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Edyta ŁASKAWIEC[1*], Mariusz DUDZIAK[1]
and Joanna WYCZARSKA-KOKOT[1]

ASSESSMENT OF THE POSSIBILITY OF RECYCLING BACKWASHING WATER FROM THE SWIMMING POOL WATER TREATMENT SYSTEM

OCENA MOŻLIWOŚCI RECYKLINGU POPŁUCZYN Z SYSTEMU OCZYSZCZANIA WODY BASENOWEJ

Abstract: The paper presents the physicochemical analysis and toxicological assessment of backwashing samples taken after the process of washing filter beds in a raw condition after the process of their aeration and dechlorination. The backwash water under investigation originated from circulation systems existing in two indoor swimming pool facilities. The backwash water, as used at the preliminary and the main stages, was characterized by different physicochemical properties. For toxicological assessment, the Mictorox® bioluminescence inhibition test, the *Chaoborus sp.* insect larva survival test and the phyto test using *Lemna minor* fine cilium were involved. The investigation presented in the paper included a preliminary phase focusing on the ecotoxic characterization of backwash water subjected to aeration and dechlorination processes. In turn, at the main stage, the effect of aeration duration on the quality of backwash water in terms of its physicochemical parameters was analyzed. The results of the preliminary stage investigation indicate that backwash water, both in a raw condition and after 30 minutes' aeration, could not be discharged directly to the environment due to the threat to living organisms caused by its high toxicity. Whereas, using 160 minutes' aeration duration contributed to a significant improvement in the quality of the backwash water and elimination of its toxic properties with respect to the indicator organisms used. The chemical dechlorination process brought about varying effects. In the case of the Microtox® test, a stimulation of bacterial bioluminescence was noted, but, at the same time, the death of individual insect larva specimens was observed. In spite of the high biomass increase in the *Lemna minor* test, a gradual discolouration of fronds under the influence of backwash water was observed. Because of the presence of numerous compounds being disinfection by-products, as well as coagulant residues in backwash water deriving from swimming pool systems, it is necessary to seek further solutions that will allow them to be recycled, which will result in a reduction of water consumption and effluent discharges.

Keywords: swimming pool water, backwashing, toxicological assessment, physicochemical analysis, biotests

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Introduction

Conducting the process of washing swimming pool filters in the correct manner and at the proper frequency makes it possible to maintain the physicochemical and bacteriological standard of not only circulating water but also washings which, in terms of quality, corresponds to surface water in quality class three. The assurance of these requirements may contribute to a reduction of the discharge of backwash water as a waste stream to the sewage system and provide the possibility of reusing it [1]. The quality and quantity of backwash water is determined by numerous other factors, including: the intensity of conducted washing, the quality of water fed to the circulation system, the quantity and types of removed impurities, as well as the type and dose of chemicals used. To assure the correct bed washing process, it is necessary to use 4 to 6 m^3 of water per each square metre of the bed, which, in the case of large facilities, entails high water and energy consumption costs [2]. Backwash water is distinguished not only by a high content of suspension, but also by residues of coagulants and disinfectants. In particular, the presence of disinfection by-products, as well as admixtures and contaminants used in the surface coagulation process is problematic from the perspective of washing reuse [3, 4]. However, from the technological point of view, the recovery of water from the waste stream is possible.

The objective of the study was to carry out the physicochemical assessment (by the measurement of the conductivity, reaction, etc.) and toxicological assessment of backwash water obtained from the filter bed washing process, as well as the analysis of the parameters under investigation after the washing aeration and dechlorination process. The assessment of the toxicity was performed based on the Microtox® bacterial test, the *Chaoborus sp*. insect larva survival test, as well as the test using a water plant, *Lemna minor* fine cilium.

Materials and research methodology

Physicochemical analysis

Backwash water used at the preliminary investigation stage was taken from the circulation system of a sports swimming pool and then subjected to analysis for selected physicochemical properties, including the reaction (pH), conductivity and ultraviolet absorbance at a wavelength of 254 nm. For the extended stage, on the other hand, backwash water was taken from the common tank of the circulation systems of the sports and a leisure swimming pools. In that part, the concentration of (free and total) chlorine, chlorides, ammonium and nitrate nitrogen, colour, turbidity and total hardness were additionally measured.

The measurement of the conductivity and pH of water samples was done with an inoLab® 740 multi-parameter meter (WTW, Measuring and Analytical Technical Equipment). The absorbance was measured using a UV VIS Cecil 1000 supplied by Analytik Jena AG, with a cuvette optical pathlength of 1 cm. The absorbance value at the wavelength of 254 nm was determined based on the UV_{254} ultraviolet absorbance

measurement method in accordance with the standards adopted by US EPA [5]. The measurement of chlorine concentration by the colorimetric method was done using a Hach® Pocket Colorimeter™ II portable instrument. The concentration of nitrate and ammonium nitrogen was determined with a photolyser 400 (Dinotec) tester. The chloride concentrations were assayed by the Mohr method. For the determination of the turbidity of samples, an EUTECH Instruments Turbidimeter, Model TN-100, was employed. The measurement of the colour was performed using a UV VIS Spectroquant® Pharo 300 spectrophotometer (Merck). The total hardness, on the other hand, was determined by the titration method using sodium versenate.

Toxicological assessment

The Microtox® test enables the determination of the magnitude of the toxic effect based on the suppression of the natural metabolic processes of bacteria in the form of bioluminescence inhibition. The toxicity analysis was carried out in conformance with the *Screening Test*procedure of the MicrotoxOmni system in a Microtox analyzer, Model 500, manufactured by Tigret Sp. z. o.o., performing the function of both an incubator and a photometer. The percentage of inhibitions relative to the control sample not exposed to the potential toxicant was measured after 5 and 15 minutes' exposure time. The toxicity effect was determined as the percentage (%) of inhibition (I) according to Equation 1:

$$\%I = \frac{100 \cdot (E_K - E_T)}{E_K} \tag{1}$$

where: E_K – the value of bioluminescence in an attempt to control,
E_T – the value of the bioluminescence in the sample with a toxic substance.

The test of the survival of animal organisms, which were *Chaoborus sp.* larvae, was performed following the authors' own methodology. Acquired from an industrial culture, the larvae were taken to a laboratory, where their mobility was evaluated. Dead or immobilized specimens were rejected from the culture. After 24 hours, the review of the culture was repeated. 3 cm^3 washing samples, with 5 specimens being placed in each of them, were used in the test. The test plates were incubated in darkness at a temperature of 20°C. The reading of the number of immobilized or dead specimens was taken after 24 and 48 hours from the start of the test, respectively. The percentage value of the toxic effect was calculated from Equation 2:

$$\text{Effect} = \frac{100 - L_{24\,\text{h}}}{L_{0\,\text{h}}} \cdot 100\% \tag{2}$$

where: L_{24h} – number of alive specimens in the sample after 24 hrs of the test,
L_{0h} – number of specimens taken to the test.

For the classification of toxicity, a system commonly used by many researchers [6] was adopted, which is based on the size of the observable effect produced in the indicator organism used (Table 1).

Table 1

The toxicity classification system [6]

Effect [%]	Toxicity class
< 25	Non-toxic
25–50	Low toxic
50.1–75	Toxic
75.1–100	Highly toxic

A preliminary toxicological assessment of the backwash water under investigation was also made based on the growth inhibition of *Lemna minor* fine cilium according to the authors' methodology complying with the OECD recommendations [7]. The frond growth and inhibition coefficients, R_f and IR_f, were determined from Equations 3 and 4, respectively:

$$R_f = \frac{\ln f_2 \cdot \ln f_1}{\Delta t} \tag{3}$$

where: f_2 – number of fronds on the last testing day,
f_1 – number of fronds on the first testing day,
$\Delta t = t_2 - t_1$ – number of testing days.

$$IR_f = \frac{R_{fc} \cdot R_{ft}}{R_{fc}} \cdot 100\% \tag{4}$$

where: R_{fc} – coefficient of frond growth in the control sample,
R_{ft} – coefficient of frond growth for successive samples.

As the inhibition signal, positive growth inhibition coefficient values (> 0%) were taken. By contrast, the growth stimulation was indicated by negative values.

An attempt to determine the influence of washing components on the dye contents of plants was also made. The concentrations of chlorophyll and carotenoids were determined by the spectrophotometric method using an acetone extract from the plants. The chlorophyll determination was made by the method described by Blamowski and Borowski [8], while for determining the sum of carotenoids, Lichtenthaler's methodology [9] was used. The basic parameters of the influence of backwash water on the plant were determined based on the changes in 7 days' tests. All biotests were carried out in three repetitions, and the presented results constitute average values obtained from the analyses.

Washing aeration and dechlorination process

The aeration process was conducted in small laboratory reactors, each of a capacity of 400 cm^3. A HAGEN ELITE OPTIMA double discharge-port pump, with a delivery of 1500 cm^3/min for each discharge port, was used for aeration. The concentration of oxygen dissolved in backwash water was controlled during the aeration process using an immersible process probe operating based on an optical measurement method, equipped with an LDO sensor (HACH LANGE). The concentration of oxygen in the backwash water used at the preliminary testing stage was 7.61 mgO_2/dm^3 and the process was conducted for 30 minutes. At the next stage, on the other hand, the oxygen concentration was increased up to a maximum of 8.80 mgO_2/dm^3, and the physico-chemical parameters were determined after 40, 100 and 160 min after the start of the process.

The dechlorination process was carried out in compliance with the US EPA recommendations [10] using anhydrous sodium sulfite, Na_2SO_3 (Stanlab). Based on the stoichiometric equation for the reaction of sodium sulfite with hypochlorous acid, HOCl, it was determined that, in order to carry out the process, 1.775 mg of Na_2SO_3 had to be used per 1 mg of free chlorine. Dechlorination was carried out only at the preliminary testing stage for backwash water from the sports swimming pool circulation system using a single sodium sulfite dose.

Results and discussion

The physicochemical analysis of backwash water performed at the preliminary stage (Table 2) indicated variations in parameters under the influence of the processes carried out. A particularly marked increase in reaction, conductivity and ultraviolet absorbance was documented in the sample of backwash water subjected to chemical dechlorination. The processes carried out contributed to a change in the nature of the suspension, which underwent sedimentation more easily compared to backwash water not subjected to the cleaning processes.

Table 2

Physicochemical analysis of backwash water examined at the preliminary stage

No.	Backwash water	Reaction pH [-]	Conductivity [μS/cm]	UV_{254} ultraviolet absorbance [m^{-1}]
1	Raw	7.38	5526	15.60
2	Aerated (30 min)	7.31	5587	19.10
3	Dechlorinated	8.36	6604	37.70

During carrying out the main testing stages concerning the aeration effects, the scope of physicochemical analysis was increased (Table 3). With the increase in backwash water aeration time, an increase in the concentration of bonded chlorine (chloramines) and chlorides was noted. A similar relationship was observed for the reaction, total

hardness and turbidity. In contrast, the longer backwash water aeration time resulted in a lowering of the concentration of ammonium and nitrate nitrogen.

Table 3

Physicochemical analysis of backwash water

Parameter/Indicator	Unit	Aeration time [min]			
		0	40	100	160
Free chlorine	$mgCl_2/dm^3$	0.05	0.06	0.05	0.04
Bonded chlorine	$mgCl_2/dm^3$	0.34	0.52	0.45	0.44
Total chlorine	$mgCl_2/dm^3$	0.39	0.58	0.50	0.48
Reaction (pH)	—	7.28	7.49	8.08	8.19
Conductivity	µS/cm	1386	1389	1396	1389
Turbidity	NTU	9.05	10.80	10.40	10.58
Colour	m^{-1}	2.00	2.00	2.00	2.00
Ammonium nitrogen	$mgN\text{-}NH_4/dm^3$	2.37	2.32	0.29	0.12
Nitrate nitrogen	$mgN\text{-}NO_3/dm^3$	17.00	12.00	12.00	8.00
Chlorides	$mgCl^-/dm^3$	188.15	202.35	205.90	205.90
Total hardness	$mval/dm^3$	7.60	7.60	7.68	7.84
UV_{254} ultraviolet absorbance	1/m	5.40	6.30	6.90	7.40

The backwash water under investigation was distinguished primarily by varying values of UV_{254} ultraviolet absorbance and conductivity. The backwash water used at the preliminary stage exhibited much higher values of these parameters, which indicates a greater fraction of swimming pool water-contaminating substances of the sample taken.

The bioluminescence inhibition test of backwash water carried out at the preliminary investigation stage showed also its high toxicity towards bacteria. After 15 minutes of exposure, the value of inhibition for raw backwash water was over 99% (Fig. 1).

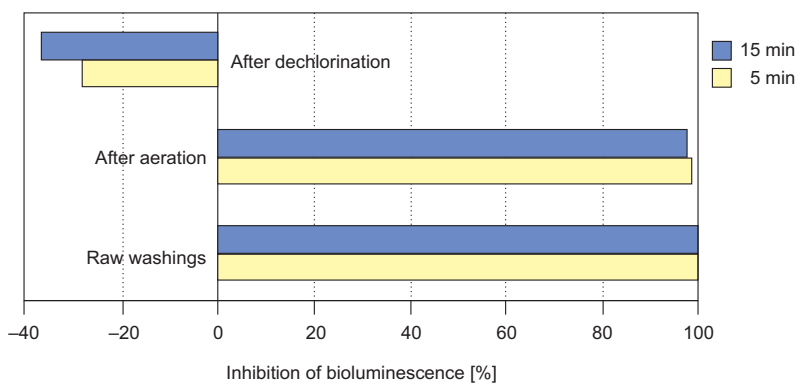

Fig. 1. The toxicity of backwash water samples in the Microtox® assay

Moreover, subjecting the backwash water to aeration did not bring about any significant reduction in inhibition value, and the bioluminescence inhibition after 15 minutes' exposure time was approx. 97%. By contrast, the dechlorination process not only completely deprived the sample of the toxic effect, but also stimulated the metabolic processes in the bacteria used in the test.

The backwash water used at the second investigation stage were characterized by a lower bioluminescence inhibition value. The bioluminescence inhibition value for the sample before the aeration process was about 78% (Fig. 2), which might have a great influence on the obtained results. Moreover, the backwash water was taken from two facilities that showed a different load with people bathing on the day preceding the sampling. The performed aeration contributed to a considerable reduction of the backwash water toxic effect on the indicator organism. Finally, the sample taken after 160 minutes of the process showed a bioluminescence stimulation at –54% of that after 15 minutes of exposure. Moreover, samples were also prepared for the sedimentation process, from which the supernatant liquid was taken after 24 hours. The fact interesting from the point of view of further research on this subject is that the bioluminescence stimulation in supernatant liquid samples was achieved already after 40 minutes' aeration time, with its value amounting to –14%.

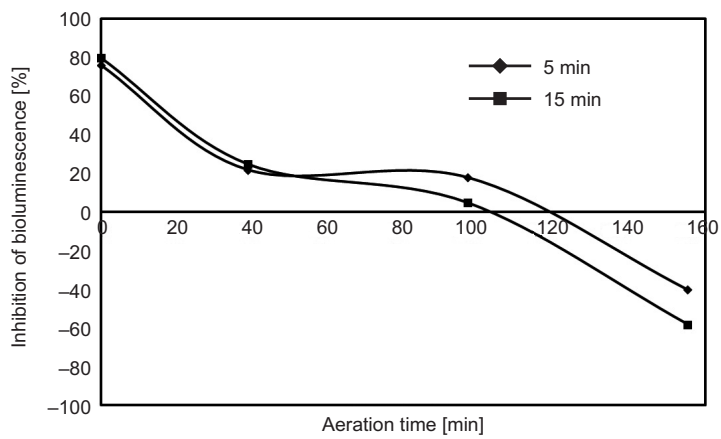

Fig. 2. Variations of bioluminescence inhibition in samples treated in the aeration process

The performed *Chaoborus* sp. insect larva survival test (Fig. 3) showed a high resistance of this organism to chemical compounds contained in the backwash water. The greatest mortality among the specimens was noted in the raw backwash water sample. The toxic effect was 27%, which classified the sample as toxic to the organisms used. Moreover, in the aerated backwash water sample the mortality of the specimens was 7%, while after the dechlorination process, 11%. The analyses were performed after 48 hours from the start of the test.

The *Lemna minor* phyto test showed a significant reduction in the content of chlorophyll-a in the fronds of plants grown both in raw backwash water and in preliminarily treated backwash water. At the same time, an increase in the concentration

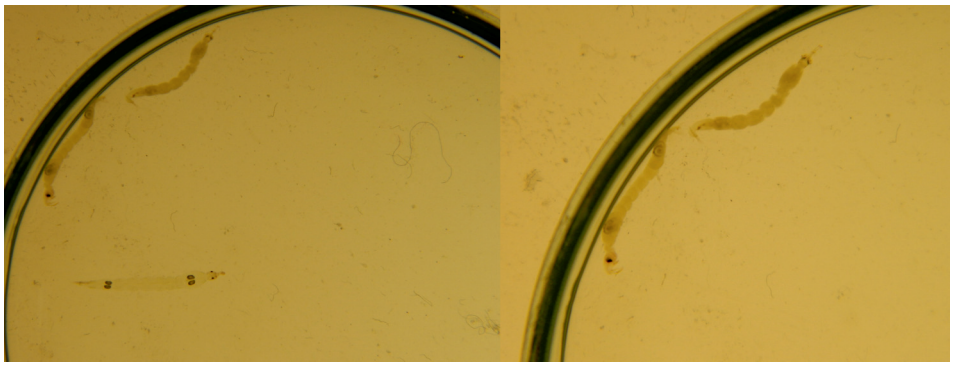

Fig. 3. The individuals of *Chaoborus* sp. – live (left photo, below one individual) and the dead (on the left and the right picture – two individuals)

of chlorophyll-b and carotenoids was noted. The increase in carotenoid contents might be caused by the activation of anti-oxidation mechanisms in the presence of impurities occurring in the test samples [11]. Whereas, the differences in values between chlorophyll-a and chlorophyll-b might be due to both the contamination of the samples and the development variations in the plants, which occur in individual phases of growth [12].

All samples taken during aeration exhibited high ability to stimulate the plant biomass increase, as indicated by the negative values of the growth inhibition coefficient (Fig. 4). The strongest stimulation was noted for raw backwash water, while the weakest stimulation, for backwash water aerated for 160 minutes. This suggests the occurrence of *Lemna minor* growth-promoting substances in the backwash water tested.

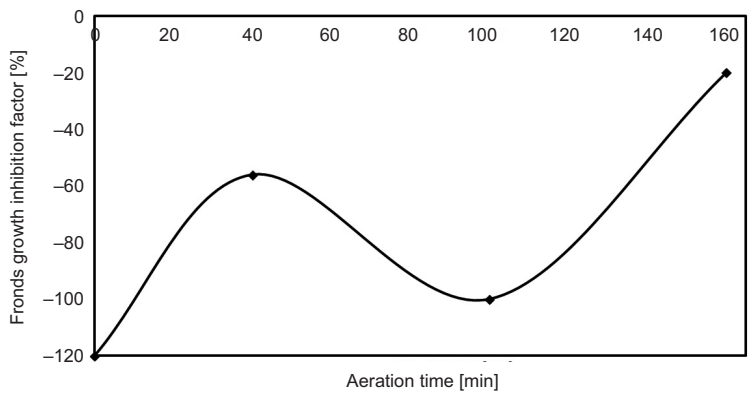

Fig. 4. Variations in the value of the growth inhibition coefficient for fronds in aerated samples

Conclusions

The performed pre-treatment processes changed the quality of the swimming pool system backwash water under investigation. The achieved final aeration results were

significantly influenced by the initial backwash water toxicity value noted in the biotests. Therefore, it is of particular importance to maintain the filter washing frequency standards. For toxicological tests, the susceptibility of particular indicator organisms is also very important, and the utmost care in their selection is necessary.

The application of the aeration or dechlorination process may bring about an improvement in the quality of the backwash water, which will allow it to be discharged directly to the soil or water. However, it is necessary to extend the research on the impact of backwash water-borne chemical compounds on the natural environment.

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OCENA MOŻLIWOŚCI RECYKLINGU POPŁUCZYN Z SYSTEMU OCZYSZCZANIA WODY BASENOWEJ

Instytut Inżynierii Wody i Ścieków
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Abstrakt: W pracy przedstawiono analizę fizykochemiczną oraz ocenę toksykologiczną próbek popłuczyn pobranych po procesie płukania złóż filtracyjnych w stanie surowym po procesie napowietrzania oraz dechlo-

racji. Badane popłuczyny pochodziły z obiegów zlokalizowanych w dwóch obiektach basenowych krytych. Do oceny toksykologicznej włączono test inhibicji bioluminescencji Mictorox®, przeżywalności larw owadów *Chaoborus* sp. oraz fitotest z wykorzystaniem rzęsy drobnej *Lemna minor*. Badania obejmowały fazę wstępną, skupiającą się na charakterystyce ekotoksykologicznej popłuczyn poddanych procesom dechloracji oraz napowietrzania. W etapie zasadniczym badań analizowano dodatkowo wpływ czasu napowietrzania na jakość popłuczyn pod względem parametrów fizykochemicznych. Wyniki wstępnego etapu badań sygnalizują, że popłuczyny zarówno w stanie surowym, jak i po 30-minutowym napowietrzaniu nie mogły zostać bezpośrednio odprowadzone do środowiska ze względu na zagrożenie dla organizmów żywych, spowodowane ich wysoką toksycznością. Natomiast zastosowane wydłużenie czasu napowietrzania (160 min) przyczyniło się do znaczącej poprawy jakości popłuczyn i pozbawienia ich właściwości toksycznych w stosunku do wykorzystanych organizmów wskaźnikowych. Zróżnicowane efekty przyniósł zabieg chemicznej dechloracji. W przypadku testu Microtox® odnotowano stymulację bioluminescencji bakterii, równocześnie zaobserwowano śmierć pojedynczych osobników larw owadów. Pomimo wysokiego przyrostu biomasy w teście z *Lemna minor*, zaobserwowano stopniowe odbarwienie frondów pod wpływem użytych popłuczyn. Niezbędne jest poszukiwanie dalszych rozwiązań umożliwiających ich recykling, co zapewni ograniczenie zużycia wody oraz odprowadzania ścieków.

Słowa kluczowe: wody basenowe, popłuczyny, ocena toksykologiczna, analiza fizykochemiczna, biotest

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Paweł WOLSKI[1]

RHEOLOGICAL PARAMETERS OF INITIALLY DISINTEGRATED SEWAGE SLUDGE AFTER FERMENTATION

PARAMETRY REOLOGICZNE WSTĘPNIE DEZINTEGROWANYCH OSADÓW ŚCIEKOWYCH PODDANYCH FERMENTACJI

Abstract: Yield point, viscosity, shear stress are technological parameters useful in practice to control the pumping of sludge, flow and other processes related to their processing. Increasing the efficiency of dewatering causes a decrease in their ability to flow through an increase in the limits of flow and thus the shear stress values. The variability of the stress and the viscosity is the result of changes in the structure occurring in the sludge during the flow. Any change in the structure of sludge by conditioning affected the same for their rheological parameters.

The aim of the study was to determine the dependence of shear velocity gradient (flow curves) pre-conditioned ultrasonic field sludge, and then fermented. In the process of sonication, four of the ultrasonic wave intensity *ie*: 2.2; 2.7; 3.2; 3.8 W/cm^2 were applied, and the time of sonication equals 600 s. The fermentation process was carried out in 10 glass flask with a capacity of 0.5 dm^3 which were models the digester. To describe the flow curves used the simplest mathematical rheological Ostwald-de Waele model. It also presents the total loss of dry mass of sludge undergoing stabilization. The studies reported an increase in shear stress with the application of higher intensity ultrasonic wave field. Reducing stress values were observed for fermented sludge with each day of anaerobic stabilization process.

Keywords: sewage sludge, rheological parameters, ultrasonic field, fermentation

Introduction

Rheology of sewage sludge is an important problem that has been explored in studies on the methods of its final use and control in the processes of stabilization and dewatering [1]. Determination of the rheological parameters allows for determination of the sewage sludge flowability during technological processes [2]. Affecting the sewage sludge structure through the application of the conditioning factors changes the value of

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stress and viscosity during the flow. Conditioning leads to the increase in the yield stress, thus intensifying dewatering ability. The increase in the ability to release water will be connected with reduction in the sewage sludge flowability [3].

Rheological properties of sewage sludge depend on its composition, concentration, temperature and pH value [4, 5]. Knowledge of these properties is useful for *eg* processes of flow, mixing and transport of heat in sewage sludge [6]. Studies have shown a correlation between rheological parameters and its properties [7]. The use of thermal, chemical and mechanical modifications and their combinations leads to changes in the values and characteristics of sewage sludge [8]. Conditioning leads to the release of intracellular matter and, consequently, to improved biodegradability of the sludge (increased biogas generation) [9–11]. Rheological properties of the excess sludge after the mechanical disintegration process point to a significant decline in viscosity, reaching 60%. Viscosity, which can be used for evaluation of the degree of disintegration of excess sludge, is reduced through the fermentation process [12].

Flow curves represent the relationship between sheer stresses and sheer rate. They can be approximated using rheological models. Determination of the rheological models of sewage sludge contributes to a more detailed description of the sludge and provides insights into the effect of the conditioning method on final parameters. The simplest mathematical rheological model used to describe the flow curve for these fluids is the Ostwald-de Waele power model [5]:

$$\tau = k \cdot (\gamma)^n,$$

where k – constant termed consistency coefficient [Pa · s];
n – exponent, termed yield exponent.

The constant k, termed consistency coefficient, and the exponent n, termed the yield exponent, are the rheological parameters determined empirically at a specific temperature. The coefficient k represents the measure that describes viscosity of a substrate. The flow coefficient n adopts varied values. The value of $n < 1$ means that the process of shear thinning is observed; if $n > 1$, shear thickening occurs; if $n = 1$, the fluid becomes Newtonian.

Material and methods

The substrate for the study was provided by sewage sludge from treatment of cellulose and paper sewage sludge. The initial dewatering of 98.32% and dry mass of 16.82 g/dm^3 were calculated based on the standard PN-EN-12880:2004 [13]. Initial conditioning of sewage sludge was performed using the energy of the ultrasonic field with the intensity of: 2.2 (40%), 2.7 (60%); 3.2 (80%); 3.8 (100%) W/cm^2. The sonication was performed under static conditions for 600 s. Initial power output of the ultrasound processor was 1500 W, vibration frequency was 20 kHz, whereas maximal wavelength at maximal intensity of 3.8 W/cm^2 was 39.42 μm (100%). The sonication process was used for sewage sludge samples with volume of 500 cm^3.

The sewage sludge fermentation process occurred in glass flasks that represented models of fermentation chambers and bioreactor. The laboratory flasks, which represented the models of fermentation chambers, were put into the laboratory thermostat (10 flasks) in order to maintain mesophilic conditions. On each day of the fermentation process, the parameters and values of the rheological models were determined after removing one of the flasks from the thermostat. Flask volume was $V = 0.5$ dm^3. The process of 25-day stabilization was performed in the bioreactor with the capacity of 5 dm^3. The Reometr RC20 rheometer was used, with shear rate of 0–200 s^{-1} for the period of 120 s.

Results and discussions

Analysis of the results demonstrated that the highest values of stress in the case of sewage sludge initially non-conditioned with the ultrasound field were found for the non-stabilized sludge (Fig. 1a). The increase in the velocity gradient led to the increase in shear stresses, and, with the shear rate of 200 s^{-1}, the highest value was obtained (2.328 Pa). Using the fermentation process with respect to non-conditioned sewage sludge led to the reduction in the parameters studied. They were lower on consecutive days of fermentation compared to the non-fermented sludge. The lowest values of shear stresses were found for the sludge after the 10th day of fermentation, for which the values of stresses at the shear rate of 200 s^{-1} were 1.565 Pa. Similar values of stress were found for sewage sludge after 25 days of fermentation in the bioreactor. Stresses in sewage sludge were correlated with its viscosity. The highest viscosity was recorded for the non-fermented sludge. Fermentation led to a reduction in this parameter, with its values for the shear rate 200 s^{-1} on the 10th an 25th day maintained at the level of 0.008 Pa · s.

Application of initial conditioning using the energy of the ultrasound field led to the increase in shear stresses and viscosity of sewage sludge on each consecutive day of the fermentation process (Fig. 1b). In the case of non-fermented sludge after initial modification with the ultrasound field with intensity of 2.2 W/cm^2, stresses at the shear rate of 200 s^{-1} were 3.419 Pa, whereas viscosity was 0.017 Pa · s. For the sludge subjected to fermentation, the obtained values were the lowest on the 10th day of stabilization, with shear stresses for the shear rate of 200 s^{-1} reaching the level of 1.888 Pa and viscosity of 0.009 Pa · s. Elongation of the intensity of the ultrasound field led to another increase in the value of shear stresses (see Fig. 1c). Analogously to the use of the ultrasound field with intensity of 2.2 W/cm^2, the stresses rose to the level of 3.604 Pa, viscosity rose to 0.018 Pa · s (non-fermented sludge) and 2.031 Pa and 0.01 Pa · s (sludge on the 10th day of fermentation and shear rate of 200 s^{-1}).

Conditioning of sewage sludge with the ultrasound field with intensity of 3.2 an 3.8 W/cm^2 yielded specific changes in the values of stresses (Fig. 1d, e). The highest stresses were recorded for the sewage sludge on the 2nd day of fermentation, for which the values at the shear rate of 200 s^{-1} was 6.252 Pa, whereas viscosity increased to 0.031 Pa · s. The analogous relationship was observed for the highest ultrasound field

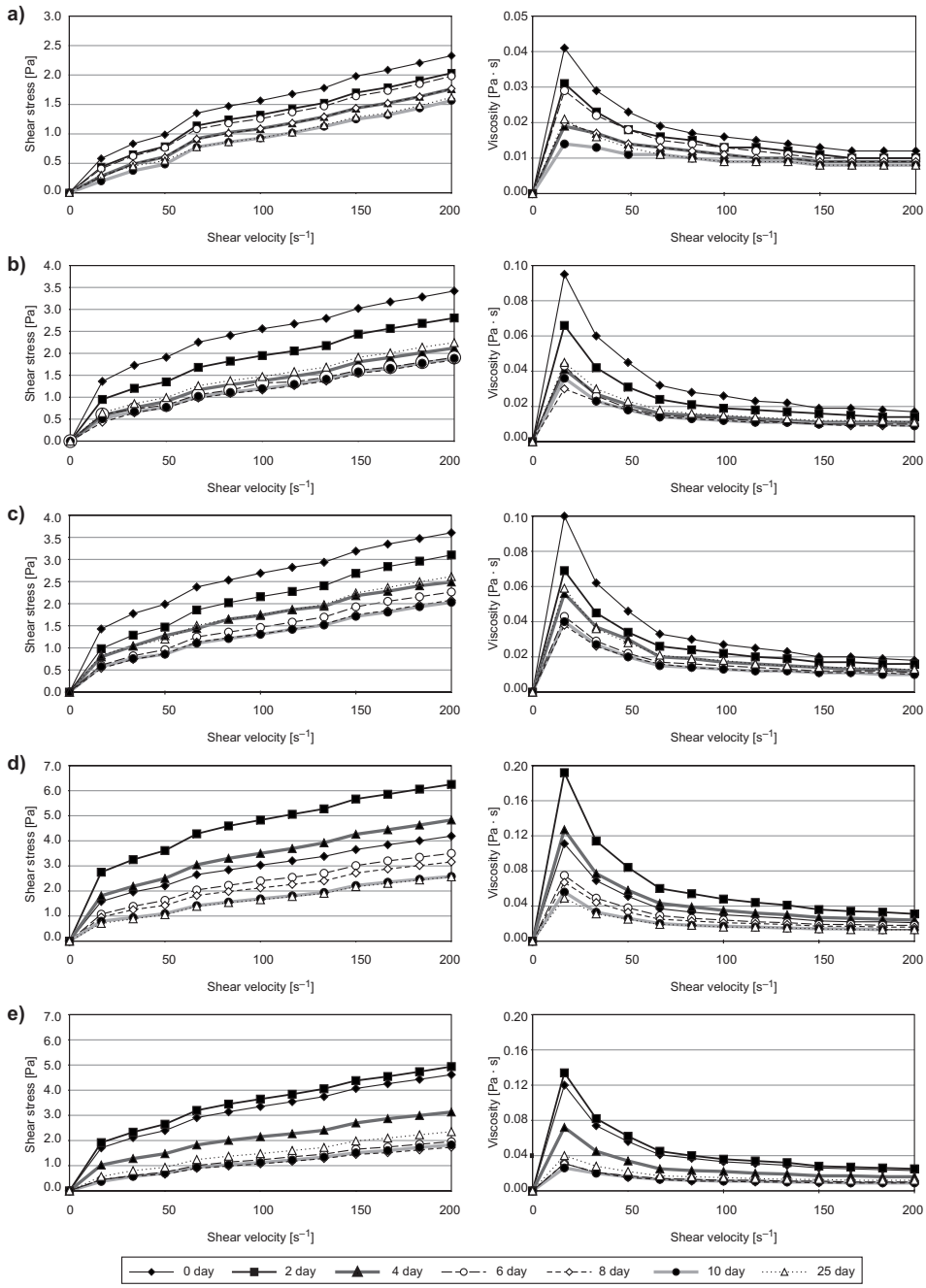

Fig. 1. Flow curves and viscosity curves for sewage sludge after fermentation: a) non-conditioned sludge; b) sewage sludge + UD40%; c) sewage sludge + UD60%; d) sewage sludge + UD80%; e) sewage sludge + UD100%

(3.8 W/cm^2), with stresses at the shear rate of 200 s^{-1} reaching the level of 4.937 Pa, and viscosity – the level of 0.025 Pa · s.

The coefficient *n* was below 1 for all the conditioning methods and fermentation times, which means that the sewage sludge was thinned as a result of the shear process (Fig. 2).

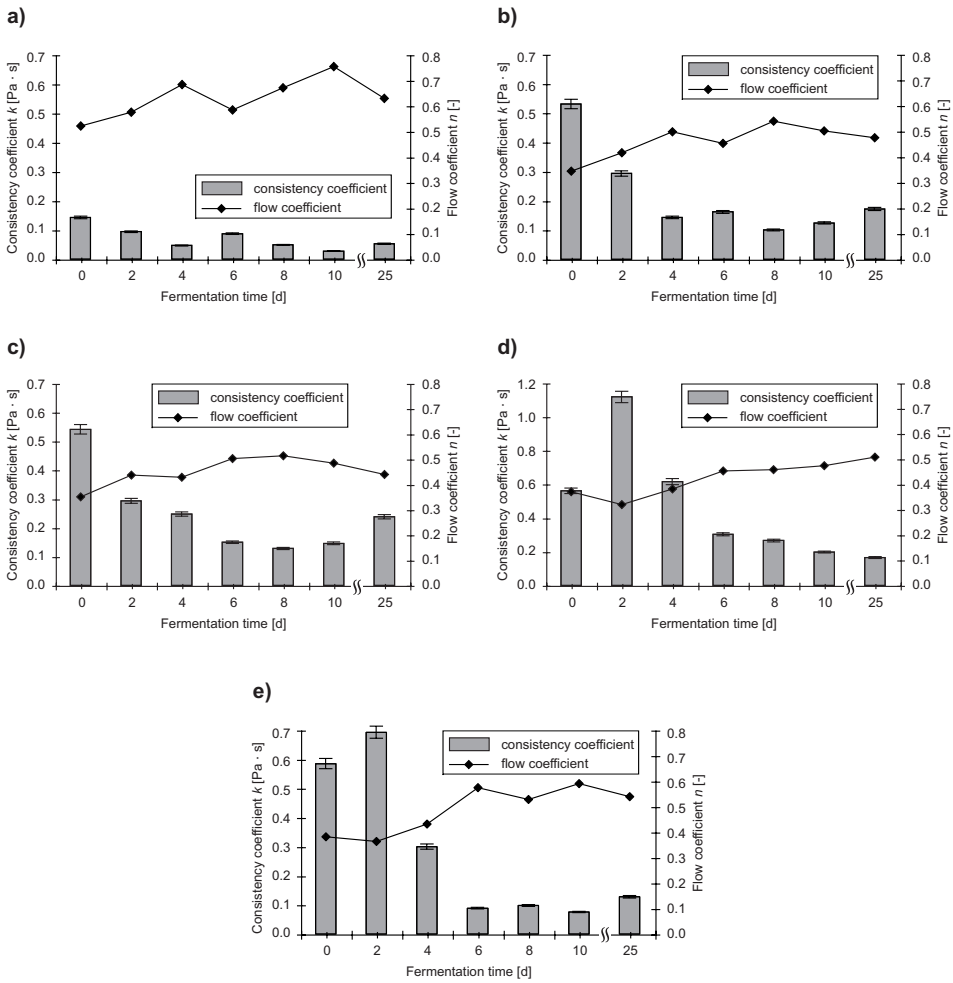

Fig. 2. Values of consistency coefficient, *k,* and flow coefficient, *n*, for the model Ostwald-de Waele sludge subjected to conditioning and fermentation: a) non-conditioned sludge; b) sewage sludge + UD40%; c) sewage sludge + UD60%; d) sewage sludge + UD80%; e) sewage sludge + UD100%

Lower values of the flow coefficient *n* for the sludge modified with the ultrasound field were also observed with respect to the non-conditioned sludge. Exposure of sewage sludge to the ultrasound field caused an increase in the value of the consistency coefficient *k*, which reflects an increase in its viscosity. In the case of the sewage sludge

modified with the ultrasound field with the highest intensity (3.8 W/cm^2), the value of coefficient k was 4 times higher compared to the non-modified sewage sludge. Regardless of the method of conditioning, sludge fermentation led to the reduction in sludge viscosity on each consecutive day of the process. The values of the parameters obtained for the model were correlated with the empirical data. The correctness and accuracy of the results obtained in the study are demonstrated by the correlation coefficients B, which, for all the samples studied, were high and ranged from 0.97 to 0.99 (Table 1).

Table 1

Values of correlation coefficient (B) and standard deviation (S) for the Ostwald-de Waele model of sewage sludge subjected to conditioning and fermentation

Parameters conditioning sewage sludge		Fermentation time [d]						
		0	2	4	6	8	10	25
Non-conditioned sludge	B	0.996	0.995	0.994	0.996	0.995	0.992	0.988
	S	0.033	0.032	0.035	0.031	0.032	0.037	0.045
Sewage sludge + UD40%	B	0.990	0.983	0.988	0.978	0.990	0.984	0.986
	S	0.063	0.076	0.054	0.063	0.043	0.056	0.060
Sewage sludge + UD60%	B	0.991	0.990	0.989	0.987	0.985	0.981	0.981
	S	0.065	0.065	0.055	0.059	0.061	0.064	0.079
Sewage sludge + UD80%	B	0.988	0.992	0.990	0.959	0.986	0.977	0.985
	S	0.090	0.096	0.094	0.079	0.083	0.090	0.073
Sewage sludge + UD100%	B	0.991	0.992	0.983	0.994	0.979	0.993	0.988
	S	0.088	0.084	0.089	0.038	0.061	0.036	0.061

The changes in viscosity and stresses caused by fermentation are connected with the depletion of the dry mass in the sludge. The use of the conditioning factor before sludge stabilization led to the increase in the dry matter content on each day of the process (Fig. 3). Total depletion in dry mass was increasing in proportion to the fermentation time and was the highest in the case of the sludge subjected to the effect of the

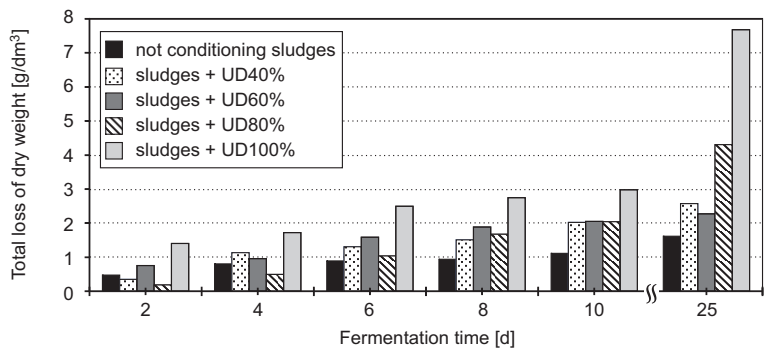

Fig. 3. Total depletion of dry mass of sewage sludge after conditioning and fermentation

ultrasound field with intensity of 3.8 W/cm^2. For the sludge after fermentation in flasks on the 10th day of the process, total depletion was at the level of 2.98 g/dm^3, whereas in the case of sewage sludge subjected to stabilization in the bioreactor, this value was 7.68 g/dm^3. Dispersion of the sludge flocs caused by the ultrasound field caused the release of organic compounds whereas stabilization led to their mineralization, which translated into the increase in the number of dry mass.

Interference with the structure induced by the conditioning factor of sludge as well as a fermentation process is shown in Fig. 4.

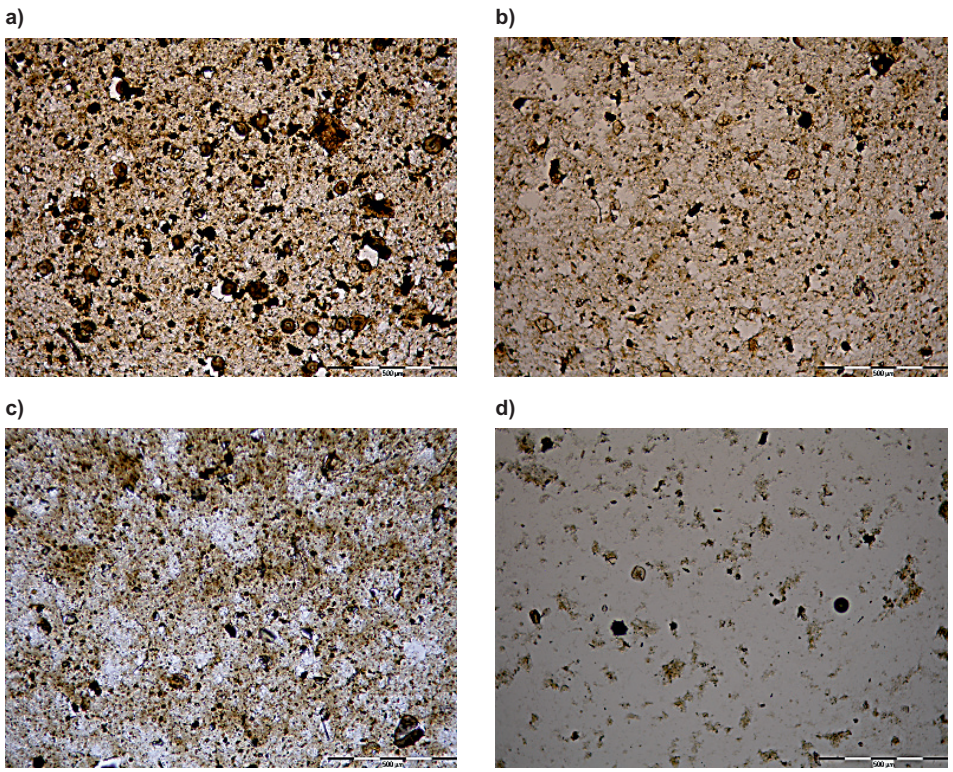

Fig. 4. Non conditioned structure and pre-conditioned of ultrasonic field sludge: a) non-conditioned sludge and unfermented; b) non-conditioned sludge on the 10th day of fermentation; c) The conditioned sludge by ultrasonic field by 3.8 W/cm^2 (100%) untreated fermentation; d) The conditioned sludge by ultrasonic field by 3.8 W/cm^2 (100%) on the 10th day of fermentation

Non-conditioned sludge on the first day of fermentation characterized by the compacted structure, homogeneous, no free water is observed. Subjecting of sludge of conditioning ultrasonic field individual clusters of sludge floc with free water areas were observed. In the view field extended sludge floc was recorded. The ten-day fermentation process caused the homogenization of the observed structures. The sludge floc with free water were mixed, forming a homogeneous mass of individual foci of sludge.

Conclusions

Knowledge of characteristics of sewage sludge in a technological line of the wastewater treatment plant can be acquired based on the evaluation of technical and technological parameters. The rheological examinations represent the basis for optimization of technological processes that occur in the wastewater treatment plant. The correlation between rheological parameters and sludge water content represents the significant property. This study allowed for development of a more accurate rheological characterization of sewage sludge after disintegration and fermentation.

The results obtained in this study lead to the following final conclusions:

– the use of ultrasonic energy in sewage sludge preparation causes an increase in shear stresses with the increase in the ultrasonic field intensity;

– stabilization of initially conditioned sewage sludge leads to a reduction in the value of shear stresses. The lowest values were recorded for the 10^{th} (flasks) and 25^{th} (bioreactor) days of fermentation;

– analysis of the Ostwald model demonstrated the increase in viscosity (expressed with the consistency coefficient) following the sonication process. Stabilization led to the reduction in the value of the parameter discussed;

– the highest total decline in dry matter of sewage sludge subjected to conditioning and fermentation (7.68 g/dm^3) was found for the highest ultrasound field intensity (3.8 W/cm^2) and stabilization performed in the bioreactor.

Acknowledgements

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PARAMETRY REOLOGICZNE WSTĘPNIE DEZINTEGROWANYCH OSADÓW ŚCIEKOWYCH PODDANYCH FERMENTACJI

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Abstrakt: Granica płynięcia, lepkość, naprężenia styczne są parametrami technologicznymi przydatnymi w praktyce do kontroli pompowania osadów, płynięcia oraz innych procesów technologicznych związanych z ich przeróbką. Zwiększenie efektywności odwadniania osadów powoduje spadek zdolności ich płynięcia poprzez wzrost granic płynięcia, a tym samym wartości naprężeń stycznych. Zmienność naprężeń i lepkości jest wynikiem zmiany struktury zachodzącej w osadach w trakcie płynięcia. Każda zmiana struktury osadów poprzez kondycjonowanie wpływała tym samym na ich parametry reologiczne.

Celem prowadzonych badań było wyznaczenie zależności naprężeń stycznych i lepkości od gradientu prędkości (krzywych płynięcia i lepkości) osadów ściekowych wstępnie kondycjonowanych polem ultradźwiękowym, a następnie poddanych fermentacji. W procesie sonifikacji zastosowano cztery natężenia fali ultradźwiękowej: 2,2; 2,7; 3,2; 3,8 W/cm^2, natomiast czas sonifikacji przyjęto 600 s. Proces fermentacji prowadzono w 10 kolbach szklanych o pojemności 0,5 dm^3, stanowiących modele komór fermentacyjnych. Do opisu krzywych płynięcia zastosowano najprostszy matematyczny model reologiczny tzw. model Ostwalda. Przedstawiono również sumaryczny ubytek suchej masy osadów poddanych stabilizacji. W wyniku przeprowadzonych badań odnotowano zwiększenie naprężeń stycznych wraz z zastosowaniem wyższych natężeń fali pola ultradźwiękowego. Zmniejszenie wartości naprężeń zaobserwowano dla osadów poddanych fermentacji z każdym dniem prowadzenia procesu stabilizacji.

Słowa kluczowe: osady ściekowe, naprężenia styczne, lepkość, pole ultradźwiękowe, fermentacja

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Iwona ZAWIEJA[1]

THE IMPACT OF EXCESS SLUDGE DISINTEGRATION ON THE CHANGES OF TOTAL ORGANIC CARBON VALUE

WPŁYW DEZINTEGRACJI OSADÓW NADMIERNYCH NA ZMIANY WARTOŚCI CAŁKOWITEGO WĘGLA ORGANICZNEGO

Abstract: The efficiency of conversion of organic substances contained in the excess sludge to the dissolved form is considered as an important factor limiting the process of anaerobic stabilization. Direct effect, occurring in the disintegrated sludge, lysis process is to increase the value of the total organic carbon (TOC), correlates with the increase of the concentration of volatile fatty acids (VFAs). The total organic carbon content is indicative of the supernatant liquid of total organic carbon in dissolved form (DOC) and suspended (SOC). Together with occurring, as a result of biochemical processes, increase the degree of decomposition of organic substances contained in the sludge decreases the value of the ratio of COD to TOC. The aim of the study was to determine the impact of the process of excess sludge disintegration on the changes of the total organic carbon values. The process of chemical disintegration of excess sludge was treated using the selected acidic *ie* HCl, alkaline *ie* KOH and oxidizing reagents *ie* H_2O_2. The modification was carried out at ambient temperature for 6 and 24 h. During sludge disintegration it was noticed the increase of total organic carbon values, disintegration degree as well as the concentration of volatile fatty acids that confirmed the susceptibility of prepared sludge to biodegradation. The highest TOC value of 2150 mg C/dm^3 obtained in case of chemical disintegration of potassium hydroxide at a dose of 12.0 g/dm^3 and preparation time 24 h. For given conditions of preparing a concentration of VFAs was 523 mg CH_3COOH/dm^3.

Keywords: excess sludge; chemical disintegration; total organic carbon (TOC), disintegration degree, volatile fatty acids (VFAs)

Introduction

Sewage sludge generated as a result of the industrial and municipal wastewater treatment, due to the hazardous substances of different nature of origin, have a harmful effect on the environment. In order to increase the effectiveness of conventional methods of disposing of looking for new technological solutions, the implementation of which would provide benefits to both environmental and economic.

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When the chemical modification used in the energy that comes from a chemical reaction, in conjunction with the specific conditions of the reaction. Introduced into the sludge chemical reagents react with the chemical contained therein organic compounds, leading to changes in the physico-chemical parameters of modified sludge. During the chemical modification of the cells lysis and the destruction of cell walls of living microorganisms in sludge is observed and the release of intracellular substances into the liquid supernatant [1, 2].

Disintegration affect the structure of the sludge and the destruction of microbial membranes, leading to lysis of microbial cells. These processes result in increased availability of organic ingredients cells as a substrate for heterotrophic biomass. While water previously associated intracellularly is released. The process of disintegration is also aimed to reduce the forces between water molecules and solid phase of sludge thus facilitating their thickening and dehydration, which may lead the same to the break chemical bonds that hinder the degradation of sludge. The result of these processes is to increase the efficiency of the hydrolysis, the waveform is essentially a spontaneous nature [2, 3].

The heterotrophic microorganisms in a variety of metabolic pathways, preferably using organic carbon as volatile fatty acids. Their content in the substrate may well be characterized by its vulnerability to biochemical decomposition [4].

Chemical methods use the energy from a chemical reaction often in combination with a well defined reaction conditions, *ie* pressure, temperature. To the most popular chemical reagents may include [5, 6]: oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide (Ca $(OH)_2$), magnesium hydroxide (Mg $(OH)_2$).

In the structure of excess sludge can be distinguished visible areas of the liquid phase and the solid phase coarse aggregates. The structure of the sludge after chemical disintegration process is characterized by significant fragmentation of the solid particles and increased liquefaction residues. The changes that can be observed in the sludge after the modification process demonstrate improved their susceptibility to biochemical degradation [7–9].

It is important for the processes of biochemical degradation under anaerobic conditions is the relationship between organic carbon and other nutrients, as well as the availability of macro- and microelements in sludge [10].

According to literature data biodegradability usually expressed by comparing the mass of the decomposed during the time period to the mass, which could theoretically be unfolded in stoichiometric proportions. Indicators for indirect assessment of the susceptibility of organic substances contained in the sludge on the biodegradation are COD or BOD_5 and TOC [11].

According to Stelmach et al [12] the maximum rate of biogas production in the case of municipal waste is observed for the carbon content in the compounds dissolved in the liquid approx. 1500 mg/dm^3. It was also found that the maximum rate of biogas production is the C/N ratio within a range of 1.5 to 2.0.

In the high processing temperatures high degree of sludge disintegration and an increase in the concentration of dissolved organic carbon is not synonymous with improvement in susceptibility sludge to biodegradation due to the formation, among others, refracting the compounds [13].

Values of BOD and COD can be influenced of organic nitrogen compounds or inorganic, reducing compounds, which may contribute to an increased demand for oxygen. The total organic carbon (TOC) is currently the only strictly defined, parameter defining the content of organic substances in wastewater and sludge [14].

Therefore, the aim of the research was to determine the effect of the chemical disintegration of excess sludge to changes in the value of total organic carbon.

Material and methods

The substrate for the study was excess sludge, which was taken from the Central Wastewater Treatment Plant "Warta" in Czestochowa. This wastewater treatment plant was the classical mechanical-biological treatment plant, and has been upgrading in terms of nitrogen and phosphorus removal and sludge management with thermal drying. Currently, wastewater is adjusted to increased regulatory requirements.

Table 1

General characteristics of excess sludge used for research

Dry mass [g/dm^3]	VFAs [mg CH_3COOH/ dm^3]	Kjeldahl Nitrogen [mg N-NH_4/ dm^3]	pH [–]	TOC [mg C/dm^3]
10.76 ± 0.15	67.5 ± 1.7	21.6 ± 2.1	7.02 ± 0.03	35.3 ± 1.5

The following physico-chemical designations were made: pH [PN-9/C-04540/05] [15], the dry mass [PN-EN-12879] [16], volatile fatty acids by steam distillation [PN-75/C-04616/04] [17] and Kjeldahl nitrogen [PN-73/C-04576/10] [18]. The evaluate the effectiveness of chemical sludge disintegration was made on the basis of the TOC by spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena). Furthermore, the degree of disintegration, assuming as reference the COD of sludge subjected to alkaline hydrolysis, was determined.

The sludge was conditioned by means of 1-mol solution of NaOH for 10 min, at the temperature of 90^{o}C, with unchanged volumetric proportion of the sludge and the solution (1 : 1). For the excess sludge pretreatment in accordance with the above methodology the COD value was equal 8125 mg O_2/dm^3.

The degree of disintegration was estimated according the following formula [19]:

$$DD_{COD} = (SCOD_1 - SCOD_2) / (SCOD_3 - SCOD_2) \cdot 100 \quad (1)$$

where: DD_{COD} – disintegration degree [%];
$SCOD_1$ – SCOD level in the pretreatment sludge, mg O_2/dm^3;
$SCOD_2$ – SCOD level in the unconditioned sludge, mg O_2/dm^3;

$SCOD_3$ – SCOD level in the sludge conditioned chemically 1-mol NaOH with ratio 1 : 1, temp. 90°C for 10 minutes, mg O_2/dm^3.

Results and discussions

During the research have been indications of selected physical and chemical parameters modified sludge, the value of which determines the susceptibility of sludge to biodegradation. Examined the pH of the sludge dry matter and Kjeldahl nitrogen, depending upon the dose of the reagent. Table 2 and 3 show the values of the selected indications physico-chemical sludge modified as appropriate for 6 and 24 h.

Table 2

Selected physico-chemical parameters of excess sludge subjected to disintegration using potassium hydroxide, hydrochloric acid and hydrogen peroxide, a contact time with reagent 6 h

Reagent	Dose of reagent	pH [–]	Kjeldahl Nitrogen [mg $N\text{-}NH_4/dm^3$]	Dry mass [g/dm^3]
KOH [g/dm^3]	0.5	8.48 ± 0.08	23.4 ± 0.5	11.23 ± 0.12
	1.0	9.62 ± 0.12	26.2 ± 0.8	12.56 ± 0.14
	3.0	10.92 ± 0.09	32.8 ± 0.6	13.89 ± 0.21
	6.0	12.38 ± 0.01	48.4 ± 1.1	14.68 ± 0.17
	9.0	12.68 ± 0.04	61.6 ± 0.9	15.02 ± 0.19
	12.0	12.84 ± 0.11	83.0 ± 0.7	16.24 ± 0.22
HCl [cm^3/dm^3]	0.5	7.84 ± 0.12	31.1 ± 1.2	11.38 ± 0.23
	1.0	7.14 ± 0.07	38.4 ± 1.7	11.45 ± 0.14
	3.0	6.93 ± 0.05	42.3 ± 0.6	11.98 ± 0.17
	6.0	6.40 ± 0.04	50.7 ± 2.1	12.36 ± 0.23
	9.0	6.05 ± 0.02	53.8 ± 2.0	13.02 ± 0.10
	12.0	5.82 ± 0.07	57.2 ± 1.6	13.89 ± 0.07
H_2O_2 [cm^3/dm^3]	0.5	7.40 ± 0.12	48.3 ± 1.2	11.01 ± 0.11
	1.0	7.45 ± 0.05	46.8 ± 2.4	11.28 ± 0.14
	3.0	7.50 ± 0.07	43.1 ± 2.2	11.89 ± 0.18
	6.0	7.43 ± 0.09	38.6 ± 1.5	11.97 ± 0.09
	9.0	7.48 ± 0.04	38.9 ± 1.6	12.06 ± 0.11
	12.0	7.53 ± 0.10	28.5 ± 1.8	12.35 ± 0.23

With increasing dose, in the case of all used reagents, there was an increase of dry matter and the Kjeldahl nitrogen. It was found that prolonged disintegration significantly influenced the increase in the value of Kjeldahl nitrogen. The highest value of tested indicator of 375 mg $N\text{-}NH_4/dm^3$ obtained for disintegrated sludge by KOH for 24 h, using a dose of 12 g/dm^3. By analyzing changes in the pH of the sludge in case of

Table 3

Selected physico-chemical parameters of excess sludge subjected to disintegration using potassium hydroxide, hydrochloric acid and hydrogen peroxide, a contact time with reagent 24 h

Reagent	Dose of reagent	pH [–]	Kjeldahl Nitrogen [mg N-NH_4/dm^3]	Dry mass [g/dm^3]
KOH [g/dm^3]	0.5	8.74 ± 0.05	38.4 ± 1.5	10.64 ± 0.11
	1.0	8.87 ± 0.07	58.1 ± 2.1	11.74 ± 0.14
	3.0	11.53 ± 0.11	63.7 ± 1.7	13.73 ± 0.21
	6.0	12.46 ± 0.23	187.6 ± 2.3	16.28 ± 0.14
	9.0	12.70 ± 0.25	336.2 ± 3.7	19.44 ± 0.24
	12.0	12.90 ± 0.16	375.6 ± 2.9	24.81 ± 0.08
HCl [cm^3/dm^3]	0.5	7.54 ± 0.32	25.4 ± 1.2	11.45 ± 0.11
	1.0	7.42 ± 0.16	26.5 ± 1.1	11.54 ± 0.21
	3.0	6.84 ± 0.43	35.8 ± 2.6	12.21 ± 0.24
	6.0	7.01 ± 0.24	42.9 ± 3.2	13.32 ± 0.16
	9.0	6.48 ± 0.25	57.2 ± 2.7	14.01 ± 0.31
	12.0	5.98 ± 0.21	58.6 ± 2.4	14.72 ± 0.29
H_2O_2 [cm^3/dm^3]	0.5	7.43 ± 0.11	55.4 ± 1.2	10.32 ± 0.21
	1.0	7.50 ± 0.26	53.3 ± 1.6	10.46 ± 0.18
	3.0	7.51 ± 0.23	52.7 ± 2.7	11.02 ± 0.23
	6.0	7.38 ± 0.18	50.1 ± 2.1	11.56 ± 0.36
	9.0	7.29 ± 0.32	49.5 ± 2.8	11.78 ± 0.54
	12.0	8.04 ± 0.37	49.6 ± 2.2	12.02 ± 0.25

modification of sodium hydroxide and hydrochloric acid were recorded an upward trend and the declining value of the index. While for modified sludge by hydrogen peroxide was observed fluctuations in pH. The prolongation of disintegration time up to 24 h, for all the tested reagents, did not affect the change in pH.

The degree of disintegration of excess sludge pretreatment by the potassium hydroxide was determined. Figure 1 and 2 show the degree of disintegration of excess sludge treated by chemical modification of the 6 and 24 h.

The highest value of 79 and 78% degree of disintegration of excess sludge conditioned with potassium hydroxide was reported for a dose of 6.0 g KOH/dm^3 of excess sludge, the contact time of the reactant 6 and 24 h. For a dose of 9 and 12 g KOH/dm^3 reported decrease in the disintegration degree value which could be due to the heterogeneous nature of the sample. Figure 3 and 4 show the changes in the TOC value and volatile fatty acids concentration of modified excess sludge by potassium hydroxide.

The highest value of TOC was observed for doses of 12.0 g KOH/dm^3 for the time 6 and 24 h respectively 1870 and 2150 mg C/dm^3, while the lowest value of 158 and 218 mg C/dm^3 for dose KOH equal 0.5 g/dm^3. The highest concentration of VFAs,

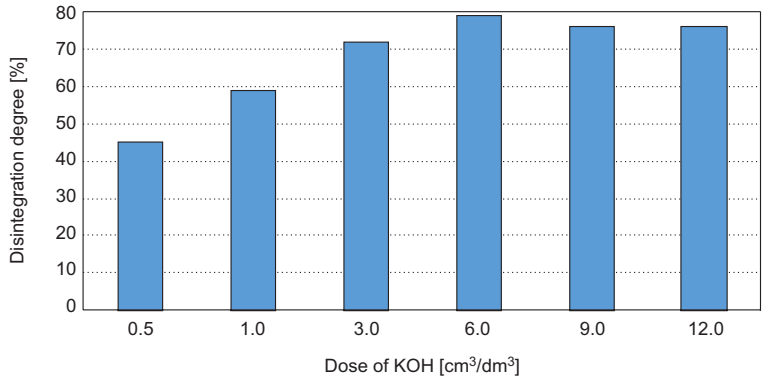

Fig. 1. Changes of the disintegration degree value of excess sludge modified by potassium hydroxide by 6 h

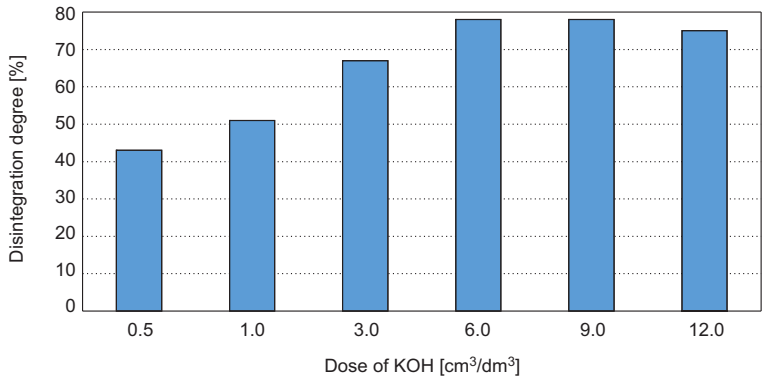

Fig. 2. Changes of the disintegration degree value of excess sludge modified by potassium hydroxide by 24 h

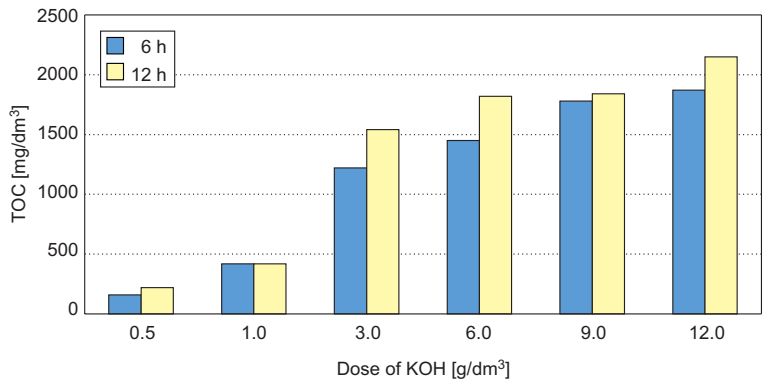

Fig. 3. Changes of the total organic carbon value of excess sludge modified by potassium hydroxide

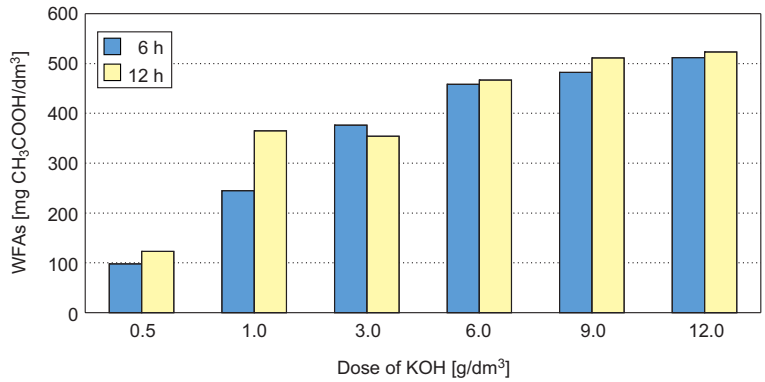

Fig. 4. Changes of the volatile fatty acids concentration of excess sludge modified by potassium hydroxide

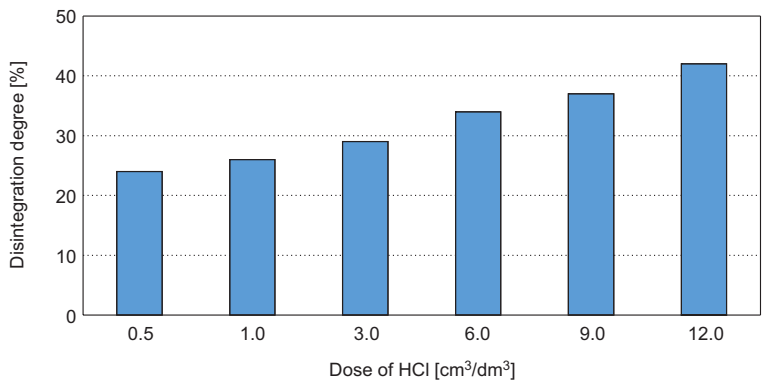

Fig. 5. Changes of the disintegration degree value of excess sludge modified by hydrochloric acid by 6 h

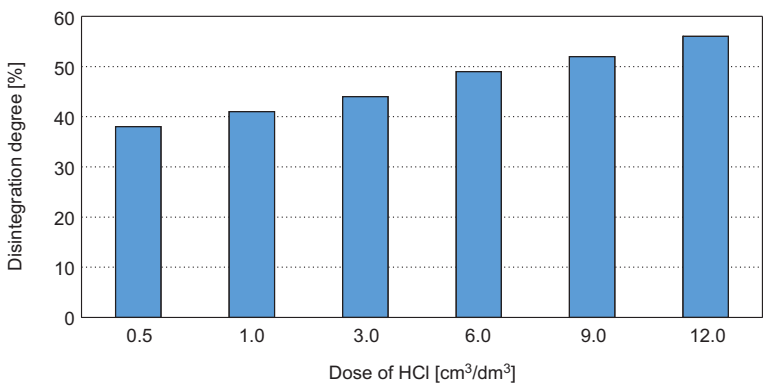

Fig. 6. Changes of the disintegration degree value of excess sludge modified by hydrochloric acid by 24 h

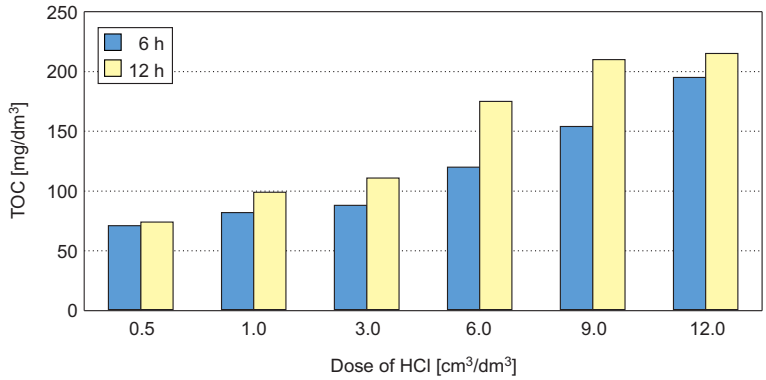

Fig. 7. Changes of the total organic carbon value of excess sludge modified by hydrochloric acid

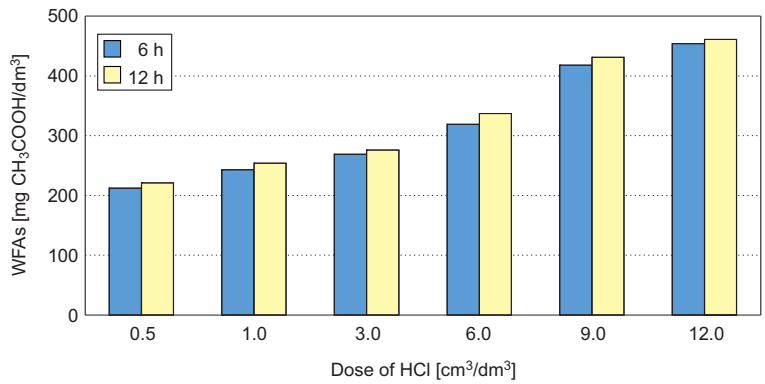

Fig. 8. Changes of the volatile fatty acids concentration of excess sludge modified by hydrochloric acid

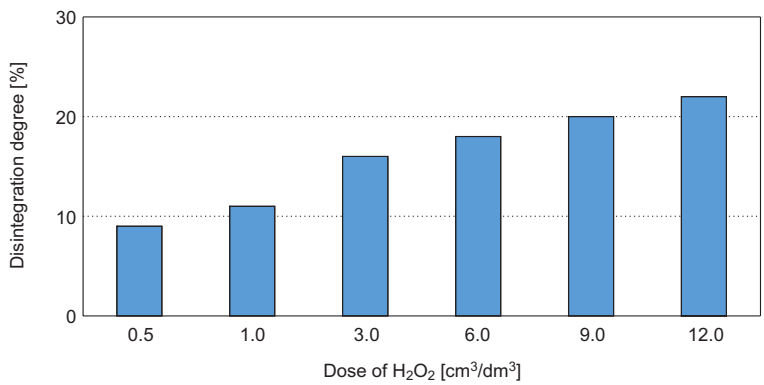

Fig. 9. Changes of the disintegration degree value of excess sludge modified by hydrogen peroxide by 6 h

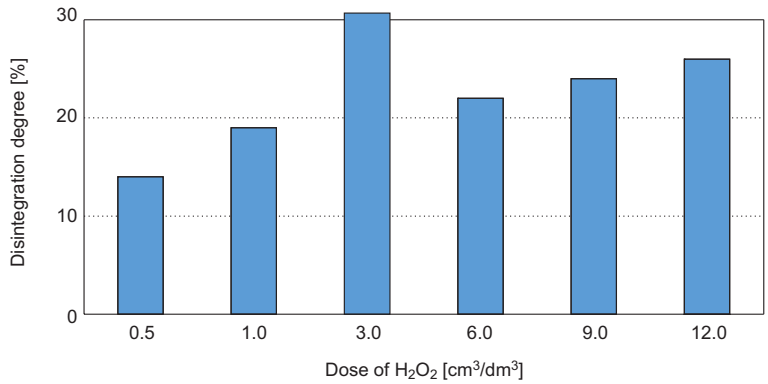

Fig. 10. Changes of the disintegration degree value of excess sludge modified by hydrogen peroxide by 24 h

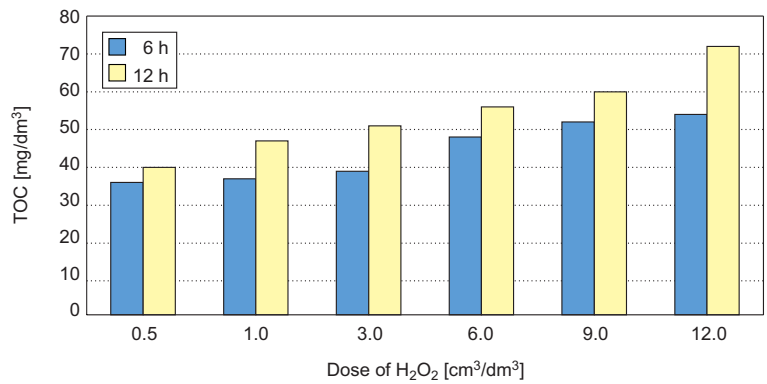

Fig. 11. Changes of the total organic carbon value of excess sludge modified by hydrogen peroxide

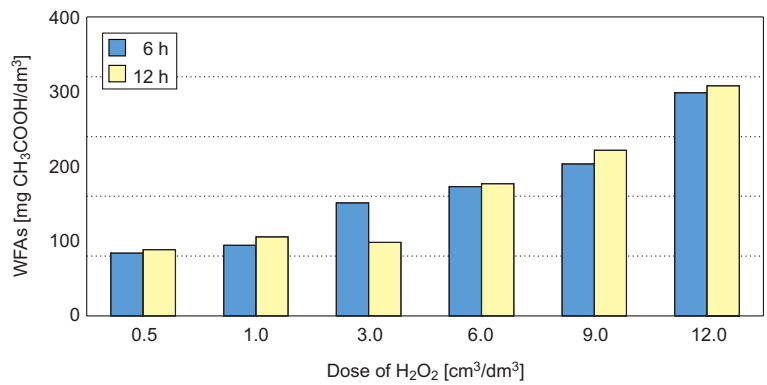

Fig. 12. Changes of the volatile fatty acids concentration of excess sludge modified by hydrogen peroxide

respectively 512 and 523 mg CH_3COOH/dm^3 was observed for the highest dose of the reagent 12.0 g KOH/dm^3 of sludge, and two periods of preparation. The lowest concentration of KOH was reported for a dose of 0.5 g KOH/dm^3 and was, respectively, for 6 h – 314 mg CH_3COOH/dm^3 and 24 h – 342 mg CH_3COOH/dm^3. Figure 5 and 6 show the changes in disintegration degree of excess sludge modified with hydrochloric acid.

The highest values of the disintegration degree of excess sludge treated with hydrochloric acid 42 and 56% was observed at a dose of 12.0 cm^3 of HCl/dm^3 of sludge and 6 and 24 hours. Figure 7 and 8 show the changes in the TOC value and volatile fatty acids concentration of excess sludge modified by hydrochloric acid.

From the Fig. 3 it can be seen that the value of TOC increased with the increase of reagent dose. The lowest value was observed for a dose of 0.5 cm^3 of HCl/dm^3 *ie* for the time 6 h – 71 mg C/dm^3 and for the 24 h – 74 mg C/dm^3. The value obtained for the highest dose of 12.0 cm^3 of HCl/dm^3 was for a time of 6 h – 195 mg C/dm^3 and for 24 h – 215 mg C/dm^3. The highest concentration of VFAs, respectively 454 and 461 mg CH_3COOH/dm^3 was observed for the highest dose of the reagent 12.0 cm^3 HCl/dm^3 of sludge, and both period of preparation. The lowest concentration of VFAs was reported for a dose of 0.5 g KOH/dm^3 and was, respectively, for 6 h – 212 mg CH_3COOH/dm^3 and for 24 h – 221 mg CH_3COOH/dm^3.

Figure 9 and 10 show the changes in the degree of disintegration of excess sludge modified with hydrogen peroxide.

The highest degree of disintegration of excess sludge chemically modified by hydrogen peroxide 22% was reported for a dose of 12.0 cm^3 H_2O_2/dm^3 of sludge and pretreatment time equal 6 h. For 24 h the highest value of disintegration degree equal 32% was reported for a dose of 3.0 cm^3 H_2O_2/dm^3 of sludge. Figure 11 and 12 show the changes in the TOC value and volatile fatty acids concentration of excess sludge modified by hydrogen peroxide.

Increase the value of TOC was observed with increasing doses of a reagent. For the disintegration time of 6 h and dose of 0.5 cm^3 $H_2O_2/$ dm^3 recorded lowest value of TOC 36 mg C/dm^3, while for a 24 h a value of 40 mg C/dm^3. The highest value of TOC 54 and 72 mg C/dm^3, respectively for the time 6 and 24 h obtained for 12.0 cm^3 H_2O_2/dm^3 of sludge. The highest concentration of VFA, respectively 373 and 385 mg CH_3COOH/dm^3 was observed for the highest dose of the reagent 12.0 cm^3 H_2O_2/dm^3 of sludge, and both period of preparation. The lowest concentration was observed at a dose of 0.5 cm^3 H_2O_2/dm^3, and was, respectively, for 6 h – 105 mg CH_3COOH/dm^3 and for 24 h – 111 mg CH_3COOH/dm^3.

Conclusions

Based on the results obtained the following conclusions were drawn:

1. By subjecting the excess sludge chemical disintegration was observed with increasing doses of reagent increase the value of the degree of disintegration, increase the value of TOC and concentration of VFAs. Increasing the value of these indicators may indicate an increase in the biodegradability of sludge, which will be confirmed in further studies regarding the process of anaerobic stabilization of modified sludge.

2. It has been found that the extension of the modification time for 24 h in the case of the concentration of VFAs did not significantly influence the value of the test indicator.

3. The highest TOC value of chemically modified excess sludge 2150 mg C/dm^3 was reported for a dose of 12.0 g KOH/dm^3 and preparation time 24 h.

4. The highest degree of disintegration of excess sludge modified chemically, *ie* 79% were obtained with a dose of 6.0 g KOH/dm^3 and preparation time 6 h.

5. The highest concentration of VFAs 523 mg CH_3COOH/dm^3 of sludge obtained for excess sludge pretreatment at 12.0 cm^3/dm^3 for 24 h. For the time 6 h a concentration of VFAs was 512 mg CH_3COOH/dm^3.

Acknowledgements

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WPŁYW DEZINTEGRACJI OSADÓW NADMIERNYCH NA ZMIANY WARTOŚCI CAŁKOWITEGO WĘGLA ORGANICZNEGO

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Abstrakt: Efektywność przemiany substancji organicznych zawartych w osadach nadmiernych do formy rozpuszczonej jest traktowana jako ważny czynnik limitujący przebieg procesu stabilizacji beztlenowej. Bezpośrednim efektem procesu lizy zachodzącego w dezintegrowanych osadach jest wzrost wartości ogólnego węgla organicznego (OWO) oraz korelujący z nim wzrost wartości stężenia lotnych kwasów tłuszczwych (LKT). Ogólny węgiel organiczny jest wskaźnikiem zawartości w cieczy nadosadowej całkowitego węgla organicznego w formie rozpuszczonej (RWO) i zawieszonej (ZWO). Wraz z zachodzącym w wyniku procesów biochemicznych wzrostem stopniem rozkładu substancji organicznych zawartych w osadach maleje wartość ilorazu ChZT do OWO. Celem badań było określenie wpływu procesu dezintegracji osadów nadmiernych na zmiany wartości całkowitej węgla organicznego. Proces chemicznej dezintegracji osadów nadmiernych prowadzono, stosując wybrane reagenty kwaśne (HCl), zasadowe (KOH) i utleniające (H_2O_2). Modyfikację przeprowadzono w temperaturze pokojowej w ciągu 6 i 24 godzin. Podczas procesu dezintegracji osadów nadmiernych odnotowano wzrost wartości ogólnego węgla organicznego, a także stężenia lotnych kwasów tłuszczowych, co potwierdziło podatność preparowanych osadów na biodegradację. Najwyższą wartość OWO 2150 mg C/dm^3 uzyskano w przypadku chemicznej dezintegracji wodorotlenkiem potasu w dawce 12 g/dm^3 i w czasie preparowania 24 h. Dla podanych powyżej warunków preparowania uzyskano stężenie LKT, wynoszące 523 mg CH_3COOH/dm^3.

Słowa kluczowe: osady nadmierne, ogólny węgiel organiczny (OWO), stopień dezintegracji, lotne kwasy tłuszczowe (LKT)

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CHANGES IN PHYSICOCHEMICAL PROPERTIES OF SOILS IN THE AREA AFFECTED BY LIME INDUSTRY

ZMIANY WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH GLEB W REJONIE ODDZIAŁYWANIA PRZEMYSŁU WAPIENNICZEGO

Abstract: Lime and cement industry belongs to the best developed branches of industry in Opole Voivodeship. The plants are located in eastern and central part of the province, in the vicinity of the city of Opole and the towns of Krapkowice and Strzelce Opolskie due to the location of the resources of calcareous raw materials (limestones and marls).The impact of lime and cement industry on the natural environment, especially soils, was studied by many authors, but these works do not concern the Province of Opole, which is one of the main centers of lime and cement industry in Poland for centuries. The article is an attempt to show changes in physicochemical properties of soils being under long lasting influence of alkaline dust emissions coming from the lime plant in Gorazdze. The research was conducted in the years 2010–2013. The range of the studies included field works in the areas adjacent to the plant, where 12 representative soil pits were arranged to collect samples for laboratory analyses. The following physicochemical parameters were determined in the samples: grain size distribution, reaction (pH), electrical conductivity and the content of calcium carbonate. The studies showed deacidification of the tested sandy soils resulting from alkaline dust deposition, which primarily concerned forest stands, which were characterized by the rise in reaction by 3–4 pH units. In the case of meadows, arable soils and wastelands, the pH values raised by 1–2 units. Moreover, alkaline falling dusts enriched the investigated soils in calcium carbonate. It concerns to the greatest extent the soil pits located nearest to the lime plant, where above 1% of $CaCO_3$ was found. The results of conductivity measurements proved low salinity of the investigated samples.

Keywords: lime dusts, proper rusty soils, pH, electrical conductivity, calcium carbonate content

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Introduction

The Province of Opole is an important center of cement and lime industry in Poland due to the presence of high-quality deposits of carbonate raw materials (limestones and marls) in the central and eastern parts of the region. The lime manufacture is the oldest branch of industry in Opole Province, concentrated in the area of Tarnow Opolski, Gorazdze, Gogolin and Strzelce Opolskie, where rich deposits of the Triassic limestones – raw materials for lime production – occur. At the end of the twentieth century, there operated six departments of lime manufacture, and these days there operate two, situated in Tarnow Opolski and Gorazdze.

By the end of the last century lime burning took place in shaft furnaces, and now mainly in modern regenerative Maerz type kilns. Lime plants produce quicklime (burnt lime) ground and in lumps, hydrated lime, calcium fertilizers (in the form of oxides, magnesium oxides and carbonates), calcareous aggregates, fodder and painting chalks, calcareous and glass flours, sorbents for flue gas desulfurization, limestone and special products.

The process of lime burning has a long tradition in the Opole Province dating from the 16th century, so the lime dust has impacted on soils of the Opole region for about 500 years, which is not without effect on their composition and properties. This is confirmed by the study of soils of Opole Province forest reserves, being under the influence of cement and lime industry, which showed increased magnetic susceptibility and the content of heavy metals and proved technogenic origin of the magnetic susceptibility, which was correlated with the content of metals [1, 2].

For decades, the main source of lime dust were shaft furnaces, which did not have any dust collection equipment and posed environmental hazard [3, 4]. According to the archive data, in the 90s of the last century lime plants emitted about 1000 Mg of dust per year, of which more than half came from shaft furnaces. The largest share in dust pollution of the atmospheric air had the lime plant in Gorazdze, hence the dust from this plant should be considered the most important from the point of view of environmental impact. Along with the increase in dust emissions, the increase in dust deposition was noted. Analyzing historical data it can be seen, that around the lime plants the allowable standard value of the fall of dust 200 $g \cdot m^{-2} \cdot yr^{-1}$ was significantly exceeded [5]. The impact on the quantity and quality of the falling dust was also close proximity to the cement plant that used raw materials coming from the same deposits.

The aim of the research, presented in this work, carried out in the years 2010–2013, was assessment of the impact of lime dust on the rusty soils in the vicinity of the lime plant in Gorazdze, by determination of changes in the physico-chemical properties of soils and diversity of features of genetic horizons. An attempt has also made to determine the extent of the impact of emitted lime dust in the selected transects.

Despite the fact, that the Province of Opole is one of the main centers of lime industry in Poland for about 500 years, the research into the impact of lime dusts on soils has not been conducted in this region so far, but mostly in the so called “White Basin” – the Swietokrzyski region.

Characteristics of the research object

The object of the study was the lime plant in Gorazdze, situated about 15 km to the south from the city of Opole, in Gorazdze village (Gogolin municipality). Nearby the plant (approximately 2 km in a westerly direction) the Gorazdze Cement Plant – the largest and most modern in Europe – is located. In the vicinity of both plants woodlands extend and in close proximity (around 5 km to the southeast from the lime plant), the Landscape Park „St. Anna's Hill" and nature reserves are situated.

The process of lime burning for decades was carried out in shaft furnaces. They were fired with the coke coming from, inter alia, Zdzieszowice Coking Plants. The fuel was introduced into the furnace together with the limestone and burned in direct contact with it. It was not until the end of the twentieth century that shaft furnaces were liquidated and two modern devices for lime burning: Maerz regenerative kiln, with a capacity of 600 Mg of lime per day and Gopex kiln – 350 Mg of lime per day. New kilns are fired with the coke oven gas or natural gas, and Maerz kiln is equipped with fabric dust collector, which resulted in the reduction in the amount of emitted dust.

According to archive data, the plant had a big share in the emissions of lime dust in the Opole Province, which amounted to almost 60%, wherein approximately 70% of lime dust emissions came from shaft furnaces [5]. According to the information provided by the lime plants, in the last decade dust emissions were high despite the modernization of technological processes. The highest values (from 81 to 157 $Mg \cdot yr^{-1}$) was recorded in the years 2007–2009, which was associated with increased, during this period, market demand for lime.

Research methods

Soil pits were located nearby the lime plant in Gorazdze, in the area of Strzelce Opolskie Forest District, the municipality of Gogolin. In order to choose the right places for the soil pits, the directions of the prevailing winds blowing in this region (W, NW, SW) and the distance from the plant were taken into account. The topographic map with a scale of 1 : 5000 was used. Soil pits were situated in relation to the plant in three transects of research:

– western (W), which included soil pits marked with symbols: G1, G2 (on grasslands), A3 (on arable soils), and F4, F5, L6, F7 (in forest areas), at a distance of 70 to 430 m from the plant;

– northwestern (NW), including soil pits marked with symbols: A10 (on arable soils), and F11 and F12 (in forest areas), at a distance of 300 to 470 m from the plant;

– southwestern (SW), which included soil pits W8 and W9, located on wasteland, at a distance of 80 to 120 m from the lime plant.

The total number of research points was 12, and the total number of soil samples collected at these points to a depth of 60 cm equaled 51. Representative samples were collected from each genetic horizon. After bringing to the laboratory, the samples were dried in trays to air-dry state, then crushed and homogenized in Retsch agate mill. Afterwords, in samples prepared this way four parameters that characterize the

physicochemical properties of the soils were determined with methods commonly used in soil science [6, 7]:

– the particle size distribution – by Casagrande areometric method in Proszynski's modification (silt and clay fractions), and by sieving method (sand fractions);

– reaction (pH) – by potentiometric method, the mass ratio of the soil to the water in the suspension equaled 1 : 2.5;

– specific conductivity – conductrometrically, the mass ratio of the soil to the water in the suspension was 1 : 5;

– the content of calcium carbonate – by Scheibler volumetric method.

The tested soils were classified according to the latest international and Polish soil classsification systems [8–11].

Results and discussion

Profile structure and particle size distribution of soils

In the course of field research it was found, that in the tested area *Rusty soils* (WRB: *Brunic Arenosols*) occurs, the subtype of proper rusty soils, with the following structure of profile: Ol-Ofh-Ah-Bv-C (soils of forest areas), A1-A2-Bv-C (soils of grasslands) and ApBv-Bv-C (arable soils). It is known from the literature, that in natural conditions such soils are formed from the poor in nutrients, carbonateless sands. They are characterized by acid reaction with the dominance of the acidifying processes, *ie* leaching, washing, podsolisation, low sorption capacity and small buffering capacity [8–12].

As a result of grain size distribution analysis one granulometric group-sands, and three subgroups (loose sands, weakly loamy sands and loamy sands) were distinguished (Table 1). A characteristic feature of granulometry of the tested soils is the presence of sand fractions only (coarse sands) throughout the soil profile, to an average depth of 50 cm. The differences that occur in the composition of the granulometric subgroups arise from lithogenic properties of substrate (bedrock), relief and soil forming processes, affecting the soil substrate [8–11].

Table 1

Schematic layuot of grain size distribution in the tested soils

Particle size distribution arrangement		Number of soil pit
Homogeneous	loamy sand	G2
	sand	F5
	sand	W9
Heterogeneous, binary	sand/loamy sand	F4, F7, F11, F12, W8
	loamy sand/sand	A10
Heterogeneous, ternary	loamy sand/sand/loamy sand	G1
	loamy sand/sand/sand	A3
	sand/loamy sand/sand	L6

Reaction (pH)

The analyzed soils are hundreds of years exposed to the alkaline dust emissions. Dusts introduced into the atmosphere by the lime plant in Gorazdze are characterized by a very high pH values in the range of 11.49 to 12.54, which affects the course of pedogenic processes in the tested soils (Table 2) [5]. Alkaline reaction of dusts results from the predominance of calcium compounds, present as calcium oxide CaO (approximately 54.9%) and calcium carbonate $CaCO_3$ (approximately 40%). Other elements have a much smaller share in the dusts, which takes the following values (in terms of the oxide forms): 2% of SiO_2, 1% of MgO, 0.4% of Fe_2O_3, 0.2% of Al_2O_3 and 0.1% of SO_3.

As a result of the alkaline deposition, naturally acidic rusty soils underwent deacidification in the whole profile, in the case of soil pits situated on grasslands to a depth of 45 cm, on arable soils to 50 cm, on wastelands to 50 cm, and on forest soils up to 50 cm. In the case of forest soils (pits marked F4–F7, located in a westerly direction from the plant and F11 and F12 – in NW), the most transformed proved to be two genetic horizons: detrital Of (pH 6.0–7.25) and humic Ah (pH 7.07–7.27) (Table 2). Moreover, in some places unnaturally high pH values in *sideric* horizon (Bv), with pH values up to 7.06 and in the bedrock – to 6.16. Taking into account that the pH values of forest soils in Strzelce Opolskie Forest District range from 3.1 to 4.2 [1], the tested forest stands are characterized by an increase in pH by 3–4 units. The reaction of litter subhorizon Ol of the tested forest soils is lower, than detrital O_f, occurring below (pH 5.39–6.00), however the difference in pH values among tested points in vicinity of the plant reaches up to two pH units. An increase in acidity of Ol subhorizon reported in forest stands may be associated with higher concentration of H^+ ions, resulting from the decomposition of debris of forest undergrowth plants and pine needles [12, 13]. Only in the case of C horizon of forest soil pits L6, F7 and F11, the pH values were within the limits given for the rusty soils under coniferous forest stands, free from strong anthropogenic pressure.

Forest soil pits located to the west of the plant, show a tendency to decrease in alkalization deep into the soil profile, whereas there was no decrease in soil reaction with increasing distance from the plant, as regards especially humic and sideric horizons. This may be related to differences in the composition of the falling dusts, as well as a diverse species composition of undergrowth and different distance between tree crowns.

The reaction of A3 and A10 soil pits, located on arable land, in the distances of 220 m and 300 m from the plant, in line with prevailing winds, is characterized by pH values above 7.0. This applies to the entire depth of the soil profile of these pits. In A3 position a slight decrease in pH values with depth was noted. The difference between the highest A1 horizon (0–5 cm), and the bedrock C (45–55 cm) equals 0.14 pH units. Different results were obtained for A10 position, where pH values do not decrease with the depth, and the lowest value occurs in A1 surface horizon. Taking into account, that most arable soils in Opole Province have pH below 5.5 [1], and the optimal pH of the soil for plant cultivation should be in the range of 5.5–6.5 [10–12], the investigated case indicates the exceedance of pH value almost by 1 unit.

Soil pits located on grasslands, overgrown with grassy vegetation (L1 and L2) and on wastelands (W8 and W9), are characterized by an increased reaction throughout entire depth. In the case of meadow pits Ł1 and Ł2, located at the following distances from the plant: 70 m and 170 m respectively, in line with the prevailing winds, pH values of soil horizons vary in the range of 7.4–7.7. Wasteland stands W8 and W9, situated at distances: 80 m and 120 m from the emitter, are characterized by lower reaction of soil horizons, with pH values in the range of 7.0–7.5. The optimum pH values for grassy vegetation growth on mineral soils range from 5.5 to 6.5 [10–12], which indicates the exceedance of pH limit value from 0.5 to 1 pH unit in the tested soil pits.

Alkalization of soils is one of the best known and widely described in the literature results of the impact of cement and lime dusts on the environment. The falling dusts, deposited on the soil surface, are the reason for breakage soil protective barriers, arising from its buffer properties. Numerous studies have shown changes in functioning of a variety of soil buffers, which does not allow to maintain the soil pH in a natural range [11–14].

Particularly noteworthy are the work concerning chemical transformations of forest soils under the long-term deposition of alkaline dusts coming from cement and lime plants in the Swietokrzyski region of Poland [15]. The author showed strong alkalization of soils, manifested in changes in their buffering properties, and the content of such metals as: Ca, Mg, Mn, Al and Fe, which led to the transformation of plant communities. She also described the transformations which the alkaline falling dusts are subjected to in the upper soil horizons. It is the process of decomposition, which releases and mobilizes dust components into the soil profile, as well as the process of binding the dusts of hydrophilic properties in poorly soluble compounds. Surface horizons of forest soils (Of, Oh, Ofh) form the filter catching alkaline dust particles, which significantly reduces their migration to deeper horizons.

The content of carbonates

The content of calcium carbonate $CaCO_3$ in the tested soils ranged from 0.0 to 3.06% (Table 2). It was fund, that the amount of this component decreases with the depth of sampling in the soil profile, and depends on the distance from the plant, which may be related to the deposition of lime dusts.

Table 2

Physicochemical properties of the tested soils

Symbol of soil pit	Location of soil pit against the plant	Depth of sampling [cm]	Soil horizon	pH [-]		Content of $CaCO_3$ [%]	Electrical conductivity [$\mu S \cdot cm^{-1}$]
				H_2O	KCl		
G1	70 m W	0–5	A1	7.84	7.41	2.23	116.5
		25–45	C	8.07	7.72	0.10	50.1
		< 45	C	8.09	7.63	0.08	48.5
G2	170 m W	0–5	A1	7.84	7.44	3.06	145.7
		15–25	A2	7.87	7.57	1.39	115.1

Table 2 contd.

Symbol of soil pit	Location of soil pit against the plant	Depth of sampling [cm]	Soil horizon	pH [-]		Content of $CaCO_3$ [%]	Electrical conductivity [$\mu S \cdot cm^{-1}$]
				H_2O	KCl		
A3	220 m W	0–5 0–30 45–55	A1 Ap C	7.45 7.47 7.64	7.10 7.01 6.96	0.27 0.31 0.02	58.3 57.1 40.5
F4	230 m W	3–2 2–0 0–15 40–60 < 60	Ol Ofh Ah ABv C	6.11 7.15 7.68 7.26 6.92	6.00 7.15 7.16 6.67 6.16	— — 0.17 0.06 0.02	321.0 167.5 102.3 43.9 24.8
F5	280 m W	3–2 2–0 0–20 20–40 < 40	Ol Ofh Ah Bv C	5.99 7.26 7.76 6.73 6.82	5.88 7.25 7.27 5.95 5.92	— — 0.21 0.02 0	288.3 132.8 90.9 28.1 28.6
L6	330 m W	7–6 6–0 0–10 10–25 < 25	Ol Ofh Ah Bv C	5.78 6.57 7.70 7.28 6.09	5.46 6.65 7.22 6.75 4.94	— — 1.25 0.02 0.02	317.3 207.7 145.7 51.6 40.0
F7	430 m W	6–5 5–0 0–10 10–25 < 25	Ol Ofh Ah Bv C	5.57 6.69 7.77 6.82 4.80	5.42 6.50 7.23 6.07 4.31	— — 0.31 0.02 0.04	313.0 145.4 106.8 38.2 47.0
W8	80 m SW	0–5 0–25 25–40 < 50	A1 A2 Bv C	7.65 7.75 7.68 7.76	7.28 7.35 7.09 7.06	0.86 0.11 0.04 0.02	84.3 78.8 39.5 30.6
W9	120 m SW	0–5 10–25 25–40 < 50	A1 A2 Bv C	7.55 7.78 7.80 7.80	7.18 7.48 7.37 6.97	0.52 0.21 0.11 0	141.9 70.5 52.4 27.2
A10	300 m NW	0–5 25–35 < 50	A1 Ap C	7.67 7.92 7.91	7.22 7.44 7.34	0.82 0.35 0.02	96.0 66.4 36.9
F11	400 m NW	3–2 2–0 0–10 10–25 < 50	Ol Ofh Ah Bv C	5.39 7.16 7.41 5.62 5.12	5.39 7.16 7.07 5.13 4.53	— — 0.73 0.02 0	358.7 169.3 236 293.3 252.7
F12	470 m NW	3–2 2–0 0–10 10–25 < 50	Ol Ofh Ah Bv C	5.83 6.78 7.72 7.68 6.79	5.78 6.87 7.20 7.06 6.16	— — 0.79 0.06 0.04	276.7 140.9 115.5 45.9 29.8

In the top layer of all tested soil pits the content of $CaCO_3$ exceeded the value of 0.1%. In the case of grassland and wasteland it concerned the layer of 0–25 cm, arable soil 0–35 cm and forest soil 0–10 cm. As it is known from the literature, when carbonate content exceeds 0.5%, the saturation of the sorption complex with alkaline cations, mainly calcium ions, may take place in organic and organo-mineral soil horizons [15]. In the case of tested soils, $CaCO_3$ content above 0.5% was noted in the upper horizons, mainly turf (A1) and humic (A2, Ah, Ap), but it concerned only some of the tested pits. The greatest amount of $CaCO_3$ were accumulated in soils closest to the lime plant, *i.e.* G1 and G2 pits.

Electrical conductivity

The results of specific conductivity measurements indicate, that alkali emissions had much less impact on the salinity of the tested soils, than on reaction (pH values) and carbonate content. Analyzed soil samples were characterized by low specific conductivity values, much less than 1000 $\mu S \cdot cm^{-1}$ (Table 2).

The tested proper rusty soils of agricultural and forest land in the vicinity of lime plant were characterized by diverse values of conductivity. The results obtained for individual soil samples ranged from 24.8 to 358.7 $\mu S \cdot cm^{-1}$. The highest values were noted in the following horizons: litter Ol: 276.7–358.7 $\mu S \cdot cm^{-1}$ (forest pits F4–F7, F11 and F12), detrital Of: 140.9–207.7 $\mu S \cdot cm^{-1}$ (forest pits F4–F7, F11 and F12) and turf A1: 84.3–145.7 $\mu S \cdot cm^{-1}$ (soil pits G1 and G2 on grasslands, and W8 and W9 on wastelands). It was also noted the increased conductivity values in humic horizon of forest soils (90.9–236 $\mu S \cdot cm^{-1}$, soil pits: F4–F7, F11 and F12) and soils overgrown with grassy vegetation (70.5–115.1 $\mu S \cdot cm^{-1}$, soil pits: G2, W8 and W9).

For most of the tested soil samples the values of specific conductivity have been decreasing with the depth of the occurrence of horizons they were collected from. An exception was the soil pit F11, where the conductivity values of mineral horizons exceeded 250 $\mu S \cdot cm^{-1}$. The increased salinity of the entire soil profile of F11 location may result from the impact of both the alkali emissions, as well as other anthropogenic factors.

There was no the decrease of specific conductivity values with increasing distance from the plant. It was noted however, that the soil pits located in line with prevailing winds, *ie* in a westerly and north-westerly direction from the plant, were characterized by the highest salinity. Most of all it refers to the forest soil pits, showing the greatest salinity in the upper horizons. The increase in the conductivity of the upper soil layer (0–2 cm) in forest soils may result from atmospheric precipitation flowing down the tree trunks. Diverse values of conductivity of the tested soils and no relationship with the distance from the plant may also be the effect of differences in the composition of the falling dusts. This is confirmed by the research into the dusts from the lime plant in Gorazdze, which are characterized by very different values of the specific conductivity in the range from 355 to 7060 $\mu S \cdot cm^{-1}$, depending on the place of their sampling [5]. The values obtained for the dusts collected in a nearby cement plant in Gorazdze were within the range recorded for the lime plant.

Conclusions

1. Long-term deposition of alkaline dusts caused the chemical transformations of the tested soils. This concerns particularly reaction (pH), and – to a lesser extent – carbonate content and salinity.

2. Alkaline dusts were the reason for the change of pH values of the tested soils from acidic to neutral or alkaline in all transects of the reaserch (W, NW, SW).

3. The increased pH values was observed mainly in the upper soil horizons (detrital, turf) and humic horizons, as well as – to a lesser extent – in sideric horizon and bedrock, to a depth of about 50 cm.

4. Lime dusts enriched in calcium carbonate mostly turf and humic horizons of grassland soils, where up to 3.06% $CaCO_3$ at pH values above 7.41 were found.

5. There was a relationship between pH values and calcium carbonate content in the genetic horizons of the tested soil pits, *ie* an increase in pH values is accompanied by an increase in the content of $CaCO_3$.

6. The tested proper rusty soils have lost their natural properties and were transformed as a result of the impact of alkaline dusts emitted from the lime plant. Only the profile structure and particle size distribution were not changed – these soil characteristics remained typical of proper rusty soils.

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ZMIANY WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH GLEB W REJONIE ODDZIAŁYWANIA PRZEMYSŁU WAPIENNICZEGO

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Abstrakt: Przemysł wapienniczy i cementowy należy do najlepiej rozwiniętych gałęzi przemysłu w województwie opolskim. Zakłady zlokalizowane są we wschodniej i środkowej części regionu, w sąsiedztwie miast: Opole, Krapkowice i Strzelce Opolskie, co wynika z występowania na tym terenie złóż surowców wapiennych (wapieni i margli). Wpływ przemysłu wapienniczego i cementowego na środowisko przyrodnicze, szczególnie gleby, był przedmiotem badań wielu autorów, ale prace te nie dotyczą województwa opolskiego, które od stuleci jest jednym z głównych ośrodków produkcji wapna i cementu w Polsce**.** W artykule podjęto próbę ukazania zmian właściwości fizykochemicznych gleb znajdujących się pod wieloletnim wpływem emisji pyłów alkalicznych pochodzących z zakładu wapienniczego w Górażdżach. Badania prowadzono w latach 2010–2013. Zakres badań obejmował prace terenowe w rejonie zakładu, gdzie założono 12 reprezentatywnych odkrywek glebowych, z których pobrano próbki do analiz laboratoryjnych. Dla każdej z próbek glebowych oznaczono następujące parametry fizykochemiczne: skład granulometryczny, odczyn (pH), przewodnictwo właściwe oraz zawartość węglanu wapnia. Badania wykazały wzrost odczynu badanych gleb piaszczystych będący efektem depozycji pyłów alkalicznych, co dotyczyło przede wszystkim odkrywek zlokalizowanych na stanowiskach leśnych, które charakteryzowały się wzrostem wartości pH o 3–4 jednostki. W przypadku łąk, gleb uprawnych oraz nieużytków wartości pH wzrosły o 1–2 jednostki. Ponadto wykazano, że opadające pyły alkaliczne wzbogaciły badane gleby w węglan wapnia. Dotyczyło to w największym stopniu odkrywek glebowych zlokalizowanych najbliżej zakładu wapienniczego, w których zawartość $CaCO_3$ przekraczała 1%. Wyniki pomiarów przewodnictwa właściwego wskazują na niski stopnień zasolenia badanych próbek glebowych.

Słowa kluczowe: pyły wapiennicze, gleby rdzawe właściwe, pH, przewodnictwo właściwe, zawartość węglanu wapnia

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BIOMASS OF SPRING BARLEY (*Hordeum vulgare* L.) IN RELATION TO FERTILISING

BIOMASA JĘCZMIENIA JAREGO (*Hordeum vulgare* L.) JAKO FUNKCJA NAWOŻENIA

Abstract: The study was aimed to determine the effect of the fertilizer dose on growth of barley. In the experiment we used calcium sulphate, which is a waste during gas desulphurisation in heat and power stations. We assumed that dihydrate calcium sulphate would react with aluminium and form insoluble $AlSO_4^+$. We weighed the biomass of barley, underground and aboveground parts separately, determined the content of chlorophyll and the change in soil reaction caused by the applied doses of fertilisers. The vase experiment with barley of the brewery variety Propino was conducted in a setting of sub-blocks with fertilizing as the one changing factor. One experimental block included 5 variants in 5 repetitions. During growth period we conducted detailed observations of growth and development of barley. Calcium sulphate has positive effect on the growth of biomass and chlorophyll content in leaves of barley. Application of a double dose of calcium sulphate did not bring measurable increase in the growth of biomass and the height of barley stems.

Keywords: biomass, mineral fertilization, grain yield, *Hordeum vulgare*

Cereals are strategic products in national and international economy, because of their multipurpose utility. Besides consumption by man, cereals are also widely use as a feed for animals. Barley grain is used specifically for production of malt, which is used in fermentation, bakery and pharmaceutical trade. The largest amounts of barley are used in brewing industry.

Mineral fertilisation is one of the most important factors that affect the size of crop. Fertilizing is efficient at maximum level only if other factors that determine its activity are optimally adjusted by agrochemical practices. Many studies showed the influence of fertilizing with nitrogen on crops of cereals, including spring barley [1–4]. Nitrogen not

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only improves productive layerage of plants but also the number of grains in an ear, which is additional factor that increases crop. Unsustainable fertilisation without supplementation with calcium leads to strong acidification of soil and considerable loss of quality of cultivated plants. Using calcium sulphate in agriculture and gardening is not a standard practice in Poland. Calcium sulphate is a waste from gas desulphurisation by both wet and semi-dry methods. The semi-dry method of gas desulphurisation is more economic than the wet methods because it uses less water. But the waste from the wet method (synthetic $CaSO_4$), which is used as a substitute of the natural calcium (VI) sulphate has buyers. Thus the chemical content of waste from gas desulphurisation will be decisive for its commercial use in agriculture.

This study was aimed to determine the effect of the type and the dose of fertilizers on the biomass of barley. The study included measurements of overground parts of plants, including the ear and grains, and of their root systems. We also determined the content of chlorophyll in leaves of plants, and tested soil for changes in its reaction and in the content of exchangeable aluminium in the effect of the used doses of fertilizers.

Material and methods

We started the two-year vase experiment with barley of the variety Propino in 2014. During the first year of study the experiment was designed as five variants in three repetitions. In the second year we modified the experiment by increasing the number repetitions to five. We used three repetitions of the experiment to assess the biomass of plants (of overground parts and roots) produced by the beginning of barley flowering. We collected the remaining plants when they were fully mature in the third decade of July, and we measured the length of ear and the number and the mass of grains. We dosed fertilisers according to the methods of vase experiments. At the base of the control (variant I), which was low-intensity cultivation without fertilizing, we set up four other variants (II, III, IV and V), in which we used mineral fertilizing by NPK fertilisers in proportions 4 : 12 : 12 at a dose of 20 g/12 dm^3 of soil. In variants III, IV and V we additionally applied fertilising by ammonium nitrate (NH_4NO_3) at two doses of 6 g/12 dm^3 of soil, one before the start of growth and before the start of growth and the second one during stem formation. Variants IV and V were fertilized with calcium sulphate ($CaSO_4 \cdot 2H_2O$) at doses of 15 and 30 g/12 dm^3 of soil, respectively [5].

Soil used in the experiment was collected from the arable layer of podsolic soil of the granulometric content of a light clay sand. Soil dried in the air was sifted through a sieve with holes of 2 mm diameter and moved to vases of the volume 12 dm^3 each. During growth of plants we maintained constant humidity of soil at the level of 60% f.w.c. (field water capacity). We sowed material of the score K1 treated with preparation Premis Universal 275 FS. We sowed barley by hand at a density of 300 seeds per 1 m^2. We kept equal distances between grains by using a previously prepared template during sowing. Sowing material was placed in the soil at the depth of 3 cm. Each time we sowed barley in the first decade of April. During the experiment, in the phase of an ear formation, the plants were sprayed against aphids with preparation

Rapid 060 CS. During growth the relative content of chlorophyll in plants was measured using chlorophyll meter CCM 200.

Before the plants formed ears, we measured the height, the length of the root (measurement of the longest root in a bundle) and biomass of the overground and underground parts of each individual in 15 vases. We used the July harvest of plants from the remaining 10 vases to estimate the crop of grains. The content of the dry mass was determined by drying and weighing plant material in 105°C until the mass was stable. We measured reaction (pH) and the content of exchangeable aluminium in soil using the method of Sokolow.

Results and discussion

During the period of growth detailed observations of development and growth of barley while constant humidity of soil was maintained. Density of plants was determined directly after germination (z_0) and after the experiment was finished (z_1). The relative density was between 0.83 and 1.0. (Table 1). Germination was similar in the control variant and in variant IV, the weakest germination was recorded in the variant where ammonium nitrate was applied (variant III). The number of individuals did not change until the end of the experiment.

Table 1

Relative density of individuals

Repetitions	Density of individuals in relation to maximum density									
	VARIANTS									
	I		II		III		IV		V	
	z_0	z_1	z_0	z_1	z_0	z_1	z_0	z_1	z_0	z_1
1	0.94	0.94	0.94	0.94	0.88	0.88	1.00	1.00	0.94	0.94
2	0.94	0.94	0.88	0.88	0.83	0.83	0.94	0.94	1.00	1.00
3	1.00	1.00	0.94	0.94	0.88	0.88	0.94	0.94	0.88	0.88
4	1.00	1.00	0.88	0.88	0.94	0.94	1.00	1.00	1.00	1.00
5	1.00	1.00	0.94	0.94	0.94	0.94	1.00	1.00	0.88	0.88

Soil used in the experiment had acidic reaction ($pH_{KCl} = 4.6$). Spring barley belongs to plants that are sensitive to acidic reaction and associated high concentration of exchangeable aluminium [6]. We used calcium sulphate for fertilizing (variant IV and V), which did not change pH of soil, despite it contains calcium. Thus, using calcium sulphate for de-acidification of acidic soils will not bring the expected effect. However, calcium sulphate would be good fertilizer in soils of alkaline reaction but with a deficit of calcium. Application of the calcium sulphate can give good effects where soil contains calcium in a form temporarily inaccessible for plants [5]. Low content of aluminium at the level of 0.6 mg/100 g of soil, was obtained by applying fertilizing by

NPK only (variant II) and in the control variant (0.5 mg/100 g of soil). Other authors [6] obtained similar results for the control sample, with the content at the level of 0.4 mmol(+) · kg^{-1}. The largest content of aluminium was found in the combination of fertilizing with NPK and ammonium nitrate (variant III), where pH was also the lowest among all analysed samples (pH_{KCl} = 3.9). The content of aluminium in this variant of fertilizing varied from 1.6 to 2.0 mg/100 g, which was caused by acidification effect of ammonium nitrate [7], which increases amount of exchangeable aluminium [8].

Production of biomass in plants is a function of their assimilation surface, efficiency of photosynthesis from a unit of this surface, and the duration of photosynthesis. The amount of biological crop of different plant species is varied and depends on their productive capacity expressed as the amount of produced dry mass, which is associated with the size of their organs. According to Pecio [9], the larger the assimilation surface grows before barley flowers the greater is the chance it produces shapely grain. We used some simplification in our two years of studies using vases. We did not measure the assimilation surface. Instead we assessed the biomass of plants before they started flowering, assuming that assimilation surface that affects the crop increases proportionally to the mass of individuals. We are aware that individual plants of the same biomass may differ in assimilation surface.

Statistical analyses showed large variation of individuals in biomass, height, length of stems and in the mass and number of grains. Biometric analysis of the root length of the spring barley showed that the longest roots occurred in these vases where we applied calcium sulphate (variants IV and V). In both these variants the length of the root was about 24 cm (Fig. 1). Thus the double dose of calcium sulphate in variant V did not cause increase of the root length proportional to fertilizing. The weakest root systems occurred in variant III, where NPK and ammonium nitrate were applied. In this variant the mean length of a root was 16 cm, the longest root had 27 cm and the shortest had 4 cm. The coefficient of variation for the length of roots was between 27% (variant I) and 54% (variant V) (Table 2).

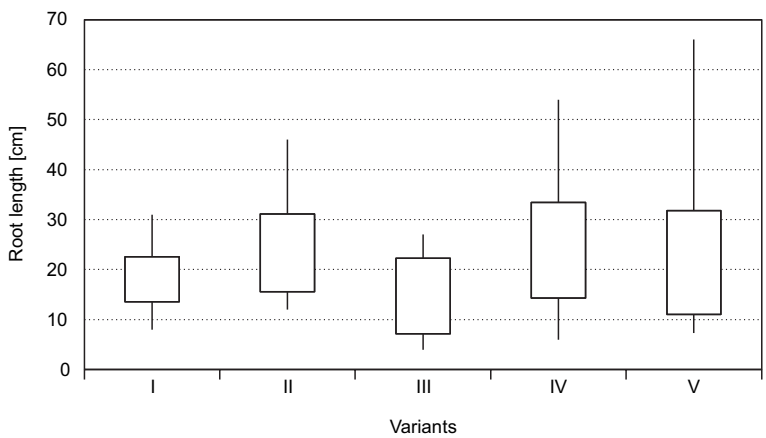

Fig. 1. Root length of spring barley depending on the dose applied fertilization variants

Table 2

Biometric parameters of spring barley of the variety Propino in relation to applied doses of mineral fertilizers, divided into overground and underground parts (harvested before flowering)

Measures of central tendency and dispersion	Biometric parameters of spring barely in the variants of the experiment									
	I		II		III		IV		V	
	Overground parts	Root	Overground parts	Root	Overground parts	Root	Overground parts	Root	Overground parts	Root
	[cm]									
Mean	65.1	18.8	57.2	23.4	58.6	15.6	61.1	23.9	51.0	23.9
SD	9.9	5.1	18.7	7.7	21.2	7.6	16.9	9.5	16.2	12.5
Min	40.0	8.0	22.0	12.0	12.0	4.0	24.0	6.0	15.0	10.0
Max	83.0	31.0	94.0	46.0	84.0	27.0	90.0	54.0	76.0	66.0
Mo	70.0	20.0	70.0	20.0	73.0	21.0	77.0	25.0	61.0	25.0
Me	67.0	20.0	63.0	22.0	72.0	16.0	64.0	23.0	55.0	21.0
v [%]	15.2	27.3	32.7	32.9	38.8	51.7	28.1	40.4	32.5	53.7

Symbols: I – control without fertilizing; II – multi-component fertilizer NPK (4%N; 12%P_2O_5, 12%K_2O); III – NPK + NH_4NO_3; IV – NPK + NH_4NO_3 + + $CaSO_4 \cdot 2\ H_2O$ – at a dose of 250 kg/ha; V – NPK + NH_4NO_3 + $CaSO_4 \cdot 2\ H_2O$ – at a dose of 500 kg/ha; Mean – arithmetic mean, SD – standard deviation, Min – minimum value, Max – maximum value, Mo – modal value, Me – median, v – coefficient of variation [%].

Similar relationships occurred in the height of individuals. Application of calcium sulphate at a dose of 250 kg/ha increased the height of plants 16% in relation to the applied dose of this fertiliser in the variant V (500 kg/ha). Thus, using high dose of calcium sulphate did not improve the height of barley. A half of studied individuals of the variant IV reached the height over 64 cm (Table 2, Fig. 2). According to the producer, the mean height of the barley of the variety Propino is 65 cm. Variation of the overground parts of plants was smaller than that of the root system, and was between 15% (variant I) and 39% (variant III).

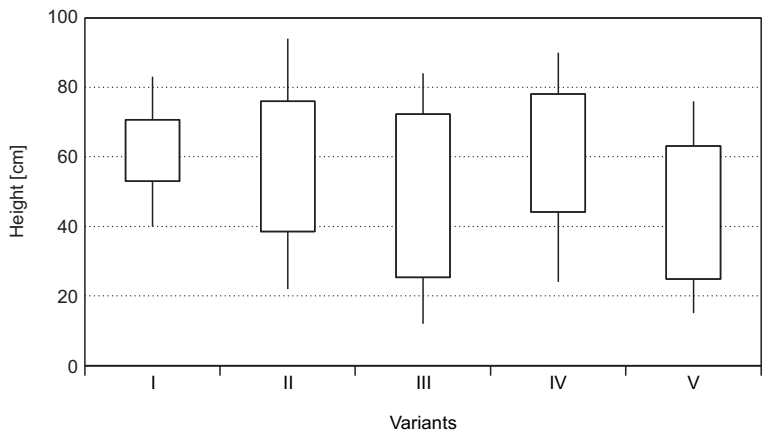

Fig. 2. The height of spring barley depending on the dose of fertilization

Fertilising had positive effect on the biomass of the underground parts and of the roots of spring barley. Individuals in vases that were fertilised with calcium sulphate at a dose of 250 kg/ha reached the largest mean biomass. Dry mass in this variant increased on average for 56% in relation to the control variant. A half of examined individuals had greater mass than 2.430 g [dry mass] (Table 4, Fig. 3). Application of the double dose of calcium sulphate caused 44% increase of biomass in relation to the control. Introducing NPK fertilizer only into the soil caused 27% increase of the biomass (variant II). Fertilizing with combination of NPK and ammonium nitrate (variant III) caused decrease in the mass of roots. General biomass of spring barley increased for 34% in relation to the control (Table 4), but the root system with this combination of fertilizers was the smallest of all four variants of fertilizing (Table 3). This situation may be associated with the content of exchangeable aluminium. According to Marschner [10] the toxic effect of aluminium affects mostly roots of plants. Badora [11] also stated that the first symptom of aluminium stress in spring barley is a significant decrease of the mass of the root system. According to this author the first symptoms of shortage of phosphorus, magnesium and calcium occur with about 70 mg of exchangeable Al per one kg of soil, which gives 7 mg/100 g. In our laboratory experiment we observed decrease of the root system already with 2 mg Al/100 g of soil [5].

Table 3

Biomass of spring barley of the variety Propino in relation to applied doses of mineral fertilizers (harvested before flowering) split into the overground parts and roots

Measures of central tendency and dispersion	Biomass spring barley depending on the fertilization									
	I		II		III		IV		V	
	Overground parts	Root	Overground parts	Root	Overground parts	Root	Overground parts	Root	Overground parts	Root
	[g d.m.]									
Mean	1.123	0.066	1.393	0.235	1.628	0.171	2.270	0.462	1.759	0.348
SD	0.421	0.036	0.732	0.166	0.844	0.122	0.930	0.338	1.104	0.266
Min	0.248	0.020	0.353	0.062	0.162	0.039	0.885	0.124	0.262	0.015
Max	1.948	0.173	3.114	0.927	3.004	0.404	5.242	1.379	4.837	1.015
Me	1.108	0.082	1.332	0.218	1.457	0.132	2.054	0.352	1.332	0.316
v [%]	37.47	54.72	52.53	70.69	51.85	71.36	41.50	74.11	62.78	76.43

Explanations see Table 2.

Table 4

Biomass of spring barley of the variety Propino in relation to applied doses of mineral fertilizers (harvested before flowering)

Measures of central tendency and dispersion	Biomass of spring barley [g d.m.]				
	I	II	III	IV	V
Mean	1.189	1.628	1.798	2.732	2.107
SD	0.430	0.854	0.881	1.160	1.293
Min	0.315	0.511	0.206	1.108	0.298
Max	2.014	3.704	3.408	6.621	5.495
Me	1.197	1.595	1.775	2.430	1.626
v [%]	36.11	52.45	48.98	43.02	61.39

Explanations see Table 2.

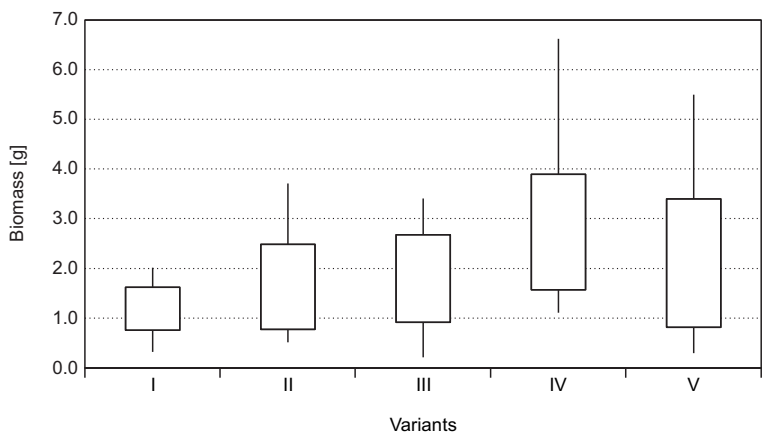

Fig. 3. The average biomass of a single individual (*Hordeum vulgare* L.) in relation to the fertilizer dose

The differences in chlorophyll content, depending on the applied fertilizer, were determined by Chlorophyll Content Index (CCI) – proportional to chlorophyll content in the sample. The lowest relative content of chlorophyll was observed in the control variant. Fertilizing with NPK (variant II), as well as adding ammonium nitrate (variant III) caused small increase in the content of chlorophyll in leaves of barley. But treating the soil with calcium sulphate doubled the content of chlorophyll in relation to the control variant.

In our experiment we determined the effect of fertilizing on features of crop structure. Statistical analysis showed that all factors in the experiment (fertilizing with NPK, ammonium nitrate and calcium sulphate) had significant effect on layerage (Table 4) and on the increase of crop (Table 5). The largest improvement of crop was obtained by fertilizing with a combination of NPK, ammonium nitrate and calcium sulphate (variant IV). Crop of grain from this variant was 5200 kg/ha, which was 36%

Table 5

The structure of yield depend on fertilization – mean values

Variants experience	Length of ear [cm]	Number of productive ears per m^2	Number of grains per ear	Weight of grains per ear [g]
I	8.2	377	17.5	0.82
II	8.6	476	19.0	0.88
III	8.5	400	18.8	0.85
IV	9.0	528	19.8	0.97
V	8.8	489	18.9	0.90

increase of harvest of grain in relation to the control (Table 5). It is known from literature [3] that nitrogen improves layering of plants and increases the number of grains in an ear, which is an additional important factor that improves crop. In all combinations of fertilizing the number of grains in a head was greater than in a control (Table 4). However, too high doses of fertilizing with nitrogen may cause decrease in the number of grains in an ear, because greater productive layering requires the plant to feed more grains. The accuracy of grain deteriorates at the same time, which means that the proportion of shapely grains in crop decreases. With a similar length of the head (variant II and III) we obtained different number and mass of grain in an ear (Table 5). Moreover, variant III caused production of low number of ears in comparison to the remaining variants of fertilizing. The recorded biomass of the overground part of barley in the variant III (mean = 1.628 g of dry mass) was greater than in the control variant and the variant with NPK fertilizing (Table 3). This indicates sufficient layering of the plants. However, a part of plants did not enter the generative phase, which could be caused by the increased content of aluminium in soil [5, 11].

Conclusions

Based on the study the we drew the following conclusions:

1. Combination of fertilising with NPK, ammonium nitrate and calcium sulphate had the greatest effect on the crop of spring barley.
2. Calcium sulphate did not change pH of soil, but had a positive effect on the biomass of the overground parts and roots and crop of grain.
3. Application of double dose of calcium sulphate did not cause measurable improvement in layering of plants and thus in crop of grain from barley.
4. In conditions of low content of exchangeable aluminium in soil, larger biomass produced by barley plants before they flower had a positive effect on production of shapely grain.

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BIOMASA JĘCZMIENIA JAREGO (*Hordeum vulgare* L.) JAKO FUNKCJA NAWOŻENIA

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Abstrakt: Dwuletnie doświadczenie wazonowe z jęczmieniem jarym odmiany browarniczej Propino rozpoczęto w 2014 roku. Celem pracy była ocena wpływu rodzaju i dawki nawozu na biomasę jęczmienia. W nawożeniu wykorzystano m.in. siarczan wapnia będący odpadem odsiarczania spalin w elektrociepłowniach. Założono hipotetycznie, że dwuwodny siarczan wapnia wejdzie w reakcję z glinem, tworząc nierozpuszczalną formę $AlSO_4^+$. Zakres badań obejmował pomiary biometryczne części nadziemnej wraz z kłosem i ziarniakami oraz system korzeniowy. Określono zawartość chlorofilu w liściach roślin, a także wykonano badania glebowe w zakresie zmiany odczynu i glinu wymiennego pod wpływem zastosowanych dawek nawozów.

Największy wpływ na wielkość plonu jęczmienia jarego miało zastosowanie kombinacji nawozowej: NPK, saletry amonowej i siarczanu wapnia. Siarczan wapnia nie wpływa na zmianę pH gleby, ale ma korzystny wpływ na biomasę części nadziemnej i systemu korzeniowego oraz plon ziarna. Zastosowanie podwójnej dawki siarczanu wapnia nie przyniosło wymiernych korzyści w plonie ziarna jęczmienia.

Słowa kluczowe: biomasa, nawożenie, plon ziarna, jęczmień jary

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Katarzyna GRATA[1]

SENSITIVITY OF *Fusarium solani* ISOLATED FROM ASPARAGUS ON ESSENTIAL OILS

WRAŻLIWOŚĆ *Fusarium solani* WYIZOLOWANEGO ZE SZPARAGA NA OLEJKI ETERYCZNE

Abstract: The purpose of this study was to evaluate the antifungal properties of sage oil, clove oil and basil oil against *Fusarium solani* isolated from white asparagus spears (*Asparagus officinalis L.*). A dual culture plate method was used for the assessment of the inhibitory effects of essential oils and volatile components on mycelium, inoculated into a PDA medium. The culturing process was conducted for 9 days at a temperature of 26°C and the fungal linear growth was measured every 1–3 days. The conidial germination of the fungus in the presence of oils was evaluated by microscope method. The results show differences in the fungistatic activity of oils, dependent on the type and dose of the oil. Generally the oils had a higher impact against the fungal spores than on mycelium growth of *F. solani*, however the type of oil and dose determined different amounts. The conidial germination was most inhibited by the basil oil (98.9% maximum inhibition), followed by the clove and sage oils at a concentration of 4% (respectively 89.9% and 85.4% maximum inhibition). In contrast, the oils had much less of an impact on the linear mycelial growth of *F. solani*. Use of the highest dose of clove oil reduced the linear growth of mycelium by 29.9%, sage oil by 14.8% and basil oil by 4%. Furthermore, gas metabolites limited the growth of *F. solani*. The degree of inhibition of mycelium amounted to 17.1% for clove oil, 15.5% for sage oil and 9.3% for basil oil used in the maximum concentration 4.0%. Based on these results, clove oil was the greatest inhibitor of mycelial growth and sporulation of *F. solani*.

Keywords: *Fusarium solani,* asparagus, essential oils, antifungal activity

Introduction

Fungi of the genus *Fusarium* are geographically widespread and occur as saprophytic organisms in the soil. They have the ability to produce highly toxic secondary metabolites (fumonisins, moniliformins, beauvericin) and therefore are classified as opportunistic organisms for plants and people [1–4].

Several pathogenic *Fusarium* species cause disease in asparagus plants (*Asparagus officinalis* L.), such as *Fusarium* stem and crown rot (FCRPR). These diseases can occur in asparagus seedlings, however they are most typically observed in mature plants

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[1, 3, 5–7]. Both white and green asparagus are easily infected by the different *Fusarium* species. Researchers have shown that the presence of *Fusarium* ranges based on region, with some regions only reporting occasional presence and others a more dominant presence. Infection of asparagus plants depends particularly on environmental conditions, agronomic practices and asparagus cultivar susceptibility [2, 5, 8–10]. This concerns mainly *F. proliferatum*, *F. oxysporum*, *F. culmorum, F. solani* and *F. redolens* [1, 3, 5, 11–15]. There have been many different approaches used towards minimizing the damage caused by *Fusarium* crown and root rot. These have included incorporating organic matter into the soil, improving soil fertility, applying arbuscular mycorrhizae (*Glomus intraradices*), chemical control and biological control (*Trichoderma* sp.) [14, 16–19].

In recent years there has been increased interest in the possibility of using natural products such as plant extracts or essential oils as biological agents of plant protection and plant disease control. The application of essential oils in particular has been evaluated as a potentially effective and safe alternative to chemicals. Plants have a limitless ability to synthesize secondary metabolites (*eg* phenols, flavones, flavonoids, alkaloids, tannins) which operate as the plant's defence mechanism against pathogenic microorganisms. Based on this process, certain essential oils in liquid phase and/or vapour phase can be used to delay or inhibit the growth of pathogenic and/or toxin producing fungi [20–27]. Many essential oils have been demonstrated to have biological activity on many fungal plant microorganisms, including *A. flavus*, *A. niger*, *Mucor* sp., *Rhizoctonia* sp. *Fusarium* sp. Some studies suggest that within an experimental system the extent of inhibition of mycelial growth and spore germination depends on the concentration of essential oils [20, 21, 28, 29].

The aim of this study was to investigate the antifungal activity of three essential oils (sage oil, basil oil and clovebud oil) against the mycelial growth and spore germination of *Fusarium solani*.

Materials and methods

The research material was the strain of *Fusarium solani* isolated from the spears of white asparagus plants (*Asparagus officinalis* L.) exhibiting signs of dry rot. The essential oils (EOs) used were sage oil (*Salvia sclarea* L.) and basil oil (*Ocimum basilicum* L.), both from plants of the *Lamiaceae* family, and clovebud oil (*Eugenia caryophyllus*) from a tree of the *Myrtaceae* family [30]. The antimicrobial effect of the tested oils (in both liquid and vapour phase) was observed by employing various antifungal assays. The sensitivity of spores and mycelium of *F. solani* to EOs was examined using the medium poisoning method (method I), disc volatilization method (method II) and cavity slide technique (method III) with a few modifications [23, 27, 29, 30–33].

I Poisoning method. The experiments were conducted on a Potato dextrose agar (PDA) medium. Fungal mycelial discs (8 mm in diameter) were cut with a sterile cork borer from the periphery of 7 day-old pure culture of *F. solani* and were placed at the centre of the medium containing the essential oils at varying concentrations (0.5%,

1.0%, 2.0%, 4.0%). Initially, in order to enhance the oil solubility, the oils were dissolved with 0.5% dimethyl sulfoxide (DMSO). In the controls tests, EOs were replaced with 0.5% DMSO solution and inoculated following the same procedure.

II Volatilization method. In order to investigate the effects of the volatile fraction of the essential oils, petri dishes containing the PDA medium were inoculated with the fungal mycelial discs (8 mm in diameter). In contrast, the suspension of each EO was not added into the medium but rather dripped onto the sterilized filter disc (6 cm in diameter) positioned on the covers of the Petri dishes. A blank sterilized filter disc with no oil treatment was used as the control. After applying the EOs, the filter discs were then immediately inverted on top of the lid and hermetically sealed with parafilm to prevent any leakage of essential vapour. All plates (from methods I and II) were incubated in the dark at 24 ± 2°C for 9 days until the mycelium in the control plates reached the edge of the plates. The radial mycelia growth was observed and measured in two perpendicular diameters at intervals of 1–2 days. The experiment was performed in four replicates, where one repeat was represented by one plate containing the growth medium with one mycelia disc. The antagonistic activity of the EOs was evaluated using the growth rate index (GRI) and additionally evaluated using the percentage of mycelial growth inhibition in comparison to the control [33].

III Cavity slide technic. The evaluation of fungistatic activity of the EOs was also carried out on the basis of spore germination of *F. solani*. Conidia of *F. solani* were harvested from the 7 day-old culture grown in PDA medium using sterile water containing 0.5% Tween 80. The conidia suspensions were then filtered through sterile gauze to remove hyphae and adjusted to a concentration of $1.65 \cdot 10^6$ spores/cm^3 using a haemocytometer Thoma. Subsequently aliquots of 30 mm^3 of the essential oil solutions at different concentrations were mixed with 30 mm^3 of the spore suspensions in a cavity slide. Then they were incubated in a moist chamber at 24 ± 2°C for 18 hours. Microscopic observation and enumeration showed varying degrees of spore germination as well as no germination. The data evaluated were the rate of conidia germination and the percentage of spore germination inhibition [34].

All experiments were conducted in triplicate and the means were statistically compared using two-way analysis of variance with a Tukey's composition test. The differences between the means were considered significant for values of $p \leq 0.01$. The data are presented as mean values ± standard deviation calculated from four determinations.

Results and discussion

The essential oils were individually tested against *Fusarium solani*. The mycelial growth and spore germination of *F. solani* was affected differently by each of the three essential oils. The inhibition effect depended on the type of oil, the amount of essential oil, the incubation period and the susceptibility of the spores and mycelia of the fungus.

All amounts of the essential oil significantly restricted the spore germination of *F. solani* with the highest inhibition activity detected for 4% concentration. Basil oil

exhibited a statistically significant negative effect on the conidia, with a germination rate of 0.64 to 16.80 compared to the control germination rate of 58.62 (Table 1).

Table 1

Effect of essential oils on the spore germination (SG) of *F. solani* (means and standard deviation ± SD)

Treatment	Clovebud oil		Sage oil		Basil oil		Mean	
Control	58.62 ± 1.48	A	58.62 ± 1.48	A	58.62 ± 1.48	A	58.62	A
0.5%	26.62 ± 1.00	B	34.29 ± 4.36	B	16.80 ± 5.43	B	25.90	B
1.0%	23.19 ± 3.77	C	27.17 ± 4.77	C	5.55 ± 1.44	C	18.64	C
2.0%	14.14 ± 2.61	D	17.28 ± 3.57	D	2.37 ± 0.65	D	11.26	D
4.0%	5.90 ± 2.16	E	8.56 ± 1.84	C	0.64 ± 1.11	E	5.03	E
Mean	25.69	B	29.18	A	16.79	C		

Values followed by a same alphabetic letter are not significantly different (capital letters $p \leq 0.01$).

All concentrations of the basil oil inhibited *F. solani* spores from 71.33% to 98.90%. Clovebud had a moderate effect with a maximum degree of inhibition reaching 89.93% for 4% concentration. Sage oil had the lowest effect with a maximum degree of inhibition reaching 85.99% for 4% concentration. (Fig. 1).

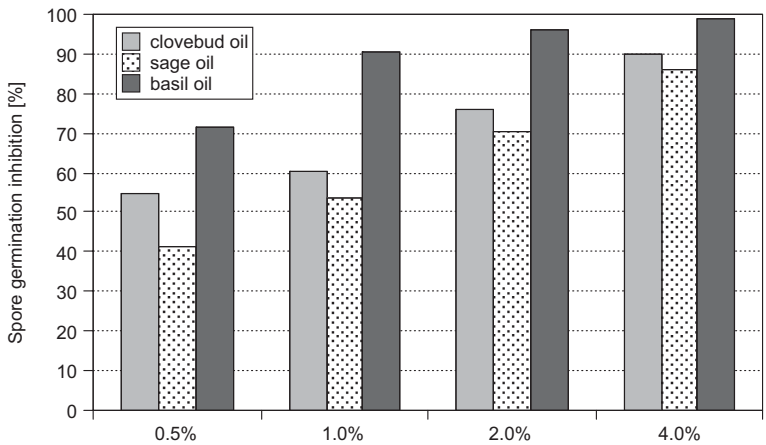

Fig. 1. Percentage inhibition of spore germination of *F. solani* at different concentrations of essential oils

In contrast, the essential oils showed a much smaller effect on the linear mycelial growth of *F. solani.* Growth inhibition was significantly influenced by the essential oil concentration and the incubation time. Increased concentration of the essential oils resulted in a gradual decrease in the linear growth of the mycelium. The clovebud oil at 4% concentration resulted in the lowest GRI value, followed by the sage oil with

a moderate GRI value, and the basil oil with the highest GRI value. At 0.5% EO concentration, the GRI ranged from 59.76 (clovebud oil) to 63.60 (basil oil), while at 4% EO concentration it ranged from 45.25 (clovebud oil) to 62.79 (basil oil) – compared to the control GRI of 64.62 (Table 2).

Table 2

Effect of essential oils (liquid phase) on the growth rate index (GRI) of *F. solani*

Treatment	Clovebud oil		Sage oil		Basil oil		Mean	
Control	64.62 ± 0.71	A	64.62 ± 0.71	A	64.62 ± 0.71	A	64.62	A
0.5%	59.76 ± 0.52	B	62.79 ± 0.68	B	63.60 ± 0.41	B	62.05	B
1.0%	58.74 ± 1.18	C	59.72 ± 0.51	C	63.21 ± 1.31	C	60.60	C
2.0%	53.22 ± 0.61	D	57.73 ± 0.58	D	62.24 ± 0.38	D	57.73	D
4.0%	45.25 ± 0.85	E	55.05 ± 1.54	E	62.79 ± 0.81	E	54.36	E
Mean	56.32	C	59.98	B	63.29	B		

Values followed by a same alphabetic letter are not significantly different (capital letters $p \leq 0.01$).

The highest degree of inhibition of mycelium was obtained for clovebud oil (29.96%), followed by sage oil (14.79%). Basil oil had the least impact on the inhibition of mycelium at only 4.01% (Table 2, Fig. 2).

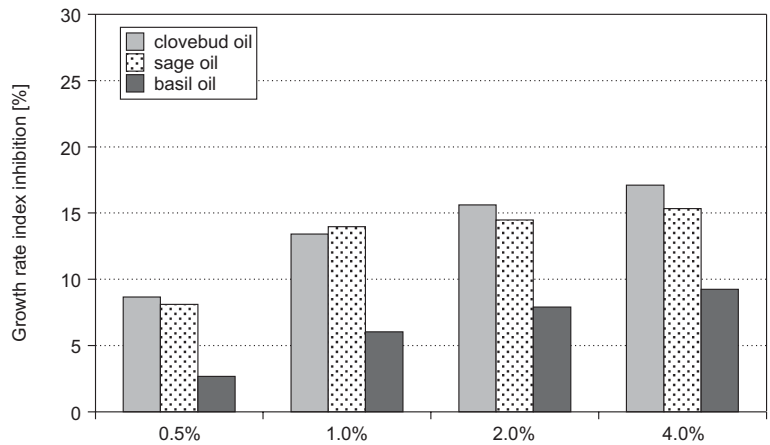

Fig. 2. Growth inhibition of *F. solani* by essential oils (liquid phase) at different concentrations

Results obtained from the volatilization method indicated that gas metabolites also significantly limited the growth of tested *F. solani*. The growth rate index was similar to that obtained for the oils applied in the liquid phase. The lowest GRI at 4% EO concentration was found for clovebud oil (52.79), followed by sage oil (53.93) and finally for basil oil (28.02) (Table 3).

Table 3

Effect of essential oils (vapour phase) on the growth rate index (GRI) of *F. solani*

Treatment	Clovebud oil		Sage oil		Basil oil		Mean	
Control	63.69 ± 0.62	A	63.69 ± 0.62	A	63.69 ± 0.62	A	63.69	A
0.5%	58.16 ± 0.31	B	58.52 ± 0.96	B	62.23 ± 0.47	B	59.63	B
1.0%	55.15 ± 0.75	C	54.78 ± 0.65	C	60.08 ± 0.55	C	56.67	C
2.0%	53.74 ± 0.24	D	54.46 ± 0.98	D	58.88 ± 0.85	D	55.69	Dd
4.0%	52.79 ± 0.24	E	53.93 ± 0.75	E	58.02 ± 0.22	E	54.91	Ee
Mean	56.71	B	57.08	B	60.58A	A		

Values followed by a same alphabetic letter are not significantly different (small letters $p \leq 0.05$); capital letters $p \leq 0.01$).

It was observed that the degree of inhibition of mycelium amounted to 17.1% for clovebud oil, 15.5% for sage oil and 9.3% for basil oil at the maximum concentration of each oil. However, the EOs in at 4% concentration volatile phase resulted in a two times smaller growth inhibition value than the EOs in 4% concentration liquid phase (Figs. 2, 3).

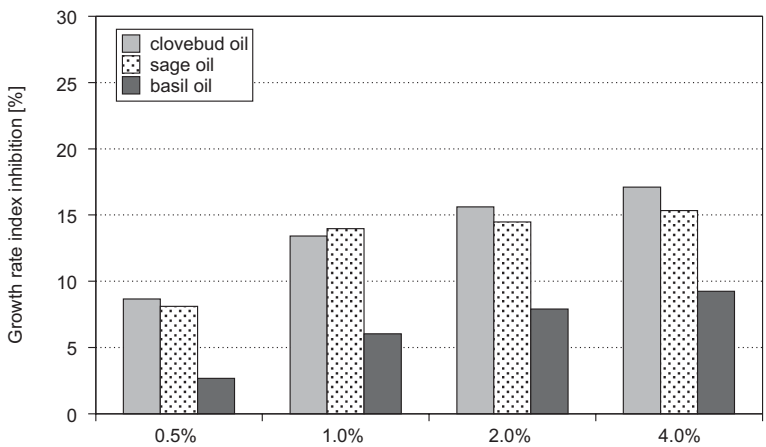

Fig. 3. Growthinhibition of *F. solani* by essential oils (vapour phase) at different concentrations

Environmental factors such as temperature, light, day length change during the vegetation period, as well as genetic factors, organ age impact on the seasonal quantitative variations in plant components [35–38].

Previous research has shown that the antifungal activity of EOs is not caused by major compounds, but is rather the result of a synergistic or antagonistic effect of different compounds present in the mixture, even if in minor percentages [36, 39, 40]. Dzamić el al [41] reported that there is a relationship between the high presence of linalyl acetate and linalool in sage oil and observed moderate antifungal activity. Some

studies suggest that the extent of inhibition of fungal growth and mycotoxin production (aflatoxin B1, G2, fumonisins, deoxynivalenol) depends on the concentration of essential oil [23, 31, 42–44].

The antimicrobial properties of sage oil have been attributed to the presence of the major oxygenated monoterpenes 1,8-cineole and camphor [36, 37, 45–48], thujone [45, 47], linalool and linalyl acetate [40, 41, 49, 50]. However Pinto et al [47] demonstrated that thujone content may not be related to the inhibition of fungal development.

Some studies found that sage oil was active in inhibiting the growth of pre- and post-harvest phytopathogenic and saprophytic fungi belonging to the genera *Fusarium*, *Aspergillus*, *Penicillium*, *Alternaria*, *Trichoderma*, *Gliocladium* [41, 43, 45, 47, 48]. Among the *Fusarium* sp. the most sensitive to sage oils were *Fusarium solani*, *F. equiseti* and *F. verticillioides* whereas *F. tricinctum*, *F. subglutinans* were the least sensitive [45]. According to Gomori et al [31] clary sage inhibited the growth of *F. culmorum* by 73.7%, *F. graminearum* by 9.26% and *A. parasiticus* by 28,05%. In another study, sage oil caused a total inhibition of *F. graminearum* growth [46]. Furthermore, Snieskiene et al [23] observed that volatile fractions of sage essential oils had the strongest fungicidal effect, after three days of incubation, on *F. sambucinum*, *F. culmorum*, *F. oxysporum* and *A. alternata* (reduction of mycelium growth amounted to more than 90%).

The high inhibition results of clove oil could be attributed to its major aromatic component, eugenol, which is known to inhibit fungal growth and fungal spore production [27, 39, 51–54]. Similarly, the main components of basil oil are eugenol, 1,8-cineole and linalool, which may exhibit antagonistic properties against certain fungi [42, 55].

Eugenol may cause morphological malformation in fungal cell, dissolve fat of fungal cell walls and therefore can interfere with the permeability of cells, destroying conidia and fungal hyphae. The inhibition levels of *F. oxysporum* by clove oil fractions containing a high content of eugenol ranged between 84.44–100% [53]. Velluti et al [51] observed that clove oil reduced *F. verticillioides*, *F. proliferatum* and *F. graminearum* colony growth by about 62%. Cosic et al [52] indicated in their results that clove oil had a stronger impact than sage oil on mycelium growth of *Fusarium* species. Sameza et al [27] showed that clove oil could significantly inhibit the mycelia growth and spore germination of *R. stolonifer* and *F. solani.* The oil caused a complete inhibition of fungal growth in all tested doses and a complete inhibition of spore germination but only at a dose greater than 31.2 ppm for *R. solani* and 250 ppm for *F. solani* [27].

These results are also in accordance with those obtained by Beg et al [56] for *A. alternata* and *F. chlamydosporum*. Their microscopic observations showed 20–40% lysis of conidia after 72 h of incubation at 5% concentration. However at higher clove oil concentration (10%), up to 20% of conidia were lysed after 24 h of incubation. Clove oil and eugenol considerably reduced the quantity of ergosterol, which is an important component of fungal cell membrane responsible for maintaining the consistency, integrity and functionality of the cells. Clove oil suppressed the growth of pathogenic fungi *Aspergillus* sp., *Fusarium* sp. and *Alternaria* sp. by a range of 41% to 65% [57].

Hussain et al [35] reported that basil essential oils and linalool possessed strong antifungal activity against *A. niger*, *F. solani* and moderate activity against *M. mucedo*, *R. solani*. It has been further observed that essential oils from winter and autumn crops demonstrated greater activity which might be attributed to be a high content of linalool and other oxygenated compounds [35]. Other studies have shown a significant impact of linalool [24] on mycelial growth of *A. niger*, *F. moniliforme,* and to a lesser extent, on *A. flavus*, *P. roquefortii* as well as an impact of eugenol [58] against *Rhizoctonia* sp., *Alternaria* sp.

The antifungal mechanisms of essential oils depend on their components and their the lipophilic nature. Therefore, volatile phenolic compounds (carvacrol, eugenol, thymol) may interfere with cell wall enzymes (enzyme inhibition), possibly through reaction with sulfhydryl groups or through interactions with proteins. They may change the cell permeability, membrane fluidity and disintegrate fungal hyphae [42, 59–62].

In this study, all of the essential oils investigated exhibited inhibitory effects on mycelial growth and the fungal spore production of *F. solani.* However, the extent of inhibition was significantly dependent upon the concentration of EOs, the type of oil, and phase type (volatile or liquid phases).

Conclusions

All three of the essential oils demonstrated antagonistic effects to a greater or lesser extent on *Fusarium solani*. Depending on the type of oil and the dose, they had a stronger effect on spore germination (even in small doses) than on mycelium growth of *F. solani*. The inhibitory effect of the essential oils increased with the increase of their concentration. In general, all amounts of the tested essential oils significantly restricted the spore germination and mycelial growth of *F. solani* with the maximum activity detected at 4% EO concentration. Additionally, it was noted that basil oil was the greatest inhibitor of spore germination (98.90%), whereas clove budoil was the greatest inhibitor of mycelial growth (29.96% in liquid phase and 17.10% in gaseous phase). The data obtained in volatilization methods established that all three of the oils in gaseous phase had fungistatic effect on *F. solani* but not to a visible degree – particularly when compared to the liquid phase data in the poisoning method. Taking into consideration both the germination of conidia and mycelial growth, the findings indicated that clove oil possesses the strongest inhibitory activity against *F. solani* isolated from white asparagus.

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WRAŻLIWOŚĆ *Fusarium solani* WYIZOLOWANEGO ZE SZPARAGA NA OLEJKI ETERYCZNE

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Abstrakt: Celem badań była ocena przeciwgrzybicznych właściwości olejku z szałwii, olejku goździkowego i olejku bazyliowego wobec *Fusarium solani* wyizolowanego z pędów szparaga (*Asparagus officinalis* L.) Ocenę właściwości antagonistycznych testowanych olejków i ich metabolitów gazowych wobec grzybni przeprowadzono metodą hodowlano-płytkową na podłożu PDA. Hodowlę prowadzono przez 9 dni w temp. 26^{o}C, dokonując pomiarów co 1–3 dni. Natomiast zarodnikowanie grzyba w obecności olejków oceniono metodą mikroskopową. Przeprowadzone badania wykazały różnice w aktywności metabolicznej testowanych olejków. W zależności od rodzaju olejku i jego dawki, stwierdzono większą aktywność wobec zarodników grzybów niż na wzrost grzybni *F. solani*. Największy wpływ na zdolność kiełkowania zarodników wykazał olejek bazyliowy, następnie kolejno olejek goździkowy i olejek szałwiowy w stężeniu 4%. Stopień zahamowania kiełkowania zarodników wyniósł odpowiednio: 98,9%, 89,9% oraz 85,4%. Natomiast zdecydowanie mniejszy wpływ wykazały na wzrost grzybni *F. solani*. Zastosowanie największej dawki olejku goździkowego ograniczyło tempo wzrostu grzyba o 29,9%, olejku szałwiowego o 14,8% a olejku bazyliowego tylko o 4,0%. Również metabolity gazowe ograniczały wzrost grzybni *F. solani*. Stopień zahamowania wzrostu wynosił odpowiednio 17,1% dla olejku goździkowego, 15,5% dla olejku szałwiowego i 9,3% dla bazyliowego. Biorąc pod uwagę analizowane czynniki, olejek goździkowy okazał się największym inhibitorem kiełkowania zarodników i wzrostu grzybni *F. solani.*

Słowa kluczowe: *Fusarium solani*, szparagi, olejki eteryczne, aktywność przeciwgrzybowa

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EFFECT OF CONVENTIONAL COOKING ON CHANGES IN THE CONTENTS OF BASIC COMPOSITION AND GLUCOSINOLATES IN KALE

WPŁYW GOTOWANIA NA ZMIANY ZAWARTOŚCI SKŁADU PODSTAWOWEGO I GLUKOZYNOLANÓW W JARMUŻU

Abstract: *Brassica* vegetables have been strongly recommended as part of human diet because of its high content of bioactive sulphur compounds, *eg* glucosinolates. The nutrient and health-promoting compounds in kale are significantly affected by traditional cooking. The study investigated changes in the levels of dry mass, ash, fat, total protein, dietary fibre as well as total and individual glucosinolates in the kale due to the traditional cooking process. As a result of cooking kale, a significant decrease was noted in the content of fat, dry matter, indole glucosinolates, and a significant growth in the content of protein, ash, dietary fibre, and aliphatic glucosinolates compared to the raw vegetable.

Keywords: kale, glucosinolates, traditional cooking, dietary fibre, basic composition

Introduction

The *Brassicaceae* family comprises about 400 genera and 4000 species of vegetables, which are commonly grown and popular everywhere in the world. They are abundant in health-promoting phytochemicals [1]. The kale (*Brassica oleracea* L. var. *acephala*), being a traditional, biannual leafy vegetable of this family, is grown worldwide. Of the *Brassica* vegetables, kale was found to have the highest antioxidant activity and large concentrations of vitamins, minerals, dietary fibre, glucosinolates, chlorophyll-associated carotenoids, flavonoids, and phenolic acids [2].

According to the epidemiological studies, there is an opposite relationship between consumption of *Brassica* vegetables and occurrence of certain cancer forms, cardio-

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vascular and degenerative diseases, immune disfunction and aged-related macular degeneration [3, 4]. Plant-derived bioactive compounds can be classified, according to their chemical structure, as antioxidants, vitamins, polyphenols, terpene derivatives, sulphur compounds, phytoestrogens, minerals, polyunsaturated fatty acids, dietary fibre, and phytic acid. The sulphur compounds are commonly found in *Brassica* or allium vegetables [5].

The glucosinolates (GLS) belong to a large group of sulfur-containing compounds occurring in all the *Brassicas* vegetables of economic importance. Usually, their structure includes: the β-D-thioglucose group, a sulfonated oxime moiety and a variable side-chain derived from methionine, tryptophan or phenylalanine, and some branched-chain amino acids. They are stored in the myrosinase-containing cells in the intact plant tissue. Upon tissue disruption, glucosinolates undergo hydrolysis by the endogenous enzyme 'myrosinase' (thioglucoside glucohydrolase EC 3 : 2 : 3 : 1) that in turn releases a range of breakdown products. Depending on the chemical structure of glucosinolates (aliphatic, aromatic, or indole glucosinolates), coexisting in vegetables factors like epithiospecifier proteins (ESP), Fe^{2+} or ascorbic acid, environmental conditions (pH value), the end products of hydrolyzed glucosinolates are different (isothiocyanates, nitriles, indoles, thiocyanates and oxazolidines) [6–10]. Furthermore, glucosinolates can also undergo thermal and chemical degradation. Some factors, like *eg*: ascorbic acid, $MgCl_2$, temperature, pH and pressure affect the activity of myrosinase. In addition, myrosinase-like activity is induced by the gastrointestinal microbiota. Ingestion of the glucosinolates-containing products in the absence of the active plant-derived myrosinase, still results in the formation and absorption of bioactive breakdown products obtained due to the gut microbiota enzymes. During digestion, such factors as the degree of cell disruption, time of gastrointestinal transit, individual genotype, meal composition, and diversity of the colonic microbiota can additionally affect glucosinolates [8, 11]. Until now, over 200 different naturally occurring glucosinolates have been identified in *Brassica* vegetables in relatively high amounts [3].

Some glucosinolates and their decomposition products have gained more widespread attention as chemopreventive agents. These are 4-methylsulphinylbutyl isothiocyanate (sulforaphane), indole-3-carbinol or 3,3'-diindolylmethane. Chemoprevention, according to its definition, is the use of natural or synthetic agents which have ability to reverse, inhibit, or prevent the development of a chronic-degenerative disease [12]. The advantageous effects of glucosinolates and their breakdown products have been thoroughly investigated. The studies revealed that glucosinolates and their breakdown products may to a certain degree regulate or adjust many essential processes like the inhibition of inflammatory processes; induction of the cytoprotective enzymes; modulation of the signaling pathways in cancer, including cellular proliferation, angiogenesis; the epithelial-mesenchymal transition; self renewal of cell in cancer stem; suppression of the diverse oncogenic signaling pathways; modulation of epigenetic alterations; and regulation of polycomb group proteins or epigenetic cofator modifiers [1, 3].

Glucosinolates along with the products of their decomposition (isothiocyanates, nitriles, thiocyanates, epithionitriles, and oxazolidines) exhibit also antioxidant, anti-inflammatory, anti-allergic, anti-fungal, anti-virus, anti-mutagenic, and anti-bacterial properties [13, 14]. As was reported by some researchers, not only breakdown products

of glucosinolates, but also intact glucosinolates could have a pro-health effect [1, 15]. The protection provided by phytochemicals occurring in the glucosinolates-containing kale is particularly important in the context of the safe and cost-effective strategy for combating several chronic diseases.

The glucosinolates content in *Brassica* vegetables prior to consumption vary markedly due to differences occurring at various stages of the food supply chain, including: cultivation; growth condition; climate; plant variety; the tissue-specific distribution in a plant parts (seeds, leaves, roots, stems); storage and packaging conditions; and culinary treatment [3, 16].

Generally, kale is not consumed immediately after harvesting. As storage and cooking affect pro-health components, heat treatment of food induces several biological, physical and chemical changes. When preparing food, cooking is the most commonly used technique in processing *Brassica* vegetables. The process has a great effect on the health-promoting bioactive compounds and elementary composition of these plants. Changes in phytochemicals due to cooking may result from two contrary phenomena: the heat-induced denaturation of enzymes which can catalyse the breakdown of nutrients and phytochemicals and an effect of matrix softening, due to which the extractability of phytochemicals increases, resulting in their higher concentration compared to the raw material. The results of previous studies concerning the effect of processing *Brassica* vegetables on glucosinolates content are sometimes inconsistent or contradictory [8, 17]. Hence, it is necessary to evaluate the availability of the phytochemicals in human diet, discovering what happens to phytochemicals before and after food processing and monitor their final concentration.

The aim of processing is therefore to enhance beneficial properties of *Brassica* vegetables by improving bioavailability of glucosinolates and other compounds as well as extending shelf life. The quality of cooked vegetables depends on quality of the raw material, parameters and methods of processing, the variety of *Brassica* vegetables, and the kind of compounds [2].

The objective of this work was also to examine to what extent the commonly used process of thermal processing of kale changes the selected parameters of its health quality such as dry matter content, total protein, fat, ash, dietary fibre, and individual and total glucosinolates, which are important and potentially health-promoting constituents of kale. In order to achieve this aim, we hypothesised that the dry matter, total protein, fat, ash, dietary fibre, as well as individual and total glucosinolates contents in the raw and cooked kale differed statistically significantly. In general, this study was undertaken to broaden knowledge on the health-promoting properties of the raw and conventionally cooked kale in terms of the above indicators.

Material and methods

Plant material

The material investigated consisted of fresh kale (*B. oleracea* L. var *acephala*) leaves and leaves after cooking to consumption consistency. The kale cultivar under investiga-

tion was *Winterbor* F_1 and was grown up at the Polan Plant and Horticultural Seed Production Centre in Krakow, Poland (Experimental Station in Igolomia). The experimental field was located in the eastern outskirts of the Krakow. The kale was grown in black soil on loess framework with neutral pH. Mineral fertilization was applied according to the fertility of soil and the nutritional requirements of the species and condition treatments were carried out during the growing season (depending on soil and weather conditions).

Vegetable samples were prepared for analyses directly after harvest. The leaves were firstly separated (5 kg green mass), then washed under running water, next tiny cut into strips 2–3 cm in width (exterior and interior parts of the plant) and mixed in order to obtain the representative average laboratory samples (a minimum of three for each analysis performed on the fresh material and the same procedure was done on material after cooking). Another part of fresh material was washed and then dried on the filter paper; shredded mechanically; frozen at –22^{o}C; and next freeze-dried in the Christ Alpha 1–4 apparatus (Christ, Germany). The material, having undergone freeze-drying, was additionally comminuted in the Knifetec 1095 Sample Mill (Tecator, Sweden) until reaching a homogenous sample with possibly the smallest particle diameter. At the same time, the other vegetable batch was cooked in the traditional way (by domestic cooking methods), in a stainless steel pot on the electric stove top. Vegetables were cooked in unsalted water and in the initial phase of hydrothermal treatment – without a lid but in accordance with the principle "from farm to fork". The proportion of water to the raw material being 5 : 1 by weight. The cooking time applied was 15 minutes. The boiled vegetables were then prepared as described for fresh vegetables.

Analytical methods

The dry matter of the prepared samples of vegetables was determined according to PN-90/A-75101/03 [18]. The determination principle comprised determining the decrease in mass upon removal of water from the product during thermal drying at the temperature of 105^{o}C, under normal pressure conditions.

In raw freshly and lyophilized kale the following analyses were also performed: protein content using Tecator Kjeltec 2200 (Tecator, Sweden); fat content, using Tecator Soxtec Avanti 2050 (Tecator, Sweden); ash content by dry mineralisation in mufl Snol 8.2/1100 (Snol, Lithuania) on oven at 525^{o}C (PN-A-79011-8:1998 [19]) and dietary fibre content with enzymatic-gravimetry method using Tecator Fibertec System E (Tecator, Sweden).

The procedure of protein determination employ mineralization of the product in concentrated sulphuric acid (IV) ("the aqueous mineralization"), followed by alkalizing the solution, distillation of ammonia released and its qualitative determination according to PN-EN ISO 8968-1:2004 [20].

Fat determination is based on the extraction of fat from the dried material with an organic solvent (petroleum ether), distilling off the solvent, drying the residue and determining the weight of the extracted "crude fat" according to PN-A-79011-4:1998 [21].

Dietary fibre content was determined according to PN-A-79011-15:1998 [22] by means of enzymatic and gravimetric methods. Lyophilized samples of kale were subjec-

ted to gelatinization with a thermally stable α-amylase, then digested by enzymes involving protease and amyloglucosidase to remove protein and starch present in the sample. Soluble dietary fibre was precipitated by adding ethanol. The sediment was then filtered off, washed in ethanol and acetone and, after drying, weighed. Half the samples was analysed for the presence of protein and the remainder incinerated. Total dietary fibre has been calculated as the weight of sediment minus the weight of protein and ash.

Determination of glucosinolates

In order to determine the content of glucosinolates, the ISO 9167-1 method with modifications described by Kusznierewicz was used [23]. For this purpose, 200 mg of each lyophilized *Brassica* sample was extracted three times with boiling methanol (2 cm^3, 70%). The known amount of glucotropaeolin (0.2 cm^3, 5 mM, AppliChem GmbH, Darmstadt, Germany*)* was added to each sample just before the first extraction as an internal standard for the HPLC analysis. The extracted glucosinolates were purified on column filled with 0.5 cm^3 of DEAE Sephadex A-25 anion-exchange resin (Sigma Chemical Co., St. Louis, MO, USA). The column was washed with 2 cm^3 imidazole formate (6 M) and twice with 1 mL Millipore water and then loaded with 6 cm^3 of each extract. Afterwards sulphatase water solution (1.67 mg/cm^3, 250 mm^3) *(Helix pomatia* type H1, Sigma Chemical Co., St. Louis, MO, USA) was introduced onto the column and the columns were incubated for 12 h at room temperature. Next day, the desulfo-glucosinolates were eluted with deionized water (2 · 0.75 cm^3) and injected (50 mm^3) into LC-DAD-ESI-MS system (Agilent Technologies, Wilmington, DE, USA) using a Grace Altima HP AQ RP-C18 column (150 · 4.6 mm, 3 mm). The mobile phase contained water (A) and acetonitrile/water (20 : 80, v/v, B). Chromatographic resolution was performed at 30°C with 1 cm^3/min flow rate and the following gradient program: linear gradient rinsing from 5% B to 100% B within 10 min and then isocratic separation with 100% B for 15 min. The chromatographic peaks were first detected by DAD (Agilent Technologies, 1200 series, Wilmington, DE, USA) at 229 nm, then the identity of individual ds-glucosinolates was confirmed by API-ESI-MS (Agilent Technologies, 6130 Quadrupole LC/MS, Wilmington, DE, USA). MS parameters were as follows: capillary voltage, 3000 V; fragmentor voltage, 120 V; drying gas temperature, 350°C; gas flow (N_2), 12 dm^3/min; nebulizer pressure, 35 psig. The instrument was operated both in positive and negative ion modes, scanning from m/z 100 to 800. The glucosinolates content of each sample was quantified by the internal standard method using glucotropaeolin – method according to ISO protocols (ISO Method 9167-1, 1992). However, in calculations of the content of individual glucosinolates, the updated UV response factors proposed by Clarke [24] were used. Glucosinolates concentrations are expressed in micromoles per gram of dry matter.

Statistical analysis

All analyses were carried out in three parallel replications and mean ± standard deviation (SD) were calculated for the values obtained (three independent pooled curly

kale samples were analysed). By the use of one-way analysis of variance (ANOVA), the significance of differences were checked between mean values of raw and cooked material. The significance of differences was estimated with the Duncan test at the critical significance level of $p \leq 0.05$. The Statistica 10.1 (StatSoft, Inc., USA) program was applied. The composition of glucosinolates was expressed as μmol/1 g dry matter.

Results

Basic composition and dietary fibre

As the dry matter content in the vegetable varies depending on the process applied, all the results presented below along with conclusions have been discussed basing on the results calculated per the dry matter unit. In consequence, only an effect of the process applied was shown.

The raw vegetable contained 17.20 g dry matter; 3.06 g proteins; 0.69 g fat; 0.51 g ash and 6.67 g dietary fibre/100 g fresh vegetable (Table 1).

Table 1

Basic composition of raw leaves of kale [g/100 g of fresh weight]

Component	Mean
Dry matter	17.20 ± 0.15
Total protein	3.06 ± 0.02
Fat	0.69 ± 0.01
Ash	0.51 ± 0.00
Total carbohydrates	13.00 ± 0.01
Dietary fiber	6.67 ± 0.00

Values are presented as mean value ± standard deviation (n = 3).

The process of cooking led to statistically significant ($p \leq 0.05$) reductions in the dry matter content and fat content, of 25.0 and 10.6%, respectively, compared to the raw vegetable (Table 2).

Table 2

Effect of cooking on basic composition in leaves of kale [g/100 g of dry matter]

Component	Raw	Cooked
Dry matter	17.20 ± 0.15^{a}	12.90 ± 0.04^{b}
Total protein	17.80 ± 0.11^{b}	20.20 ± 0.09^{a}
Fat	4.01 ± 0.03^{b}	3.59 ± 0.07^{a}
Ash	3.10 ± 0.00^{a}	3.90 ± 0.00^{b}
Total carbohydrates	75.20 ± 0.07^{b}	72.30 ± 0.05^{a}
Dietary fiber	38.80 ± 0.00^{b}	39.60 ± 0.00^{a}

Values are presented as mean value ± standard deviation (n = 3).
The values denoted with the same letters don't differ statistically significantly at $p \leq 0.05$.

Simultaneously, the same process resulted in statistically significant increases ($p \leq 0.05$) in the other components analysed like protein (13.4%), ash (25.8%) and dietary fibre (2.27%), compared to the vegetable before processing.

Total and individual glucosinolates

In the analysed kale, the following 6 aliphatic glucosinolates were identified: glucoiberin (GIB), progoitrin (PRO), sinigrin and glucoraphanin (SIN/GRA), gluconapin (GNA), glucoerucin (GER), as well as 3 indoles glucosinolates: glucobrassicin (GBS), metoxybrassicin (MGBs) and neo-glucobrassicin (neoGBS).

Total glucosinolate content in the raw kale was 2.25 μmol/g dry matter (Table 3). The content of aliphatic and indole glucosinolates in the total amount of these compounds was similar, being 49 and 51%, respectively. There was no the presence of aryl glucosinolates. The amounts of aliphatic and indole glucosinolates, expressed in absolute values, were respectively 1.10 and 1.15 μmol/g dry matter of raw material; sinigrin (SIN) and glucoraphanin (GRA) accounted for more than half of aliphatic glucosinolates (54.4%) and almost one-third of the total glucosinolates content (26.7%). Considering the absolute values, successive aliphatic glucosinolates occurring in raw kale were glucoiberin (GIB) (0.22 μmol/g dry matter) and glucoerucin (GER) (0.21 μmol/g dry matter). The proportion of aliphatic glucosinolates in total glucosinolates content was the lowest, for example, gluconapin (GNA) and progoitrin (PRO) occurred in kale in trace amounts (approx. 0.04 μmol/g dry matter).

Table 3

Content of glucosinolates in fresh and cooked kale [μmol/g of dry matter]

Glucosinolates	Kale raw	Kale cooked
Glucoiberin	0.22 ± 0.04^{a}	0.98 ± 0.04^{b}
Progoitrin	0.04 ± 0.02^{a}	0.20 ± 0.02^{b}
Sinigrin/Glucorafanin	0.60 ± 0.04^{a}	2.34 ± 0.02^{b}
Gluconapin	0.04 ± 0.00^{a}	0.10 ± 0.01^{b}
Glucoerucin	$0.21 \pm 0{,}02^{a}$	$0.17 \pm 0{,}02^{a}$
Glucobrassicin	0.53 ± 0.01^{b}	0.09 ± 0.02^{a}
Metoxyglucobrassicin	0.11 ± 0.02^{b}	0.02 ± 0.00^{a}
Neoglucobrassicin	0.50 ± 0.03^{b}	0.21 ± 0.04^{a}
Total gucosinolates	2.25 ± 0.09^{a}	4.21 ± 0.10^{b}

Values are presented as mean value ± SD (n = 3) and expressed in dry matter. Means in rows with different superscript letters in common differ significantly ($p \leq 0.05$)

Of the indole glucosinolates, the proportion of glucobrassicin (GBS) (46.5%) and neoglucobrassicin (neoGBS) (43.8%) in this group was the largest; the remainder being methoxyglucobrassicin (MGBS). In kale, glucobrassicin (GBS) content comprised 23.5% total glucosinolates amount (almost one-fourth), while neoglucobrassicin (neoGBS) 22.2%. On the other hand, after converting values to the vegetable dry matter, the

glucobrassicin (GBS) content in kale was 0.53 μmol/g, neoglucobrassicin (neoGBS) 0.50 μmol/g, and methoxyglucobrassicin (MGBS) 0.11 μmol/g.

As a result of cooking, there was a significant ($p \leq 0.05$) increase in the amount of total glucosinolates (of 87.4%) compared to the raw vegetable. In each of the analysed aliphatic glucosinolates increases were significant ($p \leq 0.05$); compared to the raw vegetables they were of 345.0% (GIB); 455.5% (PRO); 290.5% (SIN/GRA); 150.0% (GNA); and 40.0% (GER). Simultaneously, hydrothermal treatment resulted in a significant ($p \leq 0.05$) reduction in the level of indole glucosinolates: of 82.8% (GBS); 78.2% (MGBS); and 57.2% (neoGBS) compared to the raw vegetables.

Discussion

Basic composition

Dry mass

The content of dry matter in the raw kale was 17.2 g/100 g, which is similar to the results reported by other authors. According to the literature, dry mass content in raw kale fluctuates broadly from 10.4 to 21.19 g/100 g fresh vegetable [2, 25–27]. The dry matter content in the vegetable is affected by many factors, which may include variety as well as climatic conditions and agro-technical practices. This experiment revealed that during cooking dry matter content decreased by 25.0%. In the study of Florkiewicz et al [28] and Volden et al [14] cooking of fresh cauliflower and red cabbage caused significant decrease of dry matter level. A decrease in dry matter due to heat treatment in an aqueous environment may result from extraction of soluble components to water and/or absorption of the water by tissues as well as leaving some water on the surface of raw material, particularly if the surface is uneven and undulated [2]. On the other hand, in the paper of Gebczynski and Kmiecik [29] the increase of dry matter content was observed during boiling, probably because of the loss of water from the tissue and the contraction of the raw material.

Protein

The results obtained in this work are close to the values found by other authors. According to the literature data, protein content in raw kale ranges broadly from 2.4 to 9.6 g/100 g of the vegetable [27, 30, 31]. Protein in kale is regarded as the high grade protein due to large amounts of essential amino acids such as glutamic acid, aspartic acid, proline, and fewer levels of cysteine and methionine. The presence of above compounds and other exogenic aminoacids corresponds to great nutritive value of kale protein [27, 32]. As Almeida et al [33] reports, total protein content in kale is strongly affected by the conditions of cultivation (fertilization, kind and composition of soil) and variety. Deficiency of certain minerals in the soil, for example, phosphorous and potassium has an effect on the quantity and quality of protein in the vegetable [34].

This study revealed that cooking led to a 13.4% increase in protein content. Slupski et al [35] also reported that technological and culinary processing of New Zealand

spinach caused a significant increase in amino acid content in 100 g of edible portion, except for methionine and cystine in frozen products prepared for eating. On the other hand, Lisiewska et al [36] showed a 14% loss of protein during cooking Brussels sprouts, while the losses in protein content found by Czapski [37] and Florkiewicz et al [28] during cooking broccoli and cauliflower were of 15.6 and 10.5%, respectively. The increase in protein content in dry matter of the cooked kale could result from more efficient leaching of other constituents soluble in boiling water, which, in turn, increases the proportion of these constituents in 100 g dry matter.

Fat

As was reported by Ayaz et al [30], kale leaves contain mainly linoleic, α-linolenic and palmitic acids. In this work, the fat content in the examined raw kale was minimal (0.69 g per 100 g fresh weight of the vegetable) that almost fully agrees with the amounts found by Sikora and Bodziarczyk [27] and Skapski and Dabrowska [38], which were respectively 0.67 g and 0.4–1.3 g/100 g fresh vegetable. The process of cooking, investigated in this experiment, resulted in a 10.6% reduction of this component. Greater losses due to cooking, amounting to 57%, were reported by the US sources [39] and Florkiewicz et al [28] (25.3%), while Czapski [37] observed an increase in the fat content of 10.8%, when cooking broccoli.

Ash

The ash content determined in the raw kale in this work was 0.51 g/100 g vegetable fresh weight, which does not concur with the findings of other authors. Ash contents reported by other authors were within the range 1.1–2.18 g [27, 38, 40]. The process of cooking in this experiment, resulted in a 25.8% growth of this component, while Florkiewicz et al [28] reported the opposite trend. Among the green leafy vegetables, kale is an excellent source of minerals, especially accumulating high levels of calcium, phosphorus and magnesium. Calcium is easily assimilated, mainly due to the lack of oxalic acid, which limits its assimilation. Kale contains from 535 to 551 mg calcium, 117–106 mg magnesium [41], and 5.73 mg phosphorus per 1 g vegetable dry weight [30]. The most important microelements in kale are iron, zinc and manganese [30]. According Fadigas et al [41], 100 g of kale contains from 1.48 to 2.13 mg iron, 1.95–2.63 mg zinc and 1.34–2.05 mg manganese. Hence, due to these constituents this vegetable should be recommended, especially for children.

The apparent increase in ash content in dry matter of the cooked kale could result from more efficient leaching or by a potential release of cellular bound of other constituents soluble in boiling water, which increases the proportion of these constituents in 100 g dry matter.

Dietary fibre

The dietary fibre plays a significant role in the prevention of several diseases. *Brassica* vegetables are an excellent source of dietary fibre. In kale, the proportion of

non-digestible carbohydrates, *ie* dietary fibre comprising mainly water insoluble hemicelluloses and water soluble pectins responsible for the increased bacteria proliferation in the colon, is significant and ranges from 0.8 to 3.8% [31]. The content of dietary fibre in the examined raw kale was 6.67 g/100 g fresh vegetable weight, which agrees with the findings of Sikora and Bodziarczyk [27] (7.40–9.56 g/100 g). Thermal treatment of the examined vegetable, which was performed in this work, led to the small increase in dietary fibre content of 2.27%. Czapski [37] and Komolka and Gorecka [42] also observed an increase in dietary fibre content in other *Brassica* vegetables; the first in broccoli (26.9%) and the others in the white cabbage (56.7%), red cabbage (60.5%), and the Italian cabbage (38.5%). During wet heat processing, insoluble fibre can be broken into smaller fragments and then dissolved in the water.

In this study also the percentage of carbohydrates was calculated on as the difference between 100 g of fresh product and the sum of water (g), total fat (g), protein (g) and mineral compounds – ash (g). Fructose, glucose and sucrose are the major soluble sugars found in kale leaves [30]. It has been found in this work that 100 g the raw kale had 13.0 g total carbohydrates. The amounts reported by Sikora and Bodziarczyk [27] and American sources [39] were slightly lower and were respectively 10.14 g/100 g and 10.1 g/100 g. As Skapski and Dabrowska [38] demonstrated, in kale sucrose prevails over the simple sugars and the level of these constituents increases after the ground frost.

Cooking applied in this experiment caused a 3.94% decrease in the content of the aforementioned compounds. According to the USDA Nutrient Database for Standard Reference [39], the losses in carbohydrates due to cooking amounted to 35.6%; however, these noted by Czapski [37] in the cooked broccoli were much lower (10.8%).

Total and individual glucosinolates

The literature data on the total glucosinolates contents generally were close to the results obtained in this work [10, 43]. On the other hand, the value reported by Korus et al [16] much more exceeded the value obtained in the present work. According to the authors, usually there are two processes responsible for the reduction in the levels of glucosinolates: glucosinolates breakdown by myrosinase and thermal treatment of vegetables. During the first one, the enzyme initiates the process of hydrolysis that leads to an impairment of plant tissue and leakage of cell fluid [44]. The temperatures up to 60^{o}C enhance the activity of myrosinase, while higher temperatures lead to inactivation of the enzyme by denaturing the enzyme both in the cabbage and after leaking into the cooking water [45]. With regard to the second process, substantial glucosinolates losses due to this process were reported by Ciska and Kozlowska [46] and Volden et al [14]. Glucosinolates, as water-soluble, are leached out into the cooking water. Moreover, their heat resistance is various [47]. Most authors stated a decline in the amount of glucosinolates due to blanching and cooking in the selected *Brassica* vegetables, for example, in Brussels sprouts, white and green cauliflower, broccoli, and curly kale [48]; in kale [2]; in broccoli [49]; in cauliflower [14]; in broccoli [50]; in Brussels sprouts [51] or in cabbages [46, 52]. According to Kapusta-Duch et al [53] the process of

cooking *Brassica* vegetables caused a generally significant ($p \leq 0.05$) decrease in the total glucosinolates content compared with raw vegetables: 6.6% in the rutabaga; 68.9% in green cauliflower; and 69.2% in purple cauliflower. On the other hand, the authors found the increase in the levels of certain individual glucosinolates in rutabaga. As for the effects of different cooking techniques (boiling, steaming etc.) on glucosinolates content, these reported in the literature are not so clear-cut. There are however reports in the available literature, which indicate an increase in their amount resulting from cooking, which partially agrees with the results obtained in the present work. D'Antuono et al [54] reported that the total glucosinolates content was two-fold higher in boiled cauliflower in comparison to raw. The authors reported that this was due to higher extractability of these compounds in the cooked than in the raw plant tissues. According to Vallejo et al [55], inactivation of myrosinase and a breakdown of plant tissue upon heat provide partial explanation for their well-preserving or increase. Gliszczynska-Swigło et al [49] claimed that part of such molecules bound to the cell walls is released only after a breakdown of cell structures.

Ciska et al [51] found that 5-minute cooking Brussels sprouts led to a significant increase in the majority of aliphatic glucosinolates and one indole glucosinolates compared to the raw vegetable. Such trend was observed for glucoiberin, progoitrin, sinigrin, gluconapin, glucoraphanin, and glucobrassicin. However, these increases were not as high as in this work. After 15-minute cooking Brussels sprouts, an increase was significant only in case of glucoiberin and sinigrin. Extended cooking time (30 minutes) caused losses in the number of all individual glucosinolates. Ciska et al [51], Oerlemans et al [56] and Rosa and Heaney [57] noted that losses due to cooking were greatest in the case of indole glucosinolates, which is consistent with our findings. According to Vallejo et al [55], cooked broccoli contained significantly more glucoiberin, glucoalyssin, and progoitrin. Verkerk and Dekker (2004) and Oerlemans et al [56] observed an increase in total glucosinolates in steamed and conventional boiled red cabbage of 60% and 35%, respectively, compared to the raw vegetable, while the increase of total glucosinolates level determined by Roque-Sala [59] in Brussels sprouts was of 86% when compared to those before steaming (steaming time – approx. 5 minutes). Ciska et al [51] found that sinigrin and glucoraphanin showed the highest thermal stability during cooking. On the other hand, Sosinska and Obiedzinski [60] noticed that there are various factors affecting these differences, such as species, variety, storage conditions, cooking time, and the degree of sample fragmentation. As was also reported by Miglio et al [61], broccoli cooked by steaming had higher glucosinolates level compared to the fresh ones but the level was also higher when compared to those cooked by a conventional method. Numerous authors report that myrosinase is inactivated, for example, after: 5 minutes [62]; 2–5 minutes, depending on the applied treatment techniques [63]; or 4.8 minutes [58]. Researchers explain the phenomenon of an increase in these compounds by extractiveness of glucosinolates from the vegetable material after heating that in turn gives higher amounts of the glucosinolates accessible to extraction and determination [60]. In order to reach maximum activity, myrosinase, like other enzymes, must have appropriate conditions (pH, temperature, presence of co-factors such as ions of iron and vitamin C or the presence of other proteins) [64].

The differences observed in glucosinolates thermal degradation may be caused by the specific plant components negatively influencing glucosinolates stability. The higher glucosinolates content in plant tissue, the higher is their sensitivity to heat degradation. The process of cooking causes that some components, like glucosinolates, migrate into water and become diluted. Probably, there may be another mechanism affecting the variations in the glucosinolates thermal stability in different environments.

The results obtained indicate that further studies are needed to explain changes in glucosinolates contents during convectional cooking not only kale, but other *Brassica* vegetables. As the results presented by other authors and those obtained in this work are not clear-cut, the research problem seems to be interesting. Therefore, the aim should be to optimize hydrothermal processes in order to make the best possible use of pro-health substances occurring in *Brassica* vegetables in human nutrition.

Conclusions

The current study clearly shows that nutrient and health-promoting compounds in kale are significantly affected by traditional cooking. Raw kale (var. *Winterbor* F_1) was characterized by the rich primary composition and the significant content of glucosinolates.

The commonly used thermal processing method resulted in a statistically significant ($p \leq 0.05$) increase in the level of total protein, ash, dietary fibre, total and aliphatic glucosinolates and a substantial reduction in the content of fat, carbohydrates, total dry matter, indole glucosinolates compared to the raw vegetable.

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WPŁYW GOTOWANIA NA ZMIANY ZAWARTOŚCI SKŁADU PODSTAWOWEGO I GLUKOZYNOLANÓW W JARMUŻU

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Abstrakt: Warzywa kapustne są szczególnie zalecane w diecie ze względu na wysoką zawartość składników biologicznie czynnych zawierających siarkę, tj. glukozynolanów. Celem pracy było sprawdzenie jak zmieniają się wybrane parametry jakości zdrowotnej jarmużu (tj. zawartość: białka, tłuszczu, popiołu, węglowodanów, błonnika pokarmowego, suchej masy i glukozynolanów) pod wpływem tradycyjnego gotowania w wodzie. W wyniku omawianego procesu zaobserwowano istotne statystycznie obniżenie zawartości suchej masy, tłuszczu oraz glukozynolanów indolowych, a także istotny statystycznie wzrost zawartości białka, popiołu, błonnika pokarmowego oraz glukozynolanów alifatycznych, w stosunku do surowego warzywa.

Słowa kluczowe: jarmuż, glukozynolany, proces gotowania, błonnik pokarmowy, skład podstawowy

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WYKAZ ŁACIŃSKICH, POLSKICH I ANGIELSKICH NAZW MIKROORGANIZMÓW, ROŚLIN I ZWIERZĄT I ICH CZĘŚCI ANATOMICZNYCH

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INDEX OF ACRONYMS

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LKT – lotne kwasy tłuszczowe (4) 421, *31*
LNAPL – lekkie ciecze organiczne niemieszające się z wodą (3) 287, *21*
OWO – ogólny węgiel organiczny (4) 421, *31*
PCA – analiza składowych głównych (2) 127, *9*
PE-LD – polietylen o małej gęstości (1) 89, *7*; (3) 357, *27*
PET/met/PE – metalizowany politereftalan etylenu (1) 89, *7*; (3) 357, *27*
SRFs – stałe paliwa z odpadów (3) 313, *23*

Varia

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ECOpole '16 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 25th annual Central European Conference ECOpole '16, which will be held in 5–8.10.2016 (Wednesday–Saturday) in Hotel Antalowka in Zakopane, PL.

The Conference Programme includes oral presentations and posters and will be divided into four sections:

- SI Chemical Pollution of Natural Environment and Its Monitoring
- SII Environment Friendly Production and Use of Energy
- SIII Forum of Young Scientists and Environmental Education in Chemistry
- SIV Impact of Environment Pollution on Food and Human Health

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format),
- extended Abstracts (6–8 pages) in the semi-annual journal *Proceedings of ECOpole*,
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15th July 2016** and for the Extended Abstracts: **1st October 2016**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2016**) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole '16 website).

After the ECOpole ’16 Conference **it will be possible to publish electronic version of presented contributions** (oral presentations as well as posters) on this site.

Further information is available from:
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ZAPRASZAMY DO UDZIAŁU
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SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM
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