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Andrzej DŁUGOŃSKI[1]* and Marek SZUMAŃSKI[1]

USE OF RECREATIONAL PARK BIO-WASTE AS LOCALLY AVAILABLE ENERGY RESOURCE

BIOODPADY PARKÓW WYPOCZYNKOWYCH JAKO MIEJSCOWY SUROWIEC DO WYTWARZANIA ENERGII

Abstract: Biomass is the oldest and third in terms of volume renewable energy source. Biomass produced by recreational parks is organic matter (fresh of dry) produced by plants as a consequence of their normal growth. Plant waste (bio-waste) produced mainly due to leaf abscission in autumn and during maintenance works are generally transported outside park area. This results in a loss of potential profit for the manager/owner of the site. Bio-waste may be stored in composting plants or incinerated in on-site incineration plants producing energy for the park (and its environs) and thus contributing to energetic self-sufficiency of the park. The aim of this article is to estimate biomass volume available in selected Lodz city parks for use in energy production.

Keywords: Park bio-waste, recreational park, Lodz city

Introduction

Improper and uncontrolled collection as well as incineration of waste contributes to global greenhouse effect. Poland by singing the Kyoto Treaty [1] agreed to decrease greenhouse gas emissions [2]. As a consequence state policy is evolving towards gradual increase of biomass share among resources used for production of energy. At present nearly 92% of renewable energy produced in Poland derives from biomass (forestry 85.5% and agriculture 6.3%) [3]. Use of biomass as a fuel for energy production is a complex issue which requires an analysis of resources available in a given area. Currently, numerous large plantations of energy crops are set up (*eg* willow, miscanthus, ...), usually at a certain distance from urbanised areas. Such crops are characterised by rapid biomass growth in comparison to traditional crops. Crops such as these are used at an industrial scale where land conditions allow [4–9]. In cities park bio-waste may constitute an alternative source of energetic materials. Bio-waste

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such as shed leaves are a serious problem in cities. Such leaves are most often removed to city dumps, stored and sometimes composted. Removal of bio-waste from green areas in cities is associated with transportation costs (in this case: cost of service, fuel, amortization, ...). Since bio-waste produced by city green areas requires regular disposal, alternative means of its utilization should be considered [10, 11]. Parks located in city downtown zone can be thought of as reservoirs of resources which can be converted to biofuel or energy, as shown in Fig. 1. Selective waste collection (such as waste paper, glass, plastics and other) practiced in cities can be complemented with collection of bio-waste, *eg* leaves collected during autumn park maintenance. It thus seems reasonable to collect energy resources directly from urban parks.

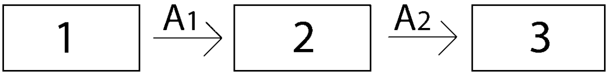

Fig. 1. An outline of energy production using bio-waste (1 – bio-waste; 2 – biofuel; 3 – electric and thermal energy; A1 – processing; A2 – converting)

Subject, goal and scope

The topic of this article is bio-waste produced in recreational parks.

The goal of this article is identification of bio-waste in recreational parks.

This article covers quantity, weight and calorific value of bio-waste from recreational parks.

Selected terminology

Park biomass – organic matter (either fresh of dry) produced by park plants as a consequence of their normal growth.

Park bio-waste – plant waste produced during vegetative period (especially leaf abscission in autumn, mowed grass as well as organic waste left behind by visitors), which are subject to natural decay.

Recreational park – a functional unit of green spaces in city serving a recreational purpose which is covered mainly in plants.

Bio-waste calorific value – 1. thermal energy produced by incineration of biofuel produced from park bio-waste (expressed most frequently as $\mathrm{MJ \cdot kg^{-1}}$ or $\mathrm{kJ \cdot g^{-1}}$); 2. calorific value of incinerated tree leaves (own definition based on: Dziewanowska and Dobek [10]).

Bio-waste incineration – one of three methods of of bio-waste management (aside from dumping and composting), involving acquisition of electric or/and thermal energy.

Research site

This article covers data collected while researching all downtown Lodz recreational parks. This area was selected due to the fact that bio-waste from those parks is transported outside of the city. The research site is shown in Fig. 2.

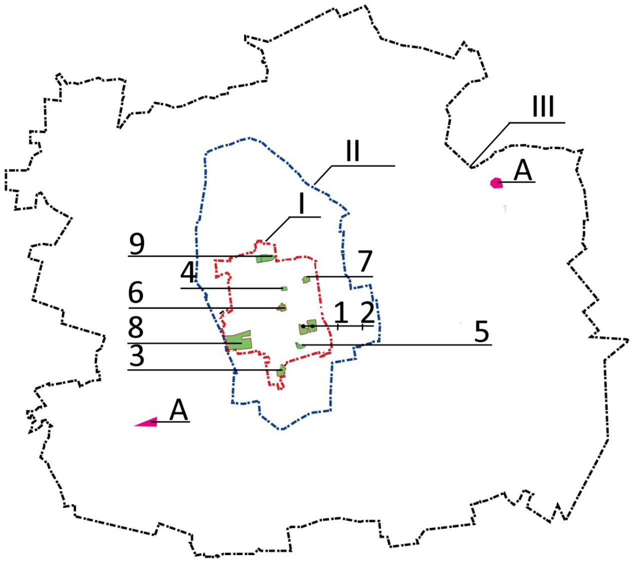

Fig. 2. Research site – recreational parks located in downtown Lodz (1–9 downtown Lodz parks' ordinal numbers, A – potential disposal destination for downtown Lodz recreational parks' bio-waste, I – boundary of downtown zone, II – boundary of residential zone, III – boundary of suburban zone / Lodz city limits

Research methods

Materials

This article is based on the following materials:

– own research and analyses conducted in downtown Lodz recreational parks (in the period between 2012–2014),

– domain literature (books and articles) on: bio-waste management, using biomass in production processes, calculating calorific value of tree leaves in green areas,

– selected legal acts.

Methods

Method used for evaluation of recreational park bio-waste volume and calorific value of deciduous trees' leaves shed in autumn is based on research, data and estimations acc. to: Dziewanowska and Dobek [10].

Arguments for use of recreational park bio-waste (current state of research)

Literature on use of biomass/ bio-waste [4–9] is mainly focused on agricultural (cultivation of energy crops) and industrial aspects rather than on studying selected problems of bio-waste management – in this case estimation of calorific value of incinerated leaves collected in city green areas [10, 11].

Waste (including bio-waste) management defined in accordance with act on waste of 2012 [12] as „collection, transportation, processing of waste including supervision of those operations...” may also include estimation/ determination of its characteristics / properties (in this case volume and calorific value of bio-waste) as well as establishing means of its disposal (such as incineration). Research by Dziewanowska and Dobek [10], Arodudu et al. [13], Lin and Cao [14] and other authors confirm this view.

It should be noted that park bio-waste (*eg* leaf abscission) is a resource which may be used to produce biofuel [11]. However, leaves may be used as fuel only after drying rather than when fresh.

What does collection and processing of waste depend on?

During routine park maintenance of urban green areas there comes a time (in Poland this is autumn) when bio-waste, including shed leaves, is collected and transported outside of the park. It may be stored and then dried. There are however other means of disposing of such bio-waste. Leaves do not need to be transported to a drying room, but may be left to dry on their own within the park (*eg* in a spot designated for storing such bio-waste). They can then be collected after reaching sufficiently low humidity.

In order to achieve the highest calorific value, bio-wastes need to be dried and comminuted after collecting. Based on domain literature leaves may be processed after they reach humidity of 15–20% in a drying process lasting 1 to 2 weeks at 293 K [10]. It’s worth noting that those values are mirrored for example in forest cover humidity parameters. Forest cover with 0–20% humidity is classified as 3rd fire danger class and as such is most susceptible to ignition.

According to research conducted by Dziewanowska and Dobek [10] dried leaves nearly double their calorific value and lose half their weight compared to when fresh. They may be used directly as fuel (after comminuting) or converted to briquette. Comminuting leaves seems more beneficial than converting them into briquette, since comminuted leaves have higher calorific value compared to briquette. For example of 1 gram of comminuted dry leaves has a mean calorific value of 15.4 kJ, while the same amount of briquette less than – 14.0 kJ. Additionally comminution process seems to be more cost effective.

Means of evaluation of park biomass volume and its calorific value

According to field research a single 100-year old common beech tree (*Fagus sylvatica*) has 800,000 leaves with a total surface area of 1600 m^2 [15]. Based on in-house studies of downtown Lodz recreational parks one leaf of common beech (*Fagus sylvatica*) with typical dimensions of 0.03 x 0.04 m weights 1 g (0.000001 Mg) fresh biomass on an average. This allows to estimate the biomass of shed leaves of a 100 year old tree at 800 kg (0.8 Mg), and the calculated mass may be considered standard. These two values along with number of trees in a park allow calculating an approximate/ estimated bio-waste volume (of fresh matter) for a given park.

Volume of bio-waste for autumn leaf abscission can be calculated using the following formula:

Number of deciduous trees in a park × standard biomass volume for one deciduous tree (fresh matter) = bio-waste volume after autumn leaf abscission.

Example: if in a given park there are 100 deciduous trees aged approx. 100 years, the biomass produced during autumn leaf abscission can be estimated at 80,000 kg (80 Mg).

When determining the calorific value of shed leaves it is necessary to consider that dry matter weight will be half that of fresh matter before drying [10]. Results of research by Dziewanowska and Dobek [10] show that leaves collected for measurement, dried and then comminuted has a calorific value of 15 $\mathrm{MJ} \cdot \mathrm{g}^{-1}$. Based on this it can be calculated that 1 Mg of dry matter of bio-waste (leaves) has an approximate calorific value of 15 GJ. Calculation should include biomass volume produced by one tree and number of trees in a park.

Total calorific value of bio-waste produced by trees growing in a park during autumn leaf abscission can be calculated using this formula:

Number of deciduous trees in a park · volume of biomass produced by one tree (fresh matter) expressed in Mg · 1/2 · 15 $\mathrm{GJ} \cdot \mathrm{Mg}^{-1}$ = calorific value of bio-waste produced during autumn leaf abscission of park deciduous trees expressed in GJ.

Example: given there are 100 deciduous trees in a park, each producing 0.8 Mg of leaves (fresh matter), or 0.4 Mg of dry biomass (considering that drying halves the initial leaf weight) and assuming that 1 Mg of dry matter has an approximate calorific value of 15 GJ, then total dry leaves calorific value may be estimated at 600 GJ.

Is incineration of leaves collected from urban parks practiced?

Practice of incineration of green area bio-waste is currently at a pilot stage, nevertheless it seems to gain in popularity in Poland but also abroad. Polish examples include green area bio-waste management system introduced in Otwock, where leaves are collected and transported to a warehouse, dried and finally incinerated in a bio-waste incineration plant. Abroad initiatives include a still unfinished park bio-waste management project with the use of an on-site bio-waste incineration plant in a park in Uppsala in Sweden. The project envisages converting incinerated bio-waste to electric power for use in the park as well as neighbouring residential estates [16].

Results and discussion

Studied literature allows to treat recreational park bio-waste as a locally available resource for production of energy. Available volume of this resource was estimated for downtown Lodz recreational parks. Calorific value for the resource was also calculated.

Resources available in downtown Lodz parks are presented in the Table 1.

The method described above was used to evaluate the volume of bio-mass produced in nine downtown Lodz recreational parks during autumn leaf abscission. Out of the nine downtown zone parks the greatest biomass volume can be obtained from Poniatowski Park. This park produces 3,299.2 Mg of bio-waste leaves (fresh matter). Moniuszko Park produces the least leaves by weight. This park produces 199.2 Mg of bio-waste leaves (fresh matter) – which is 16 times less than site with the largest area.

Table 1

Bio-waste volume in downtown Lodz recreational parks

No. (See Fig. 1)	Park proper name	Park area $[m^2 \cdot 10^4]$	Number of trees in park [pc]	Park biomass volume [Mg]	Park bio-waste ratio $[Mg/m^2 \cdot 10^4]$
1	Zrodliska I Park	10.6	965	772.0	72.83
2	ZrodliskaII Park	6.6	579	463.2	70.18
3	Reymont Park	6.3	562	449.6	71.37
4	Moniuszko Park	2.3	249	199.2	86.61
5	Kilinski Park	2.9	349	279.2	96.28
6	Sienkiewicz Park	4.6	464	371.2	80.70
7	Staszic Park	3.9	504	403.2	103.38
8	Poniatowski Park	41.7	4,124	3,299.2	79.12
9	Staromiejski Park	17.0	940	752.0	44.24
TOTAL		95.9	8,736	6,988.8	78.30*

* Mean average bio-waste ratio in downtown Lodz recreational parks $[Mg/m^2 \cdot 10^4]$.

By summing up bio-waste volume produced by downtown Lodz parks it can be estimated that all downtown zone parks may produce 6,988.8 Mg of leaves during autumn abscission (fresh matter). It should be noted that this biomass is currently being removed from those sites.

It can be observed that biomass volume in a given site is directly related to the number of deciduous trees and park surface area. As noted by Dziewanowska and Dobek [10] and Herezniak [15] the older the tree the more leaves it produces. However, calorific value of leaves of various tree species may differ significantly [11,14], and this requires further studies.

Estimations for nine downtown zone parks show that Staszic Park has the highest bio-waste ratio. Bio-waste ratio of this park is 103.3 $Mg/m^2 \cdot 10^4$. The lowest bio-waste ratio was found for Staromiejski Park. This ratio was equal to 70.18 $Mg/m^2 \cdot 10^4$, which is approximately 2.3 times less than on site with the highest ratio. On an average 1 hectare produces approximately 78.30 Mg of biomass.

Summing up, biomass ratio for individual downtown zone parks is not proportional to their area. Parks with small area but a large number of trees have higher bio-waste ratio.

Potential calorific value of biomass collected from recreational parks is given in table below (Table 2).

Calorific value of leaves shed during autumn leaf abscission in nine downtown Lodz parks was estimated using the method described above. Out of the nine downtown parks the biomass from Poniatowski Park has the highest calorific value. Calorific value of biomass for this park was calculated at 24,744 GJ. Biomass which can be collected in the Moniuszko Park has lowest calorific value. The calorific value of the biomass from this park was calculated at 1,494 GJ – which is over 16 times less than for the largest park. Summing up calorific value of biomass from each of the downtown Lodz parks, it

Table 2

Potential calorific value of biomass collected from downtown Lodz recreational parks

No. (See Fig. 1)	Park proper name	Park area [$m^2 \cdot 10^4$]	Number of trees in park [pc]	Park biomass volume [Mg]	Park biomass calorific value [GJ]	Biomass calorific value ratio [$GJ/m^2 \cdot 10^4$]
1	Zrodliska I Park	10.6	965	772.0	5,790	546
2	Zrodliska II Park	6.6	579	463.2	3,474	526
3	Reymont Park	6.3	562	449.6	3,372	535
4	Moniuszko Park	2.3	249	199.2	1,494	650
5	Kilinski Park	2.9	349	279.2	2,094	722
6	Sienkiewicz Park	4.6	464	371.2	2,784	605
7	Staszic Park	3.9	504	403.2	3,024	775
8	Poniatowski Park	41.7	4,124	3299.2	24,744	593
9	Staromiejski Park	17.0	940	752.0	5,640	332
TOTAL		95.9	8,736	6988.8	52,416	587*

* Mean average calorific value ratio of biomass collected in downtown Lodz recreational parks [$GJ/m^2 \cdot 10^4$].

can be estimated that the total energy which can be produced from leaves shed in autumn in downtown zone parks equals 52,416 GJ. It should be noted that this energy may be used outside of these parks.

Calculations done for nine downtown zone parks show that Staszic Park has the highest calorific value ratio. Biomass calorific value ratio of this park equals 775 $GJ/m^2 \cdot 10^4$. Staromiejski Park proved to have the lowest biomass calorific value ratio. It was calculated at 332 $GJ/m^2 \cdot 10^4$, which is less than half compared to the site with the highest biomass calorific value ratio. On an average, approximately 587 GJ of energy can be produced from 1 ha of park.

Summing up, biomass calorific ratio for individual downtown zone parks is not directly proportional to their area. The smaller the park area with greater number of trees, and the greater volume of biomass, the higher biomass calorific value ratio.

Analysis of literature and calculations confirm the need for management of recreational park bio-waste.

The results as well as literature provide data suggest that parks may become a source of fuel, provided that during autumn maintenance works leaves are dried to proper humidity and incinerated in specified conditions.

Incineration process should be subject to constant improvement and have smallest possible impact on the park and its visitors. This should be a topic of separate studies with a goal of minimising or eliminating environmental impact of an incineration plant. Research so far indicates that biofuel which can be produced from park bio-waste may be converted to electric or thermal energy or both.

The supply of resource for production of biofuel in downtown Lodz seems to be guaranteed. Parks produce bio-waste yearly. Collecting this material does not require separate plantations or cultivation (tilling, fertilization, regular watering, etc.). Use of bio-waste produced by parks plants helps to realize the full potential of urban parks, by complementing ecological and recreational functionality of parks with an economical function. Done calculations prove that green areas in cities can provide raw material for producing energy on site.

It should be noted that the raw material produced by the recreational parks is first and foremost beneficial to park's direct environs, providing health benefits for denizens, but is also a production site allowing yearly collection of shed leaves and using them for production of biofuels and energy for the environs.

The strategy of using biomass to produce biofuel should cover a few parks and rely on transporting collected bio-waste to an incineration plant located in the vicinity or in the largest of the parks. According to authors the minimum park area where setting up an incineration plant would be feasible is 40 ha. This requirement is met by Poniatowski Park in Lodz.

The key issue is cost-effectiveness of bio-waste incineration. This requires further research and calculations. Research in this field should be correlated with refinement of ecosystem services discussed by Bolund and Hunhammer [17], Constanza et al. [18] and Fisher et al. [19].

Conclusions

1. Parks can be treated as production site of energetic materials within cities. In this certain dualism in park functionality can be seen – on one hand they should service daily and weekly recreational traffic, and on the other hand – produce raw materials for production of biofuel.
2. Studies prove that parks do provide raw materials for production of energy in the form of tree leaves collected during autumn maintenance jobs.
3. Results show that the nine downtown Lodz parks produce approximately 6,988.8 Mg of fresh biomass (leaves alone) a year which when processed can provide energy equal to approximately 52,416 GJ enough to heat approx. 52,416 m^2 of a flat = one thousand 3-room flats for a year.
4. One hectar of park grounds produces approximately 78.3 Mg of bio-waste with the calorific value of 587 GJ, which can later be converted to electricity or thermal energy allowing to heat approx. 587 m^2 of a flat = ten 3-room flats for a year.
5. The idea of collecting bio-waste from recreational parks and using them to produce energy should become an incentive to broaden the list of ecosystem services provided by recreational parks.

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BIOODPADY PARKÓW WYPOCZYNKOWYCH JAKO MIEJSCOWY SUROWIEC DO WYTWARZANIA ENERGII

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Abstrakt: Biomasa to najstarsze i trzecie co do wielkości na świecie naturalne odnawialne źródło energii. Biomasę parków wypoczynkowych stanowi substancja organiczna (w postaci świeżej lub suchej) powstająca podczas naturalnego rozwoju roślin na obszarze parku. Pozostałości roślinne (bioodpady) nagromadzone głównie podczas jesiennego opadu liści i prowadzonych zabiegów pielęgnacyjnych w parku są przeważnie wywożone poza jego teren. Taka sytuacja wiąże się utratą potencjalnych dóbr dla zarządcy/właściciela terenu. Bioodpady mogą być magazynowane w kompostownikach lub spalane w spalarniach na miejscu, wytwarzając energię dla parku (jak i otoczenia) i przyczyniając się w ten sposób do samowystarczalności parku pod względem energetycznym. Artykuł zawiera szacunkowe obliczenia dotyczące możliwości pozyskania biomasy na cele energetyczne na przykładzie wybranych parków Łodzi.

Słowa kluczowe: bioodpady, spalarnie bioodpadów, wytwarzanie energii, park wypoczynkowy

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OPTIMIZATION OF CARBON DIOXIDE CONCENTRATION IN THE DIDACTIC ROOMS BY THE REGULATION OF VENTILATION

OPTYMALIZACJA STĘŻENIA DITLENKU WĘGLA W SALACH DYDAKTYCZNYCH POPRZEZ REGULACJĘ WENTYLACJI

Abstract: Poor ventilation of didactic rooms can interfere with students' ability to concentrate and even cause them to suffer headaches. This is a significant issue as the ventilation systems of most lecture buildings in Poland do not provide proper air exchange. This paper presents findings of research on air parameters research in the didactic rooms of various sizes. Rooms for classes should ensure climatic comfort i.e. proper humidity and air temperature, physical and biological air quality, and low concentration of carbon dioxide. The research suggested that natural ventilation should not be used, and further research was done after the upgrading of ventilation systems and installation of exhaust fans. The coefficients of carbon dioxide emissions by one student depend on the number of people and size of the room were calculated. Designated coefficients will be used in the algorithm for determining the parameters of the fans in the ventilation system of the classrooms and lecture halls.

Keywords: carbon dioxide concentration, didactic rooms, optimization, regulation, ventilation

Introduction

Educational buildings are a specific kind of public utility facilities. What is characteristic of them is the fact that large numbers of people are present in individual rooms at the same time. A situation of this kind makes it particularly important to ensure that the people who study can do so in proper conditions while staying in this type of rooms [1]. Each person teaching classes to large groups of students can notice that after a few hours of lectures the level of concentration of participants significantly drops. However, this is not brought about by the fact of being bored by the class, but mainly by worse air quality in the rooms where these classes are held [2]. The issue of internal conditions quality in classrooms in school buildings has been raised in multiple

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scientific studies, yet they concerned the relation between air quality, energy efficiency and costs of heating these buildings only to a slight degree [3].

The quality of internal conditions in educational buildings means, first of all, suitable interior comfort in the rooms where classes are held for large groups of students [4, 5]. In Poland, the conditions concerning interior comfort in educational buildings have been specified by the requirements of the PN-EN 13779, 2008 Standard: Ventilation for non-residential buildings – Performance requirements for ventilation and room-conditioning systems [6]. Pursuant to the above mentioned standard, interior comfort is influenced mainly by the following:

- air temperature,
- air humidity,
- physical and biological quality of air,
- CO_2 concentration [6].

Until the present moment, most administrators of educational facilities (at the level of primary, secondary and higher education) have only paid attention to the temperature inside the classrooms being compliant with the standards, and they have not been aware of the significance of the remaining parameters ensuring proper interior comfort [7]. While analyzing operating costs of classrooms, the owners use calculations made by numerous experts showing that heating costs constitute about 70% of costs connected with maintaining public utility facilities, including buildings of higher education centers. Taking into consideration the fact that in Poland about 60% of residential buildings and public utility facilities are heated with the use of centralized sources, it is difficult to optimize heating costs by changing the source of heat or fuel used. Therefore a significant majority of thermal upgrading work, aiming at the reduction of operating costs of educational buildings, comes down solely to improving insulation properties of building envelope, that is exchanging the existing windows for energy efficient ones and extending the layer of insulation of external walls [8]. Increasing the airtightness of rooms makes the operation of ventilation system much worse, it reduces heat losses through ventilation and reduces heating costs, however, it causes far too low air exchange and brings about significant worsening of air quality in classrooms as a result [9, 10]. The parameters of building ventilation should be selected in such a manner that heating cost reduction is not achieved as a result of worsening room air quality.

While drawing up the algorithm for the optimization of ventilation systems in educational facilities, what was assumed as a basic optimization criterion was maintaining in rooms where large groups of people spend time such air parameters that comply with the requirements pursuant to the PN-EN 13779, 2008 Standard [6]. This shall be implemented on the basis of the analysis of three basic air parameters inside rooms, that is:

1. Concentration of carbon dioxide, which can be easily measured although as an odourless substance it is not perceptible by the people being present inside the room. In the course of research carried out in classrooms, the concentration given in 1858 by a German physiologist Pettenkofer amounting to 1000 ppm [11] was assumed as the limit value of concentration in rooms where people spend time. This value is, at the same time, recommended by the European division of World Health Organization (WHO) [12].

2. Air temperature is the second air parameter being analysed. Maintaining temperature complaint with the Standard in a winter season is connected with heating rooms. However, taking into consideration the fact that over 40% of heat lost in buildings is discharged to the atmosphere through the ventilation system along with the used air, this air discharged from buildings together with the used air was assumed as an important optimization criterion of working parameters of ventilation systems.

3. Air humidity inside rooms is the third parameter to be taken into consideration while optimizing work parameters of ventilation systems. Excessive humidity holding inside rooms for a prolonged time can lead to mildew appearing on the inside wall surfaces and this can possibly be a result of poor thermal insulation or its entire lack, as well as improper ventilation and insufficient heating, which in practice denotes improper operation and maintenance of the facility [13].

The analysed parameters might be differentiated depending on the activity level of students who spend time in given classrooms, as well as on possible disruptive factors. One should also remember that air temperature and humidity that guarantee thermal comfort inside rooms where people spend time, assume different recommended values during and outside the heating season [14]. In the summer, the recommended values amount to: inside temperature 20–22^{o}C, relative air humidity 30–50%, whereas in the winter they should be: inside temperature 24–26^{o}C, relative air humidity 45–60%.

On the basis of the above assumptions, research was carried out aiming at the determination of the optimum ventilation parameters of classrooms for the climate zone in which Poland is located.

Materials and methods

In Poland, most buildings in which classes are held for students are equipped with natural ventilation systems. Therefore, while preparing the studies of ventilation systems of classrooms, two facilities were selected, that is classrooms of different sizes, however both located in a building equipped with gravity ventilation systems. The building in which these two classrooms are located is an old educational facility where no thermal upgrading work has been done and where old windows have not been exchanged for new ones. Fresh air enters the rooms through leakages in window and door framing.

A lecture hall (shown in Fig. 1) with the area of 51.5 m^2, in which there are two ventilation ducts VD1 and VD2, is the first facility.

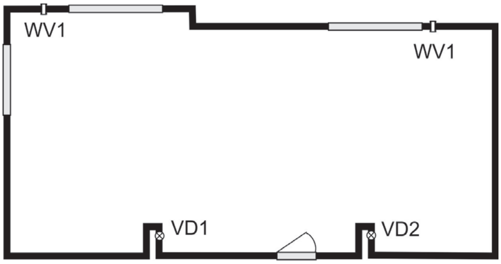

Fig. 1. Didactic room 1 with the area of 51.5 m^2

A seminar room (shown in Fig. 2) with the area of 29 m^2 and a single ventilation duct VD1, is the second facility.

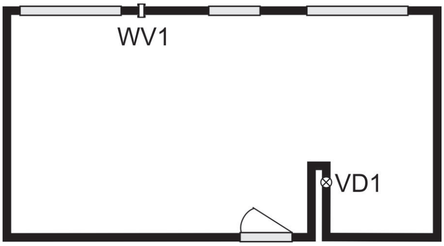

Fig. 2. Didactic room 2 with the area of 29 m^2

Measurements of air parameters inside the test facilities were taken during classes with different numbers of students and various activities. In the primary series of tests, there was only natural ventilation working in the rooms. The following were recorded in the course of research: carbon dioxide concentration, air temperature and humidity inside the rooms, air temperature outside the building, as well as the speed of air flow in the ventilation ducts. All tests of the interior air quality were done at the head level of people inside the room. The measurements were taken during the entire day with air parameters being recorded every 15 minutes, also during break times between classes. The measurements in the rooms vented solely with the use of gravitation ventilation were carried out in the period from October until April, that is both during the heating season and at the time were classrooms were not heated.

With natural ventilation working, it was necessary to open the windows to air the rooms during break times. In situations when the temperatures outside were low, the flow of air entering from the outside while airing the rooms, reaching the average values corresponding to the air exchange rate in the room of about 8 h^{-1}, significantly reduced the inside temperature, even to below 12°C. Such a situation was noncompliant with the minimum allowable temperature for classrooms amounting to 18°C, and at the same time it created a significant discomfort for people entering the room. Due to the above reason, a decision was made to carry out modernization work consisting in the following: mounting exhaust fans in ventilation ducts (marked in Figs. 1 and 2 with VD symbols), as well as installing wall ventilators (marked in Figs. 1 and 2 with WV symbols). Because of the fact that classrooms are characterized by changing occupancy during the day, the use of mechanical ventilation allows to control the flow of air discharged from them. After the modernization was carried out in both facilities, the next series of measurements was performed with measurements taken within the period from May to June and from September to December. The performance period for the second series of tests was selected so that it comprised both the heating season and the time outside the heating season, which allows to compare the results obtained in the test series before the modernization with the results reached after the ventilation was changed from natural to forced one.

Results and discussion

The carried out research of inside air parameters in both test facilities with natural ventilation showed that after students had spent several dozen minutes in the classrooms the concentration of carbon dioxide, air temperature and humidity exceeded the limit values pursuant to the PN-EN 13779 Standard [6].

The outside air parameters recorded during the tests corresponded to the average parameters in the climate zone I of Poland although, according to the PN-EN 12831:2006 Standard – Heating systems in buildings. Method for calculation of the design heat load, the building is in fact located in the climate zone III [15]. On the basis of the carried out measurements, the background of CO_2 in the outside air was determined at the level of 400 ppm.

As it is generally known, anyone who spends time inside a closed room is a source of carbon dioxide emission. Depending on the activity during various forms of classes, as well as individual students' metabolism, particular emissions of carbon dioxide by any given student can assume different values. After the analysis of the obtained results, it was assumed, for calculations for the sake of ventilation system optimization, that each person spending time in a classroom is a source of emission of 12 dm^3 of carbon dioxide per hour. After the analysis of the obtained results was performed, it was determined that relative air humidity in a classroom increases on average by 3% within one hour. This value, of course, depends to a large degree on the number of students and the type of physical activity they perform.

Sample sequences of changes in the carbon dioxide concentration, air temperature and relative humidity in the tested classrooms were presented in Fig. 3.

While checking the effectiveness of natural ventilation in the classrooms, an attempt was made to check to what degree the air tightness of a building in which classes are held is responsible for so low efficiency of room ventilation by a gravitation method. In order to increase the inflow of fresh air to the rooms, tests were carried out in which the rooms were untightened by opening windows and doors. However, this was quite burdensome for the teaching process due to the noise from the outside. For this reason, a decision was taken to air the classroom solely during break times. A sample comparison of natural ventilation of a lecture room without opening windows with airing the room three times during breaks between classes was presented in Fig. 4.

As it can be seen in the diagram presented in Fig. 4, even if we air a classroom a few times during a day, it is impossible to keep the level of carbon dioxide concentration below 1000 ppm in a room only aired by means of gravitation ventilation. Airing rooms by opening windows at intervals brings about temperature drops of the air inside below the values recommended by the PN-EN 13779 Standard [6]. It should thus be expressly stated that natural ventilation, which does not provide a possibility to adjust the ventilation air flow in a room, should not be used in such rooms in which classes with students are held. It is only mechanical ventilation that can assure proper adjustment of ventilation airflow and that is why further tests were carried out only after modernization work consisting in the following: mounting exhaust fans in ventilation ducts, as well as installing wall ventilators, had been carried out in both test facilities. In order to adjust working parameters of ventilators precisely, controllers were installed which

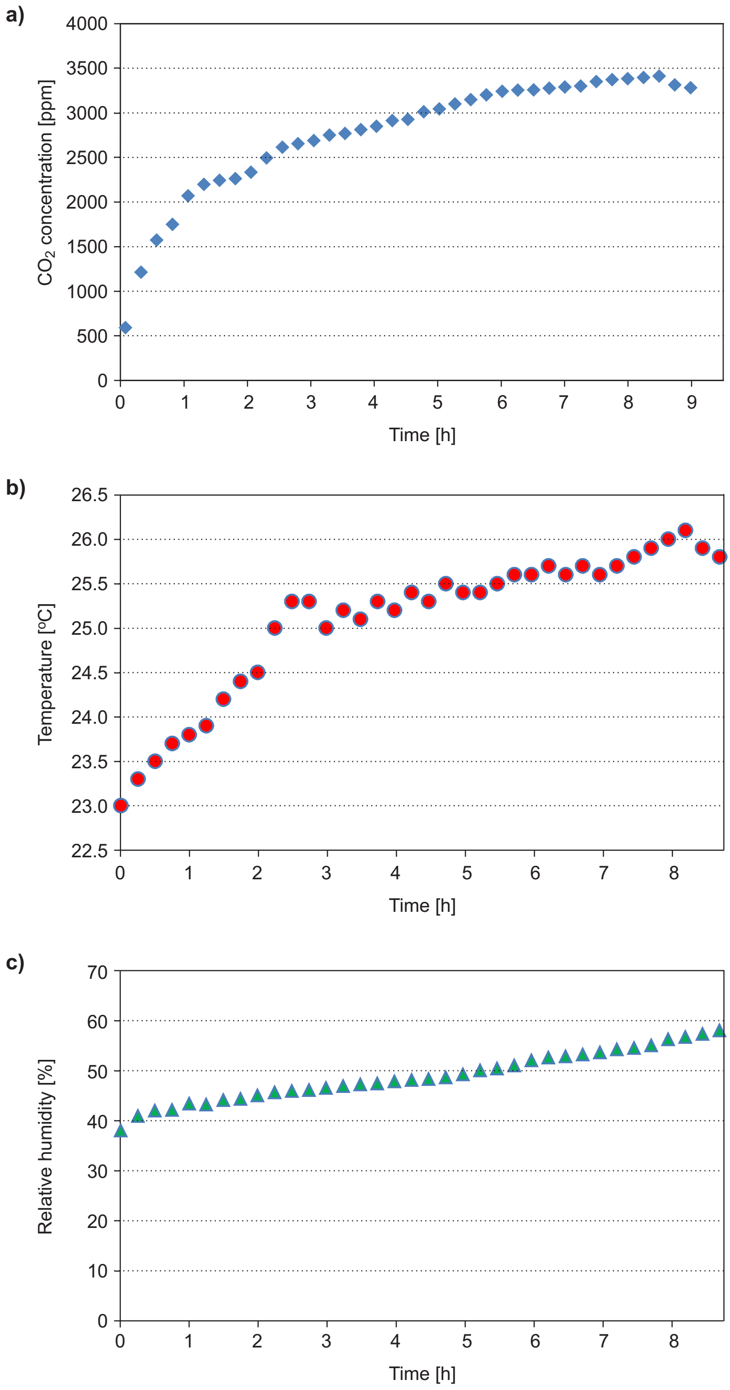

Fig. 3. CO$_2$ concentration (a), temperature (b) and relative humidity (c) variation in classroom

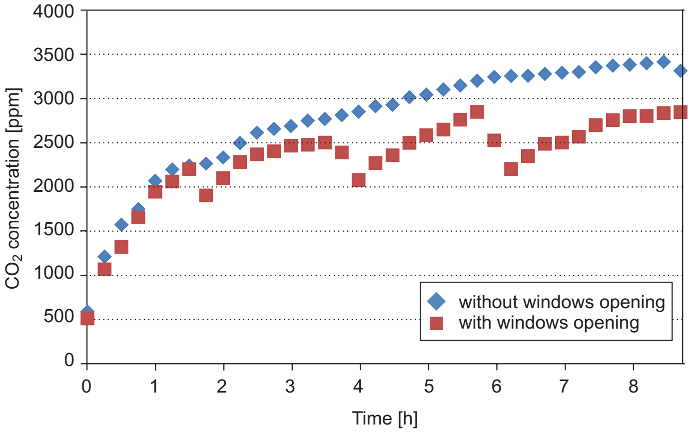

Fig. 4. The variation of CO_2 concentration variation in classroom with and without windows opening

made it possible to determine the number of work cycles per hour and their duration. Thus modified mechanical ventilation system allows to adjust the flow of air discharged from the tested rooms, which is indispensable in order to obtain the air exchange rate in a classroom which is assumed for a given series of measurements.

Tests recording air parameters inside the rooms and outside the building were carried out in both classrooms following the modernization of their ventilation systems. The tests conducted both in the smaller seminar room and in the bigger lecture hall showed similar change trends in air parameters when calculated per a single student. A sample course of changes of the most important parameter, that is carbon dioxide concentration in a lecture hall, was presented in Fig. 5. As it can be observed the use of exhaust fans allows to reduce the level of carbon dioxide concentration in the course of classes. With no precise adjustment of the ventilation system, connected with continuous monitoring

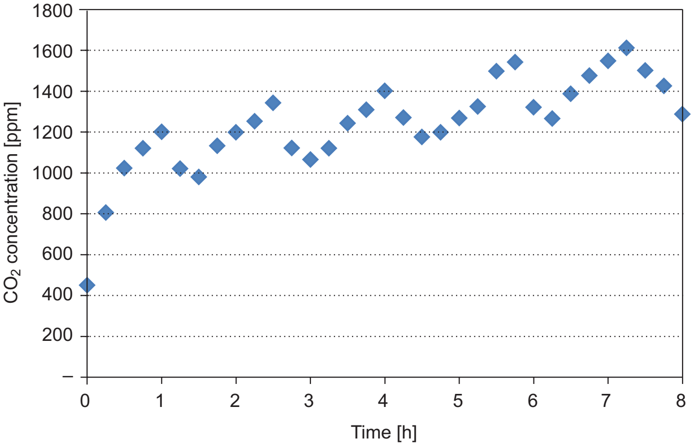

Fig. 5. CO_2 concentration variation in classroom after modernization

of air parameters, it was impossible to maintain carbon dioxide concentration at the level below 1000 ppm.

To select such parameters for the adjustment of mechanical ventilation system that guarantee maintaining air quality as recommended by the standards, and the recommended value of carbon dioxide concentration amounting to 1000 ppm in particular, classroom ventilation parameters should be optimized. In order to optimize quality parameters of air inside classrooms, assumptions had to be adapted which would allow to select adjustments of the ventilation system that would be most favourable with respect to carbon dioxide concentration, air humidity and internal air temperature, which is, during the heating season, inseparably connected also with the heating costs of these rooms. Due to the fact that over 40% of heat from a building is lost along with the used air discharged through its ventilation system, each change of ventilation airflow brings about the change of energy requirement for heating the tested rooms. Calculations of heat requirement for heating the building with the central heating system for each series of measurements were determined with the use of algorithms contained in the Regulation of the Minister of Infrastructure and Development on methodology of determining the energy performance of buildings [16].

Selection of the optimum work parameters of the ventilation system of classrooms is best represented by the sample diagram shown in Fig. 6.

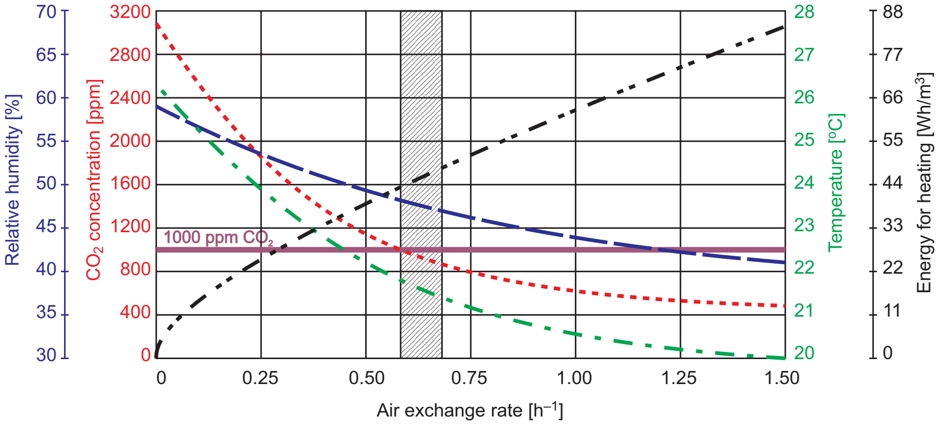

Fig. 6. Selection diagram of the didactic room ventilation parameters for air exchange rate optimization

As it can be seen in the sample diagram, the optimum parameters of air quality with the lowest possible energy consumption for heating 1 m^3 of air are achieved when the air exchange rate in a classroom at the level of 0.6–0.7 exchange per hour is selected (the optimum range of values of air exchange has been crosshatched in the diagram). Concentration of carbon dioxide and energy consumption for heating 1 m^3 of air discharged through the ventilation system are the most important parameters deciding about which adjustments of the ventilation system to select.

By using the factors of carbon dioxide emission determined in the course of research and the optimum range of the air exchange rate in the rooms, as well as on the basis of the recommended parameters of air quality as described in the standards, a mathematical model was prepared which allows to determine the optimum flow of used air discharged through the ventilation ducts, dependent on cubic capacity of rooms, the number of students present and the external air parameters (carbon dioxide concentration, temperature, relative humidity).

With the use of the developed model, when one knows the efficiency of exhaust ventilators and the cubic capacity of rooms, they might select such periods of ventilator work and cross sections of wall ventilators that ensure optimum value of the air exchange rate, which further guarantees air quality in a classroom complaint with the PN-EN 13779 Standard [6]. The selection of optimum work parameters of the mechanical ventilation system with the use of the determined model allows, at the same time, to reduce the operation costs of an educational building.

Conclusions

It was shown in the tested classrooms equipped with natural ventilation that the limits stated in the standards concerning carbon dioxide concentration and relative air humidity were exceeded, which in practice excludes the use of gravitational ventilation in classrooms.

Modernization of the ventilation systems in the tested rooms, which was suggested in the course of research and implemented by way of mounting exhaust fans in ventilation ducts, as well as installing wall ventilators, allows to guarantee interior comfort pursuant to the PN-EN 13779 Standard [6] in educational buildings where there is no technical possibility to install intake and exhaust ventilation with heat recovery.

Factors of CO_2 emission by students, depending on the cubic capacity of rooms and the number of people inside, were determined from the results of the carried out research. The averaged value of carbon dioxide emission by a single student within one hour, applied to determine the work parameters of the ventilation system, was assumed at the level of 12 dm^3/h. Also, the average value of a relative air humidity increase in classrooms was determined and it amounted to 3%.

In case of mechanical ventilation of classrooms, the optimum value of the air exchange rate by the system was determined within the range 0.6 to 0.7 of the entire exchange in the room within one hour. This exchange rate meets the air quality requirement of the PN-EN 13779 [6]. Standard for classrooms, and at the same time it allows to reduce heat losses through the ventilation system.

With the use of the developed mathematical model of ventilation system control, one can determine optimum work parameters for a ventilation system allowing at the same time to minimize costs relating to heating a building.

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OPTYMALIZACJA STĘŻENIA DITLENKU WĘGLA W SALACH DYDAKTYCZNYCH POPRZEZ REGULACJĘ WENTYLACJI

Samodzielna Katedra Inżynierii Procesowej
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Abstrakt: W artykule zamieszczono wyniki badań parametrów powietrza w pomieszczeniach dydaktycznych różnej wielkości. W pomieszczeniach, w których realizowany jest proces dydaktyczny z udziałem dużych grup studentów, powinien być zapewniony odpowiedni komfort klimatyczny, na który mają wpływ przede wszystkim: temperatura oraz wilgotność powietrza, jakość fizyczna i biologiczna powietrza, koncentracja

CO_2. W wyniku przeprowadzonych analiz wykazano, iż w pomieszczeniach dydaktycznych wentylacja grawitacyjna nie powinna być wykorzystywana. Po modernizacji pomieszczeń i zainstalowaniu w systemach wentylacji wentylatorów wyciągowych dokonano pomiarów, na podstawie których wyznaczono współczynniki empiryczne emisji CO_2 przez studentów, uzależnione od kubatury pomieszczeń i liczby osób. Współczynniki te uwzględniono w algorytmie wyznaczającym parametry pracy wentylatorów w systemie wentylacji.

Słowa kluczowe: stężenie CO_2, sale dydaktyczne, regulacja, wentylacja

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THE POSSIBILITY OF THE LIGHT NON-AQUEOUS PHASE LIQUIDS MIGRATION IN THE LAYERED POROUS MEDIUM

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Abstract: The light non-aqueous phase liquids (LNAPLs) percolating into the soil and groundwater present a threat to the subsurface environment. When LNAPL is present on the groundwater table the initial step of remediation should be its recovery. Proper design and monitoring of LNAPL recovery require an estimation of the actual LNAPL thickness or LNAPL specific volume. These parameters are mostly calculated on the base of the apparent LNAPL thickness (LNAPL thickness measured in the monitoring well). This apparent thickness can be even several times greater than the actual LNAPL thickness in the porous medium surrounding monitoring well. This difference depends on the properties of soil and the properties and amount of LNAPL on the water table.

The major aim of this study was to investigate if LNAPL present in the observation well can contaminate the high permeable soil lenses lying below the LNAPL layer on the groundwater table. Results show that the considerable amount of LNAPL penetrated the high permeable soil lens that was hydraulically connected to the well. Additionally, the free product percolation into the high permeable soil lens has influenced the value of apparent LNAPL thickness. Such a situation can complicate the estimation of the actual thickness or specific volume of LNAPL on the groundwater table.

Keywords: LNAPL, actual thickness, apparent thickness, confined LNAPL, layered porous medium

The light non-aqueous phase liquids (LNAPLs) access the subsurface as a result of spills from the underground storage tanks and damages of pipelines and cisterns transporting fuels [1, 2]. A little amount of petroleum product infiltrates into the soil and groundwater with the leachates percolating from unsealed landfills [3] and due to the coal deposits exploitation [4]. Generally, migration of the LNAPL spilled into the porous medium comprises three steps [1, 5]: (a) vertical infiltration through the vadose zone due to the gravity and capillarity forces, (b) horizontal spread of LNAPL plume on

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the groundwater table due to the buoyancy forces and relative permeability; it produces concurrent displacing of the capillary fringe; at this step LNAPL forms lens within the capillary fringe and some soluble constituents dissolve into the groundwater, (c) stabilization of the lateral spread of LNAPL plume and migration of dissolved contaminants in the direction consistent with the groundwater flow.

LNAPL comprises a special risk for soils and groundwater [2, 6]. When it is released into the subsurface it infiltrates downward through the unsaturated zone and can accumulate and float on the groundwater table. Then LNAPL can migrate laterally in the direction of groundwater flow [1, 7]. A portion of petroleum product can be adsorbed on the soil grains or entrapped in the voids of porous medium by capillary forces, posing the residual or entrapped LNAPL coexisting in the pores with water and air [8]. Mechanisms prompted the trapping of LNAPL in the porous media are: snap-off and bypassing [9, 10]. Snap-off mechanism prevails in pores that have high values of aspect ratio (pore body is much larger than the pore throat). Bypassing mechanism takes place when wetting fluid flow (water flow) disconnects the nonwetting fluid. In this case LNAPL ganglia are trapped in clusters of large pores [9–11]. In the water-wet saturated zone, the trapped non-aqueous liquid remains as disconnected and immobilized “ganglia” or “blobs”, referred to as the residual LNAPL (residual oil) [10, 11].

Mobile as well as immobile (residual) LNAPL is the source of soil and groundwater contamination [12]. It can act as long-term source of highly toxic substances [13]. LNAPLs usually consist of different substances (mixtures) with very diverse physical, chemical and biological properties [13].

Especially hazardous for groundwater resources are very soluble constituents originating from LNAPLs [13]. Polycyclic aromatic hydrocarbons (PAHs) are poorly soluble in water, but in specified conditions they can be leached out from contaminated rock and pose a threat to aquifer [14].

A certain part of LNAPL compounds evaporates easily due to high vapor pressures [13]. Both solubility and volatility of these constituents leads to the change of LNAPL composition and properties over time [13, 15].

The hydrocarbon contamination may influence the selected geological-engineering properties of clay soils. Clays contaminated with LNAPLs lose their plasticity and behave like a noncohesive soils [16]. This situation can lead to loss of insulating properties of clays and to the increase of risk of aquifer contamination [16]. The presence of LNAPL in the subsurface produces not only changes in soil morphology but also the disturbance of the biological processes on account of the pollution with toxic compounds [17].

The degree of risk for the subsurface environment associated with LNAPL spills is influenced by: the type and properties of contaminants (hydrocarbons), the volume of mobile LNAPL and its age, the migration pathways of contaminants, and the possibility of reaching and contamination of the water supply resources and systems [18, 19].

If the aquifer is contaminated with hydrocarbon, it is crucial that the remediation should be started as early as possible [20]. When sufficient amount of LNAPL is present on the groundwater table the initial step of remediation should be free product recovery.

After this process a certain amount of residual or trapped LNAPL remains in the soil pores due to capillary forces [20].

This immobile contamination can be removed from porous medium during further steps of remediation guided with use of the physical, physicochemical and biological processes [21]. The proper design of remediation strategy, requires the determination of the vertical and horizontal extent of the LNAPL body, the amount of LNAPL that can be recovered (mobile LNAPL), and estimation of the free product migration direction [2, 8, 20].

The free product volume is usually assessed on the base of thickness of LNAPL lens overlying the groundwater [19, 22] or on grounds of the LNAPL specific volume [22–24]. This thickness (the actual LNAPL thickness or the formation LNAPL thickness) or LNAPL specific volume can be assessed on grounds of the free product thickness measured in the observation wells installed in contaminated aquifer (the apparent thickness) [20]. Unfortunately, the apparent LNAPL thickness measured in the well is always different from the thickness of free product in the porous medium surrounding the borehole (the actual thickness) [18, 19, 22]. This difference depends on the hydrogeological properties of the aquifer and the amount and properties of released LNAPL [18]. Furthermore, the groundwater table in an observation well is always depressed by the overlying hydrocarbon plume and the LNAPL overlying the water in the porous medium surrounding the well may or may not penetrate through the capillary fringe and it is dependent on the flow rate through the unsaturated zone [19].

The notion of “apparent thickness” is relevant to conceptual model describing the vertical LNAPL distribution in the porous medium developed in the 1980s (a “pancake” model). This model assumes that LNAPL can spread horizontally on the groundwater table or on the capillary fringe forming the continuous separate layer. The “pancake” model didn’t take into account the phenomenon of capillarity [25]. This model assumes that almost whole pore space within the LNAPL lens floating on the groundwater table is filled with hydrocarbon so the LNAPL saturation within this lens amounts to nearly 100 percent [25].

The next conceptual model describing LNAPL distribution in the subsurface, developed in the 1990s is “the multiphase model” or “equilibrium model” (Fig. 1). This model is based on idealized relationships between capillary pressure and immiscible fluids saturation [22, 24, 25]. “The multiphase model” takes into account that water and air coexist with LNAPL in the pore space of contaminated zone of porous medium and LNAPL saturation do not reach 100 percent. The maximal LNAPL saturation amounts to approximately 70 percent [22, 25] and is observed near the water table [23, 25]. By “the multiphase model” the best parameter that enables estimation of recoverable free product volume is the LNAPL specific volume [22]. It is the volume of LNAPL per unit of area of soil surface [22].

Estimation of the actual thickness and the LNAPL specific volume requires the evaluation of the apparent LNAPL thickness [25]. The apparent thickness can be even several times greater than the actual thickness. Additionally, the lower limit of LNAPL layer in the well lies significantly below the lower limit of LNAPL layer in the adjacent geological formation [18, 22, 26, 27]. Thereupon the observation wells enabling the

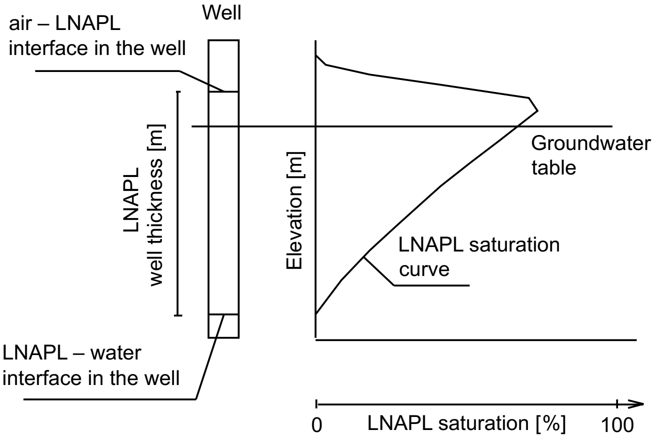

Fig. 1. LNAPL saturation curve in "multiphase model" (on the base of [25])

visibility of the whole LNAPL layer should be adequately deep. The presence of LNAPL in the observation well can be the result of presence of LNAPL on the groundwater table and its presence in the macropores (fissures, fractures) under the groundwater table which are in hydraulic contact with the LNAPL lens [28]. It is possible, that only a small part of LNAPL is present on the groundwater table, and the majority is located in the good permeable layer under the groundwater table having the hydraulic contact with LNAPL lens (so-called confined LNAPL) [28–30].

LNAPL layer can by confined within both: confined and unconfined aquifer [31]. The confined LNAPL in the confined aquifer can occur when LNAPL infiltrates into the classic confined aquifer, where high permeable soil layer is situated below an impermeable, semipermeable or low permeable porous medium (aquitard, aquiclude). In this situation LNAPL can migrate downwards through a low permeable zone within the network of higher permeable macropores, fissures, fractures, etc. The impermeable (semi- or low permeable) porous medium acts in this case as the confining layer [31].

On the other hand LNAPL can be confined in unconfined aquifer due to: lower historical water levels and LNAPL hydrostatic head and lateral migration. When the water table level in unconfined aquifer decreases LNAPL may infiltrate down to a coarser grained porous medium situated below the finer grained soil. The subsequent increase of groundwater table level may lead to submergence and confining of LNAPL within coarse grained porous medium [31]. Furthermore, the free product can penetrate some distance below the water table due to its hydrostatic head resulting from the LNAPL release. In this case LNAPL may access a coarser grained (high permeable) porous medium layer and migrate horizontally [31, 32].

The goal of experiment described in this paper is to examine how behaves the LNAPL layer in the observation well, that is located in layered, inhomogeneous porous medium and when the high permeable soil layer lies between low permeable soil layers. The additional goal of experiment was to confirm if such a situation may result in secondary contamination of low permeable porous medium located above the high permeable soil layer.

Materials and methods

The experiment was performed with use of 3 soils including 2 types of sandy soils (soil 1 and soil 2) characterized in [33] and 1 type of gravel with grain diameter range from 5 to 20 mm. The effective grain sizes of soils 1 and 2 amounted respectively: 0.20 and 0.19 mm. Hazen's uniformity coefficients of soils 1 and 2 amounted respectively: 1.25 and 1.58 and their hydraulic conductivities amounted about 12.8 and 13.1 $m \cdot d^{-1}$.

As LNAPL was used the rapeseed oil with the density of 918 $kg \cdot m^{-3}$ and the dynamical viscosity of 0.07 $kg \cdot m^{-1} \cdot s^{-1}$ (at the temperature of 20^{o}C).

The experiment was carried out in plexiglas column with diameter of 10 cm and height of 70 cm, with perforated tube having a semicircular cross-section as monitoring well (diameter of 3.5 cm). The filter wall was protected with nonwoven fabric to prevent the sand to get across the filter holes into the well. In the experimental column was also inbuilt the 3 cm diameter equalizing column with perforated bottom used to the changing of the water table elevations during the experiments.

The column was packed with the following layers of soils, starting at the ground surface: 0–32.4 cm – soil 1; 32.4–37.5 cm – soil 2; 37.5–43.5 cm – gravel; 43.5–54.0 cm – soil 1; 54.0–58.0 – soil 2; 58.0–64 cm – gravel. These values are the medium depths to the boundaries of specified layers, because these boundaries courses were not ideally horizontal. The good permeable layers (gravels) were separated from less permeable layers (sands) with use of non-woven fabric so that the sand does not pour into the gravel layer voids. The perforated tube for injection of LNAPL was located into the upper part of soil. Then the experimental column was filled with water until the water table reached the assumed elevation (below the outfall of perforated tube). After 4 days 100 cm^3 of LNAPL was injected into the column directly above the capillary fringe zone. LNAPL was stained with the dye – Sudan III for better visibility of the liquid in the column. After next 4–5 days the apparent LNAPL thickness was measured in the well. This procedure (LNAPL injection and consequent apparent thickness observation) was repeated 5 times (the volume of 5th portion of LNAPL was only 45 cm^3 on the grounds that the lower limit of LNAPL layer in the well declined near the bottom of column). The water table in equalizing column was kept constant during experiment and amounted 17.2 cm ± 0.1 cm below soil surface. The top of experimental column was protected against LNAPL evaporation by the cover. Experiment was carried out at the temperature of 20 ^{o}C ± 2°C [33].

Results and discussion

Figure 2 shows the depths to upper and lower LNAPL limits in the well (the air-LNAPL interface and the LNAPL-water interface, respectively) for changing LNAPL volumes in the column.

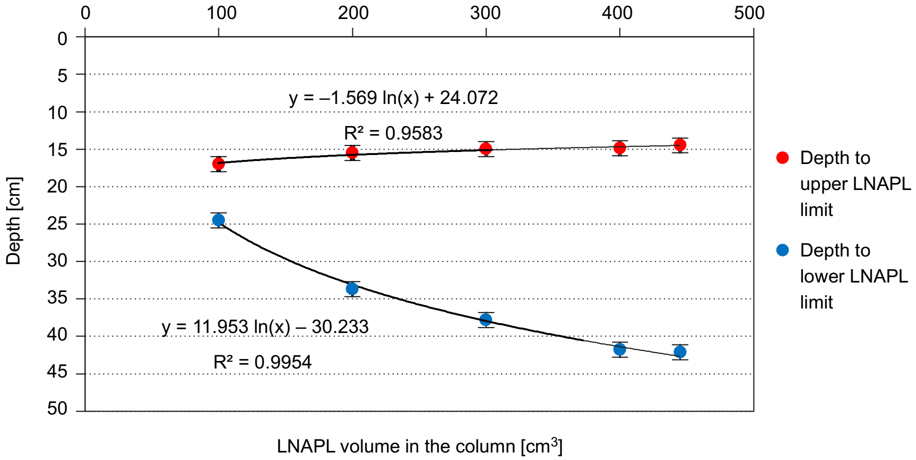

Fig. 2. Depths to upper LNAPL limits in the well (air-LNAPL interface) and lower LNAPL limits in the well (LNAPL-water interface) for changing LNAPL volumes in the column [33]

Figure 3 shows the changes of LNAPL apparent thicknesses depending on the LNAPL volume in the experimental column. Obtained results show that the biggest increases of the apparent LNAPL thickness were observed at the beginning of experiment, especially after the second LNAPL addition, when the thickness increase was 10.7 cm ± 0.4 cm (for the apparent thickness 18.2 cm ± 0.2 cm). The thickness increases after third and fourth injections were distinctly lower and amounted to: 4.6 cm ± 0.4 cm and 4.1 cm ± 0.4 cm, respectively. The least increase of apparent thickness amounted to (0.7 ± 0.4) cm was observed after 5th addition of LNAPL (by 450 cm^3 of LNAPL in the column). Diminished increases of apparent thickness after 3rd and

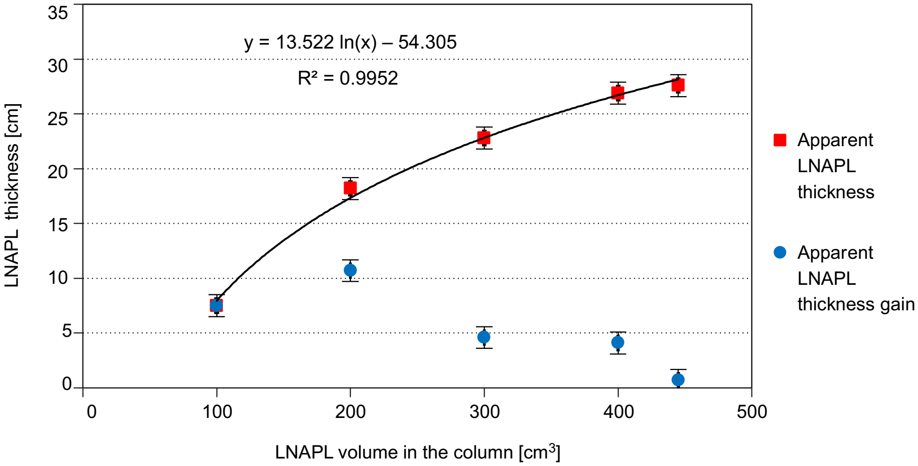

Fig. 3. Fig. 3. Relationship between apparent LNAPL thicknesses and LNAPL volumes in the column (upper graph) and apparent thickness gains for changing volumes of LNAPL (lower graph) [33]

4th additions of LNAPL were caused by get of lower limit of LNAPL layer in the well to the upper high permeable layer of soil in column and filtration of LNAPL from well into the gravel layer (Fig. 4).

Fig. 4. LNAPL visible in the upper high permeable layer 1 day after its fourth addition (on the left) and 5 days after its fourth addition (in the middle and on the right [33])

Results presented in Figs. 2 and 3 show LNAPL layer distribution in the well a few days after each LNAPL addition. In the meantime, from the 3rd LNAPL addition, the lower limits of LNAPL layers observed just after LNAPL addition was located lower than the limits stabilized after a few days due to the slow LNAPL infiltration into the good permeable layer. Figure 4 shows that one day after 4th LNAPL addition oil is present in the well and in the whole good permeable layer (photo on the left). Five days after oil addition only the upper part of the gravel layer (about two-thirds of its pore space) was occupied by LNAPL and the lower part of gravel layer (about one-third of its pore space) was occupied by water. Initially, after 4th oil portion addition the apparent LNAPL thickness was a few centimeters greater than final value given in Fig. 3, what indicates the light residue on the column wall directly under the LNAPL layer (Fig. 4). Nonetheless, the excess of LNAPL little by little infiltrated through the high permeable layer into the low permeable layer, leading up with the apparent thickness decrease. On the other hand distinct retardation of the thickness increase after 5th LNAPL injection was caused not only due to the addition of the minor portion of LNAPL (only 45 cm^3), but primarily due to the continuous LNAPL infiltration into the high and low permeable layers. As a result of this infiltration a few days after 5th LNAPL addition the lower limit of LNAPL layer raised and stabilised at the depth (41.8 ± 0.1) cm below soil surface (just as in the case of 4th LNAPL addition).

Further observations conducted about 2 months after the last LNAPL addition indicated that during this period occurred slow vertical upward LNAPL percolation from the upper high permeable layer (alternatively directly from the well) into the commanding weakly permeable layers composed of soils 1 and 2. In the end the significant amount of LNAPL was immobilized near the water table and the capillary fringe level (Fig. 5).

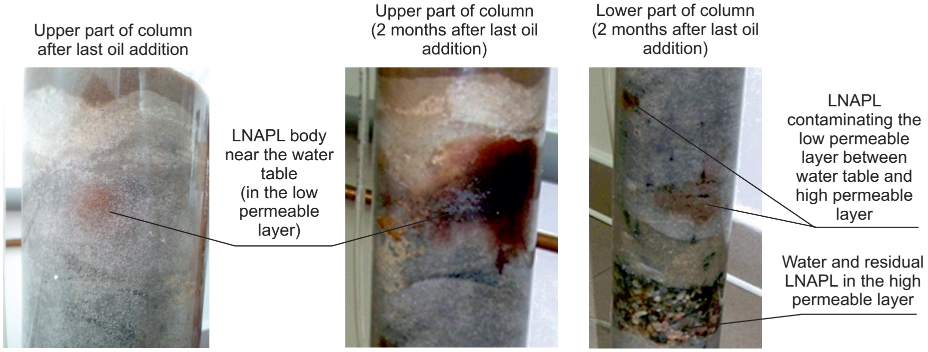

Fig. 5. LNAPL contaminating the low permeable layers 2 months after last addition of oil

The soil across which LNAPL percolated, located between upper high permeable layer and the water table, was distinctly contaminated with residual phase of oil. The source of this contamination was probably LNAPL present initially in the high permeable layer as confined LNAPL in the unconfined aquifer, described in [29–32]. However it is possible, that the source of soil contamination was also LNAPL infiltrating directly from the observation well. This means that there is a need for further more exact investigations to clarify LNAPL behavior in the subsurface, especially when LNAPL occurs in confined conditions. The aim of further research can by the investigation of the persistence of confined LNAPL in high permeable layer in the unconfined aquifer and its dependence on the grain size distribution of the overlying, water saturated soil layer.

Obtained results show that it exists real possibility of aquifer saturated zone contamination (even below the water table) when LNAPL present in the monitoring well reaches the high permeable soil layer. Additionally in this case the part of saturated zone located above the high permeable layer can be contaminated with LNAPL residual phase. The obtained results confirm that existence of high permeable layers having hydraulic contact with LNAPL layer present in the filtered well has an influence on the value of apparent LNAPL thickness and thereby on the accuracy of estimation of the actual thickness or specific LNAPL volume on the groundwater table and subsequent volume of LNAPL that can be recovered during initial remediation.

Conclusions

1. When the high permeable soil layer stays in the hydraulic contact with filtered well filled with LNAPL the light non-aqueous phase liquid can percolate into this layer.

2. The existence of high permeable layers having contact with the filtered well can have an influence on the apparent LNAPL thickness and thus on the accuracy of

estimation of the organic liquid volume that can be recovered during initial stage of remediation.

3. The results show that the considerable amount of LNAPL probably can percolate vertically from high permeable layers having contact with monitoring well into the commanding worse permeable layers of aquifer and can float towards the groundwater table.

4. Drilling of boreholes in the LNAPL contaminated aquifer can lead to the uncontrolled augmentation of range of the hydrocarbon contaminated zone. Therefore, after well drilling and installation the LNAPL recovery action should be began promptly.

5. LNAPL saturation depends on the soil grain size distribution. Coarse grained soil can accumulate more LNAPL than the fine grained soil.

6. There is a need for further investigations to clarify confined LNAPL behavior in the subsurface and to examine the persistence of confined LNAPL in high permeable soil layers in the unconfined aquifers.

Acknowledgements

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MOŻLIWOŚCI ROZPRZESTRZENIANIA SIĘ LEKKICH CIECZY ORGANICZNYCH W OŚRODKU POROWATYM O BUDOWIE WARSTWOWEJ

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Politechnika Częstochowska

Abstrakt: Lekkie ciecze organiczne niemieszające się z wodą (LNAPL), które infiltrują do środowiska wodno-gruntowego, stanowią dla niego bardzo poważne zagrożenie. Gdy na zwierciadle wody podziemnej jest obecna warstwa LNAPL (tzw. wolny produkt), wstępny etap remediacji powinien obejmować jej sczerpanie. Prawidłowe zaprojektowanie, a także monitorowanie operacji sczerpywania wolnego produktu wymaga znajomości rzeczywistej miąższości lub jednostkowej objętości LNAPL, które ustala się na podstawie miąższości LNAPL zmierzonej w studni obserwacyjnej (tzw. miąższości pozornej). Miąższość pozorna różni się od rzeczywistej i może być od niej nawet kilka razy większa. Różnica między wskazanymi miąższościami zależy m.in. od właściwości gruntu, a także od właściwości i ilości LNAPL na zwierciadle wody podziemnej.

Celem badań opisanych w artykule było ustalenie, czy wskutek obecności LNAPL w studni obserwacyjnej, zlokalizowanej w ośrodku porowatym o budowie warstwowej, może dojść do wtórnego zanieczyszczenia warstw dobrze przepuszczalnych, znajdujących się poniżej plamy LNAPL na zwierciadle wody.

Otrzymane wyniki wskazują, że część LNAPL może infiltrować ze studni obserwacyjnej do strefy ośrodka porowatego o wysokiej przepuszczalności, jeżeli pozostają one w hydraulicznym kontakcie. W takiej sytuacji może dojść do uformowania się tzw. napiętej soczewki LNAPL, która może występować zarówno w warstwie wodonośnej o zwierciadle napiętym, jak i w warstwie wodonośnej o zwierciadle swobodnym. Poza tym infiltracja LNAPL do warstwy dobrze przepuszczalnej może znacząco wpływać na zmniejszenie się miąższości pozornej, co może w dużym stopniu skomplikować prawidłowe ustalanie miąższości rzeczywistej i jednostkowej objętości LNAPL na zwierciadle wody podziemnej.

Słowa kluczowe: LNAPL, miąższość rzeczywista, miąższość pozorna, napięta LNAPL, ośrodek porowaty o budowie warstwowej

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SURVEYS OF CONSUMER PREFERENCES OF THE OPERATION AND MANAGEMENT OF WATER SUPPLY

BADANIA SONDAŻOWE PREFERENCJI KONSUMENCKICH NA TEMAT FUNKCJONOWANIA ORAZ ZARZĄDZANIA DOSTAWĄ WODY

Abstract: The permanent and long-lasting development of the civilization influences the growth of the threat occurrence connected with the functioning of Water Supply System (WSS). The presented methodology can be used to describe the functioning of the public water supply using the evaluation of its proper functioning and allows for implementation to determine proper operation of water network. The expanded methodology of conducted surveys of recipients in the field of the effectiveness of the water supply system is the basis for a comprehensive assessment of its proper functioning. Consumer opinions may be used in determining water supply reliability standards and the rules for granting discounts and rebates in the case of restrictions and interruptions in water supply. A significant issue is the assessment by respondents nuisance interruptions in water supply (time and frequency), knowledge of the causes, inconveniencing and losses that causes lack of water supply. In the work the results of consumer survey during undesirable events in Polish water networks were presented.

Keywords: water network, consumer assessment, water supply system functioning analysis

Introduction

Assessment and analysis of proper water supply functioning is an important issue for policy development company, and is used to improve the existing organizational and operational state. A properly functioning collective water supply system should ensure a continuous water supply to the recipients, with a suitable quality and adequate quantity (required pressure), at a specific time. These parameters must be maintained at the required level, which in reality is not so simple.

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Water consumers increasing awareness of their rights causes that waterworks companies are more and more focused on the client. The recipient who bears costs in the form of fees is entitled to demand an adequate level of service [1]. More and more often the parameters of water supply are standards, according to which the agreement between the water supplier and the water recipient is concluded. In the agreements concluded between the supplier and the recipient, the recipient should have the right to negotiate the price if the supplier does not fulfil water quality standards. Specific identification of indicators describing the quality of water services prevents misuse of monopolistic position by the water supply company, also in public-private partnerships. The basis for such an agreement should be arrangements for customer service quality standards, therefore the establishment of the priority criteria (the parameters of water supply) and the permissible values of deviations of these parameters from the acceptable parameters, what can be determined in the conducted survey. Such a survey can consist of questions concerning inconveniences and losses occurring during undesirable events and crisis situations.

The issue related to the amount of fees that recipients would be willing to bear as to obtain a given level of services provided by the water company and therefore the Contingent Valuation Method (CVM) and the so-called Willingness to Pay (WTP), as well as Willingness to Accept (WTA) in case of interruption of water supply were described in works [2] and [3]. The test results contained in [4] indicate that the continuity of the water supply is an important factor in the assessment by consumer of water, who is willing to pay more for a reduction in the frequency and duration of interruptions in water supply.

The aim of the water supply system safety operation is to counteract against lack of water or its bad quality threatening health of municipal water pipe users and to supervise this action using processes, information resources in the given operating conditions, in compliance with the valid law and with economic justification [5]. However, legal regulations do not control the operation of water supply companies and conditions of receiving water with certain deficiencies. One example is the lack of clear rules that would strictly define minimum level of services provided to water customers by water companies. These rules are based on local legislation that is approved by the local authorities.

It is worth to mention, that consumers in water supply system functioning are exposed to numerous threats, as for example failures of each subsystems of water supply systems, lowering groundwater table, also some incidental undesirable events as droughts, floods and other factors causing deterioration of the quality of raw water. But among all these mentioned events, consumers are most prone to get water, which quality does not meet the relevant standards.

Also water companies experience the effects of negative events including penalties resulting from deliver water with inadequate quality or interruptions in the water supply, costs incurred for the failure removal, lower profits from the water sale, material cost needed to restore damaged or destroyed infrastructure, other costs related to the transport of materials. Therefore in the examined water supply systems an emphasis was put on the issue connected with water services assessment including analysis of safety functioning, as well as performed survey through conjoint analysis implementation.

The main areas of the application of conjoint analysis in water supply system consider environmental and social improvements [6], consumer's selection attribute of the bottled water on the premium market [7], evaluate participant's preferences for various attributes of recycled water for various uses and the transformation of urban water supply [8].

The proposed approach will facilitate the management, provide the centralized control and comparison of water supply companies, which will ensure that the services provided by them will be at a certain level [9–12]. It will also protect against reaching a monopoly position by a given company, such a situation could result in higher prices for supplied water while the level of service is lowering [13]. Such procedures of safety assessment of quality services involving functioning analysis or failure and losses analysis will help to protect different group of recipients [14–18].

The scientific objective of the paper is to develop an innovative methodology for operation analysis and assessment, associated with consumer's safety, in the water supply system. Also issues related to the risk of non-delivery water in everyday life in order to prevent or minimize such risk with regard to hazardous situation occurrence.

Analysis of the water supply system operation from the consumer perspective

The basic quality parameter of service is its availability, including the duration of interruptions in water supply. This nuisance is proportional to the size of failure, the number of people affected by failure and the duration of interruptions in water supply, what can be described in the following way:

$$IR = I_u / R_i \tag{1}$$

where: IR – the customer interruption;
I_u – the sum of unplanned interruptions of water supply;
R_i – the total number of recipients.

and

$$T_{avg} = D_T / I_T \tag{2}$$

where: T_{avg} – the average time necessary to restore the water supply in case of unplanned interruptions in water delivery;
D_T – the sum of the duration of all interruptions in the water supply;
I_T – the total number of water interruptions.

The average time necessary to restore the water supply in case of unplanned interruptions in water delivery in the examined water network is shown in Fig. 1.

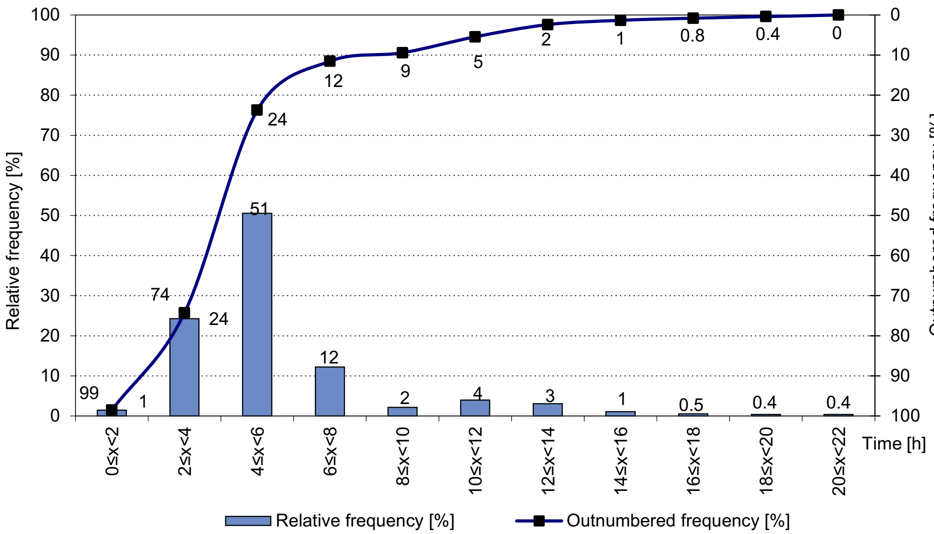

Fig. 1. Histogram of relative frequency and time-frequency summed renewal curve of water pipes

The service availability determined quotient of the time of the continuous water supply throughout the year and the time when there was the demand for water, can be reflected through following expression:

$$SA = (R_i \cdot 1 \text{ year} - R_i \cdot D_T) / (R_i \cdot 1 \text{ year}) \tag{3}$$

where SA is the availability service indicator.

The average values of presented indicators from 7-years period of time, on the example of the examined water supply system, were as follow: IR = 1.4 no of failures per recipient and year, T_{avg} = 2.5 h per failure and SA = 0.9127.

As to find the importance of calculate indicators from customers point of view, the initial survey was conducted among the recipients, concerning summary of loss and inconveniences caused by lack of water supply and kind of complaint for failure of not meeting quality standards of water supply. Based on this analysis three parameters where chosen to perform the further dissection: the service availability, price of delivered water and possibility to negotiate the discount for not delivered water.

Assessment of interruption in water supply through assumptions of willingness to accept method

In the preliminary study surveyed respondents were asked if the water supplier, in this case water company should compensate financial losses associated with the lack of water supply.

In the Fig. 2 the dependence between the response to the question of compensation by the supplier financial losses associated with the lack of water supply land the gender of the respondents.

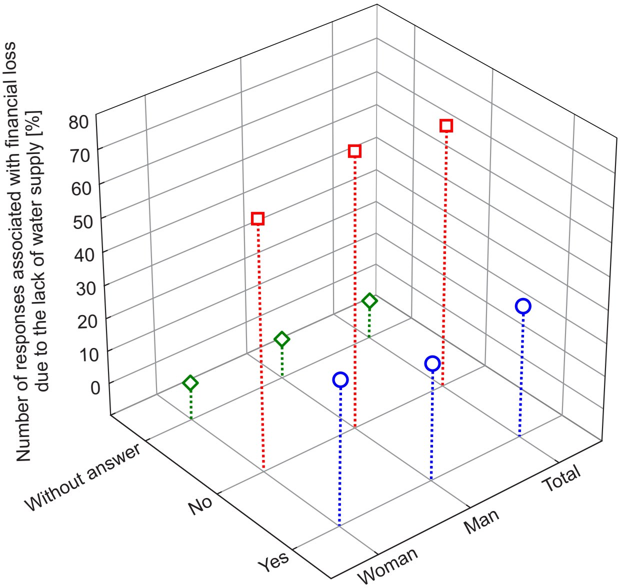

Fig. 2. Dependence between the response to the question of compensation the financial loss associated with the lack of water supply by the water supplier and the gender of the respondents

Among the surveyed about two-third answered that the supplier should not compensate the financial losses occurring during a lack of water supply. A different opinion have 29.5% of the respondents, while 1.5% did not answer this question. When taking into account the gender of the respondents, 65% of women and 73% of men believe that the supplier do not need to pay compensation for failure to meet certain parameters of water supply. Based on these results, it is concluded that gender does not have much connection with the opinion on compensation for financial losses due to the interruption of water supply. In the case of age category the highest percentage (about 70%) of people who believe that the supplier should compensate the resulting financial losses are people from 36 to 50 years old. The detailed analysis showed that people with the lowest income do not demand any compensation for financial losses for lack of water supply.

In the next question the respondents were asked about consent to pay higher water bills in return for reducing the number of interruptions in water supply.

In the Fig. 3 the dependence between the response to the question of approval for payment of higher water bills in return for reducing the number of interruptions in the water supply and the respondents gender was presented.

The majority of respondents, as many as 79%, did not agree to pay higher bills, the remaining 21% expressed such a willingness. As can be seen, the respondents are reluctant to agree to increase water charges in return for reducing interruptions of water

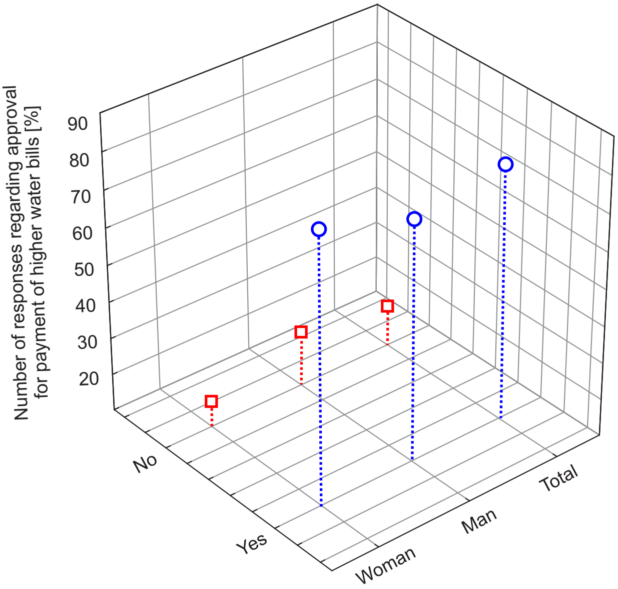

Fig. 3. The dependence between the answer to the question of approval for payment of higher water bills in return for reducing the number of interruptions in water supply

supply, which may be caused by the lack of certainty as to reducing the risk of lack of water supply. In detail, 75% of men and 83% of women do not agree to increase the water bills in return for a reducing the number of interruptions in the supply. Considering the dependence between the response to the question of approval for paying higher water bills and respondents age, in case of disagreement on the increase in bills, the largest percentage (about 88%) occurs in the youngest age group, between 18 and 25 years. In other age group, the results are not varied enough to say on this basis that the age of the people is important for the agreement to increase the bills in return for reducing the number of interruptions of water supply. Identical situation as in the previous question was for net income per family member, when in the least-earning group, 90% of respondents did not agree to an increase in water bills.

Another question concerned the maximum amount of increase in water bills in return for reducing the number of water interruptions. To this type of question only those people respond who in the previous question have agreed to pay higher bills. The respondents had unlimited choice in terms of the amount of the maximum increase of bills in return for reducing the number of interruptions of water supply. In the Fig. 4 the results of the analysis were shown.

Most people, as many as 65% would agree for payment of higher bills, provided that it will not increase by more than 5 EUR. In other categories, the number of people systematically decreases along with the increase in water bills. Nearly 90% of the respondents gave the increase of the bills should not exceed 12 EUR. The respondents generally do not decide to highly increase the bills in return for reducing the number of interruptions of water supply.

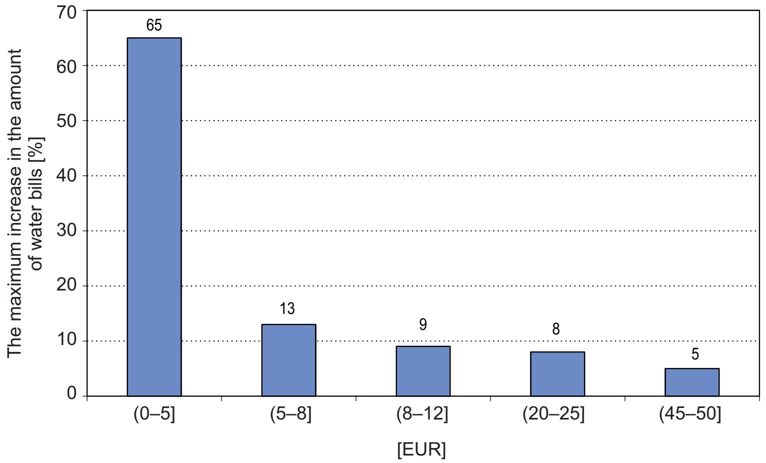

Fig. 4. The maximum amount of increase in the water bills for reducing the number of interruptions in the water supply

Determination of the risk of lack of water supply based on the performed consumers survey

The important issue in the assessment of the operation of water supply systems is risk analysis, an essential component in developing Water Safety Plans recommended by the WHO. They are considered as a basis for taking effective preventive measures to increase the level of protection of water consumers.

Risk is the product of the probability of undesirable event occurrence and the possible losses related to this event [10]. After having the answer to the question: Do You experience any interruptions in the water supply during last year? the probability of the risk associated with such event was calculated, also losses associated with the lack of water supply were established.

The next step was to determine the risk of non-delivery water according to the formula [10]:

$$R = \Sigma P \cdot C \tag{4}$$

where: P – the probability of undesirable event occurrence;
C – the amount of losses caused by the occurrence of undesirable event.

The empirical probability of the occurrence of undesirable event in the last year in the consumer’s opinion is:

$$P = 0 \text{ – if the number of failures is zero,}$$

and

$$P = 1 \text{ – if the number of failures is greater than zero.}$$

The calculations were made in two groups: to the first group were included all the respondents and to the second group only those recipients who take water from the public water supply.

The risk of lack of water supply in both groups is the same, approx. 4050 EUR. This is due to the fact that all people who do not have the access to the public water supply, although sometimes experienced interruptions in water supply, assessed the water losses at 0 EUR. The risk value determines the losses that consumers would incur in the lack of water supply. Based on these results the further statistic was made.

The value of the average financial loss per a recipient for people using the public water supply system is 11 EUR, and for all the people 6 EUR.

Greater losses affected the recipients having access to the public water supply system, which is associated with the same level of the total financial losses.

Also the standard deviation for the financial loss was determined, which for all the respondents is $\sigma = 24$ EUR, and in the case of using public water supply system is $\sigma = 29$ EUR. The standard deviation characterizes the dispersion of data around the arithmetic mean. Results of the recipients having access to the public water supply system are more dispersed than for all the respondents.

Based on the answers of the respondents in several intervals relating to interruptions experienced in the last year, the average amount of financial losses for one break in water supply was calculated.

A smaller average amount of financial losses for one break in the water supply concerns all the respondents and slightly exceeds the amount of 5 EUR, while for people provided with tap water from the public system this value is about 6 EUR.

Conjoint analysis as a method of measuring the customers' preferences

In order to propose a contract for the water supply, concluded between the water supply company and the various categories of customers, de-compositional method was used, based on multivariate measurement (*ie* measuring the total coexistence of variables) – conjoint analysis [19–21].

In this method, the recipients make an assessment of attribute sets of provided services. The choice of attributes involves information regarding the services characteristics, on this basis the decomposition of generalized priorities preferences relating to the levels of services characteristics is made.

As a result, the preferences are aggregated, and therefore the preference measurement occurs at the level of services characteristics. The steps of conjoint analysis are shown in Fig. 5 [20, 21].

Firstly, the subject of research was defined, that is the choice of the individual parameters describing the service and levels. In the next stage the model form was specified, then the method of data collection and the choice of preference measurement scale were defined. In the last step the method for model estimation was assumed and the total utility was interpreted and used to assess the performance of the proposed service.

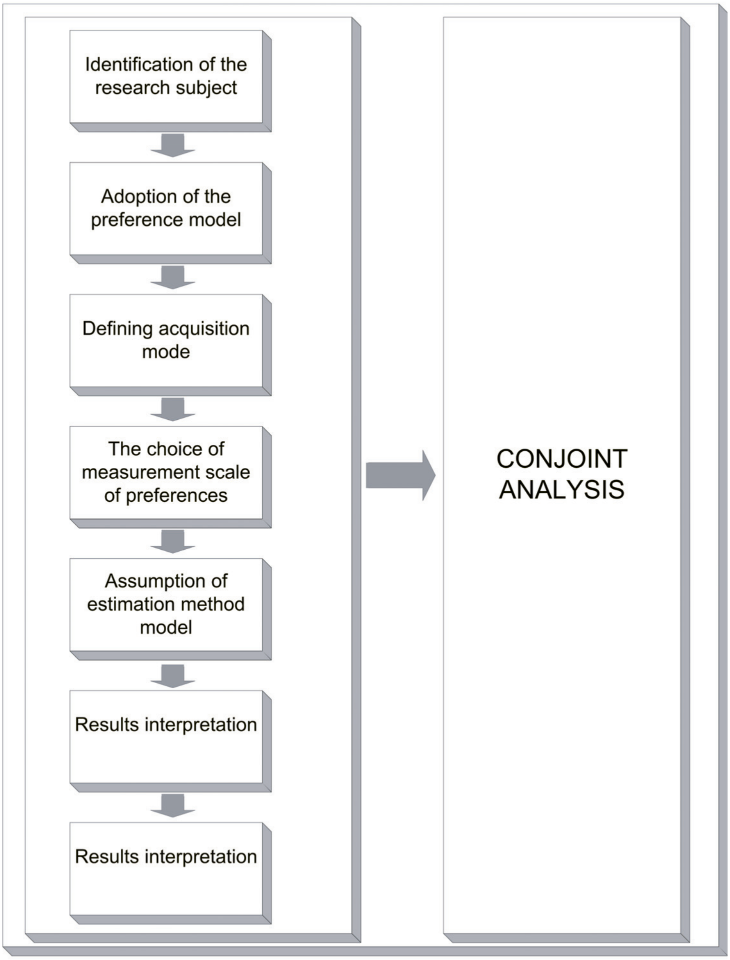

Fig. 5. Steps of conjoint analysis

Conjoint analysis was performed using Statistica software. Developing a proposal for an agreement between the supplier and the recipient, three variables and categories that describe the variable data, were distinguished:

– price levels for 1 m^3 of delivered water: 5 EUR, 7 EUR, 12 EUR, 15 EUR,

– the availability ranges of water services depended on the duration of interruptions in water supply throughout the year: $\leq 6\ h \cdot a^{-1}$, $(6–10]\ h \cdot a^{-1}$, $(10–12]\ h \cdot a^{-1}$, $(12–16]\ h \cdot a^{-1}$, $> 16\ h \cdot a^{-1}$,

– the possibility to negotiate discounts for failure to meet water supply standards: yes, no.

At the beginning of the analysis the subject matter of research was defined, that is the choice of the individual parameters describing the service and levels. In the next stage the model form was specified, then the method of data collection and the choice of preference measurement scale were defined. In the last step the method of estimating model was assumed and the total utility was interpreted and used to assess the performance of the proposed service.

On the basis of certain variables and their levels 32 product variants were created. However, such situation does not resolve the dilemma of the product purchaser, because he does not know which version of the product would be best for him. This situation is more difficult, when there are more options of contract to choose from. In order to facilitate the option choice by the customer it is proposed to implement a conjoint analysis.

This method consists in selecting 6 the most contrasting options of given product or service, which significantly reduces the number of options helping customers in choice. After analysis the most contrasting contracts, a total of eight contrasting contracts, were proposed to recipients. In this way, a customer can easily rank them from the most to the least preferred [19].

Total utility for the *i*-th offer and *j*-th respondent is calculated as follows [20]:

$$X_{ij} = \sum_{k=1}^{m} X_{ik}^{j} + b_{0j} \tag{5}$$

where: X_{ij} – total utility for *i*-th offer for *j*-th respondent;
X_{ik}^{j} – total utility of category of *k*-th attribute, which occur in the *i*-th offer;
b_{0j} – is absolute term for *j*-th respondent.

For each respondent the indicator of the relative importance for various parameters of offer was determined as [20]:

$$W_{k}^{j} = \frac{\max\{X_{ik}^{j}\} - \min\{X_{ik}^{j}\}}{\sum_{k=1}^{m} (\max\{X_{ik}^{j}\} - \min\{X_{ik}^{j}\})} \tag{6}$$

where: W_{k}^{j} – the relative importance of *k*-th attribute of offer for *j*-th respondent;
X_{ik}^{j} – theoretical partial utility of *i*-th level of *k*-th attribute for *j*-th respondent.

Zero-one coding was applied, because the independent variables are qualitative in nature and, therefore, will be presented by means of artificial variables. In the zero-one coding *n*-categories of variables are replaced by $n - 1$ artificial variables, where the omitted category is the reference category [20]. Then the utility function coefficients were calculated, thereby obtaining the utility of each category. Utilities have been designated for each respondent and individual profile. In this way, the information on the utility of each profile, defined by a given category assessed by individual respondents, was obtained. On this basis, the ranking of individual profiles was calculated.

Determination of the utility functions of three important variables for each individual customer and its partial utility were as follows:

– price per 1 m^3 of delivered water: 5 EUR (0.27), 7 EUR (0.1), 12 EUR (0), 15 EUR (–0.4),

– the availability of water services depended on the duration of interruptions in water supply throughout the year: $\leq 6\ h \cdot a^{-1}$ (0.38), (6–10] $h \cdot a^{-1}$ (0.34), (10–12] $h \cdot a^{-1}$ (–0.36), (12–16] $h \cdot a^{-1}$ (–0.41), > 16 $h \cdot a^{-1}$, (–0.55),

– the possibility to negotiate discounts for failure to meet water supply standards: yes (0.7), no (–0.1).

The partial utility of the variable describing the price is a decreasing function, the lowest price is preferred. The largest decline occurred in the interval between 12 and 15 EUR, so recipients negatively react to changes associated with higher price levels. In the case of ranges of water services availability, we deal with a nominal scale. Preferred in this case are the category of water interruptions lasting less than 6 hours, also the possibility to negotiate discounts for failure to meet water supply standards is chosen.

The final step of the analysis was to obtain information about the relative importance of each factor for each respondent.

Determination of the utility functions of three variables for each individual customer, including validity factor were as follows:

– price per 1 m^3 of delivered water: 5 EUR (31%),

– the range of services availability depending on the duration of interruptions in water supply during the year: $\leq 6\ h \cdot a^{-1}$ (32%),

– the possibility to negotiate discounts for failure to meet water supply standards (36%).

Preferences of the respondents in the entire group were the most influenced by the ability to negotiate discounts for failure to meet water supply standards, then the availability of water services, the weakest factor proved to be the price per 1 m^3 of delivered water.

According to the statistical analysis the highest-ranked agreement made by the recipient of water supply system was the contract containing the following attributes: price per 1 m^3 of delivered water: 5 EUR, the range of services availability depending on the duration of interruptions in water supply during the year: $\leq 6\ h \cdot a^{-1}$ and the possibility to negotiate discounts for failure to meet water supply standards.

If it turns out that the contract with the highest degree of preference cannot be realized, then the producer (in this case, the water company) will have knowledge of the alternative contract – the next best in terms of preference. The proposed analysis of services level assessment provided by the water companies using the conjoint analysis enables the presentation of characteristics differentiation indicating which water supply systems are characterized by high quality services.

Conclusions and perspectives

This paper considers the application of the survey analysis method, in order to assess the water quality services proposed by the water company. Using conjoint analysis the importance and order of the individual preferences of recipients can be determined, by adjusting the profile of the needs of the market and the possibility to adjust the criteria for services to customer needs. An important advantage of survey analysis is the study of the market in real conditions.

Continuation of the subject of the work should be directed to assess the financial losses caused by lack of water supply, as to develop quality standards for water service levels taking into account the consumer and water companies opinion. The presented methodology and the results obtained using the survey through risk analysis is an important set of information from the water consumers point of view.

The proper management of public water supply consequently will allow to control the quality of services related to the supply of drinking water of the required parameters.

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BADANIA SONDAŻOWE PREFERENCJI KONSUMENCKICH NA TEMAT FUNKCJONOWANIA ORAZ ZARZĄDZANIA DOSTAWĄ WODY

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Abstrakt: Stały i długotrwały rozwój cywilizacji wpływa na wzrost występowania zagrożeń związanych z funkcjonowaniem systemu zaopatrzenia w wodę (SZW). Prezentowana metodologia może być stosowana w celu oceny prawidłowego funkcjonowania wodociągów. Opinie konsumentów mogą być stosowane przy określaniu standardów niezawodności usług wodociągowych oraz zasad udzielania bonifikat i upustów w przypadku ich niedotrzymania. Ważnym zagadnieniem jest ocena przez respondentów uciążliwości (czasu oraz częstotliwości), uniedogodnień, a także wielkości strat finansowych spowodowanych brakiem dostawy wody. W pracy przedstawiono wyniki badań oceny konsumentów podczas zdarzeń niepożądanych w polskich systemach wodociągowych.

Słowa kluczowe: sieć wodociągowa, ocena konsumencka, analiza funkcjonowania systemu zaopatrzenia w wodę

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MEMBRANE PROCESSES IN THE UTILIZATION OF WASTEWATER GENERATED DURING WASTE GASIFICATION

WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI WÓD POPROCESOWYCH ZE ZGAZOWANIA ODPADÓW

Abstract: Gasification, regardless of the fuel type, is always accompanied with the generation of highly loaded wastewater. Those streams are formed during cooling and cleaning of process gas and comprise of tars, condensed water vapor and a range of organic and inorganic compounds. Nowadays, there are no treatment systems of those wastewater, especially dedicated to small and medium size gasification plants, operated with alternative fuels, *ie* biomass and wastes, what is the main limitation in the technology popularization and industrial commercialization. On the other hand, conventional methods proposed for the treatment characterize with the narrow spectrum of action dedicated, mainly to the removal of tar substances. In the presented paper the possibility of utilization of waste gasification wastewater by means of membrane processes is proposed. The technology was based on the two stage treatment system enabling the separation of tars by spontaneous sedimentation/floatation and low pressure drive aqueous phase filtration. Polymeric, ultrafiltration membranes of various cut off were investigated due to the contaminants removal effectiveness and capacity. It was shown, that the use of membrane processes assures the concentration of soluble organic contaminants to the rate enabling their recycle to the gasifier. The filtrate obtained during the process characterized with much decreased load of contaminants and after the proper polishing could be directly deposited to the environment.

Keywords: wastewater, tars, gasification, alternative fuels, SRFs

Introduction

The process of gasification of alternative fuels, *ie* wastes formed to SRFs (solid recovered fuels) or biomass, is energetically efficient and economically attractive thermal operation, which is regarded as one of the most promising method for energy production [1–4]. The process comprises of several stages, which usually occur in one

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reactor, called gasifier, organized in co-current or counter-current flow, which is schematically presented in Fig. 1.

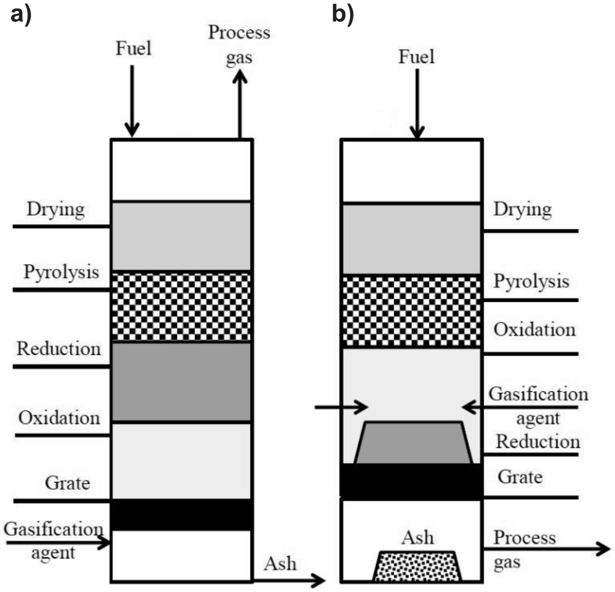

Fig. 1. Fixed bed reactor for alternative fuel (SRF) gasification: a) counter-current mode, b) co-current mode

The mechanism of gasification process can be defined as a series of thermochemical reactions, which occur during pyrolysis and combustion. As a results of those reactions and at the use of a proper gasification agent (air, oxygen, water vapor, hydrogen, carbon dioxide, etc.) and increased temperature (above 800^{o}C) the conversion of solid substrates to combustible gaseous products, which is a mixture of carbon oxide and dioxide, hydrogen, methane and water vapor, takes place [5–7].

The gas obtained during the gasification process, except of the gaseous products, contains also a range of contaminants, which need to be removed in case, when further gas processing, *eg* in chemical synthesis or cogeneration, is predicted. Two gas cleaning methods are used for this purpose *ie* wet and dry systems. In the former method, the contaminants are usually washed out from the gas by means of water or oil absorption in scrubbers and the simultaneous cooling of gas due to its contact with the scrubbing medium occurs. In the latter method, the condensable contaminants present in gas stream appear in the form of aqueous-tar mixture, while solids (dusts and ashes) are usually removed on filters [8–10].

Regardless of gas cleaning method, the highly loaded wastewater containing tars and aqueous stream contaminated with water soluble organic compounds is formed (Fig. 2). The proper management of the stream is said to be one of the most important condition for popularization of biomass gasification, especially in case of medium and small systems. Nowadays, only large installations equipped with technologically complete

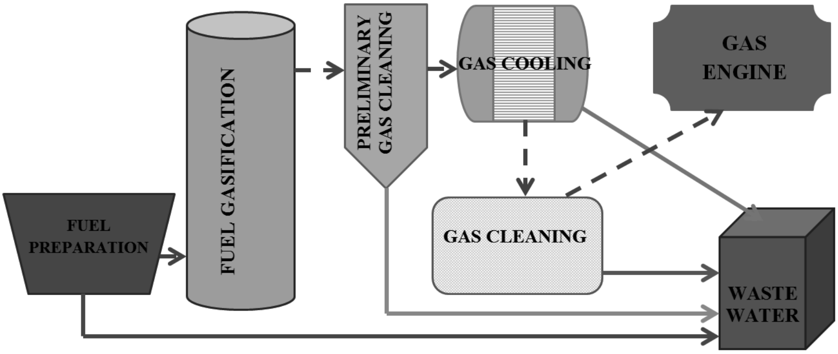

Fig. 2. Places of formation of wastewater streams generated during gasification process

wastewater treatment plants are found to be commercially available, and the lack of the method for proper utilization of smaller amount of wastewater is one of the main reason [11, 12].

In the paper, the technique for the treatment of biomass gasification wastewater obtained during the dry cleaning of gas (*ie* tar-water condensate) is discussed. The system was based on the membrane separation, and different types of membranes were used.

Methods

The process of membrane filtration was carried out in the laboratory installation by KOCH Membrane Systems, model KMS Cell CF1. The device is equipped with the feed tank of volume 0.5 dm^3 and two membrane cells arranged in a series of common separation area of 56 cm^2. The construction of the device enables to run the process in the cross flow mode. The scheme and the photography of the installation is shown in Fig. 3.

In the study two types of membranes differ in membrane material and molecular weight cut off, *ie* polyvinylidene microfiltration membrane of pore size 0.3 μm

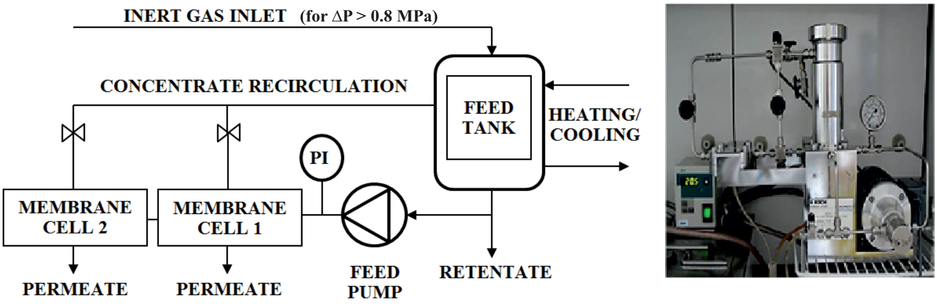

Fig. 3. The scheme and the photography of laboratory installation for membrane filtration KMS Cell CF1

(MF-PVDF-0.3) and polysulphone of cut off 30 kDa (UF-PS-30) were used. The filtration of gasification condensate was preceded by both, membrane conditioning and characterization with deionized water at transmembrane pressure of 0.1 MPa as well as with removal of tars from the treated medium by means of spontaneously occurring sedimentation and floatation of the fraction. Next, the filtration of the aqueous phase of the condensate was carried out at transmembrane pressures range equal to 0.1–0.3 MPa, increased by 0.05 MPa by the process. The difference in process pressures resulted of the dependences observed during the membrane conditioning. Both process were carried out until 80% of the feed volume was recovered in the form of permeate. After the process, the stream of deionized water was again measured, in order to evaluate the character of fouling of the membrane and possible interactions between membrane materials and contaminants present in the treated wastewater.

The feed and the filtrates obtained during the process were characterized due to the value of pH, specific conductivity, chemical oxygen demand, ammonia nitrogen and dry mass content. pH and specific conductivity were measured with the use of dedicated probes, chemical oxygen demand and ammonia nitrogen were indicated by means of HACH Lange methodology, while dry mass content was analyzed by means of conventional thermal method at 105^{o}C temperature.

Results and discussion

In Fig. 4, the capacities of clean membranes expressed as the volumetric deionized water flux at 0.1 MPa transmembrane pressure are compared.

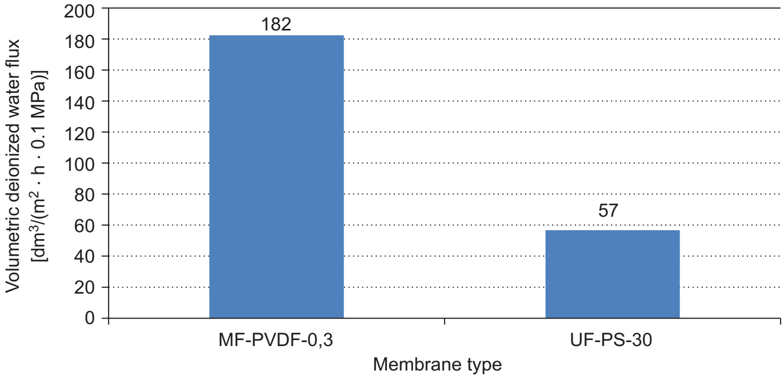

Fig. 4. The comparison of capacities determined for clean membranes

The difference in capacities between both membranes was found to be significant, and microfiltration membrane was three times more efficient than UF membrane. After the membrane characterization, the filtration of SRFs gasification wastewater was made. The processes were carried out at the transmembrane pressure range of 0.1–0.3 MPa. The results of the filtration are shown in Figs. 5 and 6.

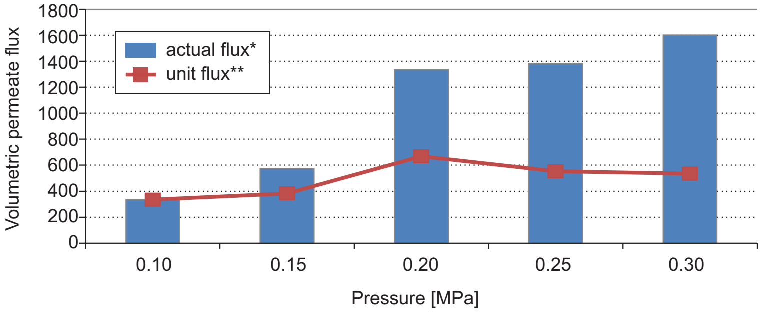

Fig. 5. The capacity of MF-PVDF-0.3 membrane obtained during SRF gasification wastewater filtration * [$dm^3/(m^2 \cdot h)$]; ** [$dm^3/(m^2 \cdot h \cdot 0.1$ M Pa)]

It was observed, for MF-PVDF-0.3 membrane, that the flux constantly increased with the pressure increase, however values obtained for 0.20 and 0.25 MPa pressure were comparable. Nevertheless, where the actual fluxes were recalculated into unit fluxes, *ie* at 0.1 MPa transmembrane pressure, it was observed, that the flux was increasing only up to 0.2 MPa pressure and then it started to decrease. It indicated that the pressure 0.2 MPa was the critical pressure for MF-PVDF-0.3 membrane, *ie* the one above which the improvement of membrane capacity was negligible.

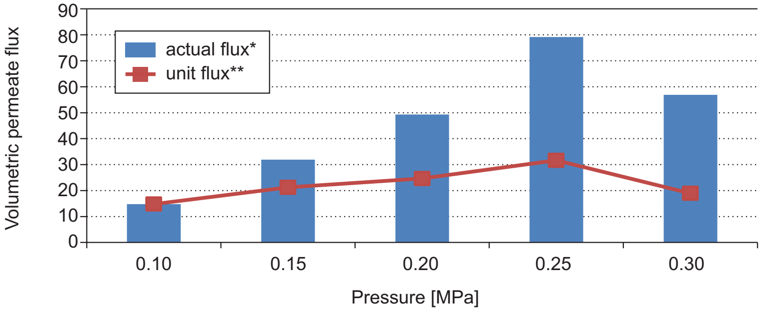

Fig. 6. The capacity of UF-PS-30 membrane obtained during SRF gasification wastewater filtration * [$dm^3/(m^2 \cdot h)$]; ** [$dm^3/(m^2 \cdot h \cdot 0.1$ MPa)]

In case of UF-PS-30 membrane the increase of the flux was observed only up to 0.25 MPa pressure, and then the decrease in the capacity was obtained. The same behavior was also noticed for the membrane unit flux. Hence, 0.25 MPa pressure was established as the critical one for UF-PS-30 membrane, and, in opposite to MF-PVDF-0.3 membrane, the pressure at which the impact and severness of fouling could be clearly marked.

In Fig. 7, the comparison of unit fluxes obtained at various transmembrane pressures for both membranes, is shown.

It was noticed, that the difference between fluxes of particular membranes obtained during wastewater filtration, where much higher than ones of deionized water. In case

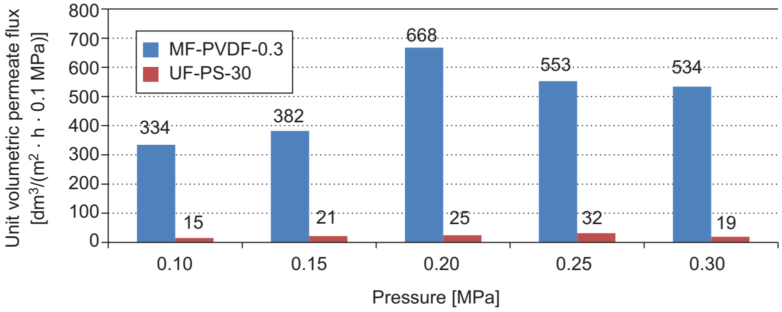

Fig. 7. The comparison of capacities obtained for both membranes used to SRFs gasification wastewater filtration

of MF-PVDF-0.3 membrane the deionized water flux was only 3 times greater than UF-PS-30 flux, while wastewater flux was ca. 20 higher for the former membrane type. Hence, it was concluded, that the process efficiency depended not only on the transmembrane pressure applied, but also on the interactions between membrane material and the treated medium. UF-PS-30 membrane was found to be more resistant than MF-PVDF-0.3 membrane.

Nevertheless, in order to confirm the impact of the wastewater properties on the membrane, after the process was finished, the volumetric deionized water flux was again measured for both membranes. The obtained results, in the form of relative permeate flux, *ie* the ratio of deionized water flux measured after the process to the deionized water flux measured for clean membrane, are shown in Fig. 8.

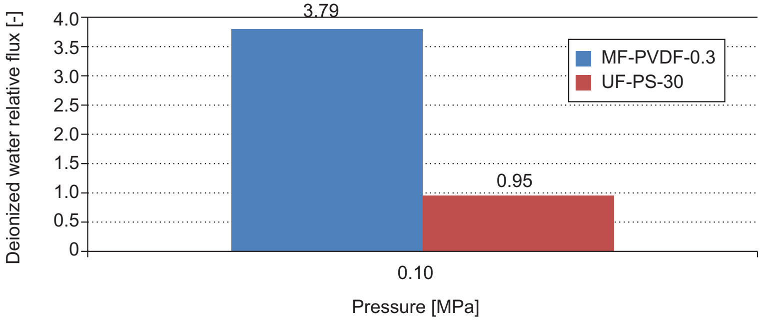

Fig. 8. The comparison of deionized water relative fluxes determined for both membranes

The comparison of relative fluxes of deionized water showed that there was a significant difference between interactions of membrane materials and treated medium. The contact of the wastewater with polyvinylidene fluoride membrane (PVDF) caused the great increase in the material hydrophilicity, hence the deionized water flux measured after the process was almost 4 times greater than the one measured before the process. On the other hand, the polysulphone membrane was found to be slightly fouled.

However, the capacity of the process must be accompanied with the efficiency of contaminants removal. In case of such open membranes the removal rate should be measured only for organic contaminants marked as COD and dry mass content. The obtained results are showed in Table 1.

Table 1

The values of parameters of process streams and removal rates of contaminants

Parameter	Unit	Feed	MF-PVDF-0.3 permeate	UF-PS-30 permeate	MF-PVDF-0.3 removal rate	UF-PS-30 removal rate
pH	—	3.51	7.63	7.61	—	—
COD	[mgO$_2$/dm^3]	67 000	62 000	42000	8	38
Dry mass	[mg/dm^3]	593	90	42	85	93

Both filtrations resulted in the production of filtrate, which needed to be undergone to further treatment. Nevertheless, the significant reduction in dry mass content, reaching 93% in case of UF-PS-30 membrane was shown. Additionally, this membrane enabled to remove almost 40% of contaminants marked as COD. Hence, if a combined system of membrane filtration and *eg* activated carbon adsorption was applied to such a wastewater purification, it was UF-PS-30 membrane, which was suggested to be used.

Summary and conclusions

The wastewater generated during solid fuels gasification, equipped with the dry gas cooling and cleaning system, is a highly loaded tar-aqueous mixture of a wide range of contaminants. The proper management of the stream is said to be crucial for popularization and commercialization of small and medium biomass gasification system. In this paper, a study on the treatment of aqueous phase of the stream by means of membrane filtration is discussed. The feed to the membrane process was the water fraction of the tar-water condensate, from which tar fraction was removed by means of spontaneous sedimentation and flotation. Two types of membranes were used, polyvinylidene fluoride microfiltration of pore size 0.3 μm 5 and polysulphone ultrafiltration of cut off 30 kDa. It was found, that both membranes should be followed by further treatment, *eg* activated carbon adsorption, in order to enable the deposition of the treated stream to sewage system or to the environment. In case of process capacity, significant differences were found between membranes, and polyvinylidene fluoride membrane was significantly affected by the treated medium, *ie* its hydrophilicity increased. On the other hand, polysulphone membrane was slightly fouled after the process. However, considering both, the membrane capacity and the effectiveness of contaminants removal, it was concluded, that the process should be carried out with the use of UF-PS-30 membrane.

Acknowledgements

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WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI WÓD POPROCESOWYCH ZE ZGAZOWANIA ODPADÓW

Instytut Chemicznej Przeróbki Węgla, Zabrze

Abstrakt: Proces zgazowania, niezależnie od typu zastosowanego paliwa, wiąże się z powstawanie wysoko obciążonych ciekłych strumieni odpadowych. Wody te formowane są podczas chłodzenia i oczyszczania gazu procesowego i stanowią mieszaninę smół, skroplonej pary wodnej oraz szeregu związków organicznych i nieorganicznych. Brak odpowiednich rozwiązań systemowych, przede wszystkim w przypadku małych i średnich instalacji powoduje, że ich popularyzacja i komercjalizacja na skalę przemysłową są znacznie ograniczone. Obecnie proponowane metody utylizacji ciekłych strumieni odpadowych charakteryzują się zawężonym spektrum działania, skupiając się na jednym z aspektów problemów jakim jest obecność substancji smolistych.

W niniejszej pracy zaproponowano możliwość zagospodarowania ciekłych strumieni odpadowych z procesu zgazowania SRF z wykorzystaniem technik membranowych. Rozwiązanie oparto o dwustopniowy system oczyszczania umożliwiający separację smół poprzez samoistnie zachodzące procesu sedymentacji i flotacji oraz niskociśnieniową filtrację membranową. W badaniach wykorzystano polimerowe membrany mikro i ultrafiltracyjnej o różnych granicznych masach molowych. Wykazano, że zastosowanie procesów membranowych umożliwia zatężenie rozpuszczonych związków organicznych w stopniu umożliwiającym ich zawrócenie do reaktora oraz powstawanie filtratu o obniżonym ładunku zanieczyszczeń, który, po odpowiednim podczyszczeniu, może zostać odprowadzony do kanalizacji lub do środowiska.

Słowa kluczowe: ścieki, smoły, zgazowanie, membrany, SRF

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Alicja MACHNICKA[1*] and Ewelina NOWICKA[1]

THE INFLUENCE OF MECHANICAL AND THERMAL DISINTEGRATION ON GRAVITATIONAL SEPARATION OF SURPLUS SLUDGE

WPŁYW DEZINTEGRACJI MECHANICZNEJ I TERMICZNEJ NA SEPARACJĘ GRAWITACYJNĄ OSADU NADMIERNEGO

Abstract: The primary effect of sewage sludge disintegration process is the physical, chemical or biological change of their structure, which causes destruction of flocs, fragmentation of microbial cells and thus release of cell contents into the surrounding liquid. Pre-treatment of the sludge can be used for the process of thickening and dewatering of sludge.

In this paper, the influence of hydrodynamic, microwave and freezing/thawing disintegration on selected properties of gravitational surplus activated sludge, were assessed. The scope of the research included the parameters characteristic of the sedimentation process, *ie* sludge density index (*SDI*), sludge volume index (*SVI*), sludge thickening speed (v), sludge concentration (C_i) and changes in the liquid phase of sludge chemical oxygen demand (*SCOD*) and turbidity.

The obtained results as well as performed calculations have confirmed the impact of used disintegration in terms of improving the properties of surplus activated sludge.

Keywords: hydrodynamic cavitation, microwave radiation, dry ice, surplus activated sludge, gravitational separation sludge

Introduction

Sludges are an inseparable element of each sewage treatment plant. They are created on different stages of a sewage treatment process line and they are a specific waste of the treatment processes. They are produced in primary settlement tanks – as the primary sludge and in secondary tanks – as the secondary sludge, they can be produced as a final product of chemical precipitation – as chemical sludge and also as a result of mixing of the primary sludge with a different one. However, they are always an essential technical problems due to large water content and mass as well as sanitary hazard. Recent

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regulations [1, 2] require the improvement of such unfavourable sludge properties by producers (sewage treatment plants).

Sludge thickening is a process of a technological line of sewage sludge in which separation of solids from liquids takes place. The sludge does not change its fluid consistency and an increase of dry weight sludge and reduction of its volume is obtained [3, 4]. Gravitation thickening takes place spontaneously in the devices called settlement tanks (primary, secondary, intermediate) or might be carried out in separate thickeners. These devices are thickening sludge in a continuous or periodic system.

Methods of sewage sludge pre-treatments are very expensive and time consuming and do not always give satisfactory results. A selection of an appropriate method of processing is necessary, while maintaining a relatively low investment and operating costs.

The main task of the sludge conditioning process is to transform its properties and composition to make thickening and drainage more effective.

Disintegration methods are processes of initial conditioning of sewage sludges. They are based on destroying flocs and rapture of microorganisms cells envelopes with the help of external forces and release of intracellular substance into the liquid phase of the sludge [5]. They are used mainly to improve efficiency of biological degradation processes, reduce a phenomenon of foaming, sludge swelling and lowering of sludge volume index.

The applied and tested disintegration methods include, the following: mechanical [6, 7], chemical [8, 9], biological [10], thermal [11, 12] and hybrid [13].

The article describes the influence of the applied disintegration methods – hydrodynamic cavitation, microwaves and dry ice, on gravitational separation of the surplus activated sludge.

Hydrodynamic cavitation results in formation of cavities (bubbles) filled with a vapour-gas mixture inside the flowing liquid, or at the boundary of a constriction devices due to rapid local pressure drop. Subsequently, the pressure recovers down the constriction (valve or nozzle) and causes cavities to collapse. The collapse of cavitation bubbles is defined as implosion and the forces associated with results in mechanical and physique-chemical effects. The physical effects include the production of shear forces, shock waves, generating local high temperatures and pressures, whereas the chemical effects result into the generation of radicals *eg* formation of reactive hydrogen atoms and hydroxyl radicals which can recombine to form hydrogen peroxide [14–16].

One of the sewage sludge disintegration methods is the usage of microwaves. Microwaves are a form of electromagnetic radiation with wavelengths ranging from one meter to one millimeter; with frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm) [17]. Some materials can absorb microwaves. Materials which absorb the energy of microwaves are heated. This is a property of dielectric substances, for example of water. In dielectrics, microwaves cause a dipole polarization. Dielectrics have a dipole structure, this causes rotation of the molecules. Microwaves vary from other electromagnetic waves in the fact that they generate the molecular move in the alternating electric field without breaking the stability of chemical bonds. The energy carried by the microwave radiation is considerably smaller than the energy of a chemical bond decay. Electromagnetic waves undergo all physical phenomena that are characteristic for wave motion [18, 19]. They can be transmitted or absorbed and also undergo reflection, refraction, deflection, interference and polarisation. Microwave radiation can be absorbed by matter through dipolar polarisation (dielectric), which is responsible for the microwave heating effect and through ionic conductivity.

Another method of sewage sludge disintegration is freezing/thawing. Several conceptual models have been developed to describe the interaction between the ice and sludge particles during freezing [20]. When the ice front approaches sludge flocs, it also pushes the flocs at a certain speed. Depending on the freezing rate and other factors, the flocs are entrapped in ice or pushed ahead of the ice front. Once the flocs is trapped in the ice, dewatering process initiates, resulting in releasing of bound water (dehydration) and more compacted sludge particles [20, 21]. On the other hand, advancing flocs ahead of the ice front results in the thickening of flocs [21]. Moreover, water freezing in microorganisms is caused break-up of cells walls and release to liquid phase organic/inorganic matter [22].

Materials and methods

The research material was surplus activated sludge (from the secondary settling tank) with a concentration of dry solid – in average – 11.81 g $\cdot$ dm^{-3}. Sewage sludge samples were taken from a large municipal waste water treatment plant in Silesia region. Wastewater treatment plant uses advanced processes simultaneously, biological removal of carbon compounds of nitrogen and phosphorus (*EBNR* – Enhanced Biological Nutrients Removal). The treatment plant was designed for the flow of 12 000 m^3 $\cdot$ d^{-1}. For the time being, the amount of flowing sewage is ca. 90 000 m^3 $\cdot$ d^{-1}, solid retention time ca. 14 days and concentration of activated sludge in the bioreactor 4.32–4.64 mg $\cdot$ dm^{-3}.

Disintegration methods of sewage sludge – the disintegration by hydrodynamic cavitation

The sample of surplus activated sludge (volume 25 dm^3) was treated by hydrodynamic cavitation. The experimental set up consisted of a 1 200 000 Pa pressure pump, rating 0.54 kWh, output 500 dm^3 $\cdot$ h^{-1}, which recirculated sludge from a container, through a 1.2 mm cavitation nozzle. The process was carried out for 15, 30, 45 and 60 minutes, which corresponded to 3, 6, 9 and 12 multiplicity flow by the cavitation nozzle.

The disintegration by microwave radiation

The sample of surplus activated sludge with the volume of 5 dm^3 was subjected to the microwave destruction. Disintegration process was carried by the frequency of microwaves 2.45 GHz and nominal power 900 W. Disintegration was carried out over periods of 30, 60, 90 and 120 seconds.

Such a short time resulted from avoiding the thermal (boiling) effect which is rising at longer acting of microwaves.

The disintegration by freezing/thawing

Dry ice, sometimes referred to as "cardice" or as "card ice", is the solid form of carbon dioxide. It is used primarily as a cooling agent. At pressures below 519 797.25 Pa and temperatures below 217.15 K (the triple point), CO_2 changes from a solid to a gas with no intervening liquid form, through a process called sublimation. The opposite process is called deposition, where CO_2 changes from the gas to solid phase (dry ice). At atmospheric pressure, sublimation/deposition occurs at 195.15 K. The density of dry ice varies, but usually ranges between about 1.4 and 1.6 $g \cdot cm^{-3}$ [23].

For disintegration of surplus activated sludge (1 dm^3), the following volume ratios of the surplus sludge to dry ice were used, *ie* 1 : 0.25; 1 : 0.5; 1 : 0.75; 1 : 1.

Sewage sludge at room temperature mixed with a certain volume of dry ice. The samples were then thawed at room temperature until completely dry ice sublimate.

Analytical method

All chemical analyses were performed for samples before and after each phase of disintegration. Soluble Chemical Oxygen Demand (*SCOD*) value and turbidity value were determined according to the procedures given in the Standard Methods for Examination of Water and Wastewater [24].

In the taken samples of surplus activated sludge content of suspended solids (*SS*) were determined according to the Wastewater Engineering Treatment and Reuse [25].

$$X = \frac{(a-b)\cdot 1000}{c} \tag{1}$$

where: X – dry weight sludge [$g \cdot dm^{-3}$];
a – weight of the crucible with the dried sludge [g];
b – weight of the crucible without sludge [g];
c – sludge weight used for the test [g].

For colorimetric determinations, a spectrophotometer HACH DR5000 was applied. Chemical analyses were measured for samples before and after each time of disintegration (microwave, hydrodynamic process) and for each volume ratio of sludge to dry ice.

The results here presented were performed 10 times, arithmetic average was calculated. The standard deviation was determined according to the estimator of the highest credibility in STATISTICA 6.0.

Sludge density index (*SDI)*, sludge volume index (*SVI*), surplus activated sludge thickening speed (*v*) and concentration of sludge (C_i)

The scope of the study included determining the sedimentation kinetics based on the curves of sludge falling and thickening speed. Kynch's theorem was applied here, which says that the falling speed of sludge particles is a function of suspension concentration in immediate vicinity [26].

Sludges sedimentation has been observed in cylinders of $V = 1000\ \mathrm{cm}^3$ capacity and cross-sectional area of $F = 26.4\ \mathrm{cm}^2$.

The following calculations have been made in the sludge samples, both in control ones and those subjected to the process of disintegration, based on Tchobanoglous et al [25]:

Sludge density index (*SDI*) – Donaldson index [$\mathrm{g \cdot cm^{-3}}$], based on the following formula:

$$SDI = \frac{m}{V \cdot 10} \tag{2}$$

where: m – mass of total suspensions in a sample [$\mathrm{g \cdot dm^{-3}}$];
V – volume of sludge read after 30 minutes of sedimentation of a sample of 1000 cm^3 volume [$\mathrm{cm^3 \cdot dm^{-3}}$].

Sludge volume index (*SVI*) – Mohlman index [$\mathrm{cm^3 \cdot g^{-1}}$], based on the following formula:

$$SVI = \frac{1}{SDI} \tag{3}$$

Sludge thickening speed (*v*) [$\mathrm{mm \cdot min^{-1}}$], based on the following formula:

$$v = \frac{v_r - v_n}{t_n} \tag{4}$$

where: v_r – sludge column height in sedimentation process 400 [mm];
v_n – sludge volume for "n" sedimentation time [mm];
t_n – sedimentation time [s].

Sludge concentration (C_i) [$\mathrm{g_{d.w.} \cdot dm^{-3}}$] **and thickening time (t_i),** based on the following formula:

$$C_i = \frac{c_0 \cdot h_0}{h_i + v_i \cdot t_i} \tag{5}$$

where: c_0 – dry mass concentration [$\mathrm{g_{d.w.} \cdot dm^{-3}}$];
h_0 – initial height of the sludge layer [cm];
v_i – falling speed in the $h_i$point [$\mathrm{cm \cdot min^{-1}}$];
t_i – any falling time [min];
h_i – height of the sediment layer after t_i time [cm].

Results and discussions

Sewage sludges, after the process of sewage treatment contain form 97 to 99.5% of water [3]. During thickening of sewage sludges, the dry mass content in the sludges is increased as a result of sedimentation of sludge particles and their compression due to the influence of gravity and is followed by a reduction of free water content. This results in a reduction of their volume. Sewage sludges thickening can be treated either as pre-processing before fermentation or as initial processing before dehydration in a sewage treatment plant, which does not use anaerobic stabilization.

In the framework of research, various methods that can be applied to improve gravitational properties, are needed.

The aim of a disintegration method used (hydrodynamic cavitation, electromagnetic radiation, freezing/thawing) was to destroy the structure of flocs and microorganisms of the surplus activated sludge [16, 27, 28].

The studies conducted showed the effectiveness of the applied hydrodynamic cavitation and electromagnetic field depends mainly on the amount of operation time. While the effectiveness decomposition of surplus activated sludge by dry ice depended on the used value relationship: sludge to dry ice.

A measure of effectiveness of disintegration methods was organic matter release from a solid into a liquid phase of sludge, as well as an increase in turbidity of the sludge liquid. Releasing of organic substances, expressed in the value of *SCOD* and turbidity of liquid phases show the effectiveness of destroying flocs and microorganisms of the sludge.

After a 60-min of disintegration by hydrodynamic cavitation the *SCOD* values in sludge liquidphase changed from 63 mg $O_2 \cdot dm^{-3}$ to 2248 mg $O_2 \cdot dm^{-3}$ (Fig. 1). The microwave radiation and destruction with dry ice caused an increase of the *SCOD* value of about 549 mg $O_2 \cdot dm^{-3}$ and 840 mg $O_2 \cdot dm^{-3}$, respectively (Figs. 2–3).

Similar results of using microwaves received Grubel and Machnicka [17].

Many researchers examined release of the organic matter during the destruction of the flocs and microorganisms by freezing/thawing. The crystallization of intra-aggregate moisture was claimed to be responsible for the damage of cell membranes and release of intracellular substances to the surroundings. Release of organic matter in the process of freezing was examined by Hu et al [29]. They obtained more than 15% increase of *SCOD* value. This level of solubilization is comparable to that from sewage sludge sample treated at 100^{o}C for 30 min [30] and with 0.8 $W \cdot cm^{-3}$ of ultrasonication for 5 min [31].

The methods of mechanical and thermal disintegration causing microbiological destruction of the structure of flocs contributed to the increase of turbidity of a liquid phase of a sludge, mainly due to the release of intracellular substance and extracellular polymers. The supernatant turbidity of the surplus activated sludge amounted to 10 NTU (Figs. 1–3). Upon the process of hydrodynamic (60 min), microwave (120 s) and dry ice (the volume ratio of sludge to dry ice of 1 : 1) disintegration, the turbidity increased by 258 NTU (Fig. 1), 17 NTU (Fig. 2) and 101 NTU (Fig. 3), respectively.

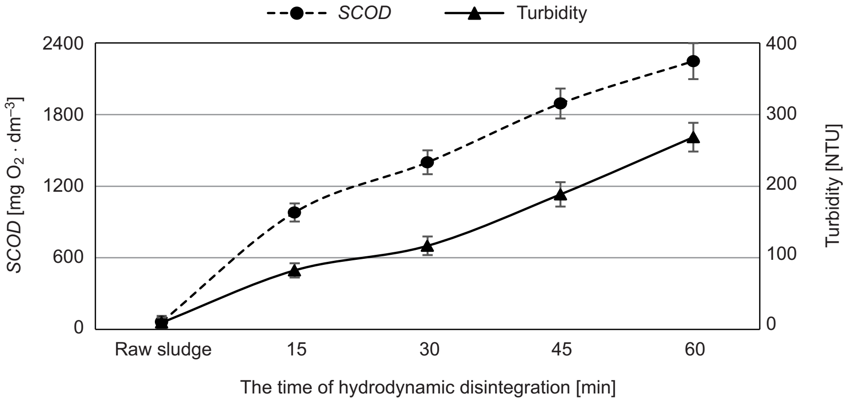

Fig. 1. The change of the *SCOD* value and supernatant turbidity during hydrodynamic disintegration

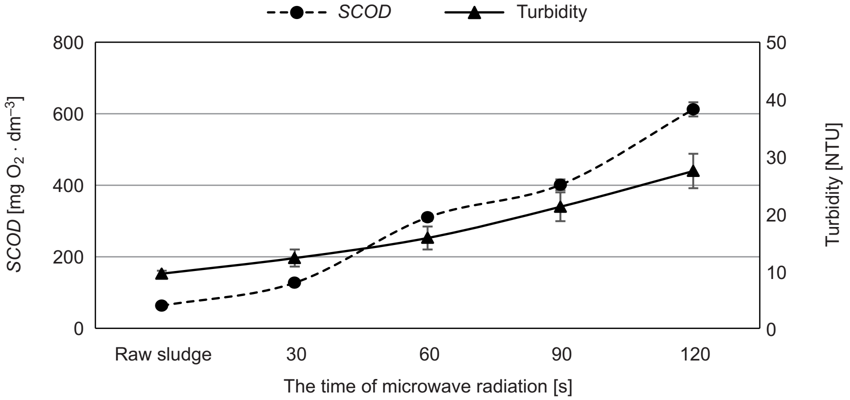

Fig. 2. The change of the *SCOD* value and supernatant turbidity during microwave disintegration

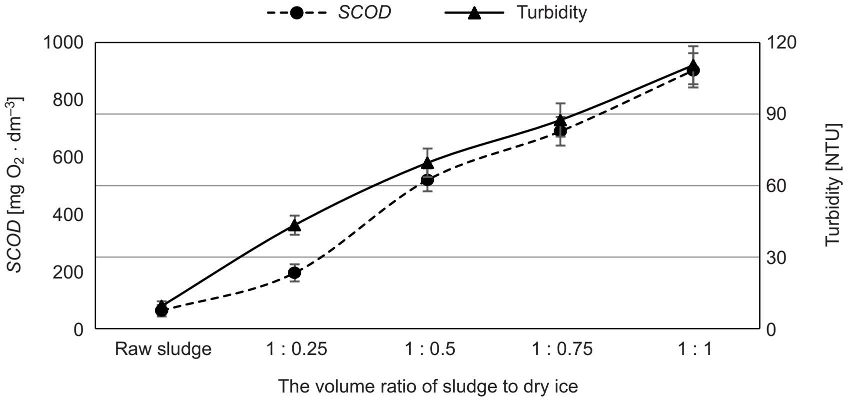

Fig. 3. The change of the *SCOD* value and supernatant turbidity duringfreezing/thawing disintegration

Interaction of electromagnetic field, hydrodynamic cavitation and low temperature on the surplus activated sludge resulted in changes of *SDI* and *SVI* in comparison to the sample of sludge, which has not been subjected to disintegration. *SDI* is defined as a mass of total suspension expressed in grams in the volume of 100 cm^3 of sludge subjected to a 30 min of sedimentation process [32]. However *SVI*, *ie* Mohlman's index, is the inverse of the Donaldson's index. It is defined as the volume (in cm^3) occupied by 1 gram of activated sludge after settling the aerated liquor for 30 min [32]. The change in the value of *SDI* and *SVI* depended on the applied action time of hydrodynamic cavitation and microwaves as well as the volume ratio of the sludge to dry ice (Figs. 4, 5).

SDI increased by 1.65 $g \cdot cm^{-3}$, 0.32 $g \cdot cm^{-3}$ and 1.17 $g \cdot cm^{-3}$ for surplus activated sludge disintegration with hydrodynamic cavitation (60 min), microwaves (120 s) and thermal disintegration (the volume ratio of sludge to dry ice of 1 : 1), respectively (Fig. 4). A disruptive action of the applied sludge conditioning methods decreased the value of *SVI*. The action of hydrodynamic cavitation on the sludge caused the biggest change in the value of *SVI* in comparison to the influence of magnetic field and freezing/thawing (Fig. 5). In case of a sludge disintegrated with a hydrodynamic cavitation within 60 min, the value of *SVI* amounted to 39 $cm^3 \cdot g^{-1}$ (Fig. 5). Reduction in the index value below 100 $cm^3 \cdot g^{-1}$ (Fig. 5) shows a high ability of surplus activated sludge to dehydration as a result of conditioning processes used.

Destruction (mechanical and thermal) of flocs and microorganisms of the surplus activated sludge caused changes in its structure and properties. The release of fixed water and biologically fixed water appeared, which contributed to faster dewatering and better thickening of the sludge.

Another parameter that was calculated was the thickening speed (v) of the activated sludge depending on the time of exposure of surplus activated sludge to applied

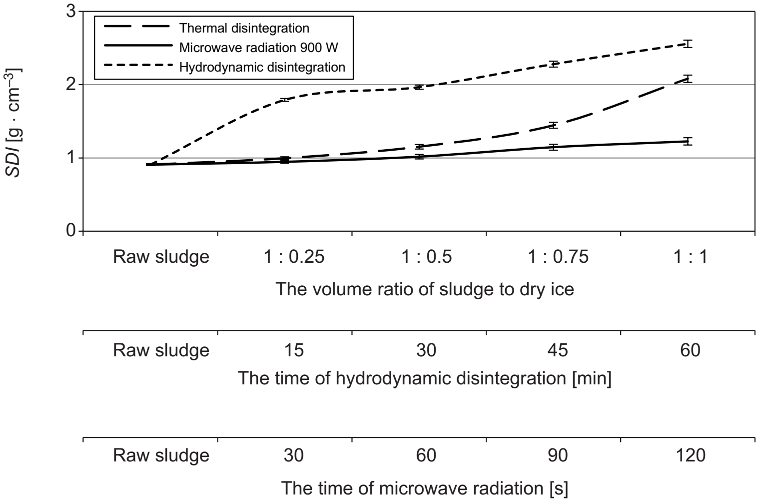

Fig. 4. The change of *SDI* during hydrodynamic, microwave and freezing/thawing disintegration

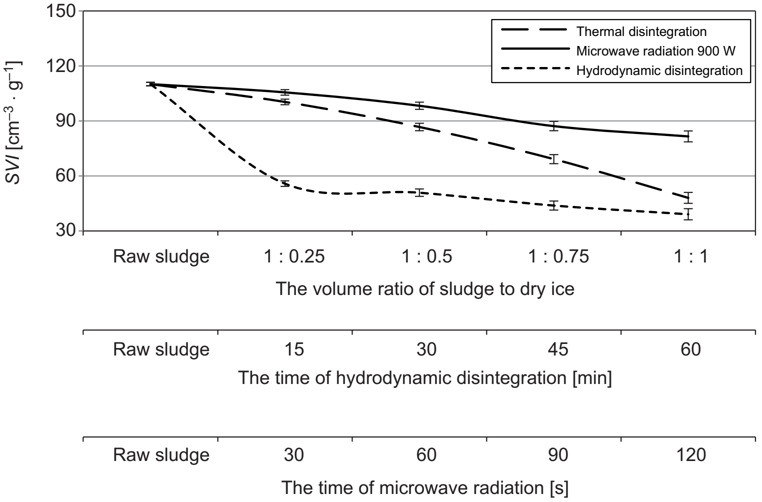

Fig. 5. Change of *SVI* during hydrodynamic, microwave and freezing/thawing disintegration

mechanical disintegration and volume ratio of sludge to dry ice. It is one of the most important parameters of assessing the sludge thickening process. Sludge thickening speed (v) is a process of particles falling of a solid in liquid by the action of gravity and inertia forces. A necessary condition for the occurrence of the phenomenon is the difference in density of solid and liquid. In case of gravitational separation, zonal falling matters. This type of falling is characteristic for flocculating suspensions or non-flocculating suspension but with a very high concentration [32]. Changes of thickening speed (v) of the surplus activated sludge under the influence of preparing with hydrodynamic cavitation, microwaves and thermal are presented in Figs. 6–8. An intensive increase in sludge thickening speed (v) of disintegrated sludge takes place in the first 5 minutes of sedimentation. It was connected with an earlier destruction of flocs and then their flocculation, formation of aggregates of higher density and lower porosity in respect to sludge deposits before disintegration.

Similar results of increase of a sedimentation phase (falling speed) of sewage sludge for thermal disintegration have been obtained by Hu at al [29] and Bien [33] for ultrasonic disintegration.

Changes in concentration of sludge mass depending on the time of sedimentation are presented in Figs. 9–11.

The initial dry weight of sludge without disintegration was 8.35 g · dm^{-3}, and after 30 min sedimentation value was 8.95 $g_{d.w.}$ · dm^{-3}. On the basis of obtained results and calculations, sludge concentration (C_i) increases with the time of exposure to a disintegration method (Figs. 9–11). After disintegration of the surplus activated sludge in a hydrodynamic process (60 min), obtained sludge concentration (C_i) increase from 8.57 $g_{d.w.}$ to 23.74 $g_{d.w.}$ · dm^{-3}, after microwave disintegration to 12.10 $g_{d.w.}$ · dm^{-3}, and after thermal disintegration to 19.77 $g_{d.w.}$ · dm^{-3}. The concentration of sludge which has not been subjected to disintegration changes definitely less intensively. Extending the

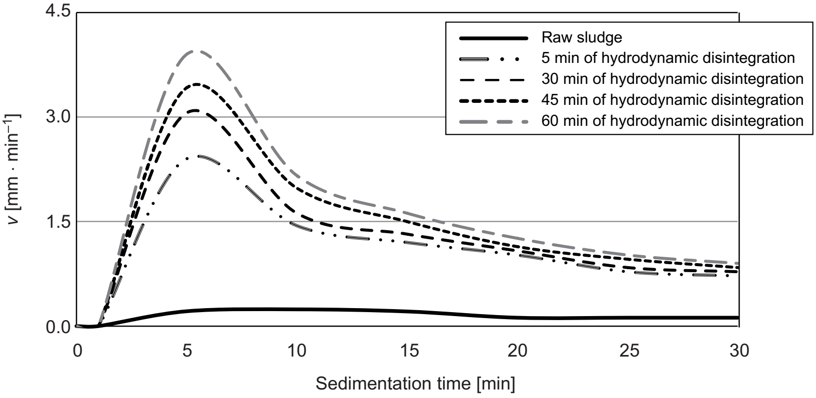

Fig. 6. Sludge thickening speed (*v*) during hydrodynamic disintegration

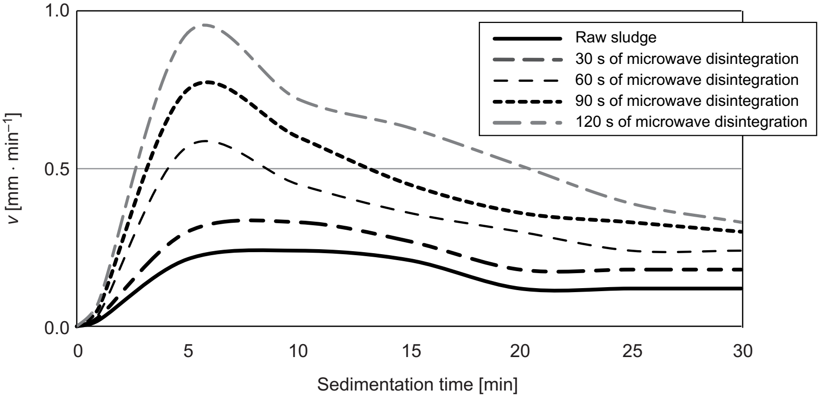

Fig. 7. Sludge thickening speed (*v*) during microwave disintegration

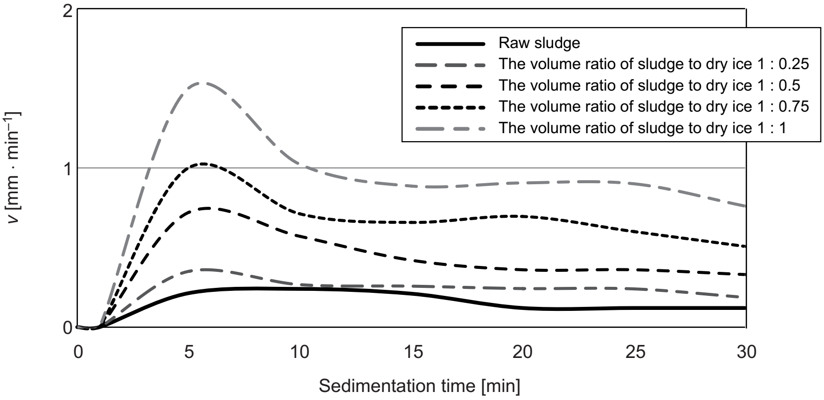

Fig. 8. Sludge thickening speed (*v*) during disintegration with dry ice

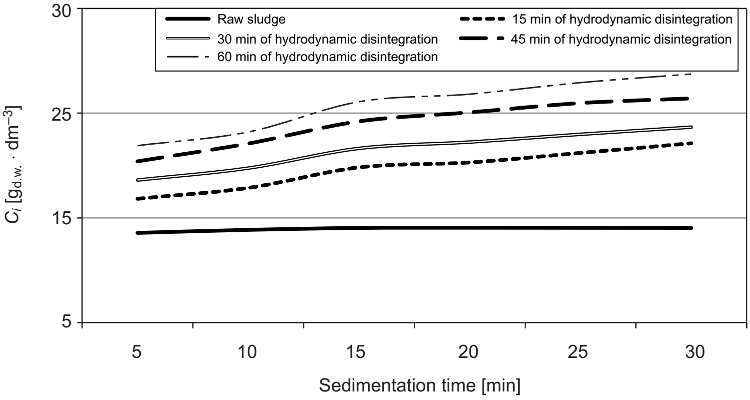

Fig. 9. Changes of sludge concentration (C_i) during hydrodynamic disintegration

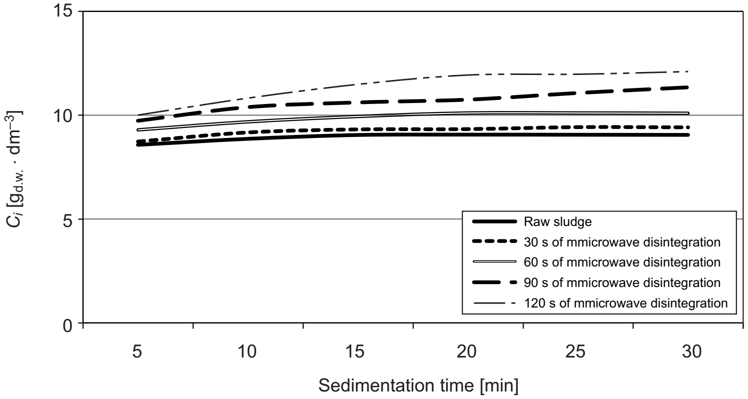

Fig. 10. Changes of sludge concentration (C_i) during microwave disintegration

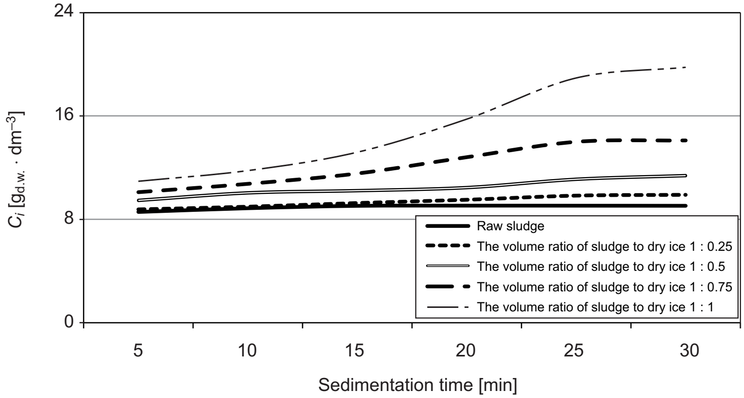

Fig. 11. Changes of sludge concentration (C_i) during disintegration by dry ice

duration of disintegration and increasing the volume ratio of sludge to dry ice, causing destruction of flocs and cytoplasmic membrane and/or cell wall of microorganisms, to faster water release during thickening as well as connecting previously fragmented flocs into larger aggregates. Water in the sewage sludge is present in free and bound water (free water, colloid water, capillary water, biological water). Free water is bound to sludge fractions. Can be separated from the sludge *eg* thickening of gravity. Colloid water is more difficult to separate. This water is related to the sludge particles, the forces of surface tension. This water can be removed only after the destruction of the structure flocs sludge. Capillary water is related to the forces of adhesion and cohesion (is removed, *eg* by centrifugation or drying). However, biological water is removed by destroying the cell covers (*eg* the methods of disintegration).

In the process with the use of hydrodynamic cavitation, the destruction of flocs and consistent structure of microorganisms cells – disrupt/lysis – took place by an increase in the speed of flow of disintegrated medium caused by reducing the cross-sectional area of the stream (the use of cavitation nozzle with a spraying angle of 0^o and a diameter of 1.2 mm). As a consequence, this caused local pressure drop of liquid (sewage sludge) to a boiling pressure. Dynamic pressure field of the liquid caused the phenomenon of mechanical cavitation associated with creation, zooming and vanishing of bubbles or other closed areas (caverns) containing a few liquids (a sewage sludge), gas or steam-gas mixture. Implosion of cavitation bubbles caused [34–36] high mechanical cutting (shearing) stress, which was so large that not only the biological phase of the sludge might have been destroyed, but even the solid structures.

The direct effect of any kind of radiation on a living cell is determined by its absorption, whereas the cellular components absorb waves of specific lengths. Microwave radiation is most effectively absorbed in the scope of wave of 10^{-3} m length [37]. Therefore, the effective application of microwave energy depends mainly on the time of its action (a radiation dose).

The process of freezing with dry ice/thawing was also the cause of destruction of flocs structure of the sludge and “cold” death of microorganisms caused by a group of factors such as: freezing and thawing speed, chemical composition of the living environment, a species of bacteria, time of freezing, temperature. However, mechanical destruction of the cells is done with the use of ice crystals, which tears them from the inside or damage them from the outside [38]. Microorganisms killed as a result of freezing/\thawing, lose their cellular components to the ground (environment). The greatest sensitivity to cold shock is shown mainly by Gram-negative bacteria and those which are in the logarithmic phase of growth. Their survival rate decreases by 10 000 times [37]. Gram-positive and Gram-negative bacteria (*eg Clostridium* sp. or *Salmonella* sp.) are common throughout the sewage sludge. Gram-negative bacteria are more vulnerable to adverse factors (physical, mechanical, chemical) such as, for instance: cavitation, microwave radiation or freezing than Gram-positive bacteria. These differences are explained by the chemical structure of the cell wall and primarily by the lower-concentration of peptidoglycan (murein) in these bacteria.

The test results obtained confirm a beneficial effect of an analysed methods of disintegration (hydrodynamic, microwave and thermal cavitation) on selected gravitational properties of the surplus activated sludge. Extending the duration of disintegration of mechanical processes and increasing the volume of dry ice to the surplus activated sludge results in elimination of expanding (volume decrease) and a change of sedimentation properties in relation to the disintegrated sludge.

However, an increase in turbidity of a liquid phase reveals effectiveness of disintegration but, at the same time, this means that a part of suspensions is suspended in the supernatant liquor. A load of suspensions in a sludge liquid might in a certain extent adversely affect gravitational separation of the sludge. There is, in fact, the probability of physical property changes due to negative modifications of solid particles and liquid-solid influences.

Conclusions

1. The disintegration of surplus activated sludge by means of hydrodynamic cavitation, microwave radiation and freezing/thawing treatment results in changing the state of organic matter from solid sediment to liquid (expressed as *SCOD*). *SCOD* increased from 63 mg $O_2 \cdot dm^{-3}$ to 2248 mg $O_2 \cdot dm^{-3}$ after 60 min of exposure to the hydrodynamic cavitation, 298 mg $O_2 \cdot dm^{-3}$ after 120 seconds of exposure to the microwave radiation and 749 mg $O_2 \cdot dm^{-3}$ for the volume ratio of dry ice to surplus activated sludge 1 : 1.

2. The sewage sludge conditioning processes have resulted in the turbidity increase of a liquid phase: hydrodynamic cavitation – 27 times, microwaves – 3 times and freezing/thawing – 11 times.

3. The disintegration of surplus activated sludge with mechanical methods and a thermal method caused, depending on the time of action and the volume ratio of sludge to dry ice, changes in its sedimentation parameters:

– an increase in the value of *SDI* (in relation to raw surplus activated sludge) amounted to 2.56 $g \cdot cm^{-3}$ for hydrodynamic disintegration, 1.23 $g \cdot cm^{-3}$ for electromagnetic field interaction and 2.08 $g \cdot cm^{-3}$ for the thermal process;

– *SVI* was reduced by 65% in case of hydrodynamic cavitation, by 26% in case of microwaves and 56% in case of freezing/thawing;

– an intensive increase of sludge thickening speed (v) of disintegrated sludge (hydrodynamicdisintegration, microwave radiation, freezing/thawing) takes place in the first 5 minutes of sedimentation;

– the concentration of the sludge (C_i) mass changes depending on the time of sedimentation. After disintegration of the surplus sludge in a hydrodynamic process (60 min), the sludge concentration (C_i) obtained amounted to 23.74 $g_{d.w.} \cdot dm^{-3}$ and after microwave disintegration to 12.10 $g_{d.w.} \cdot dm^{-3}$ and after thermal disintegration to 19.77 $g_{d.w.} \cdot dm^{-3}$.

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WPŁYW DEZINTEGRACJI MECHANICZNEJ I TERMICZNEJ NA SEPARACJĘ GRAWITACYJNĄ OSADU NADMIERNEGO

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Abstrakt: Podstawowym efektem procesu dezintegracji osadów ściekowych jest fizyczna, chemiczna lub biologiczna przemiana ich struktury, która powoduje destrukcję kłaczków, fragmentację komórek mikroorganizmów, a przez to uwolnienie treści komórkowej do otaczającej cieczy. Tak spreparowany osad może być wykorzystany w ciągu technologicznym przeróbki osadów, m.in. w procesach zagęszczania i odwadniania osadów ściekowych.

W niniejszej pracy przedstawiono wpływ dezintegracji hydrodynamicznej, mikrofalowej i termicznej na wybrane własności grawitacyjne osadu czynnego nadmiernego. Zakres badań obejmował parametry charakterystyczne dla procesu sedymentacji, tj. I.G.O., I.O.O., prędkość zagęszczania osadu, stężenie osadu oraz zmiany zachodzące w fazie płynnej osadu (ChZT$_{Cr}$ i mętność).

Uzyskane wyniki badań oraz przeprowadzone obliczenia potwierdziły wpływ zastosowanych metod dezintegracji na poprawę własności grawitacyjnych osadu czynnego nadmiernego.

Słowa kluczowe: kawitacja hydrodynamiczna, pole elektromagnetyczne, suchy lód, osad czynny nadmierny, własności grawitacyjne osadu

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BIOSORPTION OF Cr(III) FROM AQUEOUS SOLUTION BY ACTIVATED SLUDGE

BIOSORPCJA Cr(III) Z ROZTWORÓW WODNYCH PRZEZ OSAD CZYNNY

Abstract: The biosorption of Cr(III) from aqueous solution using activated sludge (AS) microorganisms was investigated under various experimental conditions regarding pH and temperature. Biosorption equilibrium parameters were determined based on the Langmuir and Freundlich isotherm model. The kinetic parameters were established using the equations of pseudo-first order and pseudo-second order. Moreover thermodynamic parameters have been calculated. Langmuir isotherm provided a better fit to the equilibrium data. The maximum experimentally determined sorption capacity 26.95 mg · g^{-1} obtained at 25°C and pH 5.0. The kinetics model of pseudo-second order row has been better describing experimental data. The negative value of free Gibbs energy (ΔG^0) proves spontaneous Cr(III) biosorption by AS biomass and its decreasing along with temperature increase. The negative value of enthalpy (ΔH^0) and entropy (ΔS^0) indicates exothermic process and limitation of degree of freedom Cr(III) ions on the interphase surface solution/biosorbent. FT-IR spectroscopy analysis indicated the contribution of carboxylate groups towards the biosorption of Cr(III) by AS.

Keywords: activated sludge, biosorption, chromium(III)

Activated sludge is a commonly used biological treatment process to remove dissolved and suspended organic compounds present in wastewaters. Although the standard role of municipal treatment plants was to remove dissolved and suspended organic compounds, metals are also frequently present in the municipal sewage due to industrial wastewaters admitted to the sewerage [1]. Chromium compounds polluting the environment in the form of wastewater, dust and solid waste are generated by many industries, such as mining, metal surface machining, fertilizers manufacturing, tanneries. Aqueous solutions can be purified of chromium by the processes of reversed osmosis, filtration, ion exchange, electrochemical precipitation or extraction [2]. Practical application of these methods is frequently inefficient, due to the generation of large

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volumes of secondary waste, technical or economic limitation, in particular regarding the waste water in which the metal concentration is not higher than 100 mg · dm^{-3} [3].

Adsorption on low cost adsorbents decreases the cost significantly. Biomass from wastewater treatment plants offers the adsorbent at low cost. The excess sludge produced in the process includes both living and nonliving microbial fractions consisting of a variety of species among which bacteria and protozoa [4, 5]. Organic compounds such as carboxyl groups, acidic polysaccharides, lipids and amino acids existing in bacteria cell membrane and wall effectively take part in heavy metal biosorption [4]. Solution pH, temperature, type and quantity of chemical groups, surface area, type of impurities to be adsorbed, type and amount of biomass as well as the presence of other ions are the main factors influencing the metal sorption capacity.

The aim of the presented research were to study the adsorption of chromium(III) ions by activated sludge microorganisms from a wastewater treatment plant. During the experiments, the influence of pH and temperature on the biosorption process was assessed; statics, kinetics and thermodynamic parameters of the process were described.

Material and methods

Activated sludge (AS), a complex consortium of micro-organisms mainly containing bacteria obtained from wastewater treatment plant located in Opole (Poland). Dry biomass pellets were obtained after centrifugation in an MPW centrifuge model 215 at 4000 rpm and then dried at 50°C until constant weight. The stock solution of Cr(III) with 500 mg · dm^{-3} concentration was prepared from $Cr(NO_3) \cdot 9H_2O$. The stock solution was reduced, if necessary. Deionized water was used from all solutions.

Chromium(III) concentration before and after biosorption were determined by spectrophotometric method, using the cuvette tests (Hach Lange) and the Photolab Spectral (WTW, Germany) spectrophotometer. Before the measurement, the sample was clarified by vacuum filtration on Whatman membrane filters with 0.45 μm pore size. Biosorption experiments were conducted in Erlenmeyer's flasks with 250 cm^3 capacity, containing 50 cm^3 of Cr(III) solution. The flasks were incubated at the temperature of 30°C and agitated at 120 rpm. The initial pH of the solutions was determined with the use of 0.1 M NaOH and 0.1 M HCl.

The effect of pH on adsorption of Cr(III) onto AS biomass was studied at pH values within the range from 2.0 to 6.0, at the biosorbent addition of 2.0 g · dm^{-3}. The quantity of Cr(III) ions adsorbed by the AS biomass was calculated from the relation:

$$q_e = V \cdot (C_0 - C_e) / M \tag{1}$$

where: C_0 and C_e are the respective initial and equilibrium Cr(III) concentrations in the solution [mg · dm^{-3}], V the solution volume [dm^3], and M the adsorbent dry weight [g]. The metal sorption efficiency of the biomass was determined by the above-described procedure in every of the following experiments unless stated otherwise.

The impact of temperature at 20, 30 and 40°C on biosorption in equilibrium conditions was analysed for Cr(III) concentrations in the solution, within the range from

11.63 to 231.1 mg · dm^{-3}, adding 2.0 g · dm^{-3} of the biosorbent and setting the solution pH at 5.0. Langmuir [6] and Freundlich [7] isotherm models were applied to this study. Langmuir model is described by the equation:

$$q_e = q_{\max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \tag{2}$$

where: K_L – Langmuir constant [dm^3 · mg^{-1}], $q_{\max}$ – maximum adsorption capacity [mg · g^{-1}]. K_L and $q_{\max}$ values were determined on the basis of linear relations $1/q_e$ from $1/C_e$.

In addition, the Freundlich isotherm was also applied:

$$q_e = K_F \cdot C_e^{1/n} \tag{3}$$

where: K_F – constant of Freudlich equation [mg · g^{-1}], n – exponent of Freundlich equation. Both K_F, and n were calculated on the basis of direction coefficients and shift coefficients of the lines determined for the relation of $\ln q_e$ from $\ln C_e$.

Analyses of temperature at 20, 30 and 40°C, on the kinetics of the biosorption process, were carried out in Erlenmeyer flasks of 1000 cm^3 capacity, containing 400 cm^3 of Cr(III) solution with concentration of 50 mg · dm^{-3} and pH 5.0.

The pseudo-first order rate expression of Lagergren [8] is:

$$(dq / dt) = k_1 \cdot (q_e - q_t) \tag{4}$$

where: q_e and q_t Cr(III) – ions biosorption volume, in equilibrium and after time t [mg · g^{-1}] respectively, k_1 – Lagergren model speed constant [min^{-1}]. The parameters q_e and k_1 were calculated by linear regression method, from the relation $\log (q_e - q_t)$ from t.

Pseudo-second order [9] can by described by:

$$(dq / dt) = k_2 \cdot (q_e - q_t)^2 \tag{5}$$

where: k_2 – speed constant of pseudo-second order model [g · mg^{-1} · min^{-1}]. The parameters q_e and k_2 were calculated on the basis of gradient and shift coefficients of the lines, from the relation t/q_t from t.

Thermodynamic parameters including the change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated from the following equations:

$$\Delta G^0 = -RT \cdot \ln K_c^0 \tag{6}$$

where: R is the universal gas constant [8.314 J · mol · K^{-1}] and T is temperature [K], K_c^0 is the equilibrium constant obtained from the Langmuir isotherm [10].

The relationship between the equilibrium constant, K_c^0 and the temperature is given by the Van't Hoff equation:

$$\ln K_c^0 = (\Delta S^0 / R) - (\Delta H^0 / RT) \tag{7}$$

The plot ln K_c^0 versus $1/T$ enables us to obtain the entropy (ΔS^0) and enthalpy (ΔH^0) values from the slope and the intercept, respectively.

The functional groups of AS microorganisms and possible chromium(III) binding sites were detected by FT-IR analysis (Fourier transform-infrared spectrometer, Nicolet Nexus, USA Nicolet Co.). The FT-IR spectra obtained at 400–4000 cm^{-1} were used to examine the activated sludge before and after metal-loaded (for 24 h in 50 mg · dm^{-3}) initial Cr(III) concentration.

All data shown are the mean values of three replicate experiments, and error bars are indicated wherever necessary.

Results and discussion

Solution pH in an important process parameter in sorption of pollutant from aqueous solution. Results are given in Fig. 1.

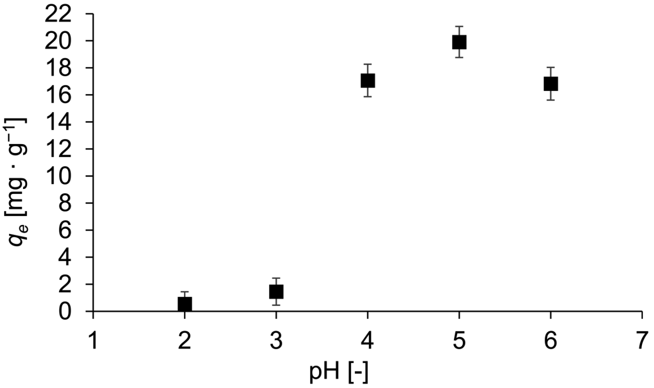

Fig. 1. The effect of pH on adsorption

The presented data show that the AS biomass sorption capacity was increasing in line with the increase of pH. The lowest value was recorded for pH 2.0, and the highest for pH 5.0, and they amounted to 0.54 and 19.91 mg · g^{-1}, respectively. At low pH, these groups are protonated and H$^+$ cations compete with chromium(III) ions for the active spots in AS biomass surface. The increase of pH causes deprotonation of functional groups, biomass surface generates negative load, which supports binding Cr(III) ions [3, 4, 11, 12]. In turn, the solution pH above 5.0 causes precipitation of chromium(III) hydroxide [2]. Other authors [13–15] have found the same trend for chromium(III) sorption by other sorbent materials.

The Langmuir and Freundlich adsorption isotherms were obtained at various temperatures and linearized Langmuir isotherm was given in Fig. 2. Table 1 presents the calculated isotherms coefficients.

The experiment data were better adjusted to Langmuir than Freundlich isotherm model. Linear regression coefficients of Langmuir model were > 0.989. The temperature increase from 20 to 40°C caused the decreased of AS biomass maximum

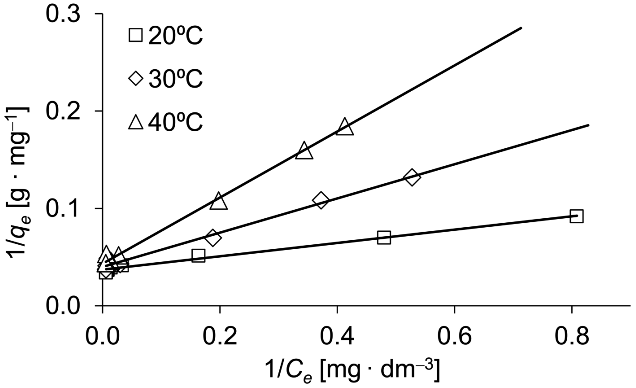

Fig. 2. Linear Langmuir isotherm plots at different temperature

Table 1

Langmuir and Freundlich isotherm constants at different temperature

Temperature [°C]	Langmuir			Freundlich		
	K_L [dm^3 · mg^{-1}]	q_{max} [mg · g^{-1}]	R^2	K_F [mg · g^{-1}]	n	R^2
20	0.542	26.95	0.990	12.19	5.675	0.935
30	0.227	25.06	0.989	7.769	4.147	0.883
40	0.127	23.15	0.996	4.795	3.134	0.924

sorption capacity (q_{max}), the respective values were 26.95 and 23.15 mg · g^{-1}. The maximum monolayer capacity of some adsorbent materials by various researches were determined as 25.64 mg · g^{-1} by using waste-activated sludge [16], 120.0 mg · g^{-1} by freeze-dried activated sludge [17], 28.16 mg · g^{-1} by algal biomass [18] and 21.64 mg · g^{-1} by soybean meal waste [19].

The correlation coefficient of linear Freundlich equation was > 0.883. The high value of K_F indicates a high adsorption. This is defined as the adsorbate adsorbed per unit weight of adsorbent. Higher the n ($n > 1$) value, higher is the intensity of adsorption [12].

The trends in Fig. 3 display that increases temperature from 20 to 40°C gave rise to a positive effect on biosorption. Many authors indicate that decreasing biosorption capacity at increased temperature indicate that the process is an exothermic [5, 12]. Therefore, the test results obtained at different operating temperatures in this study suggested that adsorption of Cr(III) on AS biomass is controlled by exothermic processes. The intensity of binding of Cr(III) by AS was highest during the first 5 minutes of biosorption, during which from 78.12 to 92.58% of chromium(III) were bound. The next stage, in which equilibrium was reached, lasted about 60 minutes. According to Fig. 3, equilibrium sorption capacity was 25.07, 20.06 and 15.95 mg · g^{-1} for 20, 30 and 40°C, respectively.

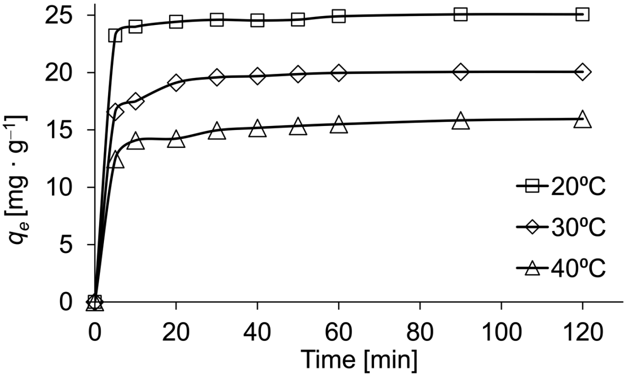

Fig. 3. The effect of temperature on sorption kinetics

The kinetic equations pseudo-first order and pseudo-second order have been applied to description of the research, in order to more fully interpret the obtained results. Both models assume reversibility and equilibrium of the adsorption process. Model parameters (determined by linearization) for kinetic experiments preformed at different temperature (20–40°C) (Figs. 4 and 5) are presented in Table 2.

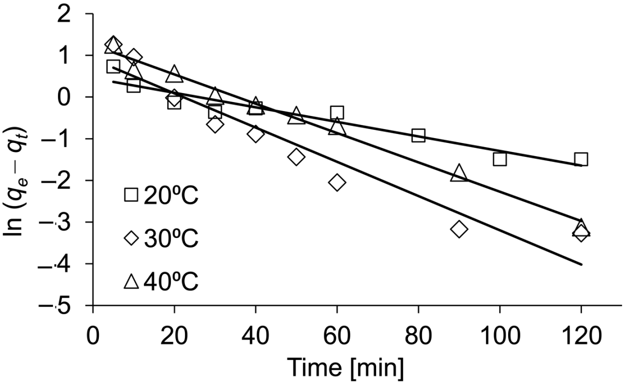

Fig. 4. Comparison of pseudo-first order sorption kinetics at different temperature

The results indicated that increase in temperature decreased both the pseudo-first and pseudo-second order rate constants for the adsorption process. The pseudo-second order kinetic model defines the measurements very well with the correlation coefficients very high (> 0.999). Also the q_e values fitted the experimental data (q_{exp}). The biosorption efficiency decreased, together with the increase of the temperature. This means that biosorption occurs is slower at higher temperatures. Also the amount of chromium(III) ions adsorbed by AS biomass decreased when the temperature of the process increased from 20 to 40°C, respectively, from 25.19 to 16.18 mg · g^{-1} (Table 2).

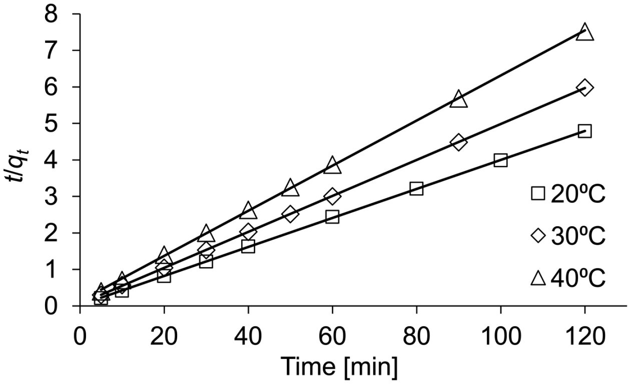

Fig. 5. Comparison of pseudo-second order sorption kinetics at different temperature

Table 2

Comparison of the pseudo-first and pseudo-second rate constants at different temperature

Temperature [ºC]	q_{exp} [mg · g^{-1}]	Pseudo-first order			Pseudo-second order		
		k_1 [min^{-1}]	q_e [mg · g^{-1}]	R^2	k_2 [g · mg^{-1} · min^{-1}]	q_e [mg · g^{-1}]	R^2
20	25.3	0.04	1.571	0.914	0.056	25.19	0.999
30	20.1	0.095	2.484	0.919	0.040	20.33	1.000
40	16	0.081	3.479	0.986	0.028	16.18	0.999

The pseudo-first order kinetic model of Lagergren was characterized by lower values of determination coefficient ($0.914 < R^2 < 0.986$) and not fit well to the whole range of contact time. It was generally applicable over the initial stage of the adsorption processes [20]. The calculated q_e values did not give reasonable value, which were too low to compare with experimental data (q_{exp}). This fact may suggest the chemisorption nature of binding of chromium(III) ions by AS biomass [12, 20, 22].

Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy change (ΔS^0) are three important parameters used to describe the thermodynamics of a process. Values of thermodynamic parameters are grouped in Table 3.

Table 3

Thermodynamic parameters

Temperature [ºC]	ΔG^0 [kJ · mol^{-1}]	ΔS^0 [kJ · mol^{-1}]	ΔH^0 [kJ · mol^{-1}]
20	–24.96	–0.104	–55.42
30	–23.62		
40	–22.89		

All negative values of ΔG^0 indicate that Cr(III) biosorption by AS is a spontaneous process. Similar conclusions have been drawn by Iddou et al. [16] and Yao et al. [17] who studied biosorption of Cr(III) by waste-activated sludge and by freeze-dried activated sludge, respectively. As reported by Horsfall and Spiff [22], values of ΔG^0 below $-20\ \text{kJ} \cdot \text{mol}^{-1}$ are characteristic for electrostatic reactions between adsorbent and adsorbate (physical adsorption), whereas those above $-40\ \text{kJ} \cdot \text{mol}^{-1}$ for covalent bonds (chemisorption). The ΔG^0 values obtained during own research, within the range from -22.89 to $-24.96\ \text{kJ} \cdot \text{mol}^{-1}$ do not explicitly suggest the biosorption type, but they may indicate the advantage of chemical sorption. The negative value of the change of enthalpy of the system (ΔH^0) indicates exothermic character of the biosorption process. In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between metal and biomass, resulting in the release of extra energy in the form of heat [23]. Negative entropy value (ΔS^0) indicates an affinity of chromium(III) from the AS surface.

FT-IR analysis of AS microorganisms was given in Fig. 6. The position of the absorption bands in the FT-R spectra is related to the change in energy of particles resulting from the stretching and bending vibration of the atoms. The FT-IR spectroscopic analysis showed strong peaks at 3401, 2926, 1653, 1538, 1413, 1244 and 1079 cm^{-1} in the absence of Cr(III). These peaks were characteristic for bonded hydroxyl group (–OH), asymmetric stretch of CH_2, stretching vibration of COO, C=O and C–N (amide I), protein N–H bend, C–N stretch (amide II), protein C–N stretch (amide III), secondary amide and Pyridine(I), respectively [23]. The AS biomass is known as a rich organic (bacteria, algae and protozoa) and inorganic mass. The biochemical composition of organic biomass are protein, lipid, extra cellular polysaccharides and nucleic acids [12].

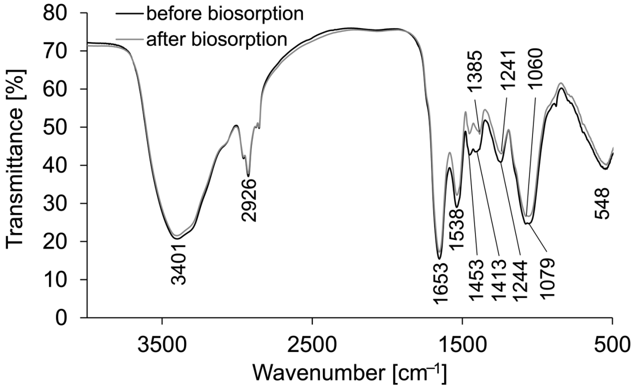

Fig. 6. FTIR spectra of AS biomass before and after biosorption

After the chromium(III) sorption experiment, using AS biomass, Cr(III) loaded AS was dried in an oven at 60°C for removal of water. The only observable change in the spectrum of the Cr(III) exposed AS was in the symmetrical stretch of the carboxyl group, which showed higher intensity. Similar change which shifted from 1413 to

1385 cm^{-1} was observed earlier by Ashkenazy et al. [25]. This shift peaks can be attributed to a change in the counter ion associated with the carboxylate anion. These data suggest that acidic groups, particularly carboxylate, contribute to the chromium(III) ion uptake [24].

Conclusions

The obtained results indicate that the optimum parameters of Cr(III) adsorption by the AS biomass were as follows: pH 5.0 and temperature 20^{o}C. The maximum Cr(III) biosorption capacity was determined as 26.95 mg · g^{-1} at 20^{o}C and pH 5.0. The batch experimental results fitted well to the Langmuir isotherms model. The biosorption capacity of AS was decreased with increasing solution temperature. The kinetic study indicates that the rate of biosorption conforms to the pseudo-second kinetic rate equation. The negative value of free Gibbs energy (ΔG^0) proves spontaneous Cr(III) biosorption by AS. The negative value of enthalpy (ΔH^0) and entropy (ΔS^0) indicates exothermic of process and limitation of degree of freedom Cr(III) ions on the interphase surface solution/biosorbent. FT-IR showed the presence of different groups on the surface of the biosorbent. Because marked change observed at carboxyl group peak (1385 cm^{-1}) in chromium(III) loaded AS, carboxyl groups were the dominant species in the Cr(III) biosorption mechanism. The obtained results confirm the usefulness of the AS biomass in the process of Cr(III) biosorption from the wastewaters.

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BIOSORPCJA Cr(III) Z ROZTWORÓW WODNYCH PRZEZ OSAD CZYNNY

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Abstrakt: W pracy badano proces biosorpcji jonów chromu(III) z roztworów wodnych przez mikroorganizmy osadu czynnego (OC), w różnych warunkach pH i temperatury. Parametry równowagowe biosorpcji wyznaczono w oparciu o modele izoterm Langmuira i Freundlicha. Parametry kinetyczne określono za pomocą równań pseudopierwszego i pseudodrugiego rzędu. Obliczono również parametry termodynamiczne procesu. Izoterma Langmuira lepiej opisywała dane równowagowe. Maksymalna pojemność sorpcyjna wyznaczona eksperymentalnie wynosiła 26,95 mg · g^{-1} przy 25^{o}C i pH 5,0. Model kinetyki pseudodrugiego rzędu lepiej opisywał dane doświadczalne. Ujemna wartość energii swobodnej Gibbsa (ΔG^0) świadczyła o spontaniczności biosorpcji Cr(III) przez biomasę OC i jej spadku wraz ze wzrostem temperatury. Ujemna wartość entalpii (ΔH^0) i entropii (ΔS^0) wskazywała na egzotermiczność procesu i ograniczenie stopni swobody jonów Cr(III) na powierzchni międzyfazowej roztwór/biosorbent. Analiza FT-IR wykazała udział grup karboksylanowych w biosorpcji Cr(III) przez OC.

Słowa kluczowe: osad czynny, biosorpcja, chrom(III)

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ASSESSMENT OF HEAVY METAL CONTAMINATION IN TOPSOIL AND SOIL INVERTEBRATES FROM THE NIEPOLOMICE FOREST

OCENA ZAWARTOŚCI METALI CIĘŻKICH W GLEBIE I BEZKRĘGOWCACH GLEBOWYCH W PUSZCZY NIEPOŁOMICKIEJ

Abstract: The purpose of the research was to determine the respective contents of heavy metals (Pb, Cd, Ni, Zn and Cu) in soil and extracted soil fauna in humid mixed coniferous forest (MHCF), fresh mixed coniferous forest (MFCF) and in fresh mixed forest (MFF) of Niepolomice Forest. The contents of heavy metals varied, depending on the forest type and trophic group. The highest values of cadmium, lead, and copper content were recorded in MFCF, while of nickel in MHCF. Analysis of variance and post-hoc Tuckey's showed significant differences between the concentrations of Zn and other metals in invertebrates in different types of forest habitats. Bioconcentration factor shows that both soil saprophages and predacious invertebrates accumulated the largest amounts of Cd and smaller amounts of Zn, while the accumulation of remaining metals depended on the type of forest habitat. In fresh mixed coniferous forest predators accumulated heavy metals in the following order: Cd > Zn > Pb > Ni > Cu, in the case of saprohages it was: Cd > Zn > Ni > Cu > Pb.

Keywords: Niepolomice Forest, heavy metals, trophic groups, saprophags, predators, bioconcentration factor values

Introduction

Soil is a major element of all land ecosystems. Processes taking place there are crucial for their sustainability and efficiency [1]. One of its characteristic features is the abundance and diversity of organisms found in it. In one square meter of soil one can find up to 1000 species of pedofauna, including approximately 200 species of arthropods. Invertebrates play significant roles in the delivery of ecosystem services by soils at plot. They participate actively in the interactions that develop in soil among physical, chemical and biological processes. Soil invertebrates are enormously diverse

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[2]. According to recent estimations, soil animals may represent as much as 23% of the total diversity of living organisms that has been described to date [3].

Anthropogenic activity brings about essential changes in the circulation of elements in the environment, which leads to the pollution by these elements of individual environmental components. Particularly hazardous is the process of accumulation of cationic trace elements of heavy metal groups. Heavy metals in excessive amounts pose serious risk to plants, animals and human beings [4–8]. The presence of trace metals in the soil, plants and in soil fauna is an environmental indicator [2, 9–11]. Accumulation of heavy metals in soil is conditioned by the form of land use as well as physical and chemical properties of the soil and by weather conditions [12, 13].

That is why there is a need to systematically monitor their concentrations in environmental components [14]. Since invertebrates are very susceptible to changes of soil conditions, they may be considered valuable indicators of soil disturbances [15–23].

The purpose of the research was to determine the respective contents of heavy metals (Pb, Cd, and Ni, Zn and Cu) in soil and extracted soil fauna in three types of forest habitats – fresh mixed coniferous forest, humid mixed coniferous forest and in fresh mixed forest of Niepolomice Forest.

Materials and methods

Niepolomice Forest is a huge forest complex situated approx. 25 km to the east of Krakow. Forests cover nearly 90% of its area. Niepolomice Forest is dominated by pine coniferous forests: mixed fresh coniferous forest (MFCF), mixed humid coniferous forest (MHCF), marshy coniferous forest (MCF); mixed fresh forest (MFF), mixed humid forest (MHF), mixed marshy forest (MMF), alder forest (AF), and ash-alder forest (AAF).

The research was carried out in three types of forest habitats: in mixed humid coniferous forest (MHCF) which occupies the largest area in Niepolomice Forest, in mixed fresh coniferous forest (MFCF) (9.8%), and in mixed fresh forest (MFF) (10.5%) [24]. The localities of taking of the samples were marked in Fig. 1.

Soil samples were taken during autumn of 2011–2012 vegetation season, in tree stands of age category III (called stickstand), where trees have between 40 to 60 years of age.

Soil samples were collected from the surveyed positions with soil frames sized 25 × 25 cm and with 1 m^2 surface area and absent of soil fauna using the dynamic method with a modified Tullgren apparatus. Soil fauna were separated into trophic groups – saprophags, predators, and phytosaprophags – in which heavy metals were then marked. The heavy metal content in soil and soil fauna was determined by FAAS after previous mineralization of the soil and animal test materials. For this purpose, animals and soil samples were dried at 105^{o}C to obtain a dry weight. After obtaining the dry weight, each trophic group was weighed. Also, 2 g of dried soil from each location was weighed.

The soil and soil organisms underwent the mineralization process in a Velp Scientifica DK-20 mineralizer in concentrated nitric acid at 120^{o}C until the tissue was completely dissolved. Then, the resulting solutions were poured into measuring flasks filled with distilled water up to 10 cm^3. In the solutions thus prepared, the heavy metal content was determined content – cadmium, lead, nickel, copper and zinc in a spectro-

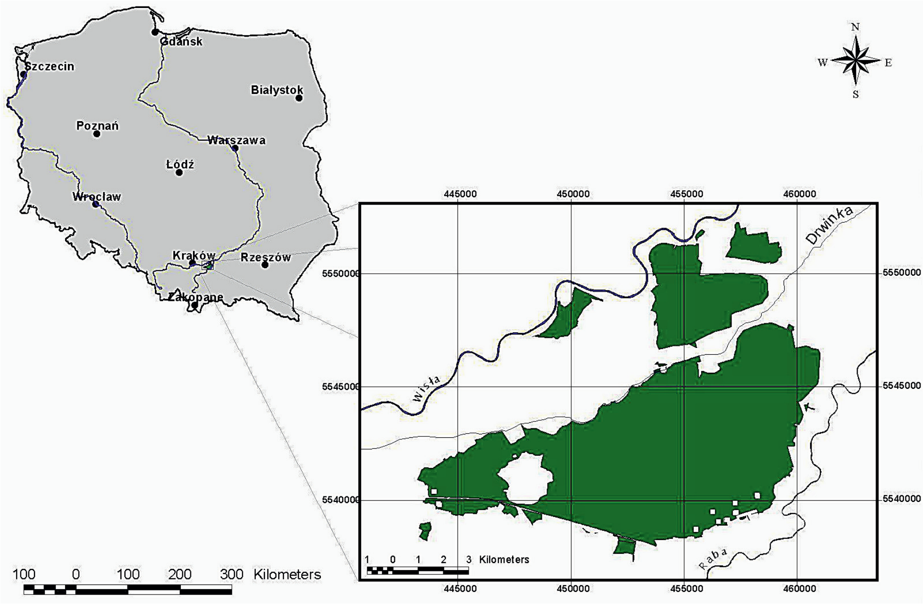

Fig. 1. Location of the study area in Niepolomice Forest

photometer. The heavy metal content in soil and soil fauna was determined by Buck Scientific 200A Flame Atomic Absorption Spectrophotometer FAAS. The AAS limits of detection (LoD) and quantification (LoQ) for Pb were set at 0.027 ppm and 0.083 ppm (mg/dm^3), respectively, for Cd 0.011 ppm (LoD) and 0.033 ppm (LoQ), for Ni 0.017 ppm (LoD) and 0.05 ppm (LoQ), for Cu 0.012 (LoD) and LoQ = 0.035 ppm and for Zn: LoD = 0.023 ppm and LoQ = 0.069 ppm. Reference material was BCR-185, Bovin Liver.

Moisture content and pH of the investigated soils were determined as well. PH of soil was measured using a WTW 330/SET-1 pH-meter (Wissenschaftlich – Technische Werkstatten 82362 Weilheim).

The paper also analyzes the significance of differences between the concentration of heavy metals in soil fauna in three types of forest habitat MFCF, MHCF and MFF. After showing the statistical significance ($p < 0.05$) a Tuckey's test was chosen [25]. The content of heavy metal in studied soil of forest habitats were compared using t-Student's test, and in the case of heterogeneous variance was used t-Student's test with the separate estimation of the variance [26]. The differences were statistically significant at $p < 0.05$. All the analyses were performed using STATISTICA 10 computer program.

Results and discussion

The analysis of the pH value showed that the studied soils had acidic pH, from 4.5 to 5.5. The types of soil found in the analysed sites included: podzolic soils, podzolic and muck soils, muck and gley soils, brown acid soils (Table 1).

Table 1

Comparison of studied habitat types of the forest (±SD)

Parameters	MFF	MHCF	MFCF
Soil pH	5.5 ± 0.2	4.5 ± 0.3	4.8 ± 0.3
Soil temperature [^{o}C]	3.1 ± 0.1	3.6 ± 0.2	4.9 ± 0.3
Area temperature [^{o}C]	7.7 ± 0.4	7.4 ± 0.6	5.4 ± 0.4
Soil moisture [%]	10.2 ± 2.3	7.5 ± 1.5	7.9 ± 1.9
Sort of soil	brown acids, podzolic	podzolic and muck, muck and gley	podzolic

The highest values of cadmium, lead, and copper content were recorded in MFCF, while of nickel in MHCF. The largest differences in content in the analysed types of forest habitats were observed with respect to lead. The overall lead content in the soil of MFF and MFCF was nine times higher than in soil of MHCF. The concentration of this metal in the soil MHCF and MFF was statistically significant ($p < 0.001$) (Table 2).

Table 2

Concentration of heavy metals in soil [mg · kg^{-1} d.m.]
(Mean, SD, significant differences between the concentration of metals in soil)

Metals	MFCF			MHCF			MFF			Limit values[a]
	Mean	SD	p	Mean	SD	p	Mean	SD	p	
Cd	0.8	0.7	ND	0.7	0.1	*	0.5	0.2	*	4
Pb	78.1	25.3	ND	8.4	0.5	***	74.4	12.4	***	100
Ni	6.4	0.2	ND	12.4	1.8	***	7.1	3.2	***	100
Cu	15.9	1.6	ND	10.4	1.6	**	8.8	3.7	**	150
Zn	89.4	20.8	ND	71.6	11.4	NS	92.6	19.8	NS	300

[a] Limit values for the heavy metal content set out in the Minister of Environment Regulation on the soil quality standards and earth quality standards for group B– (Polish Journal of Laws 2002 No. 165, item 1359 of 4 October 2002); * 0,05 > p > 0.01; ** 0.01 > p > 0.001; *** p < 0.001; NS – no significant differences; ND – no data.

It should be pointed out that the accumulation of lead in forest litter is a long-lasting process, hence the found lead concentrations may result from the total pollutant amounts from deposition lasting many years. The results indicate that the concentrations of heavy metals do not exceed the standards set out in the Regulation of the Minister of the Environment on soil quality standards and earth quality standards [27]. Rozen et al [19] showed in their study in mixed oak-pine in Niepolomice forest much higher values of Cd, Pb, Cu and Zn.

In much of the soil was cumulated zinc (71–92 mg · kg^{-1} d.m.), but its content in the studied forest was not statistically significant ($p > 0.05$). In a smaller were cumulated lead, copper, cadmium, nickel, which the concentrations in the soil were statistically significant (Table 2). Higher average content of nickel (67.5 mg · kg^{-1} d.m.) in soils in coniferous forest in Olsztyn (northeastern Poland) found Modrzewska and Wyszkowski [13].

The analysed metal content in the studied soils did not correlate with the abundance and the biodiversity of the studied fauna. The highest density was recorded in fresh mixed forest MFF, and the lowest in fresh mixed coniferous forest MFCF. The largest systematic group were Acarina, which accounted for 37% of the MHCF to 83% in the total number of MFCF. Collembola were also large numbers until reaching in MFF 10880 N $\cdot$ m^{-2} (Table 3). Also, other authors showed a similar arrangement of taxonomic groups in their studies [10, 20].

Table 3

Density of pedofauna [N $\cdot$ m^{-2}]

Systematic groups	Trophic groups[a]	MHCF	MFCF	MFF
Enchytraeidae	S	1 688		296
Lumbricidae	S	8		56
Isopoda	S			8
Collembola	S, P	7 688	120	10 880
Diptera l.[b]	S	232	8	96
Aranea	P	8		8
Symphyla	P			80
Chilopoda	P	40	16	72
Coleoptera im.[c]	P	16	32	56
Carabidae l.	P	216	200	32
Staphylinidae l.	P			56
Rhagionidae l.	P			48
Dolichopodidae l.	P		104	32
Thysanoptera	Ph		64	
Hymenoptera	P		80	272
Curculionidae l.	Ph			8
Bibionidae l.	Ph	24		
Cecidomyiidae im.	Ph	48		48
Acarina	S, P	5 992	3 008	13 160
Total		15 960	3 432	25 208

[a] Trophic groups: S – saprophag, P – predator, Ph – phytophag; [b] l. – larvae; [c] im. – imago.

Also tested was the trophic structure of pedofauna assemblages. In mixed humid coniferous forest and in mixed fresh forest were dominated by predatory invertebrates. The density of predatory forms ranged from 280 N $\cdot$ m^{-2} in MHCF to 656 N $\cdot$ m^{-2} in mixed forest fresh (Table 3). However, in mixed humid coniferous forest dominated by saprophags invertebrates, whose share was almost 85%.

The contents of heavy metals varied, depending on the forest type and trophic group. As regards lead, the largest values – between 40 mg $\cdot$ kg^{-1} d.m. and 220 mg $\cdot$ kg^{-1} d.m. – were observed in predators, while in phytophags and saprophages they ranged from 29 to 64 ad in earthworn found Rozen et al [19].

Cadmium content was higher in predators than in phytophags and saprophages and ranged from 8.0 to 22.6 mg · kg^{-1} d.m. The higher cadmium concentration was recorded in earthworm from oak-hornbeam in the northern part of the Niepolomice Forest [19]. Jelaska et al [20] showed that predators Carabides accumulated less cadmium (0.2–10.6) and lead (0.13–2.31) in forest ecosystem in Medvednicz Nature Park.

Nickel was present in the amount of 6.6 to 31.9 mg · kg^{-1} d.m., with higher values observed in predators than in saprophages and phytophags (Table 4). The highest copper contents were found in predacious invertebrates (91 mg · kg^{-1} d.m. in MHCF). Also Chrzan et al [28] showed a higher content of Pb, Ni and Cu in predatory invertebrates in forest soils.

Table 4

Content of heavy metals in trophic groups [mg · kg^{-1} d.m.] (±SD)

Metal	Saprophytophags			Predators		
	MFCF	MHCF	MFF	MFCF	MHCF	MFF
Cd	7.98 ± 1.19	13.73 ± 3.56	17.89 ± 2.34	22.61 ± 3.53	12.22 ± 1.58	13.64 ± 0.43
Pb	29.39 ± 4.6	64.38 ± 5.24	38.77 ± 15.92	220.04 ± 77.87	79.42 ± 22.11	40.03 ± 2.71
Ni	6.60 ± 0.23	10.13 ± 1.29	13.21 ± 1.59	14.78 ± 1.84	27.27 ± 4.19	31.92 ± 1.79
Cu	15.84 ± 2.53	17.99 ± 0.92	29.67 ± 4.69	18.75 ± 3.14	91.05 ± 10.97	35.79 ± 4.33
Zn	280.89 ± 36.79	860.18 ± 210.15	1081.15 ± 111.02	779.56 ± 83.41	937.96 ± 343.22	538.46 ± 156.35

Zinc is crucial for proper functioning of all cells of an organism and is present in many enzymes responsible, *inter alia*, for metabolism of proteins, carbohydrates, and fats. Zinc content in organisms is high. The highest value of 1081 mg · kg^{-1} d.m. was found in soil saprophages and phytophags. The high content of Zn in saprophagous Enchytraeides demonstrated by Rozen et al [19]. Heavy metal toxicity depends on the roles they play in the metabolic processes of the organisms and their susceptibility to bioaccumulation.

Significant correlations between the studied metals in each types of forest habitats separately demonstrated. Analysis of variance and post-hoc Tuckey's showed significant differences between the concentrations of Zn and Pb, Cd and Cu in invertebrates in different types of forest habitats (Table 5).

Table 5

Significant differences between the concentration of Pb, Cd, Zn, Cu [mg · kg^{-1} d.m.] in soil fauna of MFF and MHCF

MFCF	p	MHCF	p	MFF	p
Pb vs Cd	NS	Pb vs Cd	NS	Pb vs Cd	NS
Pb vs Zn	***	Pb vs Zn	**	Pb vs Zn	***
Pb vs Cu	NS	Pb vs Cu	NS	Pb vs Cu	NS
Cd vs Zn	**	Cd vs Zn	***	Cd vs Zn	**
Cd vs Cu	NS	Cd vs Cu	NS	Cd vs Cu	NS
Zn vs Cu	***	Zn vs Cu	***	Zn vs Cu	**

* $0.05 > p > 0.01$; ** $0.01 > p > 0.001$; *** $p < 0.001$; NS – no significant differences.

The potential risk may be expressed through the accumulation index representing the ratio between the average concentration of the element in the body to its content in the soil. Bioconcentration factor calculated for predatory and saprophytophag invertebrates, and presented in Table 6.

Table 6

Bioconcentration factor values (BCF) of the potentially toxic trace elements in saprophytophags and predators

Metal	Saprophytophags			Predators		
	MFCF	MHCF	MFF	MFCF	MHCF	MFF
Cd	10.0	19.7	35.8	28.2	17.4	27.2
Pb	0.4	7.7	0.5	2.8	9.4	0.5
Ni	1.0	0.8	1.8	2.3	2.2	4.1
Cu	1	1.7	3.4	1.2	8.8	4.5
Zn	3.1	12	11.8	8.7	13.1	5.9

Bioconcentration factor shows that both soil saprophags and phytophags and predacious invertebrates accumulated the largest amounts of Cd and smaller amounts of Zn, while the accumulation of remaining metals depended on the type of forest habitat and the trophic group.

In fresh mixed coniferous forest predators accumulated heavy metals in the following order: Cd > Zn > Pb > Ni > Cu, in the case of saprophytophags it was: Cd > Zn > > Ni = Cu > Pb. As regards fresh mixed forest, the lowest BCF value was recorded for Pb. In humid mixed coniferous forest, BCF with respect to Cd, Pb and Zn was similar both in saprophytophags and predators invertebrates. Assimilability of heavy metals by soil fauna in this type of forests was as follows: Cd > Zn > Pb > Cu > Ni (Table 6).

Conclusions

1. Content of the heavy metal in the forest soils did not exceed the limit values for forest land according to the Regulation of the Minister of Environment on standards for soil quality and earth quality standards of 4.10.2002.
2. Soil invertebrates accumulated the most of Cd and a little less of Zn.
3. Significant differences were noted between the content of Zn in soil and fauna.
4. More of heavy metals were accumulated in predatory invertebrates in humid mixed coniferous forest MHCF and in fresh mixed coniferous forest MFCF than in saprophytophags.

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OCENA ZAWARTOŚCI METALI CIĘŻKICH W GLEBIE I BEZKRĘGOWCACH GLEBOWYCH W PUSZCZY NIEPOŁOMICKIEJ

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Abstrakt: Celem badań było określenie zawartość metali ciężkich (Pb, Cd, Ni, Zn i Cu) w glebie i wyekstrahowanej faunie glebowej w trzech typach siedliskowych lasu w Puszczy Niepołomickiej – w lesie mieszanym wilgotnym, borze mieszanym świeżym i borze mieszanym wilgotnym. Zawartość metali ciężkich uzależniona była od typu lasu i grupy troficznej. Najwieksze wartości kadmu, ołowiu i miedzi odnotowano w glebie w borze mieszanym świeżym BMśw, a niklu w borze mieszanym wilgotnym BMw. Wskaźnik biokoncentracji wskazuje, że zarówno saprofagi i drapieżne bezkręgowce glebowe w największej ilości kumulowały Cd, w mniejszej Zn, natomiast pozostałe metale kumulowane były w zależności od typu siedliskowego lasu. W borze mieszanym świeżym drapieżne kumulowały metale w kolejności Cd > Zn > Pb > Ni > Cu, a saprofagi Cd > Zn > Ni > Cu > Pb.

Słowa kluczowe: Puszcza Niepołomicka, metale ciężkie, grupy troficzne, saprofagi, drapieżne, wskaźnik biokoncentracji

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INFLUENCE OF PACKAGES ON NUTRITIONAL QUALITY OF PICKLED CHILLED STORED CUCUMBERS

WPŁYW OPAKOWANIA NA JAKOŚĆ ZDROWOTNĄ OGÓRKÓW KISZONYCH CHŁODNICZO SKŁADOWANYCH

Abstract: Due to instability of fresh cucumbers during storage and their seasonal availability, different methods are used to preserve them, of which pickling is one of the most favourable. The aim of this paper was to investigate the effect of package type (bags made from low density polyethylene (PE-LD) and the metalized polyethylene terephthalate (PET met/PE) foil) on selected quality parameters of pickled cucumbers. Vegetables were analysed in 2014 before packaging and after 1, 2, 3, and 4 months of chilled storage in two types of a package. It has been found that the package type used had no statistically significant ($p > 0.05$) effect on dry matter content, vitamin C content, nitrate and nitrite contents and antioxidant activity of the pickled cold stored cucumbers. The level of total polyphenols was statistically significant ($p \le 0.05$) in pickled cucumbers stored in bags made from the metalized polyethylene terephthalate (PET met/PE) foil.

Keywords: cold-stored, packaging, pickled cucumbers, nitrates, nitrites, vitamin C, antioxidant activity

Introduction

Cucumber (*Cucumis sativus* L.) which belongs to the gourd family *Cucurbitaceae*, is one of the most popular, economically important and widely grown vegetable crops in the world [1]. Cucumber fruit is a good source of mineral compounds and dietary fibre and contain approximately 95% water, 3.6% carbohydrates, and 0.65% protein and are low in calories. They are a good source of the vitamin C (8 mg/100 g), retinol equivalent (28 μg/100 g), vitamin E (0.16 mg/100 g) and B-group vitamins, including folic acid (15 μg/100 g) and pantothenic acid [2].

Pickling cucumber is grown in many parts of the world. Pickling, as one of the biological methods of food preservation, is used since ancient times. This process runs due to lactic acid fermentation and the products obtained are characterized by longer

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shelf life, are microbiologically safe, easy digestible, simultaneously showing different properties than the initial raw material [3].

The World Health Organization has listed pickled vegetables as a possible carcinogen because of nitrites content. For this reason, the measurement of nitrite content in pickled vegetables has received increasing attention [4]. In the present study, we analyzed also the content of nitrite in pickled cucumber and the results should help to choose the kind of packaging material, which will be the most suitable for the chilled storage of pickled cucumber.

The weakness of vegetables is their seasonal availability and fact that they are perishable. In view of the above, food technology is focused on discovering and establishing the methods of storage, which will least affect their chemical composition. However, such a high amount of water determines the limited stability of cucumbers, creating good conditions for the growth of micro-organisms. Pickling cucumbers are generally stored in the brine for long-term storage. To our best knowledge this is the first study determining the effect of cold storage in different packaging type (especially innovative is one of presented packaging type – metalized foil made from PET met/PE) on selected antioxidative properties and content of some contaminants in pickled cucumbers.

The aim of this paper was to examine and compare pickled cucumber, which was chilled stored for four subsequent months, in terms of changes in the dry mass, vitamin C, total polyphenols, nitrates and nitrites content as well as antioxidant activity. The experimental material was packed in two ways: in low density polyethylene (PE-LD) bags and in metalized polyethylene terephthalate (PET met/PE) bags.

Overall, this study were undertaken to broaden knowledge on health-promoting properties of pickled cucumber, particularly in terms of the following indicators: vitamin C, total polyphenols and antioxidant activity. This study aimed also at increasing the consumer knowledge about biological value of the pickled cucumber, particularly with regard to the presence of such contaminants as nitrates and nitrites.

Material and methods

Material

The experimental material consisted of freshly pickled cucumbers, purchased in selected five sites of direct sales in the city of Krakow in 2014. Vegetables were analysed before packaging and after 1-, 2-, 3- and 4-month periods of chilled storage in the two types of the package: in the low density polyethylene (PE-LD) bags with the zipper closure (foil density: 0.91–0.92 g/cm^3; size: 230 × 320 mm); and in the bags of the similar size made of the laminate: metalized polyethylene terephthalate (PET met/PE) (a polymer from the polyester group, obtained through a polycondensation reaction between dimethyl terephthalate (DMT) and ethylene glycol (GE), CAS number: 25038-59-9, density 1.370 g/cm^3) with polyethylene. The representative samples obtained were then stored at chilled conditions (4–5^{o}C) in a fridge for four subsequent months.

Analytical methods

The experimental material taken before packing and after the established periods of chilled storage from every container was collected and then homogenized using a homogenizer (CAT type X 120) in order to obtain a mean representative sample.

Adequately prepared mean representative samples of vegetables were analyzed for vitamin C content and the levels of contaminants: nitrates and nitrites. Simultaneously, 70% methanol extracts has been prepared to determine: total polyphenols (calculated per chlorogenic acid) – through the colorimetric measurement of colourful substances formed due to the reaction between phenolic compounds and a Folin-Ciocalteau reagent (Sigma) [5] and to determine antioxidant activity based on the $ABTS^+$ free radical scavenging ability – by a colorimetric assessment of an amount of the $ABTS^+$ free radical solution, which had not been reduced by the antioxidant present in the products examined [6].

The content of vitamin C was determined as the sum of ascorbic acid and dehydroascorbic acid using 2,6-dichlorophenoloindophenol according to PN-A-04019:1998 [7]. Oxalic acid solution was used for extraction of the ascorbic acid.

The content of total phenols in the extracts was determined spectrometrically (at a wavelength of 760 nm using a RayLeigh UV-1800 spectrophotometer) according to the Folin-Ciocalteu procedure and calculated as chlorogenic acid equivalents (CGA) (in terms of milligrams) per 100 g of fresh or dry weight, based on a standard curve.

The method involved colorimetric determination of the amount of the colored solution of $ABTS^+$ free radical (2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) which was reduced by the antioxidants present in the test product. The absorbance was measured at a wavelength of 734 nm using a RayLeigh UV-1800 spectrophotometer. Values obtained for each sample were compared to the concentration-response curve of the standard trolox solution and expressed as micromoles of Trolox equivalent per gram of fresh or dry weight (TEAC).

Colorimetric method using to determinate contaminants such as nitrates and nitrites based on nitrites coloured reaction with Griess I, II reagent according to the Polish Standard [8]. Previously nitrates must be reduced to nitrites. Nitrates content was assessed using Griess I (sulfanilamide, Sigma-Aldrich) and Griess II (n-(1-Naphtyl)ethylene-diamine dihydrochloride, water solution, Sigma-Aldrich). The principle of this method is to cause a colour reaction of nitrate(III) with n-(1-Naphtyl)ethylene-diamine dihydrochloride in acidic conditions, and to measure absorbance at wavelenght 538 nm. Nitrates had tobe reduced to nitrites before to beginning of colour reaction. The described research method is recognized and widely used in assays to determine the content of nitrates and nitrites in vegetables.

Statistical analysis

All analyses were carried out in three parallel replications (n = 3) and standard deviations (SD) were calculated for the obtained mean values. The single-factor analysis of variance has been used to find the significance of differences between the mean values of the parameters investigated for the vegetable stored in two different types of package. The two-factor analysis of variance was employed to establish the significance of differences between values of the parameters evaluated for the chilled-stored vegetable depending on the package type used and length of chilled storage. The Statistica 9.1. PL program was applied for all the calculations made. In order to evaluate the significance of differences at the critical significance level of $p \leq 0.05$, the Duncan's multiple range test has been used.

Results

As the dry matter content in pickled cucumbers depending on the process applied and the container used, 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.

Vitamin C

Fresh vegetables (before packaging) contained 243 mg of vitamin C per 100 g of dry matter (Table 1). In the vegetables which were cold stored for the successive 4 months, the losses in vitamin C were statistically significant ($p \leq 0.05$) and were respectively: 17.3; 24.4; 23.4 and 26.1% in the PE-LD bags; and 24.0; 26.4; 24.3, and 27.5% in the PET met/PE bags, compared to the vegetable prior to packaging.

Table 1

The content of vitamin C in cold-stored pickled cucumbers [mg/100 g d.m.]

The kind of processing	Vitamin C	
Before storage	$243^{a} \pm 40$	
Cool storage	The kind of packaging	
	Zipper seal bags (PE-LD)	Bags (PET met/PE)
1 month	$201^{ab} \pm 24$	$184.6^{b} \pm 1.5$
2 months	$183.6^{b} \pm 1.3$	$178.9^{b} \pm 1.0$
3 months	$186.2^{b} \pm 1.9$	$183.94^{b} \pm 0.26$
4 months	$179.7^{b} \pm 1.1$	$176.20^{b} \pm 0.77$
Mean value for packaging	$199^{A} \pm 26$	$193^{A} \pm 28$

Values are presented as mean value ± standard deviation.
The values denoted with the same letters do not differ statistically significantly at $p \leq 0.05$.

It has been proved that, the type of package had no statistically significant ($p > 0.05$) effect on vitamin C content in the cold stored pickled cucumbers.

Total polyphenols

The content of total polyphenols in the examined fresh vegetables has been expressed as chlorogenic acid equivalent and was 1202 mg CGA/100 g d.m. (Table 2).

Table 2

The content of total polyphenols in cold-stored pickled cucumbers [mg CGA/100 g d.m.]

The kind of processing	Total polyphenols	
Before storage	$1202^{a} \pm 19$	
Cool storage	The kind of packaging	
	Zipper seal bags (PE-LD)	Bags (PET met/PE)
1 month	$1103^{d} \pm 15$	$1178^{b} \pm 18$
2 months	$1104.6^{d} \pm 7.0$	$1151.3^{c} \pm 7.4$
3 months	$1056^{f} \pm 25$	$1083.1^{de} \pm 8.4$
4 months	$1070^{ef} \pm 16$	$1094^{d} \pm 2.7$
Mean value for packaging	$1107^{B} \pm 57$	$1142^{A} \pm 52$

Values are presented as mean value ± standard deviation.
The values denoted with the same letters do not differ statistically significantly at $p \leq 0.05$.

In comparison with vegetables prior to packaging, in successive 4 months losses in total polyphenols in the cold-stored vegetables were respectively: 8.2; 8.1; 12.2 and 11.0% for the PE-LD bags and 2.0; 4.2; 9.9 and 8.9% for the PET met/PE bags; these losses were statistically significant ($p \leq 0.05$).

Studies revealed that the type of package which was used to store pickled cucumbers under chilling conditions, significantly affected ($p \leq 0.05$) the content of total polyphenols in the product. In pickled cucumbers stored in the PET met/PE bags, a decrease in polyphenol content was significantly lower ($p \leq 0.05$) compared to the cucumbers kept in PE-LD bags with the zipper closure.

Antioxidant activity

Antioxidant activity in fresh vegetable was 26.90 μm Trolox eq./1 g dry matter (Table 3).

Statistically significant changes in antioxidant activity ($p \leq 0.05$) occurred after only 1-month chilled storage of pickled cucumbers, when antioxidant activity decreased to 23.92 (by 11.1%) in the vegetables stored in PE-LD bags and to 24.52 μm Trolox eq/1 g d.m. (by 8.8%) in those kept in PET met/PE bags, compared with vegetables before packaging. Throughout the next 3 months of chilled storage, further significant ($p \leq 0.05$) losses in antioxidant activity were observed: of 11.9; 13.6 and 12.9% respectively in vegetables packed in PE-LD bags; and of 10.3; 12.9 and 12.6% in

Table 3

Antioxidant activity of cold-stored pickled cucumbers [µm Trolox/1 g d.m.]

The kind of processing	Antioxidant activity	
Before storage	$26.90^{a} \pm 0.52$	
Cool storage	The kind of packaging	
	Zipper seal bags (PE-LD)	Bags (PET met/PE)
1 month	$23.92^{cd} \pm 0.16$	$24.52^{b} \pm 0.20$
2 months	$23.71^{cde} \pm 0.29$	$24.12^{bc} \pm 0.00$
3 months	$23.23^{g} \pm 0.23$	$23.44^{fg} \pm 0.12$
4 months	$23.44^{fg} \pm 0.11$	$23.52^{def} \pm 0.09$
Mean value for packaging	$24.3^{A} \pm 1.5$	$24.5^{A} \pm 1.4$

Values are presented as mean value ± standard deviation.
The values denoted with the same letters do not differ statistically significantly at $p \leq 0.05$.

vegetables stored in meth PET met/PE pouches compared with vegetables analyzed prior to packing (Table 3).

The type of package had no significant ($p > 0.05$) effect on antioxidant activity of cold-stored pickled cucumbers.

Nitrates

Nitrates were determined according to the Polish Standard and the results were expressed as the amount of NO_3^- nitrate ions per kg of dry matter. The content of nitrates in fresh vegetables was 234 mg NO_3^-/kg d.m. (Table 4).

Table 4

The content of nitrates in cold-stored pickled cucumbers [mg/kg d.m.]

The kind of processing	Nitrates (NO_3^-)	
Before storage	$234^{d} \pm 23$	
Cool storage	The kind of packaging	
	Zipper seal bags (PE-LD)	Bags (PET met/PE)
1 month	$224.8^{d} \pm 1.9$	$246^{d} \pm 29$
2 months	$828^{bc} \pm 40$	$863^{b} \pm 56$
3 months	$779^{c} \pm 15$	$839^{bc} \pm 44$
4 months	$946^{a} \pm 15$	$1011^{a} \pm 30$
Mean value for packaging	$602.5^{A} \pm 345.8$	$638.9^{A} \pm 369.8$

Values are presented as mean value ± standard deviation.
The values denoted with the same letters do not differ statistically significantly at $p \leq 0.05$.

After 1-month storage, the amount of nitrates in pickled cucumbers changed in both types of package; however, this difference was statistically insignificant ($p > 0.05$). The level of nitrates in vegetables stored in PE-LD bags fell to 224.8 mg NO_3^-/kg dry matter (by 3.9%), while in those packed in Pet met/PE bags increased up to 246 mg NO_3^-/kg dry matter (by 5.1%) compared to the vegetable before packing.

A significant ($p \le 0.05$) increase in the level of nitrates in pickled cucumbers which were chilled stored in two types of package, occurred in the subsequent three months; in the vegetables stored in the PE-LD bag increased by 253.8; 232.9 and 304.3% respectively; and in the second type of package, which were the PET met/PE bags, by 268.8; 258.5 and 332.0% compared to the vegetables prior to packaging.

The type of the packing was found to have no significant ($p > 0.05$) effect on the nitrates content in pickled cucumbers stored under chilling conditions.

Nitrites

The results referring to the content of nitrites were presented as calculated on nitrite ions (NO_2^-) per kg fresh and dry matter. The content of nitrites in the fresh vegetable was 15.3 mg NO_2^-/kg dry matter (Table 5).

Table 5

The content of nitrites in cold-stored pickled cucumbers [mg/kg d.m.]

The kind of processing	Nitrites [NO_2^-]	
Before storage	$15.3^{e} \pm 3.6$	
Cool storage	The kind of packaging	
	Zipper seal bags (PE-LD)	Bags (PET met/PE)
1 month	$12.34^{e} \pm 0.72$	$14.4^{e} \pm 2.3$
2 months	$35.4^{cd} \pm 2.6$	$39.3^{bc} \pm 4.9$
3 months	$31.7^{d} \pm 2.0$	$37.3^{cd} \pm 3.2$
4 months	$45.1^{b} \pm 1.0$	$51.9^{a} \pm 2.1$
Mean value for packaging	$28^{A} \pm 14$	$31^{A} \pm 16$

Values are presented as mean value ± standard deviation.
The values denoted with the same letters do not differ statistically significantly at $p \le 0.05$.

After a period of 1-month chilled storage, the amount of nitrites in pickled cucumbers decreased in both types of package, although, the differences were not statistically significant ($p > 0.05$) compared to the vegetables prior to packaging.

Compared to the vegetable before packaging, the content of nitrites in the vegetables stored in PE-LD bags decreased up to 12.34 mg NO_2^-/kg dry matter (by 19.3%), whereas in those kept in PET met/PE bags up to 14.4 mg NO_2^-/kg dry matter (by 5.9%).

As in the case of the nitrates, in successive months of chilled storage there was a substantial statistically significant ($p \le 0.05$) increase in the content of nitrites in pickled cucumbers: of 131.4, 107.2, and 194.8% respectively for those stored in PE-LD bags; and of 156.9, 143.8, and 229.2% respectively for those from the second type of package (PET met/PE bags), compared to the vegetables prior to packaging. Studies showed that the type of package, in which pickled cucumbers were chilled stored, had no effect ($p > 0.05$) on the content of nitrites.

Discussion

Vitamin C

Vitamin C content in vegetables depends on several factors but mainly on the cultivar, stage of maturity at harvest, site and method of cultivation, agro-technique, climatic conditions, storage, as well as technology of processing and preservation [9]. The content of vitamin C in the fresh cucumber ranges in 4.6–10.8 mg/100 g fresh matter depending on the method and the year of cultivation [10] or from 9.19 to 11.15 mg/100 g fresh vegetable, as was reported by Jarosz et al [11].

In this work, pickled cucumbers prior to packing contained 12.5 mg vitamin C that do not correspond to the data available in the literature. According to the "Great tables of calories and nutritional value of food", the pickled cucumber has only 2 mg vitamin C, while in accordance with "Nutritional value of selected food products and typical dishes" this value is 4 mg/100 g fresh vegetable [12–13].

Chilled storage of vegetables causes a decrease in vitamin C content and the extent of degradation depends on its initial content in every vegetable. Compared to the raw vegetable, great losses of vitamin C (up to 80%) after 3-month chilled storage, were reported by Hounsome et al [9], who conducted similar studies but on white cabbage. On the other hand, Grzesiuk and Gorecki [14] observed small losses of this vitamin in white cabbage; after 6-month chilled storage, the losses recorded were only of 18%. Falls in vitamin C content due to chilled storage were also confirmed by the findings of Kmiecik and Lisiewska [15], who examined marinated paprika and Wojdyla et al [16], who investigated marinated pumpkin.

Acidic environment, as the only one, stabilizes the level of vitamin C. Pickled cucumbers have acidic pH ranging in 3.4–4.0 [17]. These studies revealed a sharp decline in vitamin C after 1 month of storage and milder after the second month; the level of this vitamin has stabilized only after third and fourth month of chilled storage. A fall in vitamin C content in stored vegetables could result from temperature fluctuation throughout the process discussed [18]. Losses in vitamin C may also be caused by previous technological operations such as: peeling, cutting, which lead to enzymatic decomposition of this substance or its exposure to oxygen [19]. The process of cucumber preservation generally causes a decrease in vitamin C content. However, as the solution contains more vitamin C, a direct contact surface cucumber/solution should be created in order to reduce such losses. In view of the above, cutting off cucumber ends may be a good method of vitamin C stabilization [17].

The package type has also an effect on losses in vitamin C in the chilled stored vegetables. In the case of broccoli which was chilled stored for 6 days in intended to come into contact with food open plastic boxes, Nath et al [20] recorded vitamin C losses of as much as 72%, while in the vegetables packed hermetically in polypropylene (PP) foil the losses were much smaller, amounting to 29.2%.

There was no data on the impact of the packaging type used in this work on changes in the content of vitamins in pickled cucumber.

Total polyphenols

In the pickled cucumbers examined in this work, total polyphenols amounted to 61.8 mg (expressed as chlorogenic acid – CGA) per 100 g fresh matter of the vegetable. However, since there is no literature data referring to pickled cucumbers, the results have been compared to fresh cucumber, in which Kevers et al [21] registered, on average, 20 mg total polyphenols (expressed as chlorogenic acid); the values reported by Ciz et al [22] and Chu et al [23] were respectively 24.2 mg and 14.37 mg per 100 g fresh matter of the vegetable (expressed as gallic acid). On the other hand, the content of total polyphenols, when expressed as caffeic acid, was 18.9 mg per 1 g fresh matter, as was reported by Ninfali et al [24].

The level of total polyphenols in vegetables depends on several factors such as, for example, genetic, environmental or technological. Preliminary treatment of vegetables (peeling and cutting) leads to enzymatic decomposition of these substances or their decomposition due to the presence of oxygen. In addition, the long-term storage intensifies the processes of enzymatic or chemical oxidation of these substances to an extent depending on environmental factors such as, among others, temperature, pH, water activity, time and the access to oxygen [25]. According to Vina and Chaves [26], a degree of reduction in the level of chlorogenic acid in the celery leaves stored at 10^{o}C and 4^{o}C was three and two times greater respectively than in those stored at 0^{o}C.

A fall in total polyphenols in the chilled stored vegetables may result from the temperature variations during the process. Some of the factors, however, can be controlled to optimize the concentration of total polyphenols. Effect of chilled storage may also depend on the type of vegetable. According to the literature data, the number of total polyphenols may remain unchanged (yellow pepper), increase (tomato, broccoli) or can decrease (lettuce, celery) [19, 21]. As was reported by Bunea et al [27], 24-hour storage of spinach at 4^{o}C caused a 7.6% reduction in these constituents, while after 72-hour storage the losses were greater and amounted to 11.2%. Packaging of the product stored is another important factor to be considered. There was not found even a 1% fall in the level of polyphenols in the broccoli packed in the polypropylene (PP) foil and stored at 5^{o}C for 7 days; whereas, a considerable decrease (of about 27%) was noted in broccoli stored under identical conditions but unpacked [28].

In this study, pickled cucumbers stored in PET met/PE bags was characterized by significantly higher polyphenol content compared with vegetables stored in bags made from PE-LD. There was no evidence on the impact of the packaging type used in this study on changes in the content of polyphenols in pickled cucumber.

Antioxidant activity

In this work, antioxidant activity in pickled cucumbers prior to their packaging was 1.4 μm Trolox eq/1 g fresh matter of the vegetable. However, as there is no the literature on the antioxidant activity of pickled cucumber, the results obtained in this work for antioxidant activity, as in the case with total polyphenols, were compared with the antioxidant activity of fresh cucumber. According to Cao et al [29], antioxidant activity of cucumbers ranged from 0.5 to 3.8, while this recorded by Pellegrini et al [30] was 0.43 μm Trolox eq/1 g fresh matter of the vegetable. Other authors found that antioxidant activity of fresh cucumbers, was 1.82 [24], 1.60 [21], and 1.20 μm Trolox eq./1 g fresh vegetable [22]; however, these values were determined by means of an ORAC method.

Preliminary processing of vegetables (peeling, cutting or comminuting) reduces antioxidant activity of from 20 to even 60% compare to the raw material; this is probably due to the action of enzymes (polyphenoloxidase) and the presence of oxygen [31]. Chilled storage of vegetables causes changes in the levels of antioxidants and induces their mutual interactions, which in turn leads to difficult to predict differences in antioxidant activity. Kevers et al [21] observed either an increase in this parameter (garlic, yellow paprika, broccoli) or a decrease (spinach, lettuce, leek, celery) depending on the vegetable examined. The nature of such changes is also affected by the processes applied and the additives used and is additionally associated with the oxidation-reduction reactions occurring among antioxidants. Storage, among other factors, has an effect on an increased enzymatic or chemical oxidation of polyphenols, which significantly affect antioxidant potential of the analyzed vegetables [19].

Murcia et al [32] found that chilled stored vegetables (lettuce, broccoli, and Brussels sprouts) lost about 30–40% their initial antioxidant activity after only 1-week chilled storage, while cucumber only 0.9%. The greater losses (up to 53.8%) in antioxidant activity in chilled stored broccoli were recorded by Nath et al [20].

Temperature of chilled storage of vegetables may also have an effect on their antioxidant activity, since, as reported Javanmardi and Kubota [1], antioxidant activity of tomatoes stored for one week at 5^{o}C was 1.77 higher than those kept at 12^{o}C.

However, there is no research in the available literature dealing with the effect of packaging on antioxidant activity of the chilled stored vegetables.

Nitrates and nitrites

Vegetables and vegetable products provide about 80% of nitrates in the daily food ration. These are substances of low-toxicity and most of them, in an unchanged form, are excreted from the body with urine. Part of them, however, is converted into the toxic nitrites in the gastrointestinal tract. So, the level of nitrites results from the content of nitrates. Hence, both of these constituents will be discussed together [4].

As there is no the literature concerning the contents of nitrates and nitrites in pickled cucumbers, the results obtained will be confronted with those for fresh cucumbers.

In the present study, the amount of nitrates determined in the pickled cucumbers prior to their packaging was 12.1 mg NO_3^-/kg fresh vegetable (321.3 mg $NaNO_3$/kg fresh matter). A slightly lower value, varying from 9.25 to 9.38 mg NO_3^-/kg fresh vegetable mass, was registered by Gajc-Wolska et al [33]. The result of 313.1 mg $NaNO_3$/kg fresh vegetable mass, registered by Tietze et al [34], was very similar to the result obtained in the present work; although, the levels of nitrates in cucumbers determined by Pirog et al [35], fluctuated broadly from 86.0 to 539.3 mg $NaNO_3$/kg fresh vegetable mass.

Existing legislation, such as the obligatory EC Regulation of 2011, sets maximum acceptable levels for nitrates only in selected vegetables such as fresh, preserved, and frozen spinach, fresh lettuce, rucola and Iceberg-type lettuce; the level of nitrites was not set [36].

In vegetables, the degree of nitrates accumulation depends on several factors, of which crucial are genetics, species, and the cultivar. Taking into account the ability to accumulate nitrates, vegetables can be divided into 3 groups: the first (tomato, cucumber, beans) accumulates small amounts; the second (carrots, celery leaves) gains moderate quantities; and the third (lettuce, spinach, and early cabbage) accumulating substantial quantities of such nitrates. The level of nitrates is also affected by the stage of maturity (young plants are abundant in these substances); type of soil and its pH (heavy soils, along with low pH of soli favour the accumulation of nitrate ions); fertilization (dose, form of nitrogen, and manner of fertilization); exposure to the sun's rays (a small amount of light elevates the level of nitrates); and water availability (during drought larger quantities are accumulated) [34, 37]. Their increase is also influenced by the presence of microelements in soil, particularly by the deficiency of molybdenum. Storing of the raw material under appropriate conditions is also essential, since too high temperature and oxygen deficiency may lead to unfavourable biochemical processes, which have an effect on the levels of nitrates [38].

The findings of Lisiewska and Kmiecik [39] revealed that the content of nitrates in vegetables from *Cucurbitaceae* family depends on edible part of vegetable. It has been found that when the cucumber length was rising, the content of nitrates was falling. When storing vegetables, physical, microbiological and biochemical changes, occurring in this period, have an effect on their chemical composition, including changes in the nitrates content.

In the present work, the level of the nitrites was found to be 0.8 mg NO_2^-/kg fresh matter (1.2 mg $NaNO_2$/kg fresh matter) and this result is congruent with the findings of Hou et al [4], who examined pickled cucumbers. The results obtained from 25 samples ranged from 0.14 to 9.36 mg NO_2^-/kg fresh vegetable matter of the vegetable. On the other hand, Pirog et al [35] revealed that this value was within the range 0.01–0.15 mg $NaNO_2$/kg fresh matter of the vegetable.

Ezeagu [40] conducted studies on differences in the levels of nitrites and nitrates in ogi, which is maize-fermented porridge originated from Nigeria, throughout its 8-day storage at room temperature. The author found an about 80% reduction in nitrates, while the level of nitrites increased of about 200% compared to the not stored porridge.

Throughout the period of chilled storage of vegetables, accumulation of nitrates may, although non-necessarily, be inhibited. Inadequate storage conditions may lead to an increase in bacteria containing the enzyme nitrate reductase contributing to the conversion of nitrates and other nitrogen compounds into nitrites and thereby to an increase in the content of nitrites in vegetables [4].

The studies of Niewczas et al [37] on changes in nitrates in the *Cucurbita maxima* pumpkin proved that 3-month storage reduced their level by 62.2% compared to the initial quantities; however, no differences were found in the content of nitrites. These studies showed that the levels of both nitrates and nitrites increased considerably.

In chilled stored vegetables, a package has an effect the content of nitrates and nitrites. Pickled vegetables (turnip, cucumber, and cabbage), which were chilled stored in hermetic plastic containers, contained significantly less nitrites (the mean value for all the vegetables examined: 2.73 mg NO_2^-/kg fresh matter) than the same vegetables stored without packaging (6.08 mg NO_2^-/kg fresh matter) [4].

There was no data on the impact of the packaging type used in this work on changes in the content of nitrates and nitrites in pickled cucumber.

Conclusions

This work revealed that, compared to the vegetables before packaging, a 4-month period of chilled storage of vegetables led to a decrease in the content of vitamin C, total polyphenols, as well as a fall in antioxidant activity, which was accompanied by an increase in the levels of nitrates and nitrites, regardless of the package used. The differences were statistically significant ($p \leq 0.05$).

These studies proved also that type of the package used had no statistically significant ($p > 0.05$) effect on the content of vitamin C, nitrates and nitrites as well as antioxidant activity in cold-stored pickled cucumbers.

It has been found that a decrease in total polyphenols in pickled cucumbers stored in PET met/PE bags was smaller compared to those stored in PE-LD bags with the zipper closure and these values were statistically significant ($p \leq 0.05$).

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WPŁYW OPAKOWANIA NA JAKOŚĆ ZDROWOTNĄ OGÓRKÓW KISZONYCH CHŁODNICZO SKŁADOWANYCH

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Abstrakt: W związku z nietrwałością przechowalniczą ogórków i ich sezonowością jedną z najkorzystniejszych metod ich utrwalania jest kiszenie. Celem niniejszych badań przeprowadzonych w 2014 r. było zbadanie wpływu rodzaju opakowania (torebki wykonane z folii polietylenowej o małej gęstości (PE-LD) oraz torebki z metalizowanego politereftalanu etylenu (PET met/PE) na wybrane parametry jakościowe ogórków kiszonych. Analizy były wykonywane w warzywach przed zapakowaniem oraz po 1-, 2-, 3- i 4-miesięcznym okresie chłodniczego składowania w dwóch rodzajach opakowań. Badania nie wykazały istotnego statystycznie ($p > 0,05$) wpływu rodzaju użytego opakowania na zawartość witaminy C, azotanów(V), azotanów(III) oraz na aktywność antyoksydacyjną przechowywanych w nich chłodniczo ogórków kiszonych. Istotnie statystycznie ($p \le 0,05$) wyższą zawartością polifenoli ogółem odznaczały się ogórki kiszone przechowywane w woreczkach z folii metalizowanej.

Słowa kluczowe: przechowywanie chłodnicze, opakowania strunowe z PE-LD, opakowania metalizowane PET/met/PE, azotany(V), azotany(III), ogórki kiszone, witamina C, aktywność antyoksydacyjna

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Izabela PIETKUN-GREBER[1]

DC01 STEEL CORROSION RESISTANCE IN CATHODIC POLARIZATION

ODPORNOŚĆ KOROZYJNA STALI DC01 W WARUNKACH KATODOWEJ POLARYZACJI

Abstract: The aim of the conducted research was to determine the corrosion resistance of the DC01 steel subjected to the cathodic polarization in variable conditions. The electrochemical measurements help to assess the corrosion resistance of the unhydrogenated steel subjected to the cathodic polarization and were taken using methods including the measurement of the open circuit potential as well as recording the $i = f(E)$ relation in polarization research in a tri-electrode measurement system. The measurement system consisted of a sample cell, AMEL PSW01 System 5000 potentiostat and a computer with "CorrWare" software. Hydrogenated steel was conducted in a 0.1 N water solution of the sulfuric acid with the addition of 2 mg/dm^3 of the arsenic trioxide as the penetrator promoter with the current density of 10 mA/cm^2 and 20 mA/cm^2 in the period of 3 to 24 hours. The content of hydrogen in the steel before and after the electrolytic hydrogenation process had been carried out, was marked using the LECO ONH836 analyser. It has been shown that with the hydrogen content decrease in the samples of the DC01 steel taken into consideration in the research (the amount of hydrogen depends on parameters of hydrogenation – the time and cathode current density), the value of the corrosion potential (E_{corr}) decreases. The decrease in the polarization resistance was accompanied only by the simultaneous decrease of the corrosion current density, which results in increased corrosion rate. The higher value of the cathode current density and longer time of hydrogenated, the smaller corrosion resistance of the DC01 steel in a 3% solution of NaCl.

Keywords: hydrogen, hydrogen content, cathode polarization, corrosion resistance

Introduction

The exploitation of products, structures and devices in various corrosion-aggressive environments make them exposed to damages caused by hydrogen. In relation to the time of hydrogen reaction, two types of hydrogen embrittlement: the external hydrogen embrittlement (*HEE*) and internal hydrogen embrittlement (*IHE*). In relation to the temperature, in which the process of hydrogen metal destruction is carried out, two phenomena can distinguished: high temperature hydrogen Aattack (*HTHA*) (tempera-

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tures above 200°C) and low temperature hydrogen attack (*LTHA*). Low temperature hydrogen destruction can be displayed in different ways, as: delayed hydrogen cracking (*HDC*), sulfide stress-corrosion cracking (*SSCC*), hydrogen induced cracking (*HIC*), "fish eyes" type cracking, hydrogen blisters. The intensity of the degradation process of the construction materials (metals, alloys), due to the absorbed hydrogen, is significantly dependent on the hydrogen's ability to dissolute and the diffusion rate. The hydrogen solubility in the hydrogen alloys, beside its gas pressure and temperature, depends on the crystal lattice type. The hydrogen diffusion in steel with regularly body-centred structure (*A*2), in comparison with steel with regularly-centred cubic structure (*A*1) is easier. The hydrogen atoms mobility in the latter is significantly lesser.

In construction materials, the hydrogen distribution is not uniform in the whole volume, while the local hydrogen concentration increase takes place in so-called hydrogen traps. Hydrogen traps can be divided into reversible traps (bond energy equal 60–75 kJ/mole) – decreasing the hydrogen mobility in the metal, at the same time slowing down its transport to locations of nucleation of the structure discontinuity, and irreversible traps (bond energy 25–30 kJ/mole), which accumulate hydrogen, contributing at the same time to cracking nucleation and metal delamination [1]. The difference between the reversible and irreversible traps cannot be stated explicitly. In most cases, the value of about 60 kJ/mole is taken into consideration [2]. In steel, hydrogen traps constitute structure defects, such as: non-metallic inclusions, grain boundaries, non-mantellic inclusions and alloy elements segregation, screw and edge dislocations, discontinuities [3–7]. The traps differ from one another with the hydrogen bond energy. The bond energy of Al_2O_3 with hydrogen is 79–86.2 kJ/mole [8]. Equally intense reaction can be found between the hydrogen atoms of MnS (72 kJ/mole) [9] and Fe_3C (84 kJ/mole) [5]. Significantly lesser energies of bonding with hydrogen have reversible traps (in certain temperature, hydrogen can leave the trap), *ie* grain boundaries, micro-voids as well as dislocations (screw, edge) [5]. The calculated energy of the screw dislocation bond with hydrogen equals 37–42 kJ/mole and 26–29 kJ/mole in case of screw dislocation [1].

The impact of the environment and hydrogen absorbed from it can influence the steel characteristics differently. In most cases, the impact is destructive, causing the mechanical properties, corrosion resistance as well as premature destruction to worsen. Mechanical properties degradation of steel exposed to hydrogen is revealed mostly by the decrease in their plastic properties, *ie*, contractions and elongations [10–13]. In case of stainless steel (ferritic, ferritic-austenitic) factors that can cause the decrease in plasticity include among others: complex microstructural changes in the surface layer induced by hydrogen. The changes are manifested by the creation of micro-twins, resulting in an surface relief effect in the form of needles [14]. The change of mechanical properties can be seen on the surface of fractures after the static stretching test. The hydrogen destruction causes the change in fracture characteristics leading to the trans-crystal and intergranular brittle fracture [15].

The conducted research [16–18] has shown, that electrochemical hydrogenation of metallic material causes their change in corrosion resistance. The change is revealed by the offset of electrode potential value towards stronger activity, the increase in corrosive current density as well as polarization resistance decrease. In case of stainless steel, hydrogen can considerably disturb and hinder the passivation processes. Moreover, intense defects of the surface layer caused by the hydrogen saturation, influences their pitting corrosion resistance that decreases [14]. A galvanic hydrogen cell (Fig. 1) is created together with slots in metals and alloys accompanied by the simultaneous hydrogen reaction and stretching tensions (stress corrosion). It is caused by the diversity in amount of hydrogen absorbed by the tip and walls of the split. The cell together with the stretching cell and galvanic cell are important factors contributing to the slots' length growth, which is a favourable phenomenon as far as the durability of the loaded construction component in concerned.

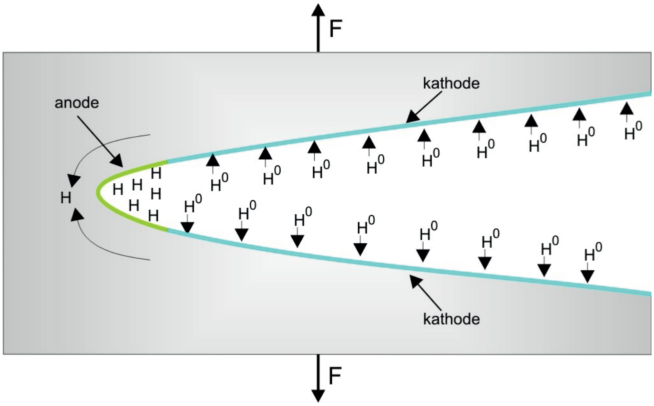

Fig. 1. The diagram of the electrochemical process present in the slot

It is of a great importance then, to conduct a research considering the changes taking place due to hydrogen, especially towards the changes in mechanical and electrochemical properties of various steel types. The results of the research can constitute not only a valuable tool in designing and creating materials resistant to hydrogen defects, and what is more, can contribute to improve the process of choosing the right materials while designing.

The aim of the research is to assess the influence of hydrogen content on the possible changes in corrosion resistance of the unalloyed DC01 steel and using the process to determine its exploitive suitability in the environment containing hydrogen. These studies complement the assessment of the steel DC01 subjected to cathodic polarization in changing conditions [19].

Studied material and research methodology

The material taken into account in the research is DC01 type of steel in a form of a cold-rolled sheet metal 2.0 mm thick. The chemical composition of the steel, made in the optical spectrometer, as well as element composition for steel according to PN-EN 10152 [20] gathered in Table 1.

Table 1

The chemical composition of the tested DC01 steel

Chemical element	Contents [wt. %]	
	PN-EN 10152	spectra analysis
C	0.12	0.04
Mn	0.60	0.29
Si	—	0.02
P	0.045	0.009
S	0.045	0.004
Cu	—	0.05
Cr	—	0.02
Ni	—	0.03
Fe	—	Bal.*

* Balance.

The process of electrolytic hydrogenation of steel samples has been carried out in 0.1 N water solution of the sulfuric acid with the addition of 2 mg/dm^3 of the arsenic trioxide. The current density of 10 mA/cm^2 and 20 mA/cm^2 in the period of 3 to 24 hours were taken into consideration. Once the hydrogenation process was finished, the samples were taken out from the sample cell intended for electrolytic hydrogenation, rinsed in distilled water, dried with absorbent paper, and then put in the measuring vessel. The measurements were taken in temperature of 21–23°C. All parameters were studied in 3 tests.

The amount of hydrogen in samples of the steel taken into account in the research and after the hydrogenation process was marked using the LECO ONH836 analyser (Fig. 2). Hydrogen marking included the melting method in the atmosphere of inert gas. The measurements of hydrogen content in steel were taken from three samples in the delivery conditions and after the hydrogen saturation. In order to limit the risk of

Fig. 2. LECO analyser of oxygen, nitrogen and hydrogen ONH836

hydrogen absorption from the alloy, until the analysis of its concentration in the sample was conducted, the samples were kept in liquid nitrogen.

The microscope observations of the steel in the delivery conditions, as well as after cathode hydrogen saturation, were conducted using the Scanning Electron Microscopy (*SEM*, *EDS*) method. The research was carried out using a Hitachi S-3400N scanning electron microscope. A 3% solution was used to pickle the steel surface samples.

Electrochemical measurements contribute to the assessment of the corrosion resistance of the unhydrogenated steel and subjected to cathode polarization, were taken using the methods including the measurement of the open circuit potential (E_0) and recording the $i = f(E)$ redundancy during the polarization research in a tri-electrode measuring system. The guidelines for the performance concerning taking the potentiodynamic polarization measurements, including the procedures and their implementation, are determined by the PN-EN ISO 17475:2010 norm [21]. The research included also a system which included a counter electrode (*CE*) and reference electrode (*RE*), AMEL PSW01 System 5000 potentiostat and a computer with “CorrWare” and “CorrView” software (Fig. 3). The counter electrode is a platinum electrode, while the reference electrode is a saturated calomel electrode (*NEK*). A 3% NaCl water solution with pH ≈ 6.0 was also used in the research, kept in temperature around 23°C. Depending on the research type, the work electrode (*WE*) were a properly unhydrogenated and hydrogenated 50 mm^2 steel samples. The samples were grinded with water abrasive paper with the 1200 grain-size, and then carefully rinsed with distilled water, avoiding greasing the grinded surface. Grinded samples were cleaned with ethylic alcohol, using a ultrasonic washer, rinsed with distilled water and dries with absorbent paper. Samples

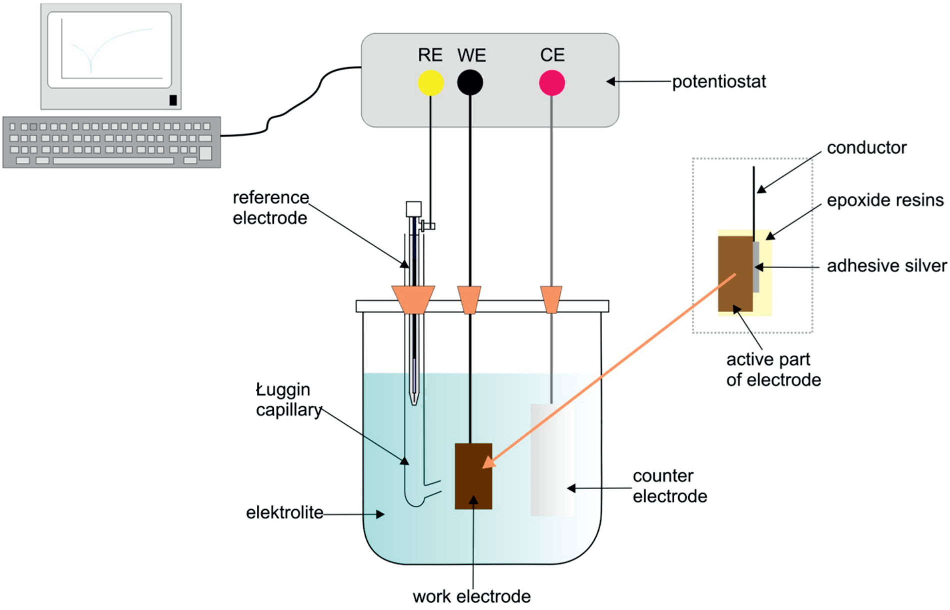

Fig. 3. The diagram of the electrochemical measurement station

prepared in such a way, depending on the research type, were placed directly in the electrochemical cell or electrolytic cell in order to saturate the samples with hydrogen.

Before commencing the polarization measurements of unhydrogenated and hydrogenated samples, the open circuit potential (E_0) measurements were taken of the researched steel in order to determine the values of the initial corrosion potential (E_{corr}). After the measured value of the open circuit potential was stabilized, their polarization was commenced; the speed of scanning of the potential was $dE/dt = 1$ mV/s in the area ±300 mV from the value of the open circuit potential (E_0). The value of corrosive current density (I_{corr}), the corrosion potential (E_{corr}) and polarization resistance (R_p) were determined using Stern method.

The results and review

The designated hydrogen content in the researched steel, in the delivery conditions, not subjected to cathode polarization was 1.26 ppm. Together with the increase of current density of the cathode polarization and its duration time, the concentration of the absorbed hydrogen decreased (Fig. 4). After cathode polarization lasting for 3 hours, with the current density of 10 mA/cm^2 and 20 mA/cm^2, the hydrogen concentration reached 13.00 ppm and 18.87 ppm respectively. Prolonging the time of hydrogenation up to 12 hours, with the current density of 10 mA/cm^2 and 20 mA/cm^2 caused the increase of hydrogen amount in relation to unhydrogenated samples for 16.04 ppm and 18.37 ppm respectively. The highest value of the hydrogen content, *ie*, 22.37 ppm, was noted in samples subjected to cathode polarization lasting 24 hours with the current density of 20 mA/cm^2.

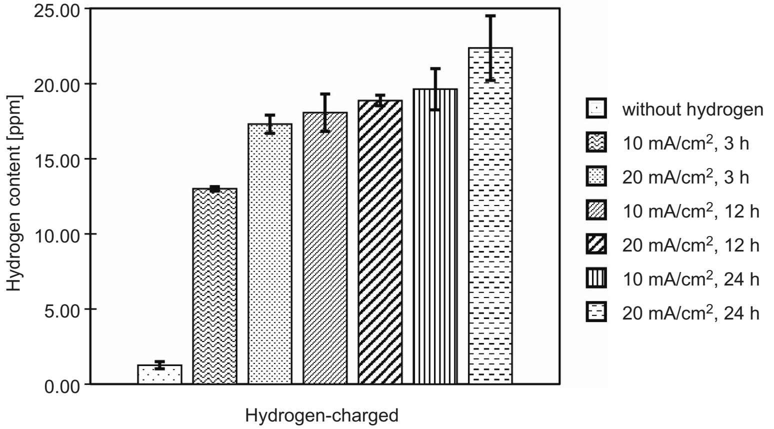

Fig. 4. Hydrogen content in the researched DC01 steel

The conducted microscope research showed, that the microstructure of the researched DC01 steel consists of ferrite grains and carbides visible on the ferrite grains boundaries as well as in their insides (Fig. 5).

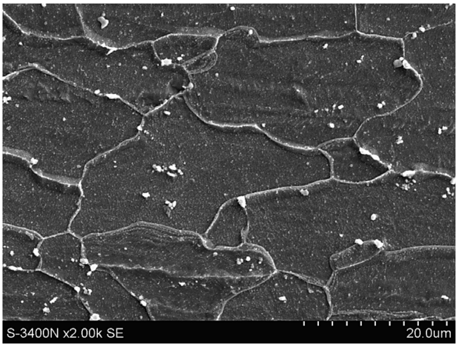

Fig. 5. DC01 steel structure

The observation of the surface of steel samples subjected to cathode polarization showed explicit changes in the microstructure caused by the hydrogen absorption (Fig. 6–8). The carried out observation showed also, that in the surface layer of samples,

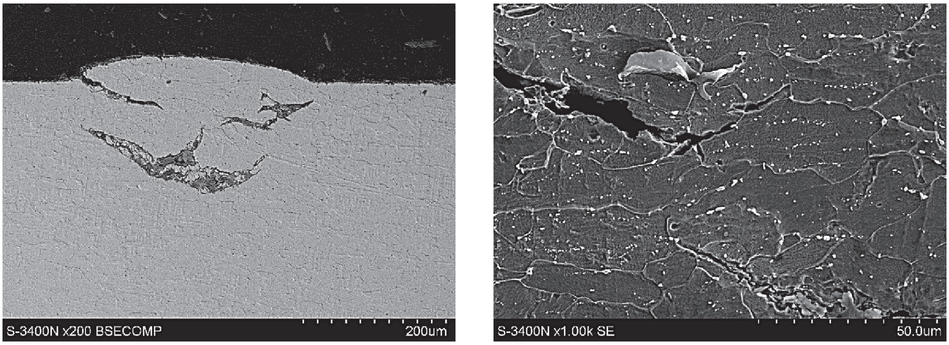

Fig. 6. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2SO_4 + 2 mg As_2O_3 with the cathode polarization current density of 10 mA/cm^2, in 12 hours

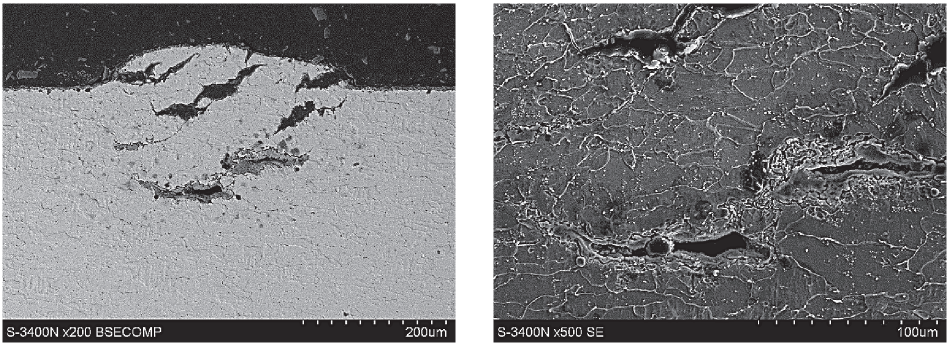

Fig. 7. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2SO_4 + 2 mg As_2O_3 with the cathode polarization current density of 10 mA/cm^2, in 24 hours

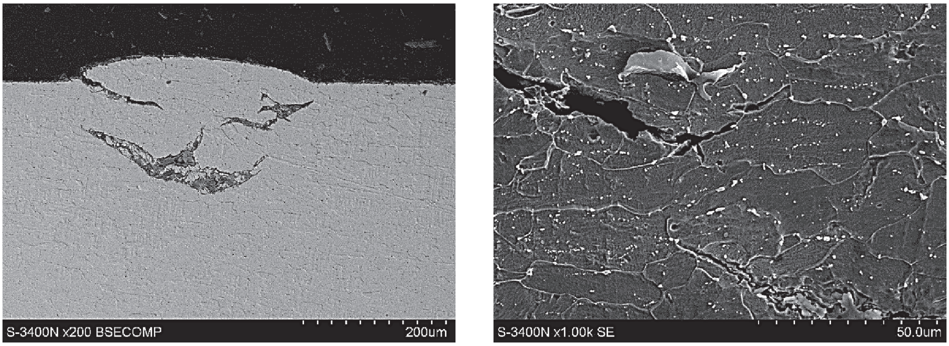

Fig. 8. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2S0_4 + 2 mg As_2O_3 with the cathode polarization current density of 20 mA/cm^2, in 24 hours

for which the hydrogen impact is the most intense, in relation to the permanent contact of the surface with hydrogen during the polarization, caused hydrogen blisters and micro-cracks to appear. Defects in form of blisters and micro-cracks are the result of a strong supersaturation of the metallic phase with hydrogen and the recombination of the atomic hydrogen around physical and chemical defects of metals (non-metallic inclusions, pores, micro-cracks).

The corrosion potential value (E_{corr}) of the unhydrogenated DC01 steel, measured in the 3% NaCl solution was –479 mV (Table 2).

Table 2

The results of potentiodynamic measurements

Sample		E_0		E_{corr}		I_{corr}		R_p	
		average	±SD	average	±SD	average	±SD	average	±SD
		[mV]		[mV]		[μA/cm^2]		[kΩ/cm^2]	
Without hydrogen		–571	8	–479	12	14.94	0.31	1.74	0.17
10 [mA/cm^2]	3 h	–599	12	–529	6	15.77	0.19	1.68	0.18
	12 h	–642	7	–546	10	18.39	0.50	1.39	0.22
	24 h	–646	5	–567	12	19.71	0.36	1.32	0.23
20 [mA/cm^2]	3 h	–659	6	–574	9	20.25	0.29	1.29	0.24
	12 h	–678	7	–584	10	22.68	0.90	1.22	0.25
	24 h	–687	6	–646	14	30.34	1.85	0.86	0.35

The results of the conducted data analysis contained in Table 2 show, that the hydrogen absorb hydrogenation by the steel causes the change in its corrosion potential value. The steel potential value, depending on the amount of hydrogen absorbed during

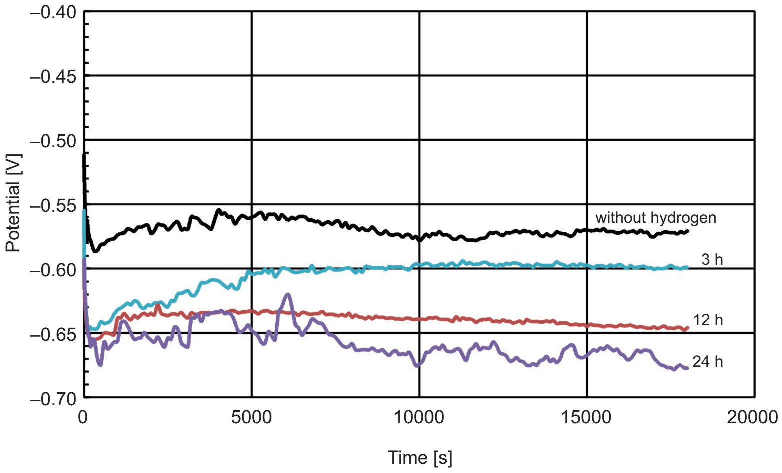

Fig. 9. The course of change in potential values of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 10 mA/cm^2

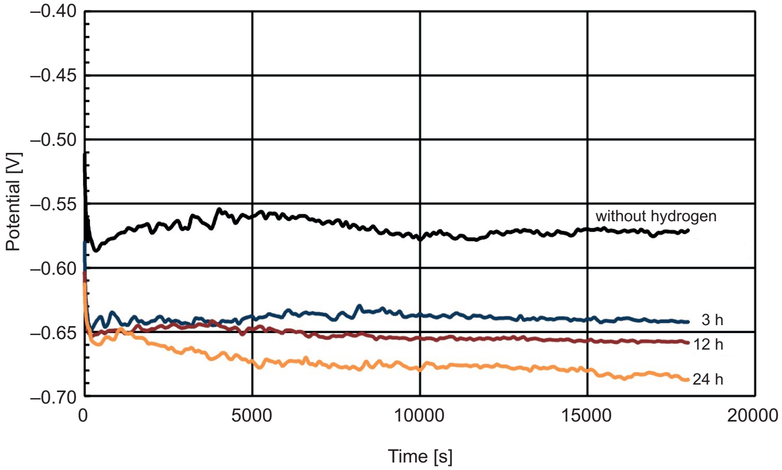

Fig. 10. The course of change in potential values of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 20 mA/cm^2

the cathode polarization was –529 mV up to –646 mV. The decrease of polarization resistance appeared only with the decrease of the corrosion current density from 14.99 $\mu A/cm^2$ to 30.34 $\mu A/cm^2$, which results in increase of the corrosion speed. On potentiodynamic curves of the researched DC01 steel samples both subjected and non-subjected to the cathode polarization, no passive range has been observed. The increase of potential value caused a constant increase of the current density (Fig. 11–12).

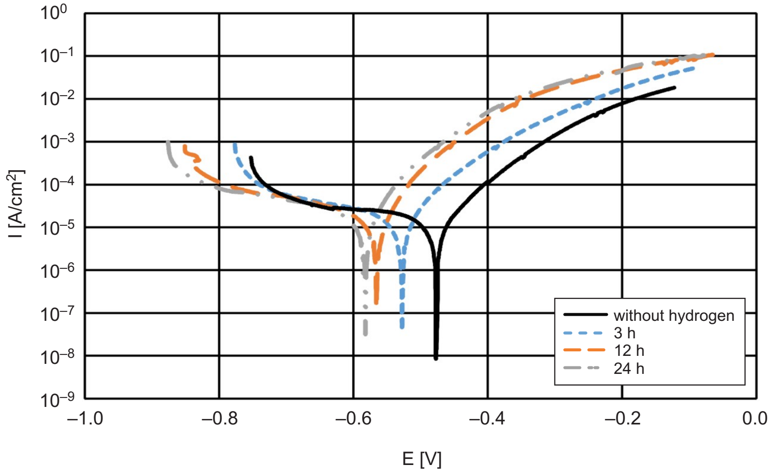

Fig. 11. Polarization curves of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 10 mA/cm^2

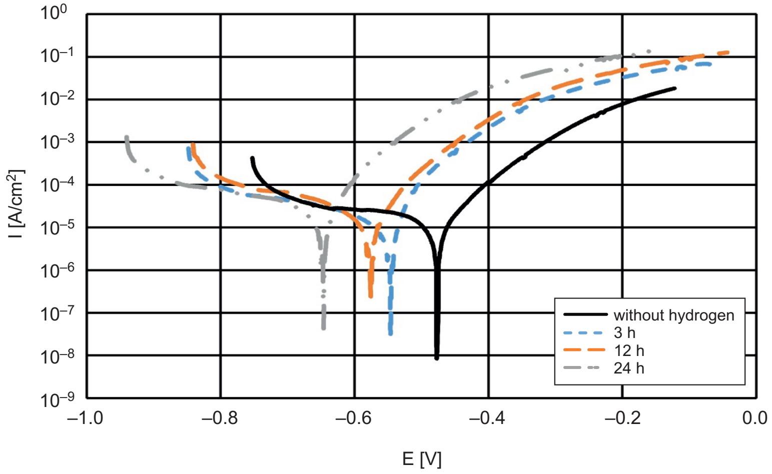

Fig. 12. Polarization curves of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 20 mA/cm^2

Summary and conclusions

The conducted research showed, that the content of the hydrogen absorbed by the DC01 steel influence the conditions of the cathode polarization being carried out. The hydrogen concentration in steel increases together with prolonging the duration of the cathode polarization, as well as the increase in the cathode current density. The hydrogen reaction in the DC01 steel leads to worse corrosion resistance measured in the 3% NaCl water solution. It has been stated, that current density of the cathode polarization and its duration cause the change in the researched corrosion resistance of the DC01 steel measured in the 3% NaCl water solution. It has been also shown, that together with the increase of the hydrogen content in the DC01 steel samples, the value of the corrosion potential (E_{corr}) decreased. The decrease of polarization resistance appeared together with simultaneous increase of the corrosion current density, which led to the increase of the corrosion rate. The higher value of the cathode current density and longer duration of hydrogenation, the lesser the DC01 steel corrosion resistance measured in the 3% NaCl water solution.

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ODPORNOŚĆ KOROZYJNA STALI DC01 W WARUNKACH KATODOWEJ POLARYZACJI

Samodzielna Katedra Inżynierii Procesowej
Uniwersytet Opolski, Opole

Abstrakt: Celem prowadzonych badań było określenie odporności korozyjnej stali DC01 poddanej katodowej polaryzacji w zmiennych warunkach. Elektrochemiczne pomiary służące do oceny odporności korozyjnej stali nienawodorowanej poddanej katodowej polaryzacji przeprowadzono metodami obejmującymi pomiar potencjału obwodu otwartego i zarejestrowania zależności $i = f(E)$ podczas badań polaryzacyjnych w trójelektrodowym układzie pomiarowym. Do pomiarów wykorzystano układ składający się z naczynka pomiarowego, potencjostatu AMEL PSW01 System 5000 oraz komputera z oprogramowaniem „CorrWare". Wodorowanie stali zrealizowano w wodnym roztworze 0,1 N kwasu siarkowego(VI) z dodatkiem 2 mg/dm^3 tlenku arsenu(III) jako promotora wnikania wodoru, przy gęstości prądu 10 mA/cm^2 i 20 mA/cm^2 w czasie od 3 do 24 godzin. Zawartość wodoru w stali przed oraz po procesie elektrolitycznego nawodorowania oznaczono przy użyciu analizatora LECO ONH836. Wykazano, że wraz ze zwiększaniem się stężenia wodoru w próbkach badanej stali DC01 (ilość wodoru zależy od parametrów wodorowania – czas i gęstość prądu katodowego) wartość potencjału korozyjnego (E_{kor}) ulegała zmniejszeniu. Spadkowi oporu polaryzacji towarzyszyło jednocześnie zwiększenie gęstości prądu korozyjnego, co skutkowało zwiększeniem szybkości korozji. Im większa wartość gęstości prądu katodowego i dłuższy czas wodorownia, tym odporność stali DC01 na korozję w 3% roztworze NaCl jest mniejsza.

Słowa kluczowe: wodór, zawartość wodoru, polaryzacja katodowa, odporność korozyjna

Varia

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