottom row). Groundwater flew from top to bottom. The Modpath module and the Zone Budget module were used to delineate the capture zone width and to calculate sub-regional water budgets.
RESULTS AND DISCUSSION

The Figure 6 shows the results of the laboratory test, i.e. the value of pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO), measured in wastewater [11].

In accordance with Figure 6, the reaction 4 proceeded quickly, evidenced by the fact that both the DO and the ORP dropped quickly as the wastewater entered the iron material. The value of ORP and DO for the first and the seventh sampling point amounted to ORP$_1$ = 332 mV; DO$_1$ = 8.24 mg/dm$^3$ and ORP$_7$ = -12 mV; DO$_7$ = 5.42 mg/dm$^3$, respectively. These parameters went down gradually.

In an iron medium, as conditions became more anaerobic in the column, pH increased (Fig. 6) as a result of reaction 4 and 7. This potential increased from 6.21 in the first sampling point and reached up to 7.20 in the second sampling point, and then it kept similar value in the remaining points.

As a consequence of pH, DO and ORP changes, it can be said that the oxidation of Fe$^0$ to Fe$^{2+}$ (and maybe to Fe$^{3+}$) causes (with time) precipitate formation and decreasing reactivity and hydraulic conductivity of the iron used as a reactive material in column test.

In order to confirm the effect of precipitate formation more measurements need to be done. Either the column influent and effluent could be analyzed for inorganic, such as anions (carbonate – CO$_3^{2-}$, bicarbonate – HCO$_3^-$ (alkalinity), nitrate – NO$_3^-$, nitrite – NO$_2^-$, sulphate – SO$_4^{2-}$, chloride – Cl$^-$, and silica – SiO$_2$(OH)$_2^{2-}$ or SiO(OH)$_3$), cations (Ca$^{2+}$,
Mg\textsuperscript{2+}, Na\textsuperscript{+}, Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Mn\textsuperscript{4+} and K\textsuperscript{+}) or the precipitate type formed in the column [3, 14].

The results of researches carried out at NAS Moffett Field and at Lowry AFB [3] show similar trends of pH and ORP changes. At NAS Moffett Field the groundwater pH rose from 7.0 to 10.9 and the ORP dropped from 134 to -821 mV in the iron, and at Lowry AFB the groundwater pH rose similarly from 6.9 to 11.5 and ORP dropped from -13 to -725 mV in the iron. DO concentration in groundwater at NAS Moffett Field dropped from 0.7 to 0.4 mg/dm\textsuperscript{3}. At both sites most of the dissolved calcium, iron, magnesium, manganese, sulphate, nitrate, and dissolved silica were removed from the groundwater flowing through the reactive barrier. Levels of alkalinity and dissolved solids were considerably reduced [3]. These constituents are likely to have precipitated out in the PRB, what confirms that problem connected with precipitate formation in zero-valent iron Fe\textsuperscript{0} may arise.

To reduce PRB costs to a minimum, the zero-valent iron should be able to maintain its reactivity and hydraulic conductivity over time. So, in order to meet these conditions:

- the hydraulic conductivity of the reactive material should be a few times higher than hydraulic conductivity of aquifer. This solution may prevent blocking up of the reactive barrier and breakdown of the whole system,

- the pyrite (or other material) could be used as a pre-treatment zone with gravel before the contaminated groundwater goes to the zero-valent iron zone. This solution may remove DO from water and prevent pH increasing [13].

In this part of paper the main observations from the hydrologic modeling carried out for evaluating dependence between the gate hydraulic conductivity and aquifer hydraulic conductivity in Funnel-and-Gate System of PRB Technology are described. In order to present this dependence, their influence on Darcian velocity within the gate and on hydraulic capture zone width was characterized. In this section:

- Figure 7 shows the dependence between the Darcian velocity within the gate (v) and aquifer hydraulic conductivity (k\textsubscript{aq}),

![Fig. 7. The Darcian velocity within the gate as a function of different value of aquifer hydraulic conductivity](image)

- Figure 8 shows the dependence between the Darcian velocity within the gate (v) and gate hydraulic conductivity (k\textsubscript{gate}),
Figure 9 shows the dependence between the hydraulic capture zone width \( z \) and hydraulic conductivity of the gate \( k_{\text{gate}} \), and hydraulic conductivity of the aquifer \( k_{\text{aq}} \).

![Graph showing hydraulic capture zone width as a function of different values of gate and aquifer hydraulic conductivities.](image)

Fig. 9. The hydraulic capture zone width as a function of different values of: a) gate hydraulic conductivity, b) aquifer hydraulic conductivity.

The graphs presented in Figures 7, 8, 9 came from some variant of the simulation on the model, because it was difficult to present all results in the paper. It was decided to do so because the results achieved from the rest of the simulations are similar i.e. the curves (the dependence) are the same but the values of the parameters are different.

In accordance with the equation 10 (Darcy’s law) the groundwater velocity (Darcian) in aquifer is rising when hydraulic conductivity of aquifer is rising for the conditions that hydraulic gradient is constant.

\[
v = -k \frac{\Delta H}{\Delta x} = -kI
\]  

(10)
where:

- $v$ – Darcian flux (velocity) [m/s],
- $\Delta H$ – head difference [m],
- $k$ – hydraulic conductivity [m/s],
- $x$ – length difference [m],
- $I$ – hydraulic gradient.

In the model on which the simulations for assessing the dependence between Darcian velocity within the gate and aquifer hydraulic conductivity were carried out (Fig. 7) the following data were used:

- the value of aquifer hydraulic conductivity amounted for each simulation to $1 \times 10^{-6}$ m/s, $2.5 \times 10^{-6}$ m/s, $5 \times 10^{-6}$ m/s, $1 \times 10^{-5}$ m/s, $2.5 \times 10^{-5}$ m/s, $5 \times 10^{-5}$ m/s, $7.5 \times 10^{-5}$ m/s, $1 \times 10^{-4}$ m/s, $2.5 \times 10^{-4}$ m/s, $5 \times 10^{-4}$ m/s respectively,
- the hydraulic gradient amounted to 0.2%,
- the gate width amounted to 10 m,
- the gate hydraulic conductivity had the same value as the aquifer hydraulic conductivity in particular simulation,
- the distance between the PRB system and the source of contaminants amounted to 35 m.

Groundwater velocity within the gate was estimated using two tools:

- Modpath module – by measuring distance that a particle covers during defined time,
- Zone Budget module – by calculating the water discharge through the gate and measuring the lateral area of the gate.

In Figure 7 it can be noticed that the velocity within the gate is rising when aquifer hydraulic conductivity ($k_{aq}$) is rising for the conditions that hydraulic gradient is constant. That is why it may be said that the groundwater velocity within the gate is strictly correlated with aquifer hydraulic conductivity and thus with the velocity in the aquifer. Moreover, on the basis of hydrologic modeling, it was noticed that due to directing a large amount of water through the much smaller cross sectional area of the gate, groundwater velocity within the gate is higher than velocity in other places of the model (velocity in the aquifer).

The gate hydraulic conductivity ($k_{gate}$) influences the velocity within the gate as well. However, on the basis of Figure 8 it can be said that this influence was not as big as when the aquifer hydraulic conductivity was changing. Moreover, after reaching some value of gate hydraulic conductivity the velocity within the gate rose very slowly. This dependence was strictly connected with the value of aquifer hydraulic conductivity. In the model by means of which the results presented in Figure 8 were achieved the following data were used:

- the aquifer hydraulic conductivity amounted to $1 \times 10^{-4}$ m/s,
- the hydraulic gradient amounted to 0.2%,
- the gate width amounted to 14 m,
- the value of gate hydraulic conductivity amounted for each simulation to $1 \times 10^{-5}$ m/s, $2.5 \times 10^{-5}$ m/s, $3.5 \times 10^{-5}$ m/s, $5 \times 10^{-5}$ m/s, $5.5 \times 10^{-5}$ m/s, $6 \times 10^{-5}$ m/s, $7.5 \times 10^{-5}$ m/s, $1 \times 10^{-4}$ m/s, $1.5 \times 10^{-4}$ m/s respectively,
- the distance between the PRB and the source of contaminants amounted to 35 m.

For Funnel-and-Gate System, the funnel part of the design is engineered to com-
pletely encompass the path of the contaminant plume and the overall design must prevent the contaminant plume from flowing around the treating zone in any direction [9]. For this configuration, hydraulic capture zone width appears to be most sensitive to funnel width [2], however, gate width and hydraulic conductivity of aquifer and gate have also some influence on hydraulic capture zone width. According to Figure 9, the hydraulic capture zone width (and the discharge through the gate) increased with the rise in hydraulic conductivity of aquifer and gate for constant value of funnel and gate width. So the change in groundwater velocity within the gate presented in Figures 7 and 8 due to changing in hydraulic conductivity of aquifer and gate had influenced hydraulic capture zone width as well.

In the model by means of which the results presented in Figure 9a were achieved the following data were used:

- the aquifer hydraulic conductivity amounted to $6 \cdot 10^{-5}$ m/s,
- the hydraulic gradient amounted to 0.08%,
- the gate width amounted to 20 m,
- the value of gate hydraulic conductivity amounted for each simulation to $6 \cdot 10^{-5}$ m/s, $8 \cdot 10^{-5}$ m/s, $1 \cdot 10^{-4}$ m/s, $1.5 \cdot 10^{-4}$ m/s, $2.5 \cdot 10^{-4}$ m/s, $3 \cdot 10^{-4}$ m/s, $4 \cdot 10^{-4}$ m/s, $5 \cdot 10^{-4}$ m/s, $7.5 \cdot 10^{-4}$ m/s, $1 \cdot 10^{-3}$ m/s, $2.5 \cdot 10^{-3}$ m/s, $5 \cdot 10^{-3}$ m/s respectively,
- the distance between the PRB and the source of contaminants amounted to 35 m.

In the model by means of which the results presented in Figure 9b were achieved the following data were used:

- the value of aquifer hydraulic conductivity amounted for each simulation to $1 \cdot 10^{-6}$ m/s, $2 \cdot 10^{-6}$ m/s, $3 \cdot 10^{-6}$ m/s, $5 \cdot 10^{-6}$ m/s, $7.5 \cdot 10^{-6}$ m/s, $1 \cdot 10^{-5}$ m/s, $2.5 \cdot 10^{-5}$ m/s, $5 \cdot 10^{-5}$ m/s, $7.5 \cdot 10^{-5}$ m/s, $1 \cdot 10^{-4}$ m/s, $2.5 \cdot 10^{-4}$ m/s, $5 \cdot 10^{-4}$ m/s respectively,
- the hydraulic gradient amounted to 0.08%,
- the gate width amounted to 20 m,
- the gate hydraulic conductivity amounted to $5 \cdot 10^{-3}$ m/s,
- the distance between the PRB and the source of contaminants amounted to 35 m.

Hydraulic capture zone width was estimated using Modpath module by measuring the width of all particles that would flow through the gate.

The simulations, whose results are presented in Figure 9, show that aquifer hydraulic conductivity had bigger impact on hydraulic capture zone width than gate hydraulic conductivity. In the case of gate hydraulic conductivity being constant, the higher value of aquifer hydraulic conductivity caused quick and continuous increase in hydraulic capture zone width, while increase in gate hydraulic conductivity caused limited increase in hydraulic capture zone width for constant aquifer hydraulic conductivity.

In accordance with Figure 9, it can be also claimed that when the value of gate hydraulic conductivity was six times higher than the aquifer hydraulic conductivity, the change in hydraulic capture zone width was very small. Hence, according to hydrologic modeling presented in the paper, when it is going to increase hydraulic capture zone width by increasing in gate hydraulic conductivity, this value should be only six times higher than aquifer hydraulic conductivity.

To sum up, hydraulic capture zone width can be controlled by changing the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity ($k_{\text{gate}}/k_{\text{aq}}$). While aquifer hydraulic conductivity is constant the gate hydraulic conductivity is the only parameter that may be changed. Moreover, according to the presented simulation, the ratio
of $k_{\text{gate}}/k_{\text{aq}}$ should amount to six because the hydraulic capture zone width hardly changes at all above this value.

Unfortunately, due to different processes in zero-valent iron, the precipitate formation in it may reduce the reactivity of this material and the hydraulic conductivity of the reactive gate. So, incorporation of adequate safety factor (larger size of iron grain) into the PRB is one of the ways of achieving satisfactory hydraulic performance. Taking this factor into account, the gate hydraulic conductivity should be higher than followed from presented hydrologic modeling. In accordance with some of the designers of PRB, the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity should amount to 10 [1, 2]. This exact value was used by designers to achieve certainty that reduction in gate hydraulic conductivity would not impact the hydraulic capture zone width when the ratio of $k_{\text{gate}}/k_{\text{aq}}$ drops below 6, at which point $k_{\text{gate}}$ becomes an increasingly sensitive parameter. It should be explained here that using larger size of grain of iron (and in this way larger gate hydraulic conductivity) than needed it is not proper for PRB efficacy, because the reactivity of the used medium decreases as a result of lower surface contact of contaminants with the zero-valent iron.

CONCLUSIONS

1. The pH, ORP and DO are inorganic parameters that give important information about the potential of precipitate formation in reactive barrier filled with zero-valent iron and are easily monitored during column tests. As contaminated water moved through the column presented in the paper, it underwent radical geochemical changes, including a reduction in ORP and DO from 332 mV and 8.24 mg/dm$^3$ to minus 12 mV and 5.42 mg O$_2$/dm$^3$ respectively, and an increase in pH from 6.21 to 7.47. In order to confirm that precipitate arose and it might affect the reactivity and hydraulic performance of the PRB, the change in inorganic constituents could be noted between the influent and effluent end of the column.

2. One of the main parameters of concern when designing a PRB is hydraulic capture zone width. It increases or decreases as the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity increases or decreases, respectively. The aquifer hydraulic conductivity is constant, thus, when it is going to increase the hydraulic capture zone width for Funnel-and-Gate System, it is important to increase in the gate hydraulic conductivity up to the value six times higher than aquifer hydraulic conductivity (according to presented hydrologic modeling).

3. As a result of studies presented in the paper it may be said that incorporation of adequate safety factor (larger size of iron grain) into the PRB is one of the ways of ensuring its efficacy and longevity. This factor (the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity) should amount to 10.

REFERENCES


ENSURING PERMEABLE REACTIVE BARRIER EFFICACY AND LONGEVITY


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ZAPEWNIEŃIE SKUTECZNOŚCI I DŁUGOTRWAŁOŚCI DZIAŁANIA TECHNOLOGII PRB

Technologia przepuszczalnych reaktywnych barier (PRB) należy do metod remediacji wód gruntowych. W technologii tej zanieczyszczenia usuwane są bezpośrednio w warstwie wodonośnej poprzez przepływ skażonego strumienia wód gruntowych przez wypełnioną odpowiednim materiałem (aktywnym) barierę aktywną.

W artykule przedstawiono problemy związane z tworzeniem się osadów w żelazie metalicznym stosowanym jako materiał aktywny technologii PRB. Osady te mogą zmniejszać aktywność materiału i jego zdolność filtracyjną. Tworzeniu się osadów mogą towarzyszyć zmiany pH, potencjału redox oraz stężenia tlenu. Zmiany te były obserwowane w badaniach laboratoryjnych przedstawionych w artykule. Ponadto w artykule przedstawiono i udowodniono następującą zasadę: aby zwiększyć skuteczność działania typu Funnel-and-Gate technologii PRB przez zwiększenie szerokości strefy oczyszczania, stosunek współczynnika filtracji materiału aktywnego do współczynnika filtracji warstwy wodonośnej (k_{gate}/k_{aq}) powinien przyjąć wartość 6. Ze względu na tworzenie się osadów w żelazie metalicznym, które mogą zmniejszać jego zdolność filtracyjną, założono jednak, iż stosunek ten powinien wynosić 10. Wartość ta daje pewność, że zmniejszenie się wartości współczynnika filtracji materiału aktywnego na skutek tworzenia się osadów, nie wpłynie w znaczący sposób na szerokość strefy oczyszczania. Przedstawione rozwiązanie może zapewnić skuteczne i długotrwałe oczyszczanie wód gruntowych w typie Funnel-and-Gate technologii PRB.

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Keywords: Lake, meromixis, conductivity, organic matter, nitrogen, phosphorus.

Abstract: Studied was a small (4.6 ha) meromictic lake situated in a deep land hollow surrounded by a high-inclination slope. The lake was made shallower two times (from 20 to 18 m) by collapsed shores. It is fed by underground waters and has relatively constant outflow. Limited water dynamics reduced the epilimnion thickness (from 4 to 2 m) and influenced the monimolimnion setting below 13 m depth with a characteristic small (0.2°C) temperature increase in the vertical profile and a permanent deoxygenation of the water below 7–11 m depth. The relationship between the organic matter parameters BOD and COD-Mn before the shore collapse revealed the dominance of matter produced in the reservoir. In the final period the situation was opposite. In the monimolimnion allochthonous matter accumulated which due to anaerobic decomposition generated large amounts of ammonium. Observed in the same water layer was also a decrease of the conductivity.

INTRODUCTION

Meromictic lakes, characteristic for limited water dynamics, make a small but expanding group of water reservoirs. Usually, they are situated in land hollows and surrounded by obstacles hindering wind access to the water table. Typically they freeze late and long lasting summer stratification sets on quickly.

There are many reasons for meromixis [5], yet the main factor fostering this phenomenon is the lakes morphometry. Crucial is the role of small surface area related to depth, expressed by the high value of the relative depth index [4]. Water dynamics is further limited by increased primary production and the resultant accumulation of decomposition products in the near-bottom water layers, inflow of salty spring waters on the lake bottom or waste water disposal.

In Poland, meromixis has been recognized in a little more than ten reservoirs [18], including Lake Zapadłe [19, 20]. Localization of this lake is the reason for reduced exposure to wind activity [13] and therefore for the diminished intensity of water circulation in the lake.

The aim of this study was to examine the selected physicochemical parameters of water collected over 16 years of research and to confirm the meromictic character of Lake Zapadłe.
MATERIAL AND METHODS

Lake Zapadłe is located in the Mazurian Lakeland, the Ostróda region, approx. 2 km east of the Łukta village. The main morphometry characteristics [16] are shown in Table 1.

Table 1. Selected morphometry characteristics of Lake Zapadłe [16]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water table ordinate</td>
<td>87.9</td>
</tr>
<tr>
<td>(m above the sea level)</td>
<td></td>
</tr>
<tr>
<td>Water table surface [ha]</td>
<td>4.6</td>
</tr>
<tr>
<td>Maximal depth [m]</td>
<td>18</td>
</tr>
<tr>
<td>Mean depth [m]</td>
<td>10.7</td>
</tr>
<tr>
<td>Relative depth</td>
<td>0.084</td>
</tr>
<tr>
<td>Maximal length [m]</td>
<td>275</td>
</tr>
<tr>
<td>Maximal width [m]</td>
<td>225</td>
</tr>
<tr>
<td>Volume [thousand m$^3$]</td>
<td>494</td>
</tr>
</tbody>
</table>

The lake is a typical postglacial melt-out reservoir. Two periods should be pointed out in its history: the first when backward erosion by the outflowing stream lowered the water table by a few meters and the second, in spring 2000, when the activity of beavers lowered the water table by 2.2 m (with parallel water surface area reduction from 5 ha to 4.6 ha). Beavers keep on being active in that area with the evidence observed many times during the field studies.

Near Zapadłe, a Lake Isąg can be found which is currently set 7 m higher. Although located in another drainage basin, it affects Lake Zapadłe in a particular way – heavy water leaking from Isąg causes ongoing shoreline destruction in Lake Zapadłe. This high input of underground waters is the reason why even at the low or periodical surface inflow Zapadłe sustains a relatively constant outflow of 30 dm$^3$·s$^{-1}$ on the average.

The lake bowl sits in a deep land hollow. The northern, western and southern shores form steep and high slopes (approx. 20 m height) covered with an old tree stand. Total drainage basin of the lake is 185.9 ha with the dominance of arable land (62%) and forests (35%). Two other lakes – Zarośnięte and Polne – occupy 3% of the area. The drainage basin draining directly to the lake is rather small, i.e., 9.4 ha and in 70% afforested. The rest of the area is cultivated land.

In this paper are presented the results of the research done in 1990–1993 and 2001–2002 (bimonthly in average). The water samples were collected four times from June 2005 to November 2006 in all seasons of lacustrine year. Water samples for the complete chemical analyses were taken from the surface layer (1 m) and at 5, 10, 12, 15 and 17 m depth, over the deepest site in the lake determined with the help of the bathymetric chart and GPS. Additionally, each time a temperature/oxygen profile was done based on the readings from every meter of the depth. Water samples were taken using 3.5-l Ruttner apparatus with an in-built mercury thermometer (0.2°C accuracy). Chemical analyses were conducted in accordance with the methods by Hermanowicz et al. [6].
RESULTS AND DISCUSSION

The distinctive feature of meromictic lakes is the lack of complete water turnover in spring and autumn that affects temperature settings in the lake (Fig. 1). In the vertical temperature profile observable is an increase towards the bottom [18]. The same tendency has been quite regularly observed in the discussed lake. At the end of the study period a small (0.2°C) characteristic temperature increase was observed between 12 and 13 m depth (June 2005) or slightly higher between 11 and 12 m depth (May 2006). On that ground, the water layer below 13 m depth was determined as the monimolimnion. Incomplete water mixis caused small temperature oscillations in the near-bottom water layers: in the range of 5.8–6.2°C at the beginning of the study and 5.2–6.3 after the water table dropped. Another outcome of the incomplete water circulation was the temperature decrease in the hypolimnion. The mean values of this parameter decreased from 6.1–6.6°C at the beginning of the research period to 5.2–5.8°C in 2005–2006. Over the years, also the epilimnion thickness has diminished. In 1990 and 1991 it was 3–4 m deep, whereas at the end of the study the thickness varied between 1 and 2 m. The main obstacle for the water exchange between the epi- and hypolimnion was the metalimnion, varying throughout the research with regard to thickness and location (4–8 m in the 1990s, 2–4 m currently). Primarily, the maximum temperature gradient was deeper, i.e., in August 1990 it was between 4 and 5 m depth and equaled 3.8°C, whereas since 2000 it has been always between 2 and 3 m. The highest temperature gradient was noted in July 2001 and it amounted to 6.4°C.

Limited water dynamics is a result of insufficient wind sheer stress on the water surface which is due to the lakes localization and enclosure by high slopes. Equally important is the relationship between the vertical and horizontal dimensions of the lake expressed as relative depth index. The relative depth, according to Halbfass, calculated for the max. depth of 20.2 m (before 2000) was 0.0993. After the shores had collapsed and the max. depth diminished the value of the index remained high (0.0839) and only a little lower than those quoted by Choiński [2] as the extreme values for the lakes of the Mazurian Lakeland.

Poor water circulation affected the oxygenation (Fig. 2). Spring turnover transferred the gas down to 8–10 m depth while the autumn circulation, even at full homothermy (28 Nov 06), to the depth of 7–11 m. The winter research (22 Jan 02, 23 Feb 06) revealed oxygen deficits, most likely caused by the decay of organic matter accumulated in the lake [15].

The quantity of organic matter can be estimated on the ground of the BOD$_5$ and COD-Mn measurements (Fig. 3). At the end of the research (2005–2006), the BOD$_5$ values below the depth of 15 m ranged from 7.5 to 8.1 mg O$_2$·dm$^{-3}$, while COD-Mn was higher: 7.4–12.2 mg O$_2$·dm$^{-3}$ at 15 m and 10.1–12.8 mg O$_2$·dm$^{-3}$ in the deepest layer (Tab. 2). The relationship between these parameters indicates the dominance of the matter imported to the lake over the autochthonous matter which seems rather obvious provided that the lake is a through-flow reservoir, the steep shores are strongly eroded, water permeates from the nearby Lake Isąg, and the way of the drainage basins use. An opposite situation had been observed before the shores collapsed in the spring 2000. The parameters of organic matter, both allo- and autochthonous, were higher and the relationship showed obvious dominance of the substance produced in the lake.
Fig. 1. Summer temperature profiles in the waters of Lake Zapadłe at the start and at the end of the research

Fig. 2. Summer oxygen profiles in the waters of Lake Zapadłe at the start and at the end of the research
Conductivity, the measurement commonly practiced in hydrochemical studies, provides information about water mineralization in relation to its feeding structure and participation of the underground alimentation [10, 11]. High values of this parameter (in the discussed lake from 440 to 484 μS·cm⁻¹) are typical for lakes fed from underground sources (in the discussed case – water percolation from Lake Isąg) and for lakes serving long time as recipients of the heavily polluted waters.

Vertical distribution of this parameter at the beginning of the research revealed no characteristic increase in the monimolimnion. An obvious increase was noted only in the deepest water layer (2-m thick) and was best observable in November 1996. In the final years, stratification of the conductivity was evident (and high concentration gradients of all examined chemical compounds), confirming a chemocline occurrence between 14 and 15 m depth.

The quantity of ions increasing along with the increasing depth is the reason for the water density changes, irrespective of the temperature. In the monimolimnion typical is the high content of dissolved gases and mineral compounds. They are characteristic for high density and even if the surface layers are considerably cooler homothermy does not occur and the density caused by the chemical factors becomes an obstacle for the settling and theoretically heavier water [14]. Conductivity in a stable monimolimnion may be about 3 times higher than in the other layers [3]. Lange [9] reported that conductivity distribution has practically no effect on the density stratification and therefore in the freshwater (characteristic for the generally low internal mineralization) studies, with sufficient accuracy, density can be considered a function of temperature. However, the studies of meromictic lakes have shown that thermal stability of water is to a large extent enhanced by chemical stability [22] which can be regarded as both the effect and the reason for
the difficulty in water circulation. In the discussed case, there is only scarce information available regarding this parameter in the early phase of the research. In 1996, before the sequent shore collapse and the resultant depth reduction, in the layer below 15 m depth the values ranged from 502 to 807 µS·cm⁻¹. Such values allowed for classifying the lake as high-conductivity reservoir [7].

Table 2. Variability ranges of the selected chemical parameters of the Lake Zapadle waters at the start and at the end of the research

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>BOD₃ [mg O₂·dm⁻³]</td>
<td>1.02–18.7</td>
<td>1.9–3.4</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>1.0–15.9</td>
<td>1.3–2.6</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>11.0–24.6</td>
<td>4.0–5.1</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>16.4–42.4</td>
<td>7.5–8.1</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>21.4–53.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>COD-Mn [mg O₂·dm⁻³]</td>
<td>6.1–14.9</td>
<td>4.6–7.4</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>6.1–12.5</td>
<td>4.8–9.0</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>7.5–21.1</td>
<td>7.4–12.2</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>9.6–16.8</td>
<td>10.1–12.8</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>10.6–25.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mineral phosphorus [mg P·dm⁻³]</td>
<td>0.01–0.627</td>
<td>0.039–0.353</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.248–0.759</td>
<td>0.329–0.576</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.581–1.139</td>
<td>0.570–1.125</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.772–1.427</td>
<td>0.623–1.894</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.594–1.706</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total phosphorus [mg P·dm⁻³]</td>
<td>0.023–0.643</td>
<td>0.147–0.420</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.297–0.789</td>
<td>0.441–1.303</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.676–1.725</td>
<td>1.206–1.498</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.894–1.597</td>
<td>1.297–1.967</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>1.161–2.178</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium nitrogen [mg N-NH₄·dm⁻³]</td>
<td>0.00–0.86</td>
<td>0.00–0.58</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.41–1.6</td>
<td>0.005–0.85</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.94–5.29</td>
<td>1.23–4.03</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>2.09–6.66</td>
<td>1.51–5.99</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>3.53–12.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrate(V) nitrogen [mg N·dm⁻³]</td>
<td>no data</td>
<td>0.005–0.247</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.00–0.12</td>
<td>0.142–0.146</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.00–0.35</td>
<td>0.006–0.183</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.11–0.31</td>
<td>0.028–0.071</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.00–0.45</td>
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</tr>
</tbody>
</table>

A vertical profile with an increase of the values in the metalimnion, like in the discussed case, is typical for fertile lakes. Fertility of a lake can be assessed on the ground of the content of nutrients: nitrogen and most of all – phosphorus. Anaerobic conditions in the deepest layers of Lake Zapadle (Fig. 2) stimulated phosphorus release from the bottom sediments [12]. Wiśniewski and Planter [23] reported that phosphorus released from the bottom sediments in winter is not precipitated during the spring turnover and almost completely feeds the summer epilimnion thus contributing to the primary production development during the vegetative period. An example is the high-significance relationship
between the circulating phosphorus content and the visibility and the chlorophyll a concentration during the summer stagnation observed in many lakes, including the meromictic Lake Starodworskie [17].

Phosphorus is the limiting element when P/N ≤ 20. In Lake Zapadłe the value was approximately 3. According to Chełmicki [1], the concentration higher than 0.005 mg P·dm⁻³ accelerates the development of algae. Intensive phosphorus uptake by plants occurs in parallel with the favorable abiotic conditions, like light and temperature. In the discussed lake such situation was observed in the last study years, from May to November, when the average concentration of this ion down to 10 m depth equaled 0.281 mg P·dm⁻³ [15] and was lower than 0.317 mg P·dm⁻³ measured at the start of the research (1991–1993). In the surface water layers mineral phosphorus was present throughout the whole study reaching the maximum levels in the early 1990s (0.297–0.627 mg P·dm⁻³).

With regard to mineral nitrogen forms, the highest measured concentrations were of the ammonium nitrogen. Like in the case of other components, its vertical stratification was obvious and the considerable increase of the concentration occurred below 14 m depth. It proves that organic matter accumulates in this water layer [18] and undergoes anaerobic decomposition. Kracht [8] explained the increase of ammonium nitrogen by its additional release from the oxygen-free bottom sediments, such as the conditions observed in the deepest waters throughout the research. According to Chełmicki [1] ammonium nitrogen can also enter the lake directly from the drainage basin. Its absence or small amounts detected in the mixolimnion reflect good oxygenation of this water layer, as confirmed by nitrate(V) nitrogen content. Occurrence of nitrate(V) nitrogen in the surface layers is an effect of the nitrification, contributing to the utilization of carbon dioxide and to alkalinity reduction. It may also be caused by the nitrogen pollution from soil fertilization in the drainage basin [3, 21] or come from the nearby Lake Isąg through water filtration.

CONCLUSIONS

The conducted observations have revealed stabilization of the meromixis qualities in Lake Zapadłe.

High temperature gradients at the epi/metalimnion interface hinder circulation of the lake water. Thickness of the epilimnion has been clearly reduced over the study period.

Vertical distribution of temperature and conductivity indicates the setting of a monimolimnion below 13 m depth. The high chemical gradients between 14 and 15 m depth are the evidence for a chemocline occurrence at this depth.

Throughout the study, the conductivity and mineral nitrogen have decreased in the deepest water layers whereas phosphorus concentrations increased.

Water deoxygenation in the winter and the values of organic matter parameters are a sign of the high fertility of the lake.

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Badaniem objęto niewielkie (4,6 ha) jezioro meromiktyczne, położone w silnym zagłębieniu terenu i otoczone skarpacej o znacznym nachyleniu. Na skutek zawałalania się brzegów zbiornik ten dwukrotnie uległ spłyceniu (z 20 do 18 m). Jest on zasilany wodami podziemnymi, posiada także stosunkowo stały odpływ. Ograniczona dynamika wód skutkowała spłyceniem warstwy epilimnionu (z 4 do 2 m), wytwarzaniem monimolimnionu poniżej 13 m głębokości z charakterystycznym niewielkim (0,2°C) wzrostem temperatury w profilu pionowym oraz stałym odlenieniem wód poniżej 7–11 m. Stosunek wskaźników materii organicznej (BZT i ChZT-Mn) przed zawałaniem brzegów jeziora świadczy przewadze materii produkowanej w zbiorniku, w ostatnim okresie obserwowano sytuację odwrotną. W monimolimnionie nastąpiło nagromadzenie materii allochtonicznej, a jej bezłenowy rozkład powodował powstawanie znacznych ilości amoniku. Stwierdzono także spadek wartości przewodnictwa elektrolitycznego w tej partii wód.
IMPACT OF THE SMALL WATER RESERVOIR PSURÓW ON THE QUALITY AND FLOWS OF THE PROSNA RIVER

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Keywords: Small water reservoir, river, water quality, eutrophication, water flows.

Abstract: The paper presents a small water reservoir Psurów located on the Prosna River (right tributary of the Warta River) in the Opolskie Voivodeship (southern Poland). Results of water quality analyses of the Prosna River flowing into the reservoir and the outflowing water, as well as water stored in the reservoir have been discussed. Water flows of the Prosna River above and below the Psurów reservoir were analyzed. The analyses were carried out from November 2006 to October 2008. The following water quality indicators were measured: PO$_4^{3-}$, NO$_3^-$, NO$_2^-$, NH$_4^+$, BOD$_5$, DO, water temperature, pH, electrolytic conductivity, TSS and chlorophyll a, for which basic descriptive statistics was calculated. The research showed that the small water reservoir Psurów contributed to the reduction of the following loads: phosphates (by about 21%), nitrates (by 26%), nitrites (by 9%), ammonia (by 5%) and total suspended solids (by 17%). It was found out that there was a statistically significant relationship (p < 0.05) between the volume of water flowing out of the reservoir and the inflowing water (Pearson’s correlation coefficient: r = 0.93). Based on the Vollenweider’s criterion the Psurów reservoir was classified to polytrophic reservoirs.

INTRODUCTION

Small water reservoirs are the main elements of the so called “small retention”. They fulfill many economic functions, protect against flood and contribute to the increase of water resources [4, 20, 21, 31]. Separating the river valley with a dam and building a water reservoir may have various impacts on the reservoir surroundings, its bed and the river valley below. Quite important is also the knowledge of the reservoir’s impact on flows and quality of water in the reservoir and below the structure [14, 19, 33]. Small water reservoirs are usually located in agricultural catchments. Since the reservoirs are built in the lowest part of the catchment they become the place where all pollutants from the catchment accumulate.

According to many authors [9, 15, 16, 31] the catchment is an element of the reservoir’s hydrological regime, which determines the quality of water and its trophy. According to Galicka et al. [8] breaking the river continuity with a stage of fall contributes to the reduction of water lift force, intensifying sedimentation processes and retention even up to 90% of the load. A considerable amount of biogenic substances is also accumulated, particularly organic and inorganic compounds of nitrogen and phosphorus, as well as
many other pollutants. This may deteriorate the quality of water stored in the reservoirs, cause their eutrophication or silting [23–25, 29, 31, 34].

Such phenomena may disturb proper operation of the reservoirs and enable fulfilling the assumed functions. According to the Water Framework Directive (2000) [7] the following actions are required in the field of surface water protection: prevention from deterioration of all water bodies, protection and enhancement of all artificial and heavily modified bodies of water in order to achieve good ecological potential and good surface water chemical status, protection and remediation of water bodies, etc. [3, 7]. Depending on the pollutant load flowing into the reservoir and its morphometry the dam reservoirs can capture up to several dozen per cent of the total amount of inflowing matter [17, 31, 32]. Small water reservoirs may also have a positive impact on intensification of self-purification of the flowing waters [5, 13, 28, 31, 32].

Only heavily polluted waters flowing into the small water reservoir can deteriorate the quality of the stored water [6, 31, 36, 37].

The aim of this paper is to analyze the impact of the small water reservoir Psurów on the quality and flows of the Prosna River flowing through the reservoir. The quality of water flowing into the reservoir, the outflowing water and water stored in the reservoir as well as flows of the Prosna River above and below the Psurów reservoir were analyzed.

**METHODS**

Psurów reservoir is located at 212.095 km of the Prosna River course in Olesno district, municipality of Radłów. It is one of nine small dam reservoirs in the Opolskie Voivodeship. The catchment in the dam section is 10.6 km². The reservoir was put into operation in 1996. The total capacity of the reservoir at the normal operational fill level is 63 000 m³ and the fill area – 4.58 ha. The average depth of the reservoir is 1.38 m. Characteristic flows of the Prosna River in the reservoir section are the following: average annual flow – 0.042 m³·s⁻¹, the lowest flow – 0.006 m³·s⁻¹, average low flow – 0.013 m³·s⁻¹. The main functions of the reservoir are: providing water for irrigation of arable land in the Prosna River valley, recreation and fishing [22, 32]. The reservoir catchment is used for agricultural purposes, including stock-farming.

The analyses of water flowing into the reservoir, water stored in the reservoir and the outflowing water were carried out from November 2006 to October 2008. Samples were collected in 3 sampling points once a month (except for January 2007 when the analyses were not made at all). The sampling point no 1 (P1) was located in the Prosna River about 300 m above its inlet to the reservoir. Sampling point no 2 (P2) was situated in the reservoir, at the dam, whereas point no 3 (P3) was at the outlet from the Psurów reservoir, 15 m below the dam (Fig. 1).

At the inlet and outlet of the reservoir water was collected from the mainstream at the subsurface layer of water. In the reservoir water was collected at the depth of 0.3 m under the water table. At all sampling points the following water parameters were determined: phosphates, nitrates, nitrites, ammonia, BOD₅, dissolved oxygen (DO), temperature, pH, electrolytic conductivity and total suspended solids (TSS). Additionally in the summer season 2007 and 2008 chlorophyll a was determined. Chlorophyll assay was made by the Voivodeship Inspectorate of Environmental Protection in Opole, according to PN-86/C-05560/02 standard. Water pH, electrolytic conductivity and temperature
were measured *in situ*, whereas other water quality analyses were made in a laboratory according to Polish standards [10]. At the sampling points P1 and P3 water flow rate was measured.

![Fig. 1. Location of sampling points and the Psurów reservoir on the Prosna River: P1 – the Prosna River – reservoir inflow, P2 – reservoir bowl, P3 – reservoir outflow](image)

To assess differences among water quality indicators for water flowing into the reservoir, stored water and the outflowing water the STATISTICA software was used. All statistical analyses were preceded by the Shapiro and Wilk’s W test for normality to check whether the analyzed variables were normally distributed [12].

The characteristics of physicochemical indicators and the impact of the reservoir on the quality of water flowing through the Psurów reservoir were determined for 2 hydrological years (1 November 2006 – 31 October 2008), for winter season (1 November – 30 April) and for summer season (1 May – 31 October).

A graphical comparison of the average values and deviations of phosphate, nitrate, ammonia, nitrite and TSS concentrations in water flowing into the reservoir (P1) and the outflowing water (P3) was presented.

To check the significance of differences between the average values of water quality indicators for water flowing into the reservoir and the stored water, as well as between the inflowing and outflowing water, a t-Student test was used for independent samples, at the significance level of \( p < 0.05 \). Hypotheses on the lack of statistically significant differences between the average values of the analyzed water quality indicators at particular sampling points were rejected.

Based on the average values of water quality indicators for the Prosna River flowing into and out of the Psurów reservoir, obtained in two research years and during hydrometric measurements made within two hydrological years, loads of pollutants [kg] flowing into and out of the reservoir were determined.

The potential risk of eutrophication of the Psurów reservoir was investigated. Therefore, calculations were made for the period of 2006–2008, based on the Vollenweider’s
criterion [30], in Benndorf’s modification [2], taking into consideration the concentration of phosphates and inorganic nitrogen in the water flowing into the reservoir (P1).

The quality of the Prosna River at the reservoir inlet and outlet, as well as for the water stored in the reservoir was assessed according to the Ordinance establishing the way of classifying the state of uniform parts of surface waters [27]. The assessment of eutrophication of the analyzed water was presented and its sensitivity to such pollutants as nitrogen compounds from agricultural sources was assessed according to the Ordinance [26].

RESULTS AND DISCUSSION

Statistical characteristics of physicochemical parameters of water flowing into the Psurów reservoir, water stored in the reservoir and the outflowing water is presented in Table 1.

Table 1. Quality of water flowing into the Psurów reservoir (P1), water stored in the reservoir (P2) and the outflowing water (P3) in the period of November 2006 – October 2008

<table>
<thead>
<tr>
<th>Index</th>
<th>Inflow to reservoir (P1)</th>
<th>Psurów reservoir (P2)</th>
<th>Outflow from reservoir (P3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minimum – maximum</td>
<td>annual mean – winter mean – summer mean</td>
<td></td>
</tr>
<tr>
<td>Phosphates [mg PO₄³⁻·dm⁻³]</td>
<td>0.038–0.59</td>
<td>0.014–0.97</td>
<td>0.015–0.57</td>
</tr>
<tr>
<td></td>
<td>0.292–0.232–0.348</td>
<td>0.240–0.144–0.328</td>
<td>0.240–0.157–0.316</td>
</tr>
<tr>
<td>Nitrates [mg NO₃⁻·dm⁻³]</td>
<td>5.50–79.00</td>
<td>0.18–62.00</td>
<td>2.30–62.00</td>
</tr>
<tr>
<td>Nitrites [mg NO₂⁻·dm⁻³]</td>
<td>0.01–0.43</td>
<td>0.003–0.36</td>
<td>0.029–0.30</td>
</tr>
<tr>
<td></td>
<td>0.165–0.177–0.154</td>
<td>0.145–0.184–0.111</td>
<td>0.154–0.181–0.129</td>
</tr>
<tr>
<td>Ammonia [mg NH₄⁺·dm⁻³]</td>
<td>0.011–0.578</td>
<td>0.026–0.656</td>
<td>0.038–0.75</td>
</tr>
<tr>
<td></td>
<td>0.158–0.247–0.077</td>
<td>0.155–0.195–0.119</td>
<td>0.157–0.188–0.128</td>
</tr>
<tr>
<td>BOD₅ [mg O₂·dm⁻³]</td>
<td>1.00–4.00</td>
<td>1.00–10.00</td>
<td>1.00–7.00</td>
</tr>
<tr>
<td>DO [mg O₂·dm⁻³]</td>
<td>7.07–9.82</td>
<td>6.09–17.11</td>
<td>6.85–11.39</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>2.00–16.50</td>
<td>1.30–24.30</td>
<td>1.30–23.80</td>
</tr>
<tr>
<td>Reaction – pH</td>
<td>6.90–8.60</td>
<td>6.90–9.80</td>
<td>6.90–9.30</td>
</tr>
<tr>
<td>Electrolytic conductivity [µS·cm⁻¹]</td>
<td>298.00–393.00</td>
<td>269.00–375.00</td>
<td>270.00–388.00</td>
</tr>
<tr>
<td>TSS [mg·dm⁻³]</td>
<td>0.00–340.00</td>
<td>0.00–280.00</td>
<td>2.00–200.00</td>
</tr>
<tr>
<td></td>
<td>70.74–108.8–35.8</td>
<td>50.17–60.36–40.83</td>
<td>62.14–65.7–59.17</td>
</tr>
</tbody>
</table>

Table 1 shows that in the water flowing into the reservoir (P1) the highest annual average concentrations of the analyzed indicators were observed for: phosphates, nitrates, nitrites, ammonia, electrolytic conductivity and total suspended solids. For other water
quality indicators such as BOD$_5$, dissolved oxygen, temperature, and pH the highest average annual concentrations were recorded for water stored in the reservoir (P2). In the outflowing water (P3) their concentrations were also higher than in the inflowing water.

From the analyses of the Prosna River flowing into the Psurów reservoir (P1) presented by Wiatkowski [32] it can be concluded that the highest average values of physicochemical parameters were recorded in the case of nitrates, phosphates, electrolytic conductivity and total suspended solids. Moreover, it can be noticed that at the sampling point located at the reservoir outlet (P3) the average concentrations of nitrates, ammonia, BOD$_5$ and water temperature were higher than at the sampling point P1 (reservoir inlet) [32].

Graphical comparison of average values and concentration ranges of phosphates, nitrates, ammonia, nitrites and TSS in the investigated waters from the Psurów reservoir area is presented in Figure 2.
Based on the above-mentioned graphical comparison it can be observed that the highest average concentrations were recorded at P1 for all water quality indicators, i.e. for nitrates, phosphates, ammonia, nitrites and total suspended solids. The higher average of nitrates, phosphates and nitrites corresponded with the lower variability of results, i.e. lower values of standard deviation. In the case of ammonia and total suspended solids the higher average corresponded with the higher value of the standard deviation, which indicates higher variability of results.

Concentrations of phosphates in the water flowing into the Psurów reservoir varied from 0.038 to 0.59 mg PO$_4^{3-}$·dm$^{-3}$, whereas in the outflowing water – from 0.015 to 0.57
mg $\text{PO}_4^{3-} \cdot \text{dm}^{-3}$ (Fig. 3). The highest concentrations of this substance in water at P1 sampling point were observed in June 2007 and at P2 – in June 2008. This might be associated with the removal of this element from arable lands during rainfall or with pouring manure onto the fields.

In the analyzed period the concentrations of nitrates in the inflowing water ranged from 5.50 to 79.0 mg $\text{NO}_3^- \cdot \text{dm}^{-3}$ and in the outflowing water – from 2.30 to 62.0 mg $\text{NO}_3^- \cdot \text{dm}^{-3}$. The highest values for nitrates at all sampling points (P1, P2 and P3) were recorded in winter months (March 2007 and 2008), whereas the lowest ones were observed in summer, during the vegetation period (July, August 2007, August 2008) [35] – Figure 4.
As far as other water quality indicators are concerned, i.e. nitrites, ammonia, electrolytic conductivity and the total suspended solids, it was observed that the highest concentrations at all sampling points were recorded in winter months (Tab. 1). The highest concentrations of BOD$_5$, water temperature and pH in the Prosna River flowing into the reservoir, water stored in the reservoir and the outflowing water were observed in summer months. In the case of dissolved oxygen the highest values in the inflowing water were recorded in summer, whereas at other sampling points – in winter.

The concentration of chlorophyll a in the water of the Psurów reservoir in 2007 varied from 15.8 µg·dm$^{-3}$ (18.07.2007) to 279.7 µg·dm$^{-3}$ (29.08.2007), whereas in 2008 it ranged from 39.0 µg·dm$^{-3}$ (06.07.2008) to 66.0 µg·dm$^{-3}$ (27.08.2007).

Out of 10 water quality indicators analyzed in the Psurów reservoir 8 (except for phosphates and nitrites) are taken into consideration in the water quality classification [27].

The analysis of the water quality of the Prosna River flowing into the reservoir (P1) and the water flowing out of the Psurów reservoir (P3) showed that the values of N-NH$_4^+$, BOD$_5$, water temperature, DO, electrolytic conductivity and water pH did not exceed the limit values of water quality indicators for uniform parts of surface waters in natural watercourses, such as rivers defined for class I. However, concentrations of N-NO$_3^-$ and the TSS exceeded the limit values of water quality indicators for uniform parts of surface waters in natural watercourses, such as rivers defined for class II [27]. The analysis of water stored in the Psurów reservoir (P2) showed that the values of chlorophyll a did not exceed the limit values of water quality indicators for uniform parts of surface waters in natural watercourses, such as lakes and other natural water reservoirs defined for class I [27].

The waters of the Prosna River flowing into and out of the Psurów reservoir were considered as eutrophic. At these sampling points the average annual concentration of nitrates exceeded the limit value (10 mg NO$_3^-$·dm$^{-3}$) of this indicator defined in the Ordinance [26]. A similar situation was in the case of chlorophyll a, the limit value of which – defined in the same Ordinance – was 25 µg·dm$^{-3}$. Moreover, the water quality analysis of the Psurów reservoir carried out in 2007 showed that the limit values of chlorophyll a were exceeded more than tenfold.

It was found out that the investigated waters were vulnerable to pollution by nitrogen compounds coming from agricultural sources because the average annual concentrations of nitrates were higher than the one recommended in the Ordinance (50 mg NO$_3^-$·dm$^{-3}$) [26].

The analysis of hydrometric parameters showed that in the period of 2006–2008 water flow rate at P1 sampling point ranged from 0.003–0.096 m$^3$·s$^{-1}$. The lowest water inflow was recorded in May 2007 and the highest in March 2007. At the sampling point P3 the water flow rate varied from 0.001–0.110 m$^3$·s$^{-1}$. The lowest outflow was observed in June 2007 and the highest one in March 2007. The average values of the water flow rate in the investigated period were: 0.029 m$^3$·s$^{-1}$ (P1) and 0.028 m$^3$·s$^{-1}$ (P3), respectively. This may be associated with the decrease of water resources in the reservoir catchment in comparison with the multi-year values determined empirically in the study [22]. The average annual discharge (SSQ) for the Psurów reservoir cited in the study was 0.042 m$^3$·s$^{-1}$.

The analysis of the relationship between the volume of water flowing into the reservoir (P1) and the water flowing out of the Psurów reservoir (P3), Pearson’s correlation coefficient ($r = 0.93$) and a linear regression equation were calculated: $P3 = -0.0043 +$
1.1072·P1, the parameters of which were determined in such a way as to minimize the sum of deviation squares. Between P3 and P1 a very high correlation was observed (0.7 < r < 1.0). This correlation is statistically significant at the significance level p < 0.05.

Among many factors having an impact on the reservoir environment the time required for a total exchange of water (i.e. water retention time) seems to be of great importance. It not only determines the hydrological state of the reservoir but also – together with the water mixing intensity – has an impact on the matter cycle in the reservoir, its trophy and the quality of the reservoir water [1].

The average retention time in the Psurów reservoir was assessed using the ratio of the reservoir capacity and the volume of water flowing into the reservoir (determined in the investigated period) [33]. The average water retention time in the Psurów reservoir in the analyzed period was 25 days. According to Wiatkowski et al. [31] the retention time in small dam reservoirs varies from more than one to several dozen days.

Based on the two-years’ research period the average loads of selected water quality indicators for the Prosna River water flowing into the Psurów reservoir and the outflowing water were calculated (Tab. 2).

Table 2. Changes in loads of phosphates, nitrates, nitrites, ammonia and total suspended solids [kg·d⁻¹] at sampling points P1 and P3 in the period of November 2006 – October 2008

<table>
<thead>
<tr>
<th>Index</th>
<th>Inflow to reservoir (P1)</th>
<th>Outflow from reservoir (P3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean – winter – summer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphates [kg P-PO₄³⁻]</td>
<td>0.236–0.282–0.149</td>
<td>0.186–0.196–0.107</td>
</tr>
<tr>
<td>Nitrites [kg N-NO₂⁻]</td>
<td>0.126–0.205–0.062</td>
<td>0.114–0.215–0.042</td>
</tr>
<tr>
<td>Ammonia [kg N-NH₄⁺]</td>
<td>0.311–0.733–0.080</td>
<td>0.295–0.570–0.106</td>
</tr>
</tbody>
</table>

Table 2 shows that after the flow of the Prosna River through the Psurów reservoir loads of pollutants decreased (phosphates by about 21%, nitrates by 26%, nitrites by 9%, ammonia by 5% and the total suspended solids by 17%). Such a significant decrease can be contributed to the absorption by primary producers (phytoplankton, macrophytes) and deposition in bottom sediments. The greatest decrease of nitrates and nitrites was observed in summer months (by about 50% and 32%, respectively), in the middle of water plant vegetation period. In the summer period (July and August) water blooms appeared in the Psurów reservoir, which rapidly and intensively decreased the concentrations of various forms of nitrogen. A similar situation was in the case of phosphate load reduction in the summer period (about 28%).

As far as the ammonia is concerned, its load in the water flowing out of the reservoir in comparison with the inflowing water increased in the summer season by 32% (from 0.080 kg·d⁻¹ to 0.106 kg·d⁻¹). In the outflowing water, if compared with the inflowing water a slight increase of nitrites was observed in the winter season (by about 5%) (Tab. 2).
In the case of total suspended solids a significant reduction (40%) was recorded in winter, whereas in summer it increased by about 30%.

Research carried out by Miernik described in [18] and carried out on a small reservoir Górny Młyn, near Końskie, in the Czysta River showed that in the water flowing out of this reservoir – in comparison to the inflowing water – the average loads of BZT, phosphates, ammonium nitrogen, nitrite nitrogen and nitrate nitrogen were lower by 9%, 51%, 99%, 68% and 81%, respectively. Similarly, the research carried out by Skonieczek and Koc [28] indicated that the small water reservoir (pond) effectively lowered phosphorus concentrations and phosphorus loads in the water of the Szabruk watercourse flowing through this pond. Generally, within the year loads of total phosphorus were reduced by 58% and phosphates P-PO$_4^{3-}$ by 60%.

In order to investigate the risk of eutrophication of the Psurów reservoir calculations were made for the period of 2006–2008. In Benndorf’s modification [2], following the Vollenweider’s criterion [30] and taking into consideration the fact that the phosphate concentration in the reservoir cross-section is 0.292 mg PO$_4^{3-}$·dm$^{-3}$ (Tab. 1), it was found out that the amount of phosphorus per 1 m$^2$ of the reservoir is 1.86 g P-PO$_4^{3-}$·m$^{-2}$·a$^{-1}$ at the ratio of average reservoir’s depth – 1.3 m to the retention time – 0.069 a. The load of inorganic nitrogen per 1 m$^2$ of the reservoir is 138 g N·m$^2$·a$^{-1}$. According to Kajak [11] the real loads are usually much higher than the dangerous ones. They may reach up to more than ten grams of phosphorus and almost 200 g of nitrogen annually per 1 m$^2$ of the reservoir’s surface. This exceeds hundred times the dangerous loads level for reservoirs of the depth up to 5 m (2.0 g N·m$^2$·a$^{-1}$ and 0.13 g P·m$^2$·a$^{-1}$). Therefore, the Psurów reservoir was classified for polytrophic reservoirs. The calculations, however, referred only to phosphorus and nitrogen supplied by inflows, the direct catchment or internal load from sediments were not taken into consideration.

In order to determine differences between average values of water quality indicators for the inflowing water (P1) and water stored in the Psurów reservoir (P2), and between inflowing (P1) and outflowing water (P3), a t-Student test for independent samples was used, at the significance level $p < 0.05$. In Table 3 statistical significance of the differences in the analyzed physicochemical indicators for the inflowing water, water stored in the Psurów reservoir and the outflowing water was presented.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Statistical significance of the difference ($p &lt; 0.05$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphates [mg PO$_4^{3-}$·dm$^{-3}$]</td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>Summer</td>
<td>$p &lt; 0.05$ (tn)</td>
</tr>
<tr>
<td></td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Outflow from reservoir (P3)</td>
</tr>
<tr>
<td></td>
<td>NS (tn)</td>
</tr>
<tr>
<td>Nitrates [mg NO$_3^{-}$·dm$^{-3}$]</td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>$p &lt; 0.05$ (tn)</td>
</tr>
<tr>
<td>Summer</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>$p &lt; 0.05$ (tn)</td>
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<tr>
<td></td>
<td>NS (tn)</td>
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<tr>
<td></td>
<td>NS (tn)</td>
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<tr>
<td></td>
<td>NS (tn)</td>
</tr>
</tbody>
</table>

Table 3. Statistical significance of the analyzed water quality indicators for the inflowing (P1) and stored water (P2), and for the inflowing (P1) and outflowing water (P3) in the period of November 2006 – October 2008; significance level marked with bold; NS – statistically insignificant difference, tn – t-Student test for independent samples.
<table>
<thead>
<tr>
<th>Indicator</th>
<th>Year</th>
<th>NS (tn)</th>
<th>NS (tn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrites [mg NO₂⁻·dm⁻³]</td>
<td>Winter</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>Ammonia [mg NH₄⁺·dm⁻³]</td>
<td>Winter</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>BOD₅ [mg O₂·dm⁻³]</td>
<td>Winter</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>p &lt; 0.05 (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>DO [mg O₂·dm⁻³]</td>
<td>Winter</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>Winter</td>
<td>p &lt; 0.05 (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>p &lt; 0.05 (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>Reaction – pH</td>
<td>Winter</td>
<td>p &lt; 0.05 (tn)</td>
<td>p &lt; 0.05 (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>p &lt; 0.05 (tn)</td>
<td>p &lt; 0.05 (tn)</td>
</tr>
<tr>
<td>Electrolytic conductivity [μS·cm⁻¹]</td>
<td>Winter</td>
<td>p &lt; 0.05 (tn)</td>
<td>p &lt; 0.05 (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>p &lt; 0.05 (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td>TSS [mg·dm⁻³]</td>
<td>Winter</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>NS (tn)</td>
<td>NS (tn)</td>
</tr>
</tbody>
</table>

Between the reservoir inlet (P1) and the reservoir bowl (P2) statistically significant differences were observed (p < 0.05) in a one year research period for five water quality indicators: nitrates, BOD₅, water temperature, pH and electrolytic conductivity. For phosphates statistically significant differences were recorded in winter between the inflowing water and the water stored in the reservoir. Statistically insignificant differences were observed for nitrites, ammonia, dissolved oxygen and the total suspended solids (p > 0.05).

As far as the inlet (P1) and outlet of the reservoir (P3) are concerned statistically significant differences (p < 0.05) in a one year research period were observed for the following water quality indicators: nitrates, temperature, pH and electrolytic conductivity. For BOD₅ statistically significant differences between the water flowing into the reservoir and the outflowing water were observed in summer months. Statistically insignificant differences were recorded for phosphates, nitrites, ammonia, dissolve oxygen and total suspended solids (p > 0.05).

CONCLUSIONS

The results obtained during the two years’ research on the impact of the small water reservoir Psurów on the quality and flows of the Prosna River allow to draw the following conclusions:

– the reservoir contributed to the reduction concentrations of phosphates, nitrates, nitrites, ammonia as well as electrolytic conductivity and total suspended solids in
the water flowing out of the Psurów reservoir (P3), if compared with the inflowing water (P1). In the case of other water quality indicators their increased values were recorded at the reservoir outlet;

- loads of phosphates, nitrates, nitrites, ammonia and total suspended solids discharged from the reservoir were lower than the inflowing ones;
- both in the water flowing into the Psurów reservoir and the outflowing water higher concentrations of mineral nitrogen, electrolytic conductivity and total suspended solids were recorded in winter. In the summer season higher concentrations of phosphates, BOD$_5$ and higher values of temperature and water pH were observed;
- the investigated waters belong to the II class of water purity due to the content of N-NO$_3$-, total suspended solids and chlorophyll a, and they are vulnerable to pollution by nitrogen compounds coming from agricultural sources;
- taking into consideration the Vollenweider’s criterion the Psurów reservoir was classified to polytrophic reservoirs;
- between P1 and P3 sampling points significant differences were observed for nitrates, water temperature, pH and electrolytic conductivity. No significant differences were recorded in the case of other water quality indicators;
- the Psurów reservoir compensated flows of the Prosna River. A high correlation was observed between the volume of water flowing out of the Psurów reservoir (P3) and the volume of the inflowing water (P1).

REFERENCES


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WPŁYW MAŁEGO ZBIORNIKA WODNEGO PSURÓW NA JAKOŚĆ WODY I PRZEPŁYWY W RZECE PROŚNIE

Praca dotyczy małego zbiornika wodnego Psurów zlokalizowanego na rzece Prośnie (prawostronny dopływ rzeki Warty) w województwie opolskim (południowa Polska). W pracy przedstawiono wyniki badań jakości wody rzeki Prosną, wodnego dopływającej i odpływającej ze zbiornika oraz wody retencjonowanej w zbiorniku. Wyko-
nano także analizę przepływów rzeki Prosny powyżej i poniżej zbiornika Psurów. Badania wykonano w okre-
sie od listopada 2006 do października 2008 r. Pomiarami objęto następujące wskaźniki jakości wody: PO$_4^{3-}$,
NO$_3^-$, NO$_2^-$, NH$_4^+$, BZT, tlen rozpuszczony, temperaturę wody, odczyn wody, przewodność elektrolityczną,
zawiesinę ogólną i chlorofil a, dla których obliczono podstawowe statystyki opisowe. Wyniki badań wykazały,
że mały zbiornik wodny Psurów redukował ładunki fosforanów (średnio o 21%), azotanów (o 26%), azotynów
(o 9%), amoniaku (o 5%) i zawiesiny ogólnej (o 17%). Stwierdzono, że między objętością wody odpływającej
ze zbiornika Psurów a objętością wody dopływającej do zbiornika istnieje wysoka zależność ($r = 0,93$), istotna
statystycznie na poziomie $p < 0,05$. Na podstawie kryterium Vollenweidera zbiornik Psurów zakwalifikowano
do zbiorników politroficznych.
THE INFLUENCE OF URBAN GREEN WASTE COMPOST ON THE PHYSICAL QUALITY OF SOIL EXPOSED TO EROSION

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Keywords: Eroded soil, compost, soil structure, water properties, air properties.

Abstract: A field experiment was conducted to assess both direct and after effects of composted urban green waste applied at the rates of 10 and 20 Mg·ha\(^{-1}\) on aggregate size distribution, aggregate water stability, water and air properties of Haplic Luvisol developed from loess exposed to surface water erosion. In the first year of the study, compost fertilization resulted in a significant reduction of an unfavorable proportion of clods > 10 mm, while air-dry aggregates with sizes of 1–5 mm and 0.25–1 mm increased within the 0–10 cm layer of the eroded soil. In the second year after compost application, there was a significant increase in the water-stable aggregate content with sizes of 0.25–10 mm in the treated soil as compared to the control plots. However, no significant differences in aggregate size distribution and aggregate water stability were stated in the third year after compost application. A direct influence of compost addition was reflected in a significant decrease in bulk density and significant increases in actual soil moisture, maximum water capacity, saturated hydraulic conductivity, total porosity, the fraction of macropores with diameters > 20 μm, and air permeability in the surface layer of the soil. At the same time, there was a significant decrease in the proportion of soil mesopores with diameters between 0.2 to 20 μm, whereas no significant differences in field water capacity and retention of water useful for plants were observed. Values of Dexter’s index \(S\) of soil physical quality in the compost-amended soil were comparable to those found in the control plots. The dose of 20 Mg·ha\(^{-1}\) turned out to be more effective.

INTRODUCTION

Soil quality can be conceptualized as the capability of soil to function within natural or agriculturally managed ecosystems, to sustain plant and animal productivity, maintain water and air quality, and support human health and habitation [17]. Physical properties suggested as soil quality indicators include soil depth, thickness of humus horizon, soil color, texture, structure, and compaction, water capacity, retention of water useful to plants, infiltration, aeration, crusting, surface runoff, and susceptibility to water erosion.

Soil erosion is a major process of physical degradation of soil cover in agricultural areas with a strongly developed relief [6, 12, 18, 21, 29]. During the process, cultivated horizons located on upper convex segments of slopes become increasingly reduced, and soil material is accumulated in hollows. This results, in turn, in more or less reduced pedons within eroded soils and overbuilt pedons within colluvial soils. Destruction of soil genetic horizons is accompanied by depletion of humus substances and nutrients in soil. In contrast to non-eroded soils, Ap horizons of eroded soils developed from illuvial hori-
zons or parent material have poorer aggregation, aggregate water stability and less favorable water-air properties [15, 25, 27, 28, 30]. Also, erosion processes tend to wash away or colmatate crop plants, and to leach mineral fertilizers and plant protection chemicals, posing a threat to the environment, particularly to surface and underground water. Affecting crops and soil fertility, erosion contributes to great losses of crop productivity and its lower quality [5, 10, 19]. In water management, erosion processes cause increased river sedimentation and colmatation of water reservoirs as well as damage to drainage facilities.

As a result of poor aggregate water stability, eroded soils are susceptible to crusting at the soil surface and further water erosion during periods of heavy runoff. Since the soils are potentially rich in plant nutrients, their water-stable aggregate structure should be restored. In order to increase soil organic matter contents and to improve soil structure and water-air properties, high doses of natural or organic fertilizers are applied together with NPK fertilization and liming [4, 9, 26]. According to some studies, organic waste compost may elevate organic carbon content in soil and enhance its physical, physico-chemical and chemical properties [1, 16, 34]. Meeting required standards, urban green waste compost is of the greatest quality [3, 7, 13]. Materials used for composting include grass, leaves, ground-up tree and bush branches, green waste from marketplaces, and garden refuse.

The purpose of the study was to assess both direct and after effects of composted urban green waste applied in moderated doses on aggregate size distribution, aggregate water stability, water and soil properties of Haplic Luvisol developed from loess.

MATERIAL AND METHODS

The study was conducted in the period of 2005–2007, in a small loess catchment typical of loess areas in Poland, located in the town of Bogucin (51°19′56″N and 22°23′18″E) on the Nałęczów Plateau (Lublin Upland). The catchment is a model research object of the Institute of Agrophysics of the Polish Academy of Sciences in Lublin, where processes of soil erosion have been studied for more than ten years [29]. The field experiment was carried out on a slope with inclination ranging from 11 to 15%, transversal to the direction of tillage. The study comprised plots with two doses of compost and control plots in 3 replications, on Haplic Luvisols affected by different erosion degrees, e.g.: the slightly eroded soil with the sequence of genetic horizons Ap-Blt-B2t-BC-Ck, moderately eroded soil with the sequence of horizons Ap-B2t-BC-Ck, and strongly eroded soil with the sequence of horizons Ap-BC-Ck (9 plots in total). The plot size (5×3 m) was limited by a distinctive mosaic pattern of the soil cover on the loess slopes, formed by patches of non-eroded soil, pedons with different degrees of erosion, and colluvial soil.

In 2005, spring wheat (Triticum aestivum L. variety Nawra) was sown, having replaced sugar beet (Beta saccharifera). Cultivation management included winter ploughing, cultivariong and harrowing in spring. Mineral fertilization per hectare was as follows: 40 kg of N (on a one-off basis, full dose before sowing, applied in the form of nitrochalk and ammonium phosphate), 23 kg of P, and 75 kg of K (applied as 60% potassium salt). At the beginning of April 2005, before wheat sowing, compost was mixed into the soil to the depth of 10 cm. Its amounts were relatively small doses of 1 and 2 kg·m⁻² (10 and 20 Mg·ha⁻¹) because compost application was designed as a supplementary agricultural treatment rather than a rehabilitation measure. The compost used in the study was produced
by P.U.H. Botom Company in Raszyn from solid green waste (grass, leaves, ground-up wood) coming from Warsaw. Dry matter content in the mature compost was 50.95%. According to the producer’s information, the chemical composition of the compost was as follows: Corg – 19.4% d.m., Norg – 1.3% d.m., P₂O₅ – 1.0% d.m., K₂O – 0.5% d.m.; contents of heavy metals were significantly below their limit values. For crop protection, Chwastox Turbo 340 SL was used (2 dm³·ha⁻¹).

For analyses of a direct effect of the compost, soil samples were collected from the surface layer of Ap horizons (at the depth of 0–10 cm). In order to determine aggregate size distribution and aggregate water stability, collective samples were taken on four days during 2005 (May 23, June 14, July 11, and August 8). Soil samples of undisturbed structure were collected on June 14 and August 8, 2005 in 8 replications to metal cylinders of 100 cm³ in volume (4 cylinders to determine water capacity and air permeability, and 4 cylinders to determine saturated hydraulic conductivity). Soil Corg content and physico-chemical properties were assayed in the samples taken in June.

After effects of the compost on aggregate size distribution and aggregate water stability were studied in 2006 and 2007, e.g. in the second and third year after its application. Cultivation management included repeated annual skim ploughing, winter ploughing, spring cultivatoring and harrowing. Spring barley (*Hordeum vulgare* L. variety Stratus) was grown twice, and mineral fertilization per hectare was the same as in 2005, viz. 40 kg of N, 23 kg of P, and 75 kg of K. Soil material was sampled on June 20, 2006 and June 15, 2007, at the depth of 0–20 cm.

Soil texture was determined according to the Casagrande aerometric method modified by Prószyński. Organic carbon content was measured by Tiurin’s method in Simakov’s modification. Soil reaction in 1 mol·dm⁻³ KCl was determined potentiometrically using a combined electrode. Soil hydrolytic acidity in mmol H⁺·kg⁻¹ was analyzed by Kappen’s method in 1 mol·dm⁻³ CH₃COONa. The sum of exchangeable basic cations was estimated after Kappen in 0.1 mol·dm⁻³ HCl. On the basis of these assays, cation exchange capacity and a degree of sorptive complex saturation with basic cations were calculated.

In order to determine aggregate size distribution [kg·kg⁻¹], 500-g representative samples in two replications were processed by dry sieving technique with a nest of sieves with the mesh sizes of 10, 7, 5, 3, 1, 0.5, and 0.25 mm. The content of water-stable aggregates (WSA) [kg·kg⁻¹] was determined in four replications through wet sieving with the use of the modified Baksheyev’s apparatus made by The Institute of Agrophysics of the Polish Academy of Sciences in Lublin. The sieving results were used to calculate mean weight diameter (MWD) values of both air-dry and water-stable aggregates using the procedure of Youker and McGuinness [33]. Aggregate stability was assessed following the method described by Le Bissonnais [20].

Specific soil density [Mg·m⁻³] was measured pycnometrically. Bulk density [Mg·m⁻³] was calculated from the ratio of the mass of the soil dried at 105°C to its volume. Actual soil moisture during sampling [kg·kg⁻¹] was measured by the gravimetric method. Water capacity in the range of soil water potential from -0.1 kPa to -1554 kPa [kg·kg⁻¹] was determined in pressure chambers, on porous ceramic plates (manufactured by Eijkelkamp and Soil Moisture Equipment Corporation). Retention of water useful to plants (within the range of potential from -15.5 to -1554 kPa) was calculated as a difference of water capacity values corresponding to the potential. Saturated hydraulic conductivity was determined with the use of Wit’s apparatus (Eijkelkamp) by calculating water filtration coef-
ficient \([m \cdot d^{-1}]\). Total porosity \([m^3 \cdot m^{-3}]\) was calculated on the basis of values of specific and bulk soil density. Distribution of pores with equivalent diameters of > 20 \(\mu m\), 0.2–20 \(\mu m\), and < 0.2 \(\mu m\) was calculated on the basis of water capacity values expressed in \(m^3 \cdot m^{-3}\). Air permeability at field water saturation of -15.5 kPa \((\times 10^8 \text{ m}^2 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1})\) was measured using LPiR-2 apparatus for the measurement of air permeability in the moulding masses (manufactured by Polish Foundry Research Institute in Cracow).

Analysis of variance (ANOVA) involving two-way classification in the completely randomised design was applied to the data pertaining to direct effects of the compost in 2005, while the after-effects in 2006 and 2007 were analyzed using ANOVA with one-way classification. The significance of differences was verified by Tukey’s test.

Dexter’s index of soil physical quality \(S^{[11]}\) was calculated on the basis of water retention curves using the computer program RETC. The index \(S\) is defined by the author as the slope value of the soil water retention curve at its inflection point and should be calculated using the van Genuchten modified equation \([32]\):

\[
S = -n \left( \theta_{sat} - \theta_{res} \right) \left[1 + 1/m \right]^{-\left(1 + m\right)}
\]

where:
\[
\begin{align*}
\theta_{sat} & \quad \text{the volumetric water content at saturation [kg·kg}^{-1}], \\
\theta_{res} & \quad \text{the residual water content [kg·kg}^{-1}], \\
n & \quad \text{the dimensionless parameter controlling the shape of the curve}, \\
m & \quad \text{the dimensionless parameter with Mualem restriction [23]: 1 - 1/n}.
\end{align*}
\]

RESULTS

Granulometrically, the studied Haplic Luvisol developed from loess was silt loam, comprising, depending upon the erosion class, 12–15% of sand (2–0.05 mm), 68–74% of silt fraction (0.05–0.002 mm), and 14–17% of clay (< 0.002 mm). Corg contents in the soil ranged from 8.04 to 9.20 g·kg\(^{-1}\) and tended to decrease with an increasing erosion degree. Soil reaction was slightly acid (pH 5.8–6.1). Soil hydrolytic acidity was between 18.8 and 26.2 mmol(+)-kg\(^{-1}\), the sum of exchangeable basic cations was within the range of 87–98 mmol(+)-kg\(^{-1}\), while cation exchange capacity ranged from 113.3 to 116.8 mmol(+)-kg\(^{-1}\). A degree of sorptive complex saturation with basic cations reached values between 76.9 and 80.8%.

According to the results, application of composted urban green waste elevated Corg contents in the surface layer of the eroded Haplic Luvisol, which reached up to 9.04–10.12 g·kg\(^{-1}\) in the plots with the dose of 10 Mg·ha\(^{-1}\) and up to 9.92–11.04 g·kg\(^{-1}\) in plots with the dose of 20 Mg·ha\(^{-1}\). The compost had a beneficial direct effect on aggregate size distribution. Significant changes in soil aggregation were found in May 2005 (at the first sampling) and they were also observed for all subsequent sampling times (Tab. 1). The proportion of clods > 10 mm decreased significantly (by 0.105 kg·kg\(^{-1}\) in the plots treated with 10 Mg·ha\(^{-1}\) and by 0.151 kg·kg\(^{-1}\) in the plots treated with 20 Mg·ha\(^{-1}\), on average). At the same time, there were significant increases in fractions of air-dry aggregates with sizes of 1–5 mm (by 0.048–0.070 kg·kg\(^{-1}\)) and 0.25–1 mm (by 0.032–0.052 kg·kg\(^{-1}\)), as compared to the control plots. By contrast, no significant differences in 5–10 mm aggregates and microaggregates < 0.25 mm were found. The mean weight diameter of air-dry aggregates decreased significantly (on average by 3.9 mm in the plot with the compost dose of 10 Mg·ha\(^{-1}\) and by 5.5 mm in the plot with the dose of 20 Mg·ha\(^{-1}\)).
### Table 1. Air-dry soil aggregate distribution in Ap horizon (mean values in 3 plots)

<table>
<thead>
<tr>
<th>Month, year [M]</th>
<th>Dose of compost [Mg·ha⁻¹] [D]</th>
<th>Air-dry aggregate content of diameter in mm [kg·kg⁻¹]</th>
<th>MWD [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 10</td>
<td>5–10</td>
<td>1–5</td>
</tr>
<tr>
<td>May 2005</td>
<td>0</td>
<td>0.293 0.145</td>
<td>0.296 0.186</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.166 0.172</td>
<td>0.347 0.218</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.155 0.155</td>
<td>0.352 0.238</td>
</tr>
<tr>
<td>June 2005</td>
<td>0</td>
<td>0.336 0.154</td>
<td>0.286 0.158</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.248 0.147</td>
<td>0.324 0.193</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.217 0.164</td>
<td>0.348 0.193</td>
</tr>
<tr>
<td>July 2005</td>
<td>0</td>
<td>0.352 0.101</td>
<td>0.209 0.177</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.315 0.124</td>
<td>0.242 0.180</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.198 0.130</td>
<td>0.301 0.222</td>
</tr>
<tr>
<td>August 2005</td>
<td>0</td>
<td>0.462 0.125</td>
<td>0.235 0.110</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.296 0.137</td>
<td>0.302 0.171</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.271 0.138</td>
<td>0.304 0.188</td>
</tr>
<tr>
<td>Mean</td>
<td>0</td>
<td>0.361 0.131</td>
<td>0.256 0.158</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.256 0.145</td>
<td>0.304 0.190</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.210 0.147</td>
<td>0.326 0.210</td>
</tr>
<tr>
<td>LSD (α = 0.05)</td>
<td>doses D</td>
<td>0.066 n. s.</td>
<td>0.030 n. s.</td>
</tr>
<tr>
<td></td>
<td>interaction D×M</td>
<td>n. s.</td>
<td>n. s.</td>
</tr>
<tr>
<td>June 2006</td>
<td>0</td>
<td>0.299 0.157</td>
<td>0.289 0.159</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.278 0.143</td>
<td>0.288 0.179</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.223 0.159</td>
<td>0.326 0.181</td>
</tr>
<tr>
<td>LSD (α = 0.05)</td>
<td>doses D</td>
<td>0.074 n. s.</td>
<td>n. s.</td>
</tr>
<tr>
<td>June 2007</td>
<td>0</td>
<td>0.369 0.138</td>
<td>0.239 0.136</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.397 0.132</td>
<td>0.240 0.133</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.345 0.138</td>
<td>0.273 0.140</td>
</tr>
<tr>
<td>LSD (α = 0.05)</td>
<td>doses D</td>
<td>n. s.</td>
<td>n. s.</td>
</tr>
</tbody>
</table>

n. s. – non significant differences

In the second year after compost application in dose of 20 Mg·ha⁻¹, the proportion of clods > 10 mm was significantly lower (by 0.076 kg·kg⁻¹), the proportion of air-dry aggregates with sizes of 0.25–10 mm was significantly higher (by 0.061 kg·kg⁻¹), and the mean weight diameter was significantly lower (by 2.5 mm), compared to the control plots. In the soil with the compost dose of 10 Mg·ha⁻¹, no significant differences in air-dry aggregates were found (Tab. 1). In the third year after compost application at the rate of 20 Mg·ha⁻¹, the reduction of clods > 10 mm was insignificant (by 0.024 kg·kg⁻¹) and the proportion of macroaggregates ranging from 0.25 to 10 mm was slightly higher (by 0.038 kg·kg⁻¹) in the Ap horizon of the eroded soil, compared with the control plots.

In the first year of the study, composted urban green waste proved to have a considerably weaker effect on aggregate stability in the surface layer of the eroded soil than on size aggregate distribution (Tab. 2). There were no significant differences in water-stable aggregates with sizes of 0.25–10 mm, which shows that soil-aggregate stabilization influenced by this fertilizer is a very slow process. A higher number of stable aggregates with
sizes of 5–10 mm in the plots with the dose of 20 Mg·ha\(^{-1}\) (by 0.008 kg·kg\(^{-1}\)) and higher MWD values (by 0.08 mm) were the only changes observed in that period.

Table 2. Water-stable soil aggregate content in Ap horizon (mean values in 3 plots)

<table>
<thead>
<tr>
<th>Month, year [M]</th>
<th>Dose of compost [Mg·ha(^{-1})] [D]</th>
<th>Water-stable aggregate content of diameter in [kg·kg(^{-1})]</th>
<th>MWD [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5–10</td>
<td>1–5</td>
<td>0.25–1</td>
</tr>
<tr>
<td>May 2005</td>
<td>0</td>
<td>0.004</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.009</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.010</td>
<td>0.042</td>
</tr>
<tr>
<td>June 2005</td>
<td>0</td>
<td>0.008</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.011</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.015</td>
<td>0.054</td>
</tr>
<tr>
<td>July 2005</td>
<td>0</td>
<td>0.018</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.022</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.030</td>
<td>0.060</td>
</tr>
<tr>
<td>August 2005</td>
<td>0</td>
<td>0.032</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.048</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.042</td>
<td>0.072</td>
</tr>
<tr>
<td>Mean</td>
<td>0</td>
<td>0.016</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.022</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.024</td>
<td>0.057</td>
</tr>
<tr>
<td>LSD ((\alpha = 0.05)) doses D</td>
<td>interaction D×M</td>
<td>0.007</td>
<td>n. s.</td>
</tr>
<tr>
<td>June 2006</td>
<td>0</td>
<td>0.004</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.012</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.010</td>
<td>0.059</td>
</tr>
<tr>
<td>LSD ((\alpha = 0.05)) doses D</td>
<td>0.008</td>
<td>0.012</td>
<td>0.032</td>
</tr>
<tr>
<td>June 2007</td>
<td>0</td>
<td>0.006</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.011</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.013</td>
<td>0.047</td>
</tr>
</tbody>
</table>

n. s. – non significant differences

In 2006, the after effect of the compost on aggregate stability was greater than its direct influence in 2005 (Tab. 2). The content of stable aggregates with sizes of 0.25–10 mm increased significantly (on average, by 0.046 kg·kg\(^{-1}\) in the plots with the dose of 10 Mg·ha\(^{-1}\) and by 0.086 kg·kg\(^{-1}\) in the plots with the dose of 20 Mg·ha\(^{-1}\)), compared to the control plots. Among all the examined water-stable fractions, greater numbers of the following aggregates were detected: those with sizes of 5–10 mm (by 0.008 kg·kg\(^{-1}\) in the plots with the dose of 10 Mg·ha\(^{-1}\)), with sizes of 1–5 mm (by 0.016 kg·kg\(^{-1}\)) and of 0.25–1 mm (by 0.064 kg·kg\(^{-1}\)) in the plots with the dose of 20 Mg·ha\(^{-1}\). Also the MWD of water stable aggregates in the soil treated with compost at the rate of 20 Mg·ha\(^{-1}\) proved to be significantly greater (by 0.11 mm).

In the third year after compost application, little impact of the treatment on water stable aggregates was observed (Tab. 2). Differences in the sum of stable aggregates with
sizes of 0.25–10 mm and in the content of particular water-stable fractions in the soil amended with compost were insignificant in comparison to the control plots.

Specific soil density in the Ap horizon of the eroded Haplic Luvisol was 2.65 Mg·m$^{-3}$. The compost dose of 20 Mg·ha$^{-1}$ resulted in its decrease to 2.64 Mg·m$^{-3}$. After compost treatment, bulk density in the layer of 0–10 cm decreased significantly (on average, by 0.06 Mg·m$^{-3}$ in the plots with the dose of 10 Mg·ha$^{-1}$ and by 0.12 Mg·m$^{-3}$ in the plots with the dose of 20 Mg·ha$^{-1}$) in comparison with bulk density in the control plots (Tab. 3). Lower compaction of the soil fertilized with compost considerably influenced some water and air properties of the soil.

### Table 3. Bulk density and water properties in Ap horizon (mean values in 3 plots)

<table>
<thead>
<tr>
<th>Month, Year [M]</th>
<th>Dose of compost [Mg·ha$^{-1}$] [D]</th>
<th>Bulk density [Mg·m$^{-3}$]</th>
<th>Actual moisture [kg·kg$^{-1}$]</th>
<th>Water capacity [kg·kg$^{-1}$] at Retention of water useful for plants [kg·kg$^{-1}$]</th>
<th>Saturated hydraulic conductivity [m·d$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.1 kPa</td>
<td>-15.5 kPa</td>
</tr>
<tr>
<td>June 2005</td>
<td>0</td>
<td>1.31</td>
<td>0.184</td>
<td>0.389</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.27</td>
<td>0.173</td>
<td>0.415</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.19</td>
<td>0.182</td>
<td>0.465</td>
<td>0.268</td>
</tr>
<tr>
<td>August 2005</td>
<td>0</td>
<td>1.31</td>
<td>0.134</td>
<td>0.388</td>
<td>0.273</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.24</td>
<td>0.144</td>
<td>0.433</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.19</td>
<td>0.148</td>
<td>0.469</td>
<td>0.281</td>
</tr>
<tr>
<td>Mean</td>
<td>0</td>
<td>1.31</td>
<td>0.159</td>
<td>0.389</td>
<td>0.267</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.25</td>
<td>0.158</td>
<td>0.424</td>
<td>0.263</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.19</td>
<td>0.165</td>
<td>0.467</td>
<td>0.274</td>
</tr>
<tr>
<td>LSD (α = 0.05)</td>
<td>doses D</td>
<td>n. s.</td>
<td>n. s.</td>
<td>0.032</td>
<td>0.011</td>
</tr>
<tr>
<td>interaction D×M</td>
<td></td>
<td>0.009</td>
<td>n. s.</td>
<td>n. s.</td>
<td>n. s.</td>
</tr>
</tbody>
</table>

n. s. – non-significant differences

Actual soil moisture during sampling showed significant differences among the plots only when combined with the sampling dates (Tab. 3). A significant increase (by 0.035–0.078 kg·kg$^{-1}$) in maximum water capacity of the soil (at the soil water potential of -0.1 kPa) attributable to compost application was detected, compared to the control plots, while no differences in field water capacity (at the potential of -15.5 kPa) in the compost-treated fields were found. Both compost doses contributed to significant increases in permanent wilting point moisture contents (at the potential of -1554 kPa), by 0.003 kg·kg$^{-1}$ and by 0.004 kg·kg$^{-1}$, respectively. As a result, compost fertilization had no considerable effect on retention of water useful to plants (within the range of the potential from -15.5 kPa to -1554 kPa). In comparison with the control plots, saturated hydraulic conductivity in the surface layer of the soil treated with compost increased significantly (by 2.05–4.75 m·d$^{-1}$ on average).

Total porosity in the soil with the compost was significantly higher (by 0.020 m$^3$·m$^{-3}$ and by 0.046 m$^3$·m$^{-3}$, respectively to increasing dose of compost) than in the control plots (Tab. 4). Compost application led to significant increases (by 0.040 m$^3$·m$^{-3}$ and by 0.070 m$^3$·m$^{-3}$) in macropores with equivalent diameters > 20 μm which determining air capacity of the soil at field water saturation. By contrast, the proportion of mesopores with diam-
eters ranging from 0.2 to 20 μm, which retain water useful for plants, decreased significantly (by 0.022–0.020 m³·m⁻³). At the same time, there were no significant differences in the number of micropores with diameters < 0.2 μm (which retain water unavailable for plants). Air permeability at field water saturation (-15.5 kPa) increased significantly (by 86.9×10⁻⁸ m²·Pa⁻¹·s⁻¹ in the plots with the dose of 10 Mg·ha⁻¹ and by 94.0×10⁻⁸ m²·Pa⁻¹·s⁻¹ in the plots with the dose of 20 Mg·ha⁻¹).

Table 4. Porosity and air permeability in Ap horizon (mean values in 3 plots)

<table>
<thead>
<tr>
<th>Month, Year</th>
<th>Dose of compost [Mg·ha⁻¹] [D]</th>
<th>Total porosity [m³·m⁻³]</th>
<th>Pore-size content [m³·m⁻³]</th>
<th>Air permeability at -15.5 kPa [×10⁻⁸ m²·Pa⁻¹·s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&gt; 20 μm</td>
<td>0.2–20 μm</td>
<td>&lt; 0.2 μm</td>
</tr>
<tr>
<td>June 2005</td>
<td>0</td>
<td>0.506</td>
<td>0.165</td>
<td>0.252</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.521</td>
<td>0.191</td>
<td>0.236</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.551</td>
<td>0.234</td>
<td>0.231</td>
</tr>
<tr>
<td>August 2005</td>
<td>0</td>
<td>0.505</td>
<td>0.148</td>
<td>0.267</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.531</td>
<td>0.202</td>
<td>0.238</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.552</td>
<td>0.221</td>
<td>0.246</td>
</tr>
<tr>
<td>Mean</td>
<td>0</td>
<td>0.506</td>
<td>0.157</td>
<td>0.259</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.526</td>
<td>0.197</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.552</td>
<td>0.227</td>
<td>0.239</td>
</tr>
<tr>
<td>LSD (α = 0.05): doses D interaction D×M</td>
<td>n. s.</td>
<td>0.019</td>
<td>0.028</td>
<td>0.011</td>
</tr>
</tbody>
</table>

n. s. – non-significant differences

Dexter’s index of soil physical quality S for the soil from the control plots, calculated on the basis of water retention curves, reached the values in the range of 0.064 to 0.078. In the soil treated with compost, the index absolute values were slightly lower, ranging from 0.061 to 0.065 in the plots with the dose of 10 Mg·ha⁻¹ and from 0.060 to 0.069 in the plots with the dose of 20 Mg·ha⁻¹.

DISCUSSION

Application of composted urban green waste at the rates of 10 and 20 Mg·ha⁻¹ increased organic carbon content in the 0–10 cm layer of eroded Haplic Luvisol, which is in agreement with the results obtained by other authors [1, 7, 16]. The beneficial direct effect of the compost, connected with, on the one hand, significant decreases in the proportion of clods with sizes > 10 mm and significant increases in air-dry aggregates ranging from 0.25 to 10 mm on the other, can be explained by reduced cohesion of soil mass due to compost application which prevented excessive cloddiness of the soil during the growing season. This positive effect of the compost on the soil was also present in the second year after the treatment in spite of partial dispersion of the compost during ploughing and other management practices.

Despite increased soil organic matter contents, compost addition only slightly increased water-stable aggregates with sizes of 0.25–10 mm in the first year. After sub-
merging in water, air-dry clods > 10 mm and macroaggregates with sizes of 0.25–10 mm broke down mostly into microaggregates < 0.25 mm. This indicates that the formation of water-stable bounds between microaggregates and soil particles stimulated by this fertilizer is a very slow process.

The after effect of compost application on aggregate stability was greater in the second year than its direct effect in 2005. A significant increase in the proportion of stable aggregates with sizes of 0.25–10 mm, as compared to the control plots, is indicative of partial and slow transformation of compost organic matter into high polymers of the polysaccharide type possessing a linear structure and demonstrating a greater ability to stabilize aggregates. In the third year of the study, strong dispersion of the compost in the soil mass occurred due to management practices, and progressing mineralization of organic matter reduced an influence of the fertilizer on aggregate size distribution and water stability.

When referring to the classes proposed by Le Bissonnais [20], based on the mean weight diameter after wet sieving, the aggregates in the layer of 0–10 cm of the control plots were assessed mainly as very unstable (MWD < 0.4 mm), and only in July and August 2005 as unstable (0.4–0.8 mm). At the same time, the aggregates from the soil amended with the compost at the rates of 10 and 20 g·kg\(^{-1}\) were classified largely as unstable (MWD 0.4–0.8 mm). Low MWD values were mainly determined by small numbers of stable aggregates with sizes of 5–10 mm and 1–5 mm. The applied doses of composted urban green waste turned out to be too small to enhance aggregate stability in the eroded soil more significantly and for a longer period of time.

A beneficial effect of composts on formation of stable soil aggregates was found by numerous authors [1, 3, 7, 34]. Bresson et al. [7] showed that incorporated municipal solid waste compost in the dose of 15 g·kg\(^{-1}\) of dry matter improved aggregate ability in the silty loam under simulated rainfall. As a result, surface crust development in the arable layer was slowed down, surface runoff was delayed, and water erosion was reduced. The results obtained by Whalen et al. [34] indicate a significantly greater aggregate stability in a silt-loam soil amended with composted cattle manure in the doses of 0, 15, 30, and 45 Mg·ha\(^{-1}\), proportionally to the application rates of the compost. Aggelides and Londra [1] reported improved aggregate size distribution and increased aggregate stability in loamy and clayey soils treated with compost produced from town waste and sewage sludge, at the rates of 75, 150 and 300 Mg·ha\(^{-1}\). In the laboratory study, Annabi et al. [3] analyzed effects of immature and mature composts made from municipal solid waste, sewage sludge, green waste and biowaste on the mechanisms of aggregate stabilization in a silt loam soil. All the composts applied improved aggregate stability preventing the soil from surface crusting, with a less persistent effect of the mature composts. Stabilization of the aggregates caused by their increased hydrophobicity was connected with increases in microbial activity, biomass of exocellular polysaccharides of microbial origin, and the abundance of soil fungi. Improvement in aggregate stability resulted from the diffusion of the organic substances into the aggregates.

According to the literature, only a part of organic matter is responsible for soil aggregate stability. Among organic compounds involved in soil stabilization, transient binding agents include microbial and plant-originating polysaccharides which are rapidly decomposed by microorganisms. Plant roots, fungal hyphae and some fungi may act as temporary binding agents [2]. Resistant aromatic humic substances associated with...
polyvalent metal cations and strongly sorbed polymers are cited among persistent binding agents. They are strongly bound inside aggregates and are derived from the resistant fragments of roots, hyphae and bacteria cells. The highest resistance of soil aggregates to the destructive action of water occurs during the summer months.

The results obtained in this study show that compost organic matter reduced gravity settling of the soil mass and effectively prevented the soil, loosened after wheat sowing, from compacting. As a result, bulk density in the 0–10 layer remained significantly lower till August as against that stated in the control plots. The decrease in bulk density of the compost-treated soil had a decisive influence on significant increases in maximum water capacity and total porosity, particularly in the higher content of macropores with MWD > 20 μm. The higher proportion of macropores had, in turn, a major impact on increases in saturated hydraulic conductivity and air permeability at field water saturation.

At the same time, compost addition had little effect on field water capacity and retention of water useful for plants. Since organic matter is able to fix water by molecular forces and retain it in micropores < 0.2 μm as unavailable to plants, increases in organic matter content in the soil resulted in higher moisture at the permanent wilting point. This led to significant decreases in mesopores with diameters of 0.2–20 μm retaining water available to plants in the compost-treated soil.

In their study into effects of compost produced from town wastes and sewage sludge at the rates of 75, 150 and 300 Mg·ha⁻¹ on a loamy and a clayey soil, Aggelides and Londra [1] found decreases in bulk density by 16.7–19.7% at the highest compost dose and increases in total porosity by 11.0–32.8% in a loamy soil and by 5.4–9.9% in a clayey soil, proportionally to the application rate. Saturated hydraulic conductivity was higher by 32.5–95.2% in the loamy soil and by 55.3–168.4% in the clayey soil. The increase of retention of water useful to plants was less evident. Compost application contributed to an increase in soil hydraulic conductivity and reduction in surface runoff, which is particularly important for soils susceptible to water erosion.

Increases in moisture in a sandy alluvial soil attributable to treatment with composted urban waste at the rates of 60 and 120 Mg·ha⁻¹ were reported by Jamroz and Drozd [14] and Licznar et al. [22]. Tester [31] investigated soil moisture at the depth of 5–30 cm after 5-year compost fertilization in the doses of 60, 120 and 240 Mg·ha⁻¹. In comparison to the control plot, soil moisture at the 5-cm depth was 1.9, 2.7 and 3.1-fold higher, and at the 30-cm depth 1.3, 1.5 and 2.2-fold higher, respectively for the applied rates. Similarly, Carter [8] found increases in field water capacity and soil retention of water useful to plants in barley and potato cultivation on a compost-amended podzolic soil developed from fine sandy loam.

Proper growth and functioning of crop plants roots require an appropriate ratio between mesopores with diameters of 0.2–20 μm retaining water useful to plants and macropores > 20 μm responsible for adequate aeration. According to Olness et al. [24], an optimal balance between near-surface soil water holding capacity and aeration may be achieved when field capacity (a sum of mesopores of 0.2–20 μm and micropores < 0.2 μm) is 0.66 of total porosity and air capacity is 0.34. In the Ap horizon of the eroded Haplic Luvisol, the relationship was close to the optimum: field water capacity was on average 0.69 in the control plots while ranging from 0.63 to 0.59 in the compost-treated plots, and air capacity values were 0.31 and 0.37–0.41, respectively. Given the above-presented criteria, both water and air properties of the studied soil can be regarded as highly benefi-
cial. Likewise, absolute values of Dexter’s index $S$ of soil physical quality above 0.050 indicate that the study eroded Haplic Luvisol, particularly its water and air properties, is of very high quality [11]. According to the author, $S$ index can be used as a valuable tool for assessment of soil physical degradation or amelioration.

CONCLUSIONS

Application of composted urban green waste at the rates of 10 and 20 Mg·ha$^{-1}$ contributed to increases of Corg contents in the surface layer of the eroded Haplic Luvisol.

A beneficial direct effect of compost on aggregate size distribution was connected with significant decreases in the proportion of clods with sizes > 10 mm as well as significant increases in air-dry aggregates ranging from 0.25–10 mm (particularly those of sizes with 1–5 mm and 0.25–1 mm) and in mean weight diameter values, as compared to the control plots.

In the second year after compost treatment, a significantly lower proportion of clods > 10 mm and a higher content of air-dry aggregates with sizes of 0.25–10 mm were observed, while comparing with the control plots.

In the first year after application of the doses of 10 and 20 Mg·ha$^{-1}$, only significant increases were stated in water-stable aggregates in the range of 5–10 mm and the mean weight diameter values.

In the second year, a significant after-effect of the compost in the plots treated with both doses was revealed, connected with a significantly higher proportion of water-stable aggregates with sizes of 0.25–10 mm and their greater MWD. However, no impact of compost application was found on aggregate size distribution and aggregate water-stability in the eroded Luvisol in the third year.

Both doses contributed to a significant decrease of bulk density and significant increases of maximum water capacity, wilting point, saturated hydraulic conductivity, total porosity, the content of macropores > 20 μm in diameter and air permeability at field water saturation in the 0–10 layer of the eroded Luvisol.

Compost addition did not influence actual soil moisture during sampling, field water capacity and retention of water useful for plants. At the same time, its application resulted in a significant decrease in mesopores with diameters of 0.2–20 μm.

The values of Dexter’s index $S$ of soil physical quality in the compost-treated plots were high but slightly lower than those obtained for the control plots.

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WPŁYW KOMPOSTU Z ODPADÓW ZIELENI MIEJSKIEJ NA JAKOŚĆ STANU FIZYCZNEGO GLEBY ULEGAJĄCEJ EROZJI

W doświadczeniu poletkowym badano bezpośredni i następczy wpływ nawożenia kompostem z odpadów zieleni miejskiej w dawkach 10 i 20 Mg·ha⁻¹ na skład agregatowy, wodoodporność agregatów, właściwości wodne i powietrzne gleby płowej typowej wytworzonych z lessu, ulegającej powierzchniowej erozji wodnej. W pierwszym roku badań stwierdzono, że nawożenie kompostem istotnie zmniejszyło niekorzystną zawartość brył o wymiarach > 10 mm, a zwiększyło zawartość powietrznie suchych agregatów 1–5 mm i 0,25–1 mm w warstwie 0–10 cm gleby zerodowanej. W drugim roku po zastosowaniu kompostu w glebie istotnie zwiększyła się zawartość wodoodpornych agregatów o wymiarach 0,25–10 mm w porównaniu z glebą poletek kontrolnych. W trzecim roku po zastosowaniu kompostu nie stwierdzono istotnych różnic w składzie agregatowym i wodoodporności agregatów glebowych. W bezpośrednim działaniu dodatek kompostu istotnie zmniejszył gęstość gleby, istotnie zwiększył wilgotność aktualną, pełną pojemność wodną, przewodnictwo wodne nasycone, porowatość ogólną, zawartość makroporów o średnicy > 20 μm i przepuszczalność powietrzną w powierzchniowej warstwie gleby. Pod wpływem nawożenia kompostem nie zmieniła się istotnie połowa pojemność wodna i retencja wody użytecznej dla roślin, natomiast zawartość mezoporów glebowych o średnicy 0,2–20 μm istotnie zmniejszyła się. Wartości wskaźnika jakości stanu fizycznego gleby S według Dextera w glebie nawożonej kompostem były zbliżone do wartości wskaźnika w obiektach kontrolnych. Bardziej skuteczne było nawożenie kompostem w dawce 20 Mg·ha⁻¹.
PYROMETALLURGICAL SLAGS IN UPPER AND LOWER SILESIA (POLAND): FROM ENVIRONMENTAL RISKS TO USE OF SLAG-BASED PRODUCTS – A REVIEW

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Abstract: Slags issued from base metal smelting industry constitute a serious environmental problem in Upper and Lower Silesia (Poland). The waste is located in heavily urbanized areas, covers large surfaces and still may contain large quantities of potentially toxic metallic trace elements. This review paper summarizes all the major problems related to slag storage in Upper and Lower Silesia, including: (i) detailed characteristics of the studied slags, (ii) potential release of toxic elements and (iii) related risks for the surrounding areas and (iv) applications of slags for commercial purposes.

INTRODUCTION

Mining and smelting activities left large quantities of waste accumulated as dumps covering large surface around former industrial sites of Eastern and Central Europe. Poland used to be the largest producer of industrial wastes in Europe, both in absolute terms and as a function of GDP (Gross Domestic Product; [16]). Since 1992, the accumulation of industrial wastes in Poland has been relatively stable, with average annual production of 120–125 million Mt among which 27% are slags issued from the pyrometallurgical industry (nearly 35 Mt/yr). The largest quantities of industrial wastes have been generated and landfilled in the Upper Silesia and Lower Silesia regions (Southern and Southwestern Poland; Figure 1; over half of the national total). With 490 Mt of tailings Upper Silesia was described as a region highly polluted by heavy metals and sulphates [18]. Dumps located in Upper and Lower Silesia most often form high and large heaps scattered throughout urban or country landscapes in the surroundings of industrial activities. They consist of a variety of waste materials such as barren rocks, flotation tailings and pyrometallurgical slags. Some of these tailings (e.g. pyrometallurgical slag) are used as cement additives or road ballast. However, the slags still contain up to several percent of trace elements (Zn, Pb, Cd, As, Sb, Cr etc.) which remain hazardous if they join food chain through water or/and soil [17]. In this review paper we will classify all these metal-
lic elements as potentially toxic elements (PTEs) and we define PTEs as all the elements that can be harmful if their concentrations exceed the toxicity thresholds in water and/or soil and/or food. Therefore, assessment of a potential release of PTEs from slags is of interest for environmental and human health purposes.

This review paper deals with the problem of solid waste derived from metallurgical plants. We propose to review some questions concerning pyrometallurgical slags in Upper Silesia and Lower Silesia where base-metal mining and smelting and coal extraction have been very active until present. The most important questions we attempt to answer are: What are the main specificities of the Silesian slags? How to examine their chemical and mineral composition and PTEs contents? How to forecast potential PTEs release? Are these products really dangerous? How to manage their storage? What about re-use possibilities? To answer these questions, we compare data obtained for several Polish sites, located mainly in Upper Silesia (Fig. 1 and Tab. 1). We present also some data on slags occurring in the Lower Silesia: the Lower Silesia region was the place of intense mining and smelting activity since medieval times, with small sites active until the 20th century. Currently the main sources of pyrometallurgical waste are large copper mines and smelters located in the Northern part of the region. The historical sites allow the assessment of long-term environmental effects of pyrometallurgical waste, and studies on more recent sites allow us to discuss broader spectrum of ores treated.
Pyrometallurgical wastes (Fig. 2) are the by-products of base-metal smelting which usually form at high temperatures (over 1000°C) and may still contain elevated levels of PTEs (e.g. Pb, Zn, Cu, Ni, Cr, As). Pyrometallurgical wastes include slags and associated mattes. The latter can be defined as denser material composed of local sulphide or metal concentrations of all sizes, whereas slags have lower density than mattes (ca. 2.5 to 3 g/cm³) and mainly consist of siliceous glass, silicates and oxides. Mattes are more abundant in older slags due to the fact that ancient smelting processes were not able to extract as much metals as recently used techniques. Zn, Cu and Ni are known as being the oligo-elements but these elements might also become toxic as demonstrated by very low toxicity thresholds for PTEs such as Zn, Cu and Ni (their admissible concentrations in water or food being of several tens to several hundreds µg/kg). In Silesia, PTEs involved in metallurgical industry come from the treated ores and also from the coal used for smelting processes (Tab. 1), most of them being extracted from Polish mines in the last two centuries. The concerned elements are mainly Zn-Pb. As a result, Upper Silesian slags mainly contain PTEs such as Pb, Zn, the first being known for its high toxicity even at low concentration.

Silesia is a heavily inhabited region (mean density = 377 inhabitants/km² for Upper Silesia and 144 inhabitants/km² for Lower Silesia). Smelting activity began on industrial scale in the early 1800 near Katowice and has continued until very recently. The economic evolution of the country over the last twenty years resulted in closing up of a major part of the mining and metal-extraction activities and the abandonment of numerous waste materials. The presence of mining and extraction sites within urban zones poses important problems for the affected towns and their future development. Abundant dumps are scattered throughout the entire region and often occur near the hearts of the towns, gathering on a local scale heterogeneous smelting waste (Fig. 2). These dumps include solid waste issued from blast furnaces mixed with coal and other solid waste of various origins [2, 19, 29, 36].

Dumps consisting of slags produced during reworking of silicate (lateritic) Ni-ores occur in the vicinity of the village Szklary (Lower Silesia, Table 1). However, the phase assemblages and chemical composition of the pyrometallurgical slags from Szklary dump are similar to those issued from sulphide ores smelting [25].

The Rudawy Janowickie area (Lower Silesia; Table 1) is also of interest because base metal mining and smelting activities began there in medieval times. Historical sources describe mining activity in the vicinity of the village Miedzianka as early as 1310.
Fig. 2: Photographs of different tailings heaps and material constituting these tailings located in: (a, b) Świętochłowice (Upper Silesia), (c, d) Katowice/Wełnowiec (Upper Silesia), (e, f) Szklary (Lower Silesia), (g, h) historical slags present in stream in Rudawy Janowickie (Lower Silesia)
During the 14th century the Rudawy Janowickie area was the largest center for mining and smelting of metals such as Cu, As and Ag [5]. Since then, mining has closed and started again several times. Exploitation was definitely abandoned in 1925, leaving unattended mine tailings and slags located in the surroundings of the villages Miedzianka and Janowice Wielkie. The area covered by dumps is estimated to be around 35 ha. Some of the medieval dumps were further reprocessed during the 17th century by dissolution of secondary Cu sulfates, the method being characterized by particularly cheap and relatively easy application [5].

METHODS FOR STUDYING CHEMICAL AND PHASE COMPOSITION OF THE SLAGS

Each step of environmental study includes some amount of uncertainty which contribute to the final results. Sampling is the first step of such studies which deal with heterogeneous material due to the various origins of the concerned ores and to the long time of their extraction and treatment. In order to minimize sources of uncertainty, each collected sample should be representative and properly chosen for further study. Before sampling, it is necessary to prepare a sampling plan that fits to the main aims of the study and that reflects the properties of the whole study area. Sampling locations should be chosen taking into account specific conditions at the studied site (e.g. vegetal cover diversity, topography, hydrology etc). The most important prerequisite for a representative sampling is to explore the whole site area to get a view of the overall material variability. Then, if an attempt focuses on the average composition and if there is no interest for studying the spatial variability of the studied materials heterogeneity, most appropriate procedure consists in randomizing the sampling.

Methods applied for studying slags are those used in classical chemistry, mineralogy and petrology. These methods are nowadays supplemented by very fine techniques: micro focused scanning X-ray fluorescence (SXRF), micro X-ray absorption spectroscopy (XAS) and micro scanning X-ray diffraction (SXRD) in order to obtain data at the atomic scale.

For bulk chemical analyses, slag samples are dried and then prepared by particle size reduction to produce a homogeneous sub-sample which is representative of the original sample. For most analytical methods, this sub-sample will undergo some forms of dissolution and decomposition. Each sample decomposition procedure has its own advantages and limitations. The final technique used for the determination of elements depends on the required detection levels of the elements of interest. Typically two principal means of determination: Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are selected for slags. ICP-AES measures the light-waves and light intensities to determine what elements are present in the solution and the quantities of each. ICP-MS measures the element concentrations by counting the atoms for each element present in the solution. Generally, ICP-MS can determine concentrations that are 1 to 2 orders of magnitude lower compared to ICP-AES.

X-ray powder diffraction patterns provide important information on phase composition of studied slag samples. However, even by using Rietveld refinement, it is impossible to point out the presence of minor and trace phases (< 5% of the bulk sample) using this
method. Optical and Scanning Electron Microscopy (SEM) on polished sections or rough material coupled with Energy Dispersive Spectrometry (EDS) analyses allow to observe relationships between phases present in the studied material. Furthermore, complementary characterization of slags at nanoscale using transmission electron microscopy (TEM) is useful and allows to identify small inclusions which often occur within the glass (Fig. 3) and which generally contain high amounts of PTEs [38, 25].

![Fig. 3. Transmission electron micrographs of glass containing nanometric inclusions of PTE bearing phases: (a, c) coupled with selected area electron diffraction patterns (b, d)](image)

Microprobe analyses using Wavelength Dispersive Spectrometry (WDS) system provide information concerning the chemical composition of a given phase when its size is larger than the focus of the electron beam. The EDS system can be also used for quantitative analysis. For many combinations of elements, however, the EDS system is less precise than WDS because corrections must be made for overlapping peaks and the background noise is much higher, lowering the detection levels. WDS analyses results in a
spectral resolution and sensitivity an order of magnitude better than is possible with EDS. Changes in window aperture (from 4 nA to 500 nA) and rising in accelerating voltage (from 20 to 35 keV) allow to detect metallic element present at very low levels (several up to dozens of mg/kg) depending on the element [13].

FORECASTING POTENTIAL PTES RELEASE FROM SLAGS

Within slags storage, potential risks related to the waste evolution are often estimated only on the basis of the total PTEs contents. Indeed, knowledge of PTEs solid speciation, which corresponds to the identification of the PTEs chemical and structural bonding forms, gives more exhaustive information about their potential mobility, bioavailability and toxicity [41]. The solid speciation of PTEs in slags can be assessed in two ways. The most used way consists of application of several types of chemical extractions. Chemical reagents are supposed to preferentially dissolve specific groups of waste components in a given type of previously defined conditions (e.g. acidic, reduced). On the basis of such chemical extractions, Alter [1] defined a copper slags as non-hazardous using an aggressive test consisting on leaching by buffered acetic acid. However, experimental conditions applied during these chemical procedures do not account for all possible environmental factors.

The second way of studying the PTEs speciation from waste comprises detailed mineralogical and petrological study of slags. Those methods consist in (i) identification of weathering conditions and processes leading to crystallization of secondary phases and ii) determination of chemical and structural (mineralogical) composition of the materials exposed to the meteoric agents. Interpretation of such studies is done according to the known stability conditions of the identified PTEs-bearing phases. Observations of secondary phases crystallizing in cracks or at the periphery of the parent material enable to assess the stability of the primary phases and to provide information about the mobility of the concerned elements. These observations coupled with spectroscopic techniques (e.g. Raman, Mössbauer) are particularly of interest to point out transformation of some primary phases (e.g. willemite – Zn$_2$SiO$_4$) to secondary phases (e.g. hemimorphite – Zn$_4$Si$_2$O$_7$(OH)$_2$·(H$_2$O)) by hydration [43].

Despite their names which sound very good (fraction bounded to carbonates or to oxides, extraction procedure toxicity test etc.), the chemical methods which are often automatically and solely applied, do not correctly reproduce the actual environmental conditions nor the ultimate potential release in a given situation. In spite of approximations they imply (e.g. carbonate fraction is rarely the real and entire carbonate fraction), their reproducibility justify their use in most official national and European norms for regulation. Twardowska and Szczepańska [42] point out the inconsistency of the laboratory leaching tests particularly when equilibrium conditions are imposed by kinetically determined reactions. These authors also underline that such tests reflected entirely wash-out of phases and dissolution that does not comprise delayed PTEs release.

In contrast, mineralogical studies enable the solid speciation of PTEs to be determined and the PTEs-bearing phases in slags to be characterized. As a consequence, mineralogical examinations provide information about the actual rate of PTEs release in the real weathering conditions, whereas the chemical extractions give a view of the potential release in given experimental conditions. Hence, in most recent studies, authors use de-
tailed mineralogical examinations as a complement of the chemical laboratory experiments. This can be done in equilibrium conditions by examining of the solid residue obtained after specific chemical extractions [24]. Other studies attempt to simulate natural conditions over long periods of time (several months) using mineralogical observations in order to assess the actual slags weathering. These include leaching tests performed on the surfaces of polished sections [9, 30] or crushed samples in batch [34, 35] and in column tests [37]. In most cases, these experiments show that significant amounts of PTEs are released from the slags [34, 35].

Fig. 4: Photographs of slag weathering products:
(a) small needles of gypsum from Katowice/Wełnowiec slags, (b) aggregates of carbonates (aragonite) on the surface of slag from Katowice/Wełnowiec smelter, (c, d) weathered slag particles from cultivated soil located in the vicinity of the Szklary smelter, (e) secondary Fe oxy-, hydroxides replacing sulphides in historical Cu slag from Rudawy Janowickie, (f) needles of secondary zincite occurring in slags from Katowice/Wełnowiec.
ARE PYROMETALLURGICAL SLAGS REALLY DANGEROUS?

All freshly generated anthropogenic materials are not geochemically stable and not environmentally safe when abandoned on surface climatic conditions. However, waste issued from pyrometallurgy is different than mine tailings waste because it was subjected to industrial treatment of various kinds. They also include numerous solid phases such as silicate glass and silicate and oxides deemed to be more stable because they present lower solubility in water [44] in the most frequent environmental conditions than sulphide or sulphates. Therefore, slags are generally considered as chemically stable. However, numerous studies have shown that PTEs can be mobilized from slags and may contaminate soils and streams and have then deleterious effects on the environment [2, 30, 31, 35, 39].

It is important to point out that potential environmental risk related to PTEs release from slags strictly depends on weathering processes which are very complex. They not only depend on the solid speciation of PTEs in the waste but also on numerous different factors such as: (i) textural characteristics and permeability of the material, (ii) local climatic and environmental conditions, (iii) human activities in the site of the slags storage, and (iv) time of residence of the wastes in a given site. Therefore, risk assessment related with slags, landfilling of such wastes or their possible re-use require a systematic survey of many factors influencing local weathering conditions.

**Solid speciation**

Solid speciation is one of the most important factors controlling potential risk of PTEs release related to the slags. Solid speciation in slags varies according to the processes applied to extract metal from the ore. For example, Ettler et al. [7] collected four different types of slags in the same area in Přibram (Czech Republic) where the smelting of Pb-Zn ores has been used since the 6th century BC. The oldest period of Zn-Pb ores reworking consisted of smelting at low temperatures, while present technological process involves battery processing and smelting at high temperatures. Total metal content is higher in the oldest slag material from Přibram. Each type of slag was characterized by different proportions of glass and different assemblages of metal bearing phases due to the variation of the efficiency of smelting processes and to temporary procedures that were used for valorizing subordinate elements such as Sb in lead ores. Hence, the knowledge of the smelting history enables to forecast not only main feature of the chemical speciation but also feature of physical speciation such as proportion of glass and textural characteristics.

Metallurgical slags are dominated by silicates, oxides (commonly spinel) and silicate glasses. In silicates, PTE are either concentrated in phases with pure metallic end member (for example willemite or hardystonite for Zn) or as few percentage metals occurring as replacement of other cations such as Mg – Zn substitution in olivine or in pyroxenes [36]. In mattes, numerous types of sulphides or arsenides are still present. Alloys or intermetallic compounds are also frequent because the mutual metal solubility (e.g. Pb in Sb or Sb in Pb) is important at a relatively low temperature [10, 11]. Alterability of these reduced phases when placed in oxic environment is high and as a consequence, in a given sample, they can be considered as weak zones through which the destabilization of all the surrounding material can begin. Conversely, silicates and well crystallized oxides (e.g. spinels) are more resistant to weathering [8, 25]. For example, Soubrand-Colin et al.
observed spinels as the only phases unaffected by weathering from topsoils where none of other primary minerals was preserved. Usually glasses are well known to be less resistant to weathering than crystallized material and Goldich’s series give a well-known classification of the susceptibility to weathering of the most spread phases. However, this classification is based on standard alteration conditions which are not well defined. In smelter products, proportion of oxides is more important than in natural material. Finally, glasses are not always “true” glasses because PTE found by punctual EMPA analyses are included in glasses as small nanometric inclusions of sulphides and intermetallic compounds. This fact was reported by Seignez [37] and by Kierczak [23] following TEM investigations (Fig. 3).

**Textural characteristics and permeability**

Some physical characteristics of waste such as porosity or particle size distribution play an important role in PTEs release from slags. For example, a good penetration of water within a porous waste material allows for better exchanges and the renewal of percolating water and as a consequence better release of PTEs. On the contrary, compact and dense slags (Fig. 2) may significantly delay water penetration, progress of weathering and crystallization of secondary phases. Textural characteristics, such as proportion of glass considered as more susceptible to weathering than crystalline phases, are also important to predict the PTEs release. Weathering of glass containing small inclusions of sulfides and intermetallic compounds, generally considered as environmentally hazardous and the most important PTEs carriers, may expose them to atmospheric conditions and increase the rate of PTE release from slags [25].

**Local climatic conditions**

The knowledge of the local climatic conditions in the area of the wastes storage is another important factor which has to be considered to predict potential environmental hazard related with the slags. Climatic effects are very often transitory thus sites of slags storage require continuous inspection. For example, abundant secondary phases named evaporative efflorescences usually crystallize during summer after dry periods on Rio Tinto historical smelter site [31]. These phases include ubiquitous more or less hydrated Ca or Mg sulphates but also more or less complex metal sulphates (Zn, Cu, Pb or Fe). España et al. [6] show that the most soluble phases disappear during consecutive rainy episodes in autumn when they are not sheltered from falling waters or runoff. On abandoned slag tailings other secondary minerals grow resulting in the formation of metallic oxides or hydroxides, iron oxy-hydroxides, etc. containing PTEs at concentrations as high as several percent [2, 10].

**Local environmental conditions**

Local environmental conditions constitute also an important factor controlling weathering and PTEs release from the slags. Thus, it is fundamental to collect as much information as possible about the site of the slags storage. Kierczak et al. [25] pointed out that weathering of Szklary slags issued from silicate ores appears to be less advanced than that of the slags issued from sulfide ores processing. It is probably due to both phase assemblage and their composition, but also because the local environmental conditions in Szklary, such as soil pH, are unfavorable for chemical weathering of silicate phases. Furthermore,
Kierczak *et al.* [25] compared secondary products issued from the same Ni slags collected in a heap located at Szklary. Glassy slags exposed to weathering within surface horizons of a cultivated soil were more altered than the same glasses exposed to weathering on the top of the heap poorly colonized by vegetation. The differences in the rate of weathering are probably caused by agricultural treatments and lower pH values for the cultivated soil than those predominating on the waste dump. Alteration phenomena are generally more important in acid environments than in alkaline ones. However, Sobanska *et al.* [39] found that after fifty years, the slags fragments issued from the same lead smelting factory from Northern France were more altered in alkaline soil than in acidic environments. This was explained by the influence of several possible factors, such as organic matter content in the acidic soil which may slow down the slag weathering. Another assumption is the more hydromorphic conditions in the alkaline soil which limit precipitation of iron oxides that currently prevent soluble phases from alteration in the more acidic soil. Hence, there is no general rule giving one effect to one specific factor.

**Importance of human activities**

Human activities can act as a favorable or as a limiting factor of the PTEs stability in slags. As mentioned above, soil drainage or re-vegetation of the waste heap can enhance formation of stable secondary PTEs bearing phases and contribute to limitation of the environmental risk of PTEs release. In contrast, smoke emissions cause acidification and further soil pollution. It was pointed out that some compounds dissolved in particulate matter of industrial fumes, have strongly acidified (to pH 3) rainfalls [20]. Worsztynowicz and Mill [45] highlighted that this excessive acidification of precipitation occurs in Upper Silesia region due to hard coal burning. In the authors’ opinion, “Leaving this system out of control can result in spontaneous release of heavy metals and their migration into soil, surface and ground waters. This may lead to unforeseen consequences the more dangerous that addressed to one of the most populated areas in Europe”.

**Importance of residence time**

The next important factor which determines potential risk related to PTEs release from slags is time. When permeability of metallurgical tailings is high enough to allow formation of secondary products which are stable at local climatic and environmental conditions, the concerned tailings are considered to be in equilibrium. One can indeed believe that slags dumped for long periods (several centuries) have reached an equilibrium state with the surface conditions depending on the rate of weathering penetration. However, historical mining and smelting activities generally left highly polluted soils and sediments and caused irreversible changes to the environment [15].

**HOW TO MANAGE THE SLAGS STORAGE AND WHAT ABOUT RE-USE POSSIBILITIES?**

Regarding the social perception of metallurgical waste, three periods can be distinguished. Until 1980 metallurgical slags were not considered as tailings, thus they were abandoned without any care in the surroundings of mines or factories. Main difference between mine and metallurgical tailings is that the latter are more often abandoned in inhabited areas. This is particularly the case in Silesia where urban tailings are visible until now, for
example in Bukowno, Świętochłowice or Welnowiec in the surroundings of Katowice. However, the good news is that pyrometallurgical slags are not as finely crushed as their mining equivalents and generally form decimetric to metric boulders, which are potentially more resistant to weathering (Fig. 2).

Since 1980 until now, pyrometallurgical slags have been considered as waste. They are either stocked in secure landfill sites or partially used as material for roads or concrete production. Waste stocking is very expensive because it requires: (i) location and preparation of appropriate site and (ii) transfer of huge quantities of polluted material onto several kilometers or more. Recently, due to their composition, stability and mechanical properties [14], slag wastes are used as quarries supplying materials which appear to be the best way to get rid of these harmful products. Hence, pyrometallurgical slags have been often used as road ballast or backfill material, as sandblasting agents, as cement additives, even if they contain high concentrations of potentially toxic metals [35, 45]. Though advantage of addition of granular blast furnace slags in high performance concrete is not so obvious and within some ratio, it can lead to a deleterious decrease of the concrete resistance to freeze-thaw and to compression strength [46]. Furthermore, as shown by numerous studies [12, 30, 31, 32] risks of PTE release are still high because most reuse operations resulted in placing the slags in oxidizing and well drained conditions. The best conditions of PTEs immobilization are obtained for slag inclusions in cements [19] because of their basicity.

Blast furnace slags have also been widely used in wastewater treatment and pollution control technology for the removal of phosphate, heavy metals and organic pollutants. High phosphate sorption capacity of slags has been demonstrated by batch and column experiments as well as field research [21, 22, 28]. Slags are used as filter and adsorbent in on-site wastewater treatment systems, such as constructed wetlands and industrial soil filtration systems [4, 21]. The major advantage of slag is cost effectiveness and abundance, which makes the treatment process economical. On the other hand, in such processes, slags are confined in reductive water saturated conditions that are considered to facilitate the PTEs immobilization. However, within such water treatment system, there is neither regulation nor systematic survey of the actual evolution of the slag speciation.

Very recently, due to the increasing cost of raw materials and ongoing prices of metals, a new technologic goal arises in examination of perspectives of metal extraction by the re-use of slags. In spite of their sharp decrease in 2008, prices of metals have indeed increased in a rate over 200% for the last ten years (266% for Ni, 249% for Cu and 229% for Pb), except for Zn for which the price is 69% of the price of year 1999 (Fig. 5). As for mine tailings [3], due to changes in economic context and to improvement in extraction techniques, waste can be regarded as a profitable resource. In particular, slags can be treated as ore being added to the melts instead of raw materials in metallurgic processes, for example as fluxes or only as metal supplier. Some studies [33] are performed in order (i) to know bulk composition of the slags, (ii) to assess potential stock of heavy metals which can be salvaged, and (iii) to get a precise knowledge of the solid speciation of heavy metals in order to define processes which must be used for their recovery. Upper Silesia and Lower Silesia are surely very good experimentation areas for such studies.
Poland is one of the UE countries which is the most affected by the storage of slags derived from smelting industry. The main part of pyrometallurgical waste dumps occurs in Upper and Lower Silesia. Even if the present review mainly focused on four sites, it is representative for the case diversity that can be found in Silesia. Studied sites include various types of technological processes, diverse ore origins implying different metals (Zn, Pb, Cu, Ni). Moreover, slags from studied areas have been stored for a long period of time.

Pyrometallurgical slags in Poland constitute a real and serious hazard for the environment. In order to answer the question: “What could we do to protect us against consequences of PTEs release from slags?”, we should define first the current stage of the slags weathering and stability, and secondly the final aim consisting of possible re-use or landfilling of such waste. A variety of experiments coupled with in situ monitoring should
be applied in order to estimate the real risk related with the pyrometallurgical slags. Interest of detailed mineralogical examinations has been underlined. These methods should be used as a complement to the chemical methods which are the only ones generally required by the legislation. If the slag material is too hazardous to be re-used as additive, it should be stored in secure landfills. However, it was shown that factors determining the slags weathering are complex and quite impossible to forecast. The areas of the hazardous slag dumping have thus to be constantly controlled.

Pyrometallurgical wastes are not safe for the environment when exposed to atmospheric conditions, either at the disposal site, or in the case of its bulk use for construction purposes or water treatment. Although slags constitute potentially reusable materials, as highlighted by Twardowska and Szczepańska [42], it does not provide the best possible solution, either from an economic or environmental point of view, to consider them from the category of ‘waste’ as ‘secondary raw materials’ or ‘by-products’, or just ‘materials’.

Due to increasing prices of metals some slags (e.g. Ni-rich) would better be reused as new ore, rather than being only “hidden” somewhere or landfilled. However, it requires a detailed study which responds what technological process should be used to extract the metal content remaining in the waste. In the case of slags where metal content is too low to make the extraction profitable, its reuse rather as a construction material is the best way for environmental preservation.

Finally, it is important to point out that slags do not constitute the only problem related to mining and smelting industry in Silesia. There are also huge quantities of mine tailings, fly ashes and smoke emissions which contaminate the whole area.

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COMMUNICATION

Keywords: Sedimentation, mine waters, suspended matter, water treatment.

Abstract: The results of investigations into suspended matter sedimentation from mine waters in the settling tank at the Ziemowit coal mine as well as in the relevant model of the settling tank were presented. It was shown that variations in the performance of the tank are caused by improperly accumulated sediment, which generates privileged water flow in superficial layers. Additionally, impetuous periodical water discharges seem to be important. The investigations performed on the settling tank model were focused on estimating the influence of temperature, flow rate and the aeration of mine water on the suspended matter sedimentation. Reasons for inefficiency of the settling tank were determined, and technological changes enhancing the process of suspensions removal were suggested.

INTRODUCTION

Coal exploitation from mines located in the Upper Silesian Industrial Region makes it necessary to pump out significant volumes of mine waters onto the ground surface. Preliminary observations showed that the waters were polluted with suspended matter whose concentration varied from tens to several hundreds of mg/dm$^3$, depending on local conditions and the technologies employed [1, 2, 5]. Such values of suspended matter concentration in mine waters (after discharging them into surface waters) lead to the mudding of riverbeds, and in the case of high flow rates, can be the reason for secondary pollution of the rivers.

In the mines, the coarse-grained suspended matter is already removed at individual exploitation levels in so-called main drainage galleries. However, these often do not operate satisfactorily, and the content of suspended matter in the waters pumped out into on-ground settling tanks is still considerable. Periodical (daily and weekly) discharging of mine waters into a settling tank causes varying concentration of suspended matter at the tank inlet. Lowering the efficiency of suspended matter sedimentation can also result from privileged flow streams existing in superficial layers of the settling tanks. These
are induced by mud banks, technical difficulties in controlling the water level at the tank spillway, as well as significant temperature differences between the pumped-out and the in-tank water [1]. These reasons are the most valid if sedimentation time is sufficient in relation to proper flow. Therefore, precise knowledge of the phenomena influencing the work of a settling tank is desirable in order to eliminate variations in its performance and make the process of removing mechanical suspensions from mine waters more efficient.

This paper discusses the results of investigations into the natural sedimentation of mine water suspension in real conditions in an existing settling tank at the Ziemowit coal mine as well as in laboratory conditions in a model of a settling tank. The range of the investigations included the assessment of the influence of temperature, water flow rate and water aeration on the sedimentation of suspended matter in the tank.

**METHODOLOGY**

The process of suspended matter sedimentation from the Ziemowit coal mine waters was analyzed by measuring the total suspended matter in the water samples taken from the settling tank spillway. The water flew out of the settling tank through 6 outlet boxes spaced equally along the longer side of the tank, opposite the feeding channels (Fig. 1) [4]. The concentration of suspended matter was determined according to [3, 6].

Fig. 1. The settling tank at the Ziemowit coal mine with supplementary objects

In order to assess the influence of the flow rate, temperature and aeration on sedimentation of suspended matter, certain investigations were performed on a settling tank model in laboratory conditions. The model of the settling tank was a plexiglass container,
filled with mine water of the volume of 0.08 m³ (200×20×20 cm), simulating conditions occurring in real settling tanks for salt mine waters (Fig. 2).

![Diagram of the model of the tank](image)

Fig. 2. Diagram of the model of the tank (1 – auxiliary container, 2 – stirrer, 3 – dosing pump, 4 – feeding channel, 5 – horizontal settling tank, 6 – spillway, 7 – water outflow, 8 – barriers)

The settling tank was supplied with mine water from an auxiliary container by a pp1-05 pump. Two flow rates were used: 7.2 dm³/h and 36 dm³/h. The auxiliary container was equipped with a stirrer preventing sedimentation. The stirring rate was 400 rpm. The model was placed in a closed room, at a temperature of 20 ± 1°C, with access to light and atmospheric air.

The investigations were carried out in the following four stages:

- **Stage I** – the tank was filled with mine water to a level of 5 cm, and the investigations on sedimentation were performed for two flow-rates: 7.2 dm³/h and 36 dm³/h (water retention time equal to 11 h and 2 h, respectively). Next, the measurements were repeated for a water depth equal to 10 cm.

- **Stage II** – the tank was filled with mine water to a level of 10 cm. A barrier, submerged 5 cm below the water level, was fastened adjacent to the water inlet in order to decrease the energy of the supplied water, and distribute it along, or partially under the barrier. Due to the barrier application, a rise of settling efficiency was expected. This experiment was carried out at a flow rate of 7.2 dm³/h.

- **Stage III** – the investigations were performed for aerated water. The water was aerated in the auxiliary container for 30 min. After aeration, the water was pumped at a flow-rate 7.2 dm³/h into the tank.

- **Stage IV** – the influence of mine water temperature on suspension sedimentation was investigated. Determining the sedimentation rate as dependent on temperature is reasonable, because differences in temperature between summer and winter in open settling tanks for mine waters are significant. The tank was placed in a cool room and filled with mine water of the temperature of 7°C to a level of 10 cm. The tank was supplied with water of the temperature of 18°C at a flow rate of 7.2 dm³/h. The auxiliary container was placed in an ultrathermostat. Apart from the thermometer belonging to the ultrathermostat, two additional thermometers were placed in the auxiliary container, at different depths, in order to control the water temperature.
Temperature oscillations did not exceed ± 0.3°C. The experiment was repeated with a barrier submerged 5 cm below the water level.

During the process of suspension sedimentation from mine waters in the model, the measurements of total suspended matter and turbidity of the water samples from the tank outflow were made. Three samples were taken every 30 minutes. In addition, grain composition of the suspension left after sedimentation was determined with an LAU-10 laser analyzer.

RESULTS AND DISCUSSION

The observations of water flow in the settling tank of the Ziemowit coal mine confirmed the underperformance of the tank. They indicate the probable occurrence of local, privileged superficial currents. The basis for this assumption is the observed tint of the water flowing through the settling tank from feeding channels to outlet boxes. The analysis of water samples taken from the central and the two outermost outlet boxes also suggests it. The concentrations of suspended matter in the samples taken from the inlets of the outlet boxes were 98, 36.4 and 59 mg/dm³, respectively.

A possible way of improving the tank’s performance is removing the accumulated sediment and ensuring homogeneous water flow through the settling tank. When acquiring the samples for analysis, a natural barrier made from mud and sand was visible near the first two feeding gutters. Water sample taken from the outlet box situated opposite the barrier had the lowest concentration of suspended matter, equal to 36.4 mg/m³.

The settling tank is fed from a central collector through 10 pipes spaced equally along the longer side of the tank. The water flowing from the outflows is intensively aerated in a natural way (the water falls from about 1.5 m height), and then flows into the settling tank along concrete gutters. The reason behind the unsatisfactory performance of the settling tank may also be linked to temperature differences between the water pumped out from the mine (average temperature about 18°C) and the water already in the settling tank, especially in winter (about 6°C).

The measurement results for total suspended matter and turbidity of mine water taken from the spillway of the model of the settling tank are shown in Tables 1 and 2. The efficiency of sedimentation was verified by analyzing the grain composition of the suspension. The results are shown in Figure 3.

Table 1. Results of analysis for sedimentation of mine water suspension in the model of the settling tank for water depth 5 cm

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>Total suspended matter</th>
<th>Reduction of total suspended matter</th>
<th>Removal percentage</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[dm³/h]</td>
<td>[mg/dm³]</td>
<td>[mg/dm³]</td>
<td>[%]</td>
<td>NTU</td>
</tr>
<tr>
<td>36</td>
<td>579</td>
<td>337</td>
<td>41.8</td>
<td>137</td>
</tr>
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<td></td>
<td></td>
<td>321</td>
<td>44.6</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>39.5</td>
<td>138</td>
</tr>
<tr>
<td>7.2</td>
<td>579</td>
<td>177</td>
<td>69.4</td>
<td>85.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>167</td>
<td>71.2</td>
<td>81.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>162</td>
<td>72.0</td>
<td>78.9</td>
</tr>
</tbody>
</table>
Table 2. Results of analysis for sedimentation of mine water suspension in the model of the settling tank for water depth 10 cm

<table>
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<td>216</td>
<td>62.7</td>
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<td>83.9</td>
<td>64.6</td>
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<td>103</td>
<td>82.2</td>
<td>67.2</td>
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<tr>
<td></td>
<td></td>
<td>102</td>
<td>82.4</td>
<td>68.6</td>
</tr>
<tr>
<td>with the barrier placed near the inflow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>579</td>
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<td></td>
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<td>61</td>
<td>89.5</td>
<td>54.2</td>
</tr>
<tr>
<td>with water aeration at the inflow</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>7.2</td>
<td>579</td>
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<td></td>
<td></td>
<td>131</td>
<td>77.4</td>
<td>78.8</td>
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<td>in-tank water temperature 7°C, supplying water temperature 18°C</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>579</td>
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<td>69.3</td>
<td>100.2</td>
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<td></td>
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<td>95.0</td>
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<td>201</td>
<td>65.3</td>
<td>96.3</td>
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<tr>
<td>in-tank water temperature 7°C, the barrier placed adjacent to the inflow</td>
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<tr>
<td>7.2</td>
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<td></td>
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<td>131.6</td>
<td>77.4</td>
<td>84.0</td>
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<td></td>
<td></td>
<td>129</td>
<td>77.7</td>
<td>80.9</td>
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</tbody>
</table>

Fig. 3. The results of grain composition analysis of mine water taken from the spillway of the model of the settling tank
Aerating the mine waters at the inflow lowered the sedimentation rate of the suspended matter. Its concentration increased by 30 mg/dm$^3$ (from 100 to 130 mg/dm$^3$) at the spillway. This was also confirmed by sedimentation analyses carried out in an Imhoff cone, the results of which are presented in Figure 4.

![Fig. 4. Kinetics of mine water suspended matter sedimentation for various aeration times](image)

When introducing a larger amount of air into the mine water, the particles forming the suspension remain suspended, which significantly increases the sedimentation time. The depth of the tank has an influence as well, because suspended particles aggregate, becoming larger and larger, and their falling velocity rises. The results obtained for the flow rate of 7.2 dm$^3$/h and the tank depth of 5 cm showed a decrease in the efficiency of sedimentation of about 13%, in relation to the efficiency for a tank depth of 10 cm, and for the flow rate of 36 dm$^3$/h – even by 30%.

The investigations into the natural sedimentation of mine water suspended matter in the model of the settling tank (despite the scale difference), reflected to a certain degree the conditions occurring in the actual settling tank, indicating relationships between causes and effects. The results presented in Tables 1 and 2 show that a fivefold increase in flow rate (from 7.2 to 36 dm$^3$/h) disrupts mine water suspended matter sedimentation. The total reduction in suspended matter, as a percentage, was about 40% for a tank depth of 5 cm and 60% for 10 cm when the flow rate equaled 36 dm$^3$/h. A significantly greater percentage was obtained for the flow rate of 7.2 dm$^3$/h – 70% and 80%, respectively. The unsatisfactory performance of the settling tank at a flow rate of 36 dm$^3$/h was confirmed by the presence of a coarser grain class 13–48 μm in the spillway water. In the model of the settling tank, considerable differences in suspended matter falling velocity were observed due to differences in temperature between the supplied mine water (18°C) and in-tank water (7°C) at the same flow rate. During an 11 h sedimentation, the concentra-
tion of total suspended matter fell to about 200 mg/dm$^3$, i.e. it decreased by about 60%. In summer conditions, at the temperature of 20°C, the sedimentation efficiency was about 30% higher. Temperature differences and, related to them, differences in density between in-tank waters and inflowing waters generate density currents. In the model, a visible stratification could be observed – inflowing water flowed in a superficial layer, which negatively affected the process of suspension removal. Setting a barrier in the model near the feeding channel at a depth of 5 cm decreased the flow cross-section, and improved the performance of the model. The suspended matter reduction percentage obtained was about 90% for identical temperatures of inflowing and in-tank water (20°C), and about 78% for the above-mentioned differences in temperature (at a flow rate of 7.2 dm$^3$/h). After installing the barrier, the efficiency of the model rose by about 15%, the same for natural conditions, i.e. at the temperature of 20°C, as well as for conditions with temperature differences. However, the barrier did not reduce the suspended matter concentration to the permissible value (30 mg/dm$^3$), it only improved its performance.

CONCLUSIONS

The observations performed on the model of the settling tank make it possible to state that:

- both aeration and differences in temperature between the in-flowing and in-tank water negatively affect the sedimentation process in the tank model. Water aeration caused a decrease in tank model efficiency by about 10%, and differences in water temperature by about 20%,
- after installing a barrier near the water inlet efficiency rose by about 15%.

There is no doubt that superficial currents occurring in the settling tank have a negative influence on the sedimentation of the suspended matter. These disturbances to the performance of the settling tank can be avoided by removing accumulated sediment and ensuring a uniform flow rate by installing flowing barriers to block the currently privileged superficial flow. Submerging flowing barriers to a depth of about 0.5 m and locating them straight in front of the outlet gutters of the settling tank should disperse the energy of the in-flowing water and distribute it along and partially under the barriers. This solution should significantly improve the sedimentation process in the Ziemowit’s settling tank. At first, the barriers may be sited near some outlet gutters only. Comparison of suspended matter concentration in water samples taken from the outlet boxes located straight in front of the barriers with samples from outlets without the barriers should indicate whether the barriers are effective. After confirming that they have a beneficial impact, such barriers should be installed near all inlet gutters. If the above-mentioned operations do not bring satisfactory results, it would be useful to consider aiding the sedimentation process by chemical treatment using suitable coagulants and flocculants.

The analyses carried out on the settling tank model indicate that it is necessary to redesign the inlet box in the existing settling tank. This should reduce water aeration and make water flow as uniform as possible in any cross-section of the settling tank.
POLOWE I MODELOWE BADANIA SEDYMENTACJI ZAWIESINY W OSADNIKU WÓD DOŁOWYCH KWK „ZIEMOWIT”

Przedstawiono wyniki badań nad sedymentacją zawiesiny zrzutowych wód kopalnianych KWK „Ziemowit” na osadniku ziemnym oraz w warunkach laboratoryjnych na osadniku modelowym. Zbadano przyczyny złej pracy osadnika kopalni i zaproponowano zmiany technologiczne pozwalające uzyskać zrzuty wód o ustabilizowanej zawartości zawiesin i usprawnić proces oczyszczania wód kopalnianych z zawiesiny mechanicznej. Wykazano, że zaburzenia w pracy osadnika spowodowane są nagromadzonym osadem, powodującym uprzywilejowany przepływ wody po powierzchni, a także gwałtownymi periodycznymi zrzutami tych wód. W badaniach modelowych oceniono wpływ temperatury, prędkości przepływu wody i napowietrzenia wody kopalnej na proces sedymentacji zawiesiny.

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