The study was aimed at determining the effect of microwave radiation on transformations of organic compounds in the reactor equipped with a biological membrane. The test stand was designed in such a way that only the biological membrane, and not the wastewater being treated, was radiated.

It was found that microwave radiation reduced the amount of organic compounds in the wastewater treated. The part of biosynthesis in removing organic contaminants was reduced in the reactors subjected to radiation. Due to the temperature effect brought about by microwaves, anoxic zones appeared and nitrate respiration was facilitated.

1. INTRODUCTION

The effect of electromagnetic radiation on bodies depends on the amount of energy carried by quanta or, in a wave approach, on the frequency of the electromagnetic wave, i.e. on the wavelength. If the quantum energy exceeds $1 \times 10^2$ eV (X or $\gamma$ radiation) an electron can be knocked out of an atom and then ionised. Low values of the energy of UV radiation are sufficient to reduce the strength of molecular bonds and to break them. The energy of the quanta of visible and IR radiation is sufficient to excite electrons of the outer shells only. This may take molecules up to excited states and consequently enable them to create certain chemical bonds.

Microwaves are a part of the electromagnetic spectrum, with a wavelength ranging from 1 mm to 1 m and with corresponding frequencies from 300 MHz to 300 GHz. The energy carried by quanta of microwave radiation is not high enough to be absorbed by electrons – it neither excites them nor knocks them out of the atoms. The interaction between microwave radiation and molecules does not bring about any
change in their structure. The interaction between electromagnetic field of a microwave frequency and various materials depends on the type of the latter – to be precise: on their dielectric properties, i.e. their ability to carry electric current.

For the materials such as metals with a high conductivity and low capacitance (capacitance retention) the dielectric loss factor is high. When the dielectric loss factor is very high, the penetration depth is close to zero. Materials of such dielectric properties should be treated as reflecting microwaves (reflectors). Materials whose dielectric loss factor is low are characterised by a very high penetration depth (plastics). As a result, a small portion of energy is absorbed in the material and such a body is penetrated by microwaves. Microwaves provide energy for those materials whose dielectric properties are within this range. Water is an example of such a substance. It is assumed that a temperature rise during material interaction with microwaves is due to oscillations of dipolar molecules rather than migration of ions (this applies only to solutions) [8], [15]. The energy of the microwaves is dispersed as heat from internal rotation, which means that the moving dipolar molecules disperse by friction their energy being earlier absorbed from microwaves; this results in the temperature rise.

The effects of microwave electromagnetic energy on living organisms are divided into two groups – thermal effects and non-thermal (athermal) effects. The interaction of electromagnetic energy with a given organism always means the transfer of energy and usually leads to a temperature rise; the term “athermal” refers to the effects of the interactions of microwaves which are specific to electromagnetic energy; they are not observed during conventional heating [13].

In living organisms, which contain a lot of water, it is difficult to determine unambiguously the effect of microwaves because of the high absorbance of water molecules [15]. Two mechanisms may lead to absorption of energy by a protein molecule. The first of them consists in a direct interaction of the molecule with a microwave field which causes rotation of dipolar protein molecules. In the second mechanism, a solution absorbs the energy of microwaves; this is followed by the absorbance of the resulting thermal energy by protein molecules. The electric charge is distributed in protein molecules in a certain way (isoelectric point). They contain polar chains, which may be the reason for their rotation due to microwave energy. Water molecules in the hydrated layer of proteins may also be excited by electromagnetic energy to rotate [14].

This study was aimed at determining the effect of microwave radiation on the efficiency of organic compound transformation in a reactor with a biological membrane.

2. METHODS

The experiments were conducted with a drip reactor with a biological membrane placed inside a chamber, where it was subjected to microwave radiation. The casing and filling of the reactor were made of a material transparent to microwave radiation.
The working volume of the reactor $V$ was 145 cm$^3$, while the proper area of the filling $s$ was 202 m$^2$/m$^3$, and theoretical working area of the reactor $F$ was 0.029 m$^2$.

The microwave radiation was produced by a magnetron, from which it was sent by a wave-guide to the chamber with the reactor. The total power of the reactor was 800 W, it produced microwave radiation of 2.45 GHz frequency with an efficiency of 52%. The magnetron emitted radiation with a constant efficiency, whereas the amount of energy supplied to the reactor was controlled by the duration of its work–rest cycles. Controlling the work of the microwave generator was synchronised with supplying the reactor with wastewater. Before the microwave generator was switched on, the supply of wastewater to the reactor was shut off, so the microwave energy was absorbed by the biological membrane rather than by the treated wastewater. After completion of the radiation phase the wastewater-dosing pump was restarted and the system was restored to the wastewater treatment phase (table 1).

<table>
<thead>
<tr>
<th>Radiation phase/treatment phase</th>
<th>Dose of energy supplied</th>
<th>Temperature after the radiation phase [°C]</th>
<th>Temperature after treatment phase [°C]</th>
<th>Hydraulic load, frequency of exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 s/20 min</td>
<td>1.3 W/s</td>
<td>24.3</td>
<td>22.2</td>
<td>0.05 m/h 7 × d</td>
</tr>
<tr>
<td>15 s/10 min</td>
<td>2.5 W/s</td>
<td>25.3</td>
<td>24.0</td>
<td>0.15 m/h 21 × d</td>
</tr>
<tr>
<td>15 s/5 min</td>
<td>5.0 W/s</td>
<td>28.6</td>
<td>27.7</td>
<td>0.45 m/h 63 × d</td>
</tr>
</tbody>
</table>

Due to the microwave radiation a temperature inside the biological reactor rose. The highest temperature of the biological membrane was measured immediately after the work phase of the microwave generator and depended on the amount of the radiation absorbed. Its value soon lowered with the duration of the treatment phase (table 1). The temperature of the control reactor and of the surroundings was maintained at a constant level of 18 °C.

Municipal wastewater was used for the research. It was taken daily directly from the municipal collector at a constant time. After being collected, the wastewater was subjected to sedimentation for 0.5 hours and analysed. The average ratio of BOD$_5$ to COD was 0.7. The ratio of the total nitrogen to BOD$_5$ equalled 0.26. (table 2).

The experiment was conducted in a periodical arrangement. Once a day the whole volume of wastewater in the retention reservoir was replaced. The wastewater from the retention reservoir was passed on to the bioreactor and returned (figure 1). Under the hydraulic loads applied $q_1 = 0.05$ m$^3$/m$^2$-h, $q_2 = 0.15$ m$^3$/m$^2$-h and $q_3 = 0.45$ m$^3$/m$^2$-h within 24 hours, the entire volume of wastewater passed through
the biological reactor with the frequency \( n = 7 \times d \), \( n = 21 \times d \) and \( n = 63 \times d \), respectively.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Unit</th>
<th>Average value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>[mg O(_2)/dm(^3)]</td>
<td>220</td>
<td>21.1</td>
</tr>
<tr>
<td>BOD(_5)</td>
<td>[mg O(_2)/dm(^3)]</td>
<td>175</td>
<td>14.4</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>[mg N(_{eq})/dm(^3)]</td>
<td>45</td>
<td>5.6</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>[mg N–NH(_4)/dm(^3)]</td>
<td>25</td>
<td>5.3</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>[mg P(_{eq})/dm(^3)]</td>
<td>18</td>
<td>3.8</td>
</tr>
<tr>
<td>Phosphates</td>
<td>[mg P–PO(_4)/dm(^3)]</td>
<td>12</td>
<td>3.7</td>
</tr>
<tr>
<td>Total suspensions</td>
<td>[mg /dm(^3)]</td>
<td>240</td>
<td>81.5</td>
</tr>
</tbody>
</table>

A proper area of the reactor loaded with organic pollutants expressed as COD reached 4.3 g O\(_2\)/m\(^2\)-d.

Fig. 1. Diagram of the experiment layout:
1 – biological reactor; 2 – microwave chamber; 3 – retention reservoir;
4 – sewage supply to the reactor; 5 – microwave generator;
6 – wastewater exchange in the retention reservoir (one per day) (A).
Diagram of the operation of the experiment setup (B)
For the sake of comparison, the research was conducted in the reactor which was not exposed to radiation but which otherwise worked in identical hydraulic conditions and was loaded with pollutants.

The effect of microwave radiation on transformations of organic compounds was analysed. It was assumed that the whole load of carbon compounds that flowed into the reactor was used for biomass synthesis and oxidized during the substrate respiration process in aerobic conditions or during the denitrification process. The remaining, non-decomposed part of organic pollutants was carried off the system and was measured as COD in the wastewater treated. The following formulae were used in the calculations:

- The load of organic compounds used for the growth of biomass [g/d]

\[ Q_{syn} = \left( \frac{Y \cdot (C_o - C_e) \cdot V}{1000} \right), \]

where:
- \( Y \) – biomass growth factor [g/g],
- \( V \) – intensity of pollutant flow [m³/d],
- \( C_o \) – concentration of in-flowing organic compounds equivalent to COD [g/m³],
- \( C_e \) – concentration of out-flowing organic compounds equivalent to COD [g/m³].

- The load of organic compounds used in denitrification [g/d]

\[ Q_{den} = \frac{N_{red} \cdot 2.6 \cdot V}{1000}, \]

where:
- \( N_{red} \) – concentration of the nitrogen removed in denitrification [g/m³],
- 2.6 – the amount of organic compounds used for the reduction of 1 g of oxidised nitrogen [17] [g O₂/g].

- The load of oxidized organic compounds [g/d]

\[ Q_{oxy} = Q_{sup} - Q_{syn} - Q_{den} - Q_{elf}, \]

where:
- \( Q_{sup} \) – the load of organic compounds supplied to the reactor [g/d],
- \( Q_{syn} \) – the load of organic compounds used for biomass growth [g/d],
- \( Q_{den} \) – the load of organic compounds used in denitrification [g/d],
- \( Q_{elf} \) – the load of organic compounds carried off the reactor [g/d].

3. RESULTS AND DISCUSSION

Exposing a biological membrane to microwave radiation affected certain transformations of organic compounds. In the bioreactors being exposed to microwave
radiation, organic compounds were oxidised both in aerobic conditions and in the process of nitrate respiration. In the comparable conditions without microwave radiation, no nitrate respiration was observed. The magnitude of the hydraulic load of the reactor area was crucial. As the reactors worked periodically, an increase in their hydraulic load caused an increase in the exchange between the retention reservoir and the bioreactor, thus increasing the frequency of contacts between the wastewater and the biological membrane.
The effect of microwave radiation on organic compounds

Fig. 2. The per cent share of particular unit processes in the transformations of organic compounds

Table 3

<table>
<thead>
<tr>
<th>Q_{oxy}</th>
<th>Q_{den}</th>
<th>Q_{syn}</th>
<th>Q_{elf}</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD load oxidised in aerobic conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD load used in denitrification</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD load used for biosynthesis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD load carried off with the treated sewage</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Loads of organic compounds (mg COD/d) in particular unit processes
The load of organic compounds carried off with the treated wastewater testified to the treatment efficiency. The microwave energy reduced the amount of remaining organic compounds. The process was most efficient when the microwaves supplied were on the level of 2.5 W/s, and its efficiency increased with an increase in the frequency of the wastewater exchange in the reactor. Under the maximum hydraulic load of 0.45 m³/m²·h, the amount of the organic compounds which flowed from the microwave-modified reactor reached 6.0 mg COD/d which was three times as low as that in the control reactor (18.0 mg COD/d, figure 2). Using disk beds, HAMODA and AL-GHUSAIN [6] found a linear relationship between the amount of the removed load of COD and the hydraulic load. They reported that an increase in hydraulic load is followed by an increase in the amount of the pollutant removed as long as the transport of substrate or oxygen is provided. They pointed out that the efficiency of organic pollutant removal raises in a certain interval – the more frequent the contact between the membrane and the wastewater, the higher this efficiency [2]. The results obtained

<table>
<thead>
<tr>
<th></th>
<th>0.05 m/h</th>
<th></th>
<th>0.15 m/h</th>
<th></th>
<th>0.45 m/h</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 s/20 min</td>
<td>15 s/10 min</td>
<td>15 s/5 min</td>
<td>Control</td>
<td>15 s/20 min</td>
<td>15 s/10 min</td>
</tr>
<tr>
<td></td>
<td>1.3 W/s</td>
<td>2.5 W/s</td>
<td>5.0 W/s</td>
<td>n</td>
<td>δ</td>
<td>n</td>
</tr>
<tr>
<td>$Q_{odp}$</td>
<td>20.3</td>
<td>12.3</td>
<td>26.2</td>
<td>2.4</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>$Q_{syn}$</td>
<td>28.4</td>
<td>21.6</td>
<td>44.1</td>
<td>3.1</td>
<td>41</td>
<td>2.6</td>
</tr>
<tr>
<td>$Q_{ten}$</td>
<td>20.6</td>
<td>44.4</td>
<td>38.7</td>
<td>3.3</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>$Q_{ult}$</td>
<td>29.7</td>
<td>35.7</td>
<td>35.8</td>
<td>3.4</td>
<td>59</td>
<td>3.6</td>
</tr>
</tbody>
</table>

$x$ – average load, mg COD/d.

$\delta$ – standard deviation.

$Q_{odp}$ – COD load carried off with the treated sewage.

$Q_{syn}$ – COD load used for biosynthesis.

$Q_{ten}$ – COD load used in denitrification.

$Q_{ult}$ – COD load oxidised in aerobic conditions.
in the control layout showed that an increase in the frequency of wastewater pumping from \(7 \times d (q_1 = 0.05 \text{ m}^3/\text{m}^2\cdot\text{h})\) to \(63 \times d (q_2 = 0.45 \text{ m}^3/\text{m}^2\cdot\text{h})\) produced the reduction of the non-removed organic compounds to only about 7 mg/d (table 3). It may be assumed that in the experimental conditions, the system reached its maximum capacity for organic pollutant removal.

Microwave radiation affected the aerobic conditions inside a biological membrane. According to the theory of mass transfer, an increase in temperature should result in a higher oxygen diffusion to the liquid because of the greater effect of temperature and, indirectly, because of a drop in the liquid viscosity. However, many researchers report that the speed of oxygen transfer in biological systems depends, to a limited extent, on the liquid temperature only. According to Boogerd et al. [3] the speed of oxygen penetration changes only slightly within the temperature ranging from 15 to 70 °C. Vogelaar et al. [18] found that the speed of oxygen transfer is constant within the temperature range of 20–55 °C. In the reactors exposed to microwave radiation, organic compounds were oxidised both in the process of oxygen respiration and denitrification (table 3). No nitrate respiration was observed in the control reactors. Microwave energy heats a body for a short time; taking account of a small thickness of the membrane compared to the penetration depth of microwaves, it may be assumed that the membrane is heated evenly through the whole section. At a higher temperature, oxygen is used up faster in the outer, more active layers of the membrane, which leads to the creation of anoxic zones in the deeper layers. The relationship between the creation of anoxic zones and the temperature of the biological membrane is confirmed by the research conducted by HAO et al. [7], who found that the depth of oxygen penetration decreases with a decrease in temperature.

The possibility of simultaneous oxygen and nitrate respiration in the sedimentary biomass has been widely documented in literature [4], [9], [16], [19]. Due to oxidation of organic compounds and ammonium nitrogen the anoxic zones in deeper layers of the membrane are created [1], [9]. 1.3 W/s microwave energy at the load as low as 0.05 m³/m²·h was responsible for the use of 20.6 mg COD/d only for denitrification (table 3). When the dose of radiation was increased to 2.5 W/s, the amount of COD used for denitrification increased to 44% of the total available load (figure 2). A three-fold increase in hydraulic load, from \(q_1 = 0.05 \text{ m}^3/\text{m}^2\cdot\text{h}\) to \(q_2 = 0.15 \text{ m}^3/\text{m}^2\cdot\text{h}\), did not increase the use of organic compounds in denitrification. At 2.5 W/s, about 37% of the available load was oxidised in anoxic zones, whereas nearly 39% was oxidised in the oxygenated layer (figure 2.). When the dose of radiation was higher, i.e. 5.0 W/s, 38.9 mg COD/d (31%) was used for respiration in anoxic conditions, and 34 mg COD/d (27.1%) in oxygenated zones (table 3.). This shows a similar activity of heterotrophic bacteria in the temperature range of 20.3 °C–28.6 °C observed at this dose of radiation. The ability of heterotrophic bacterial cells to form colonies, which was tested by Mayo and Nokke [12], showed that there is no difference in the rate of the process at 20 °C and at 35 °C. Lim et al. [11] found that decomposition of organic compounds is slowed down
in a much narrower temperature range. They treated wastewater with high concentrations of organic compounds in aerobic conditions at 20 °C to 60 °C. The rate of BOD₅ removal increased with a temperature increase from 20 to 50 °C, and decreased sharply when the temperature rose from 50 to 60 °C.

In addition to the amount of the radiation supplied, an increase in hydraulic load up to 0.45 m³/m²·h was caused by the part of an increasing oxidation in the transformations of organic compounds taking place in the oxygenated part of the membrane. At a higher hydraulic load, the shearing force of the wastewater increased, which reduced the thickness of the biological membrane. This is unambiguously proved by the amount of organic compounds participating in nitrate respiration. When the dose of microwaves equalled 2.5 W/s, about 75.9 mg COD/d was oxidized in aerobic conditions, whereas 17.4 mg COD/d took part in nitrate respiration and 15.7 mg COD/d of the available organic compounds took part in biosynthesis. Due to a smaller dose of the energy supplied, i.e. 1.3 W/s, per cent share of biosynthesis and oxidation (together with denitrification) in organic compound removal was similar to that in the control reactor (figure 2). It should be stressed that due to additional energy, oxidation in both aerobic (33.1%) and anoxic (25.6%) conditions was observed.

Taking account of the per cent share of the removal of organic compounds (figure 2), it was claimed that the utilisation of microwave radiation is responsible for a lower biomass synthesis. When the energy of the microwaves supplied was 1.3 W/s and the hydraulic load reached 0.05 m³/m²·h, about 28% of the total load of organic compounds took part in biomass synthesis (figure 2). An increase in the dose of energy to 2.5 W/s brought about a reduction in the biomass synthesis to 18.9% and was nearly half of that in the control system, where synthesis accounted for over 32.8% of the load removed (figure 2). An increase in the frequency of wastewater contact with the biological membrane by increasing the hydraulic load to 0.45 m³/m²·h caused a reduction of the share of synthesis in organic compounds transformation. 13.7 mg COD/d was the lowest amount used for synthesis. It accounted for a mere 9.1% of the available load. The same result was achieved when the dose of the energy supplied was 5.0 W/s. Under identical hydraulic conditions, without microwave radiation, as much as 42.8 mg COD/d was used for biomass synthesis (table 3.) It seems that the reduction in biomass production may have been due to a higher temperature and an increased activity in the systems exposed to microwave radiation. A reduction in biomass production with a temperature rise was confirmed by STOVER and SAMUEL (quoting after [10]). They treated synthetic wastewater at temperature of 55 and 60 °C and obtained over 90% efficiency at a biomass growth of 0.13 and 0.07 mg d.m./mg COD. Also COUILLARD and ZHU [5] reported a lower biomass growth at higher temperature.
4. CONCLUSIONS

Exposing biological membrane to microwave radiation affected the intensity and type of organic compound transformation.

A decrease in the consumption of organic compounds for biomass production was observed in the reactors being radiated. In extreme case, it was three times as low as in the control reactor.

Due to microwave radiation, organic compounds were oxidised in nitrate respiration. In biological membrane heated by microwaves, anoxic zones were formed. Recirculation of wastewater enabled denitrification that was observed at very small doses of radiation, when the temperature inside the reactor ranged from 20.3 to 24.3 °C.

Biological membrane exposed to microwave radiation limited the load of untreated organic compounds.

The results obtained testified to the significance of not only the dose of radiation and the temperature effect it brings about, but also of the way in which the process is carried out. 2.5 W/s microwaves produce better results compared to 5.0 W/s ones.

REFERENCES


Wpływ mikrofalowego promieniowania elektromagnetycznego na przemiany związków organicznych w reaktorze z błoną biologiczną

Celem badań było określenie wpływu promieniowania mikrofalowego na przemiany związków organicznych w reaktorze z błoną biologiczną. Stanowisko badawcze przygotowano tak, aby napromieniowaniu ulegała jedynie błona biologiczna, nie zaś oczyszczane ścieki.

Stwierdzono, że dzięki zastosowaniu promieniowania mikrofalowego zmniejszyła się ilość związków organicznych odprowadzanych w oczyszczonych ściekach. W reaktorach poddawanych działaniu mikrofał spadł udział biosyntezy w usuwaniu zanieczyszczeń organicznych. Wywołany działaniem mikrofał efekt temperaturowy spowodował powstawanie stref anoksycznych i umożliwił zajście oddychania azotanowego.