Abstract: Study was conducted in order to check sorption properties of activated sludge which has undergone thermal transformation. For this purpose, anaerobically digested and dewatered activated sludge was dried at 105 °C to constant weight. Next this sludge was milled to a particle with a diameter of 0.5–1.0 mm and subjected to thermal activation in a muffle furnace at 600 °C. In this way obtained a powder activated carbon based on activated sludge (so called SAC – “sludge-based activated carbon”). Studies of static sorption of two dyes (Lissamine Scarlet 4R and Rhodamine B) were conducted for activated carbon prepared as described above. The reaction pH was 2.5 and 7.0 respectively for the dye Lissamine Scarlet 4R and Rhodamine B. During the tests for both dyes a sorption kinetics (for two different values of the ratio of dye weight and SAC weight) were made. Then, for a predetermined time sorption (selected based on the results of the kinetics) sorption isotherms were made for both dyes. Studies have shown that the dye Rhodamine B was well sorbed by activated carbon produced from activated sludge. In the case of Rhodamine B in order to achieve an effective level of removal of that dye it was required only 0.5 hours of contact time. However, in the case of Lissamine Scarlet 4R it required a much longer contact time. That was required two hours of contact time to achieve a relatively high reduction of concentration of this dye. Also, the results obtained during determining the sorption isotherms of these two dyes, have confirmed that conclusion. The adsorbed charge of Rhodamine B per gram of SAC was significantly higher than the adsorbed charge of the second dye. These differences may have been due to the size of the pores of generated SAC. On the basis of sorption of these two dyes can be supposed, that the SAC was characterized by a pore smaller than the size of molecules of Lissamine Scarlet 4R. Therefore, the sorption process of that dye was limited. In contrast, molecules of Rhodamine B, which are smaller than the molecules of Lissamine Scarlet 4R, were much better adsorbed by the SAC. Additionally, it can be supposed that the surface charge of the generated SAC was negative, because the cationic dye (Rhodamine B) was better adsorbed by this sorbent.

Keywords: activated sludge, activated carbon, dyes, sorption isotherm, sorption kinetics
Introduction

The process of sorption at the liquid-solid system can be defined as the occurrence of compacting of the substance in the surface layer of solid, or within the pores of a solid. Sorbed substance is called ‘sorbate’, while the solid which adsorbed other substances on its surface is called ‘sorbent’. Thus, near the surface of the sorbent increases the concentration of the substance in comparison with its concentration occurring within the solution. Depending on the type of interaction between the solid’s molecules and the substance’s molecules sorption can be divided into physical and chemical. In the case of physical sorption the bonding forces between adsorbed substance and solid are van der Waals interactions. This process is reversible and generally sorption is a multilayer. Moreover, the process is exothermic with evolution of a small amount of heat (comparable to heat of condensation), and when the temperature increases the desorption process occurs (adsorbed substance is released). However, in the case of the chemical sorption the bonding forces between sorbate and sorbent are chemical interactions. Typically, the forces responsible for the chemisorption are covalent forces. Chemisorption is usually an irreversible process and the sorbate molecule is bound to the sorbent as a single layer (monolayer sorption) [1–3].

Sorption rate mainly depends on the rate of diffusion of removal substance in liquid and then in the pores of sorbent. The first step is the diffusion of substances from the interior of the solution near the solid (sorbate). In the second stage diffusion occurs in the boundary layer near the surface of a solid. The third step includes the diffusion of a substance inside the pores of the adsorbent. Finally, it comes to locating a substance in an active points of sorbent [2, 3].

The process of sorption of contaminants from solution onto a solid surface is used in water treatment, treatment of industrial wastewater as well as in the water renovation. Sorption process is used to remove from liquids (water or wastewater) specific, dangerous, toxic or valuable substances (which for example can be reused). In the case of treating water sorption is mainly used for removal of hazardous substances, soluble organic compounds both natural or anthropogenic origin. Moreover, there can also be removed free chlorine and chloramines, viruses, and partially some inorganic compounds (eg heavy metals) from water. In the case of renovation of the water (ie the third stage of wastewater treatment) sorption is used for removing of refractive organic compounds, heavy metals, as well as phenols, ammonia nitrogen, detergents and pesticides. In the case of industrial wastewater treatment adsorption is often applied for recovery of valuable substances which may be reused in the production process. Furthermore, sorption is also used for removal of dyes from wastewater [2, 4–10].

Because of the wide variety of applications the sorption process in water and wastewater treatment there can be used many different types of sorbents. However sorbents are divided into two main groups: natural and synthetic ones. However, regardless of the type of sorbent, it should characterized by a high surface area and porosity, selectivity for removal of contamination, mechanical strength as well as being safe for the environment (not emit toxic or harmful substances in its application). The
most commonly used sorbents are activated carbons, silica gel, activated alumina, zeolites, and natural clays rocks. Activated carbon can be produced from many different materials (such as peat, lignite and coal, anthracite, wood material, material of animal origin – eg from the bones, etc.). In the case of zeolite, otherwise known as molecular sieves, they are crystalline aluminosilicates of alkali metals or alkaline earth, which include spatially arranged tetrahedrons of \( \text{SiO}_4 \) and \( \text{AlO}_4 \) [11].

For the preparation of activated carbon it may also be used organic waste materials such as palm kernel shell, cashew nut shell, bamboo waste, municipal solid wastes, waste rubber tires as well as wastewater sludge. The last of listed materials can be processed in different ways in order to obtain activated carbon. The first step is always a process of dewatering and drying, and then grinding. Then, sludge is subjected to combustion, wherein there may be different pyrolysis conditions. The pyrolysis process may be conducted over a wide temperature range from 450 °C to 850 °C even. In addition, sludge combustion can be realized in different atmospheres. There can be used nitrogen, air, steam, and carbon dioxide. For example SAC can be prepared using raw sewage sludge from paper mill. Li et al [12] generate the SAC by carbonization of raw sludge at 300 °C for 60 min and then by activation at 850 °C for 40 minutes in steam atmosphere. They used that SAC for dye sorption from aqueous solutions. Furthermore, in order to produce activated carbon from wastewater sludge, chemical activation can be applied. For this purpose, the strong mineral acids (\( \text{H}_2\text{SO}_4 \), \( \text{HCl} \), \( \text{H}_3\text{PO}_4 \)) and \( \text{ZnCl}_2 \) and \( \text{KOH} \) are used. Chemical activation is conducted either before the process of pyrolysis or after burning the sledge. Chen et al [13] activated the anaerobically digested sludge using \( \text{ZnCl}_2 \) and thereafter they conducted a pyrolysis process of that sludge at 500 °C under nitrogen atmosphere. Moreover, to form a sludge-based activated carbon may be used raw sludge (not undergone digestion process) and stabilized sludge (both in aerobic and anaerobic way) [7, 9, 10, 12–20].

Sludge based activated carbon may be used for removing different kinds of substances. There can be remove dyes, phenols, 4-chlorophenol, nitrobenzene and many other organic compounds [13, 15, 16, 21, 22].

The aim of the research described in this paper was to examine the sorption capacity in relative to the two dyes of thermally transformed anaerobically digested sewage sludge.

**Experimental**

During the tests anaerobically stabilized and dewatered sludge (mixture of excess and raw sludge) was used. The sludge was dried in 105 °C to constant weight, ground in a laboratory mill and combusted in a muffle furnace. The combustion process was divided into two phases – the first sludge was calcined in 300 °C for 45 minutes. Next the temperature raised up to 600 °C and the combustion was continued for a further 45 minutes. Sorption process was carried out for such a transformed sludge.

Sorption studies (both kinetic and isotherm) were carried out in a static system. Activated carbon (based on the sewage sludge), in an amount of 0.1 g, was introduced into a closed Erlenmeyer flasks with a capacity of 50 cm³. To the flask was added
50 cm³ a solution of the dye (Rhodamine B or Lissamine Scarlet 4R) of a suitable concentration. The flasks were placed on a laboratory shaker to ensure constant stirring contents of the flasks.

During the studies two different dyes were used to check the sorption properties of SAC. Namely Lissamine Scarlet 4R and Rhodamine B were examined. The chemical structure of both dyes is shown on Fig. 1 [23, 24]. Rhodamine B is a cationic dye and according to nomenclature of Colour Index is called Basic Violet 10 number C.I. 45170. In contrast Lissamine Scarlet 4R is anionic dye, and according to nomenclature of Colour Index is called Acid Red 18 number C.I. 16255.

The tests were only a preliminary experiments in aimed to check, if generated sludge-based activated carbon has any sorption properties. Therefore, the pH value used in this study was the same as is used in determining the specific surface area of the activated sludge (using Rhodamine B and Lissamine Scarlet 4R) [25].

It is required different value of pH for both dyes when specific surface area of activated sludge is measured. It is connected with chemical structures of those dyes and the value of electric charge of dye and electric charge of surface of sorbent. The surface of flocs of activated sludge are characterized by negative electric charge. In contrast Lissamine Scarlet 4R is anionic dye. Therefore it is necessary to change the electric charge of floc surface. That is achieved by reducing pH value of the solution to 2.5.

In the case of Rhodamine B, decreasing of pH value is not required, because it is cationic dye. For that reason there should not be electrical repulsive forces between dye molecules and surface of SAC.

In the case of Lissamine Scarlet 4R the pH of reaction was 2.5, while in the case of Rhodamine B the pH value was equalled to 7.0 [25].

In the first stage of research sorption kinetics studies were performed. There were examined two different initial concentrations of both dyes. The final dye concentration was measured after different times of their contact with the sludge-based activated carbon (Table 1). The concentration of the dye was determined photometrically on the basis of the calibration curve. In the second stage, based on the results of sorption kinetics, sorption isotherm were determined for both dyes.
Table 1

Parameters of sorption kinetics

<table>
<thead>
<tr>
<th>Kind of dye</th>
<th>Initial concentration of dye [mg/dm³]</th>
<th>Weight of SAC [g/dm³]</th>
<th>Reaction time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lissamine Scarlet R4</td>
<td>50</td>
<td>2</td>
<td>0.5, 1.0, 1.5, 2.0</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td></td>
<td>2.5, 3.0, 4.0</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results and discussion

Kinetics

Research has shown that the shape of sorption kinetics depends on kind of dye. In the case of Rhodamine B after half an hour of reaction time, concentration of the dye after the process has reached a constant low level. The degree of reduction of Rhodamine B was in range 82.8–84.7 % and in range 84.1–85.5 % when the initial concentration of dye was respectively 50 and 700 mg/dm³ (Fig. 2 and Fig. 3).

However, in the case of the second dye (Lissamine Scarlet 4R) there has been no such a high efficiency of removal of that dye. The decrease of concentration of Lissamine Scarlet 4R after adsorption process was only equaled to 26.7 % and 15.8 % when the initial concentration was respectively 50 and 700 mg/dm³ (Fig. 4 and Fig. 5). In addition, when Lissamine Scarlet 4R was using there was required much longer contact time to achieve a constant degree of adsorption of dye on the SAC. Namely, when the initial concentration was 50 mg/dm³ the greatest degree of reduction of dye concentration achieved after 3 h of reaction. However, for the initial concentration

Fig. 2. Sorption kinetics of Rhodamine B – initial concentration 50 mg/dm³
Fig. 3. Sorption kinetics of Rhodamine B – initial concentration 700 mg/dm³

Fig. 4. Sorption kinetics of Lissamine Scarlet 4R – initial concentration 50 mg/dm³

Fig. 5. Sorption kinetics of Lissamine Scarlet 4R – initial concentration 700 mg/dm³
equaled 700 mg/dm\(^3\) the lowest dye content was observed after 1.5 and 2 hours of reaction. Moreover, in the case of Lissamine Scarlet 4R observed large variations in the dye concentration in subsequent times of measurement. The reason of that phenomenon may be due to the small SAC sorption properties (generated during the studies) in relation to this dye. This could result in desorption of previously adsorbed molecules of Lissamine Scarlet 4R. Then reported an increase of its concentration after sorption process in comparison with concentration equaled in the previous measurement point. That phenomenon was mainly observed in the case of initial concentration equaled 50 mg/dm\(^3\) (Fig. 4). In the case of higher content of Lissamine Scarlet 4R, that variations of effectiveness was not so large, however it also occurred. It is possible that, the bonded forces between SAC and dye were not enough strengths to immobilize molecules of the dye on surface of SAC.

**Sorption isotherm**

On the basis of studies of the kinetics, the contact time for both dyes were determined. In case of Rhodamine B, the required contact time was 0.5 hour. While in the case of Lissamine Scarlet 4R it was obtained, that the most favorable time was 2 hours. For such a chosen reaction times the sorption isotherm studies of both dyes were determined.

Studies have shown that produced sludge-based activated carbon had much better sorption properties in relation to Rhodamine B. The amount of adsorbed charge of Rhodamine B by SAC reached a much higher values in comparison with Lissamine Scarlet 4R. In the case of Rhodamine B adsorbed charge of dye was even equaled to 727 mg/g\(\text{SAC}\). When Lissamine Scarlet 4R was examined the charge of adsorbed dye was only 174.6 mg/g\(\text{SAC}\).

That shape of curve of isotherm characterizes a kind of sorption – whether it occurs single-layer or multi-layer sorption. According to the literature there are few different kind of shapes of isotherm curve depending on kind of sorption. That various shapes of isotherm curves shows Fig. 6. In the case of Fig. 6a the curve shows a single-layer

![Fig. 6. Shapes of isotherm curve: a) single-layer sorption, b) and c) multi-layer sorption](image-url)
sorption. Other curves show a multi-layer ones. The single-layer is described be isotherm of Freundlich and Langmuir. In contrast the multi-layer sorption is described by isotherm of BET.

On the basis of the shape of the sorption isotherm of both dyes can be concluded that there occurs the multi-layer sorption (Fig. 7 and Fig. 8). In both dyes during the first stage can be observed gradual increase of value of adsorbed charge with increasing equilibrium concentration of dye. Then in the second stage it can be seen parallel section to the abscissa (so called ‘Plateau’) on the curve of isotherm. It is then while the first layer of surface of sorbent was filling by dye molecules. Therefore, despite the increase of concentration of the dye was not followed by an increase of the adsorbed charge by SAC. Only a relatively large excess of the dye led to further adsorption of dye molecules in the second layer. It is connected to the coverage of all active spaces on the first layer of surface of SAC by molecules of dye. However in the case of Rhodamine B this parallel section of curve line occurred when the charge of adsorbed dye was about

Fig. 7. Sorption isotherm of Rhodamine B

Fig. 8. Sorption isotherm of Lissamine Scarlet 4R
500 mg/g\textsubscript{SAC}. In the case of Lissamine Scarlet 4R it occurred for much lower value of adsorbed charge of dye – about 60 mg/g\textsubscript{SAC}. It means that generated SAC had adsorbed much more amount of Rhodamine B than Lissamine Scarlet 4R.

This difference may be due to the particle size of molecules of both dyes. The molecule size is directly related with the surface coverage by single molecule. In the case of Rhodamine B coverage surface of single molecule equals 160 Å\textsuperscript{2}. While Lissamine Scarlet 4R is characterized by larger particles, and the coverage surface of single molecule reaches a value of 196 Å\textsuperscript{2}. It can therefore be assumed that the pore size of the generated SAC is smaller than the particle size of Lissamine Scarlet 4R molecules. Such a size of pores of SAC could have limited the adsorption of that dye. It is possible that molecules of Lissamine Scarlet 4R did not penetrate the pores of SAC and molecules of that dye were adsorbed only near the surface of SAC. Moreover for this reason the bonded forces between dye and sorbent were not strong enough to immobilize the molecules of Lissamine Scarlet 4R effectively and desorption occurred while establishing kinetics of sorption of that dye.

**Conclusions**

The study showed that the wastewater sludge may be use as a material from which an activated carbon can be produced. Subjecting the sewage sludge only into thermal transformation allowed to generate a sorbent capable to adsorb Rhodamine B. Based on the results obtained during kinetics of sorption of that dye it can be observed that it was required only 0.5 hour to obtain high efficiency of removal of Rhodamine B. Moreover, after half an hour of contact of SAC and dye the stable value of concentration occurred. In contrast performed studies have shown that the much longer contact time was required to achieve the highest efficiency of sorption of Lissamine Scarlet 4R on SAC. After about 2 hours of reaction observed a relatively high effectiveness of dye removal was observed. However the efficiency degree was not stable and sorption and desorption process occurred alternately in the following measurement points. It manifested by an alternating decrease and increase of dye concentration after sorption process.

The results of isotherm sorption also showed the difference of sorption properties of generated SAC according to examined two dyes. Much higher amount of Rhodamine B was sorbed by SAC in comparison with Lissamine Scarlet 4R. However in case of both dyes occurred a multi-layer sorption. The shape of curve of isotherm sorption shows it. It can be observed the section of parallel line to abscissa. Beyond this section it can be observed an increase in value of adsorbed charge with increase value of equilibrium concentration of dye. Therefore for both dyes it can be concluded that physical sorption occurred. It is known that multilayer sorption occurs when forces bonded molecules and solid surface are van der Waals interactions. This forces can interact The impact of these forces is greater than the size of single molecules sorbed on the surface. Therefore, it is possible the formation of subsequent layers of molecules of substance on the surface of the sorbent.
Differences between sorption effectiveness of both dyes could have been connected with size of their molecules. Rhodamine B has smaller molecules then molecules of Lissamine Scarlet 4R. It is possible that pore size of SAC was relatively small and this could have limited the sorption of Lissamine Scarlet 4R. Moreover that dye has anionic character while Rhodamine B has cationic one. It could be possible that generated SAC has an negative charge of surface. Maybe pH 2.5 was not enough low to change anionic charge of Lissamine Scarlet 4R what affected the sorption efficiency of that dye.

However, that were preliminary studies when used pH of the reaction was such as is used in determining the specific surface area of the activated sludge using these two dyes. Therefore, it may be that in the case of using a different pH in the case of Lissamine Scarlet 4R, the efficiency of its sorption will increase. This implies the need for further research aimed at verifying a wider range of properties of the produced SAC.

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WSTĘPNE BADANIA WŁASCIWOŚCI SORCYJNYCH TERMICZNIE PRZEKSZTAŁCONEGO OSADU CZYNNEGO

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Abstrakt: Przeprowadzono badania mające na celu ocenę właściwości sorpcyjnych osadu czynnego, który został poddany termicznej obróbce. W tym celu ustabilizowany beztlenuo i odwodniony osad czynny wysuszono w 105 °C do stałej masy. Następnie osad ten zmielono do ziaren o średnicy 0,5–1,0 mm i poddano termicznej aktywacji w piecu muflowym w 600 °C uzyskując w ten sposób pylisty węgiel aktywny bazujący na osadzie czynnym (tzw. SAC – czyli “sludge-based activated carbon”). Dla tak spreparowanego węgla aktywnego przeprowadzono badania procesu sorpcji statycznej względem barwników: Lissamine Scarlet 4R i Rodamina B. W badaniach pH reakcji wynosiło 2,5 oraz 7,0 odpowiednio dla barwnika Lissamine Scarlet 4R i Rodaminy B. W badaniach wykazały dobre właściwości sorpcyjne wytworzonym odsaju względem barwnika SAC. W przypadku SAC wymagany był jedynie pół godzinny czas kontaktu. Natomiast w przypadku Rodaminy B wymagany był znacznie dłuższy czas kontaktu. Również wyniki otrzymane w trakcie wyznaczania izotermy sorpcji obu barwników potwierdziły te wnioski. Wartość zabsorbowanego ładunku Rodaminy B była znacznie większa niż w przypadku drugiego badanego barwnika. Również te mogły wynikać z wielkości porów wytworzonych SAC. Na podstawie badań sorpcji tych dwóch barwników można podejrzewać, że wytworzony SAC charakteryzował się wielkością porów mniejszą od wielkości cząsteczek Rodaminy B.