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## Biosorbents for waste water cleaning from coloring agents

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**Abstract.** The objective of the experimental work was to determine the removal efficiency of selected dyes from aqueous solutions using an adsorption process. Studies of adsorption from aqueous solution on a laboratory scale were performed for the two dyes, bromocresol green and methyl orange. Activated carbon from coconut shell, lignite from Bełchatów mine and biosorbent from orange peel as an alternative adsorbent were used. For the study were selected grain fractions of  $\phi=1.0-1.5$  mm. The experiment was carried out at constant room temperature for 30 minutes in static conditions of contact. The influence of both dye concentration in the solution, and the dosage of sorbent to the dye sorption capacity is stated. The results are presented as isotherms. Biosorbent preparation process should be modified in order to avoid its decay under dye sorption from an aqueous solution. Biosorbent is comparable porous material to active carbon AC1 for bromocresol green when they have adsorption capacity  $a_m$  [mmol·g<sup>-1</sup>] 0.0199 and 0.0209, respectively. In the case of methyl orange adsorption capacity is 0.2061 for AC1 and 0.0135 for biosorbent. It means that in second case biosorbent is weak adsorbent for water cleaning, even worse than lignite Be ( $a_m=0.0399$  [mmol·g<sup>-1</sup>]). Finally, this kind of biosorbent is not suitable for adsorption cleaning of water for methyl orange at this stage of processing because maceration of material and freeing of natural dye occur.

### 1. Introduction

Dyes and pigments are important pollutants of the environment among the wide range of organic compounds. They are supplied to sewage from various industries, mainly the dyeing, textile, rubber, paper or cosmetic industries. Dyes in sewage, even at low concentrations, have an effect on the aquatic food chain or aquatic biocoenoses. In addition, some dye decomposition products already in small quantities may be carcinogenic, mutagenic and toxic [1-3].

Dyes are synthetic aromatics which are classified according to their use and the chemical structure. They are characterized by complex molecular structure, high stability and various substituents [3]. The rapid changes in dye production technology, the varied composition of waste water, and the specific properties of dyes themselves and auxiliaries, unfortunately, constitute a major obstacle in the development of an effective, economic and simultaneously simple method of dye removal from waste water.

Generally, the methods of treating dye containing wastewater are divided into four groups: mechanical, chemical, physical and a combination of the aforementioned methods. The biological degradation methods used for purification of sewage prove to be ineffective because the dyes are not biodegradable [4]. Among chemical, physical methods effective in dye removal one could distinguish: chemical and electrochemical oxidation, membrane processes, flocculation coagulation, ion exchange



as well as widely used adsorption [2,5-8]. The most developed nowadays use of biosorbents is the purification of waste waters from heavy metal ions [9] and specific solutions are the subject of patent claims [10].

Adsorption, among the aforementioned methods, also proved to be the most effective method of removing dyes from aqueous solutions. Porous synthetic adsorbents (activated carbons, ion exchange resins, zeolites, silicates, etc.) are used for this purpose, but natural adsorbents such as montmorillonites and smectites can also be used. However, for each of the adsorbents, it is necessary to regenerate them before reuse. The most common method of regeneration (desorption) is to raise the temperature with simultaneous lowering of pressure, in the case of adsorption of gases, or washing of the adsorbent bed with solvent in case of adsorption from liquid solutions. Desorption generally does not lead to the recovery of the original sorption capacity and over time the sorbent is consumed. The high costs of obtaining synthetic adsorbents and problems with the regeneration of used sorbents tend to seek unconventional adsorbents, efficient and inexpensive natural, waste materials, biosorbents, as well as waste materials from industry or agriculture [4].

The aim of the experimental work was to use biosorbent from selected waste material - orange peel to determine the effectiveness of removing selected dyes from aqueous solutions using the adsorption process. Special goal of the research was to produce cheap adsorbent with minimal technological treatment need to clean waste water.

## 2. Materials and methods

The influence of bromocresol green and methyl orange concentrations in the solution was determined (using a set of 8 solutions diluted from the base solution for the calibration curve of the spectrophotometer, then five solutions of dye with different concentrations were used to determine the sorption isotherm and sorption capacity.

### 2.1. Characteristic of investigated sorbents

Activated carbon from coconut shell (AC1), orange peel and flesh-free peel and lignite from Bełchatów mine (Be) with a  $C^{daf}$  content of 65.9% ( $V^{daf}$  57.39%) were used as absorbing substances. The helium density was determined using the Micrometrics - AccuPyc 1330 [11] apparatus and the ash content was measured after incineration of the samples in the furnace for the tested sorbents. The results are summarized in Table 1. The orange peel grain fraction size slightly influences the helium density. For sorption studies, grain fraction of orange peel was selected: 5x5mm cube, 1.0-1.5 mm and  $\phi < 1.0$  mm. For activated carbon from coconut shells and for lignite, a grain fraction of 1.0-1.5 mm was used.

**Table 1.** Helium density and ash content values for selected sorbents.

Sample		Helium density [g·cm <sup>-3</sup> ]	Ash content [%]
<b>BIOSORBENT</b> <b>(orange peel with</b> <b>flesh)</b>	$\phi$ 1.0-1.5mm	1.4327	3.22
	$\phi < 1.0$ mm	1.4364	
<b>ACTIVE CARBON</b>			
<b>AC1</b> <b>(coconut shell)</b>	$\phi$ 1.0-1.5mm	1.9992	1.57
<b>LIGNITE</b> <b>Bełchatów (Be)</b>	$\phi$ 1.0-1.5mm	1.43 <sup>a</sup>	3.8 <sup>a</sup>

<sup>a</sup>Data taken from the publication [12]

<sup>1</sup>daf - dry-ash-free basis

The raw orange peel was cut into pieces of about 0.5x0.5 cm size, initially dried at room temperature in an open atmosphere in a well-ventilated laboratory room, preventing decay or mold. The moment of transition to the next stage was assessed visually and by trying to pour pieces (i.e. they did not stick each-other and to the base surface), then it was dried in a laboratory drier at 105°C to a constant weight. The possibility of using extraction residues of essential oils (including limonene) was also considered. However, pieces of orange peel in this case are partially macerated and require another method of preparing a solid biosorbent. Dry orange peel pieces were crushed in the mill and various sieves were selected in sieve analysis. The raw skin weight was determined, after drying and weight loss after drying (Table 2).

The orange peel, independently of the particle fraction, showed not only the sorption potential but also the swelling property and the higher viscosity of the solution in the filtrate. The unfavorable phenomena described above have greatly affected the difficulty in separating the sorbent from the solution after sorption. Hence, a grain size of 1.0-1.5 mm was selected for testing to uniformize the grain fraction for both sorbents.

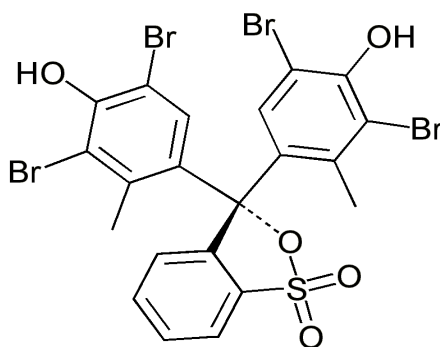
AC1 activated carbon was a commercial adsorbent of a given fraction of grain. Carbonaceous adsorbent was obtained from coconut shells and chemically activated (pH of the extract ~ 10.5 according to Polish Standard [13]).

**Table 2.** Effects of drying of orange peel at 105 °C.

	Raw sample mass [g]	Dried sample mass [g]	Mass loss [%]
<b>With flesh</b>	76.25	24.83	67.43
<b>Without flesh</b>	55.53	17.67	68.18

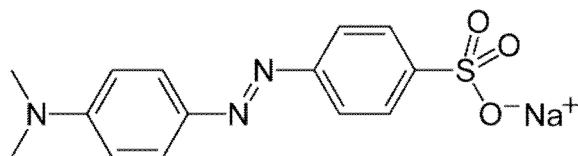
## 2.2. Dyes used in the study

Adsorption experiments from aqueous solutions on laboratory scale were made for two colours: bromocresol green (Figure 1) and methyl orange (Figure 2). Dyes used in the form of an aqueous solution as a pH indicator, bromocresol green mainly in organic analytics, and methyl orange being used in alkalimetric titration and as an ingredient in blends for impregnating indicator papers. In addition, methylorange is used for dyeing fabrics and fibres.



**Figure 1.** Bromocresol green 2,6-Dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9λ6-thiabicyclo[4.3.0]nona-1,3,5-trien-7-yl]-3-methyl-phenol [14].

Bromocresol Green -  $C_{21}H_{14}Br_4O_5S$  (molar mass: 698.04 g·mol<sup>-1</sup>) is obtained by bromination of m-cresol purple in an alcohol medium. Bromocresol green is a solid with colour from white to creamy.



**Figure 2.** Methyl orange Sodium 4-{{4-(dimethylamino)phenyl}diazenyl}benzene-1-sulfonate [14].

Methyl orange, helianthine -  $C_{14}H_{14}N_3NaO_3S$  (molar mass:  $327.34 \text{ g}\cdot\text{mol}^{-1}$ ) is a chemical compound of the azo dyes group. It is an azobenzene derivative containing a dimethylamino group and a sulfonate group. At room temperature it is an orange-colored crystalline solid [14,15].

### 3. Results

An aqueous base solution of bromocresol green at  $5\cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  and methyl orange at  $3\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$  was used for the studies. By diluting the basic dye solutions in  $100 \text{ cm}^3$  volumetric flasks, 8 working solutions of bromocresol green were prepared with concentrations from  $2.00\cdot 10^{-4}$  to  $1.00\cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$  and for methyl orange from  $1.22\cdot 10^{-3}$  to  $6.11\cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . The pH stability of the dye solutions was maintained by addition of  $10 \text{ cm}^3$  of acetate buffer pH 5.5 [16].

Prepared sorbents, washed to an inert pH, comminute and dried pH, were placed in  $100 \text{ cm}^3$  conical flasks, respectively (0.2 g, 0.15 g, 0.1 g, 0.09 g, 0.08 g). Subsequently,  $50 \text{ cm}^3$  of the highest concentration of dye solutions (base solutions) and selected five solutions from the prepared 8 working solutions were added to the flasks. All vessels were shaken for 30 minutes at velocity 40 rpm, after this time two phases were separated on the filter, i.e. the solid - the spent sorbent and the liquid - dye solution. The adsorption isotherm of each dye was measured separately and two measurements were made for each dye. The isotherms shown in Figures 3-5 and 7-9 contain average values from the two measurement series.

Concentrations of the dye for 8 working diluted solutions and for those after sorption were determined by spectrophotometric method. For this purpose, a UV/VIS Spectrophotometer was used, the transmittance (T) and the absorbance (A) were determined. For eight starting solutions, the dependence of A (or T) on the solution concentration (A or T = f(c)) is plotted. The correlation A or T versus concentration (standard curve) was used to determine the concentration of individual dyes in the solution after sorption on the tested sorbents. Wavelength was chosen 550 nm for methyl orange [18] and for bromocresol green 615 nm [19]. Subsequent samples of the dye solution before sorption and after sorption were pipetted from a conical flask into a plastic cuvette, placed in a spectrophotometer reading chamber, and values of A and T for the respective dye were read at the appropriate wavelength. A buffer solution which was used to prepare the test dyes ( $10 \text{ cm}^3$  of buffer pH=5.5 per  $100 \text{ cm}^3$  of solution) was applied as a reference sample.

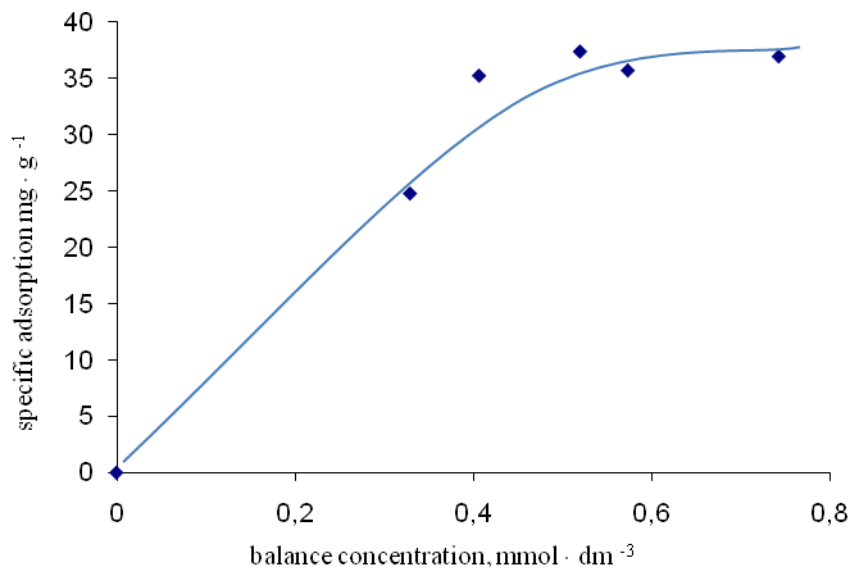
The standard curves for the individual dye solutions based on eight working solutions were plotted in the first step, then the equilibrium concentrations after sorption were measured for the respective values of A or T. Then the specific adsorption expressed in moles of the dyes substance per gram of adsorbent  $\text{mmol}\cdot\text{g}^{-1}$  were calculated basing on known dye concentrations in solution  $C_0$  and read from the calibration curve dye concentrations after sorption  $C_i$ . For this purpose, Guggenheim-Adam's dependence (1) was used [19], justified for diluted solutions:

$$a = \frac{V(C_0 - C_i) \cdot 1000}{m_C} \quad (1)$$

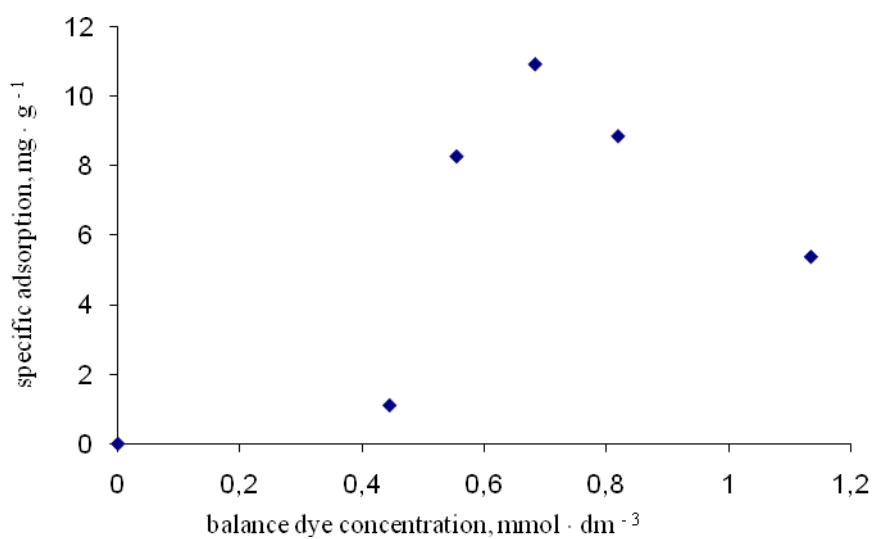
where:  $a$  specific adsorption  $\text{mmol}\cdot\text{g}^{-1}$ ,  $C_0$  and  $C_i$  are starting and balance concentrations of dye  $\text{mol}\cdot\text{dm}^{-3}$ ,  $V$  - volume of the solution  $\text{dm}^3$  and  $m_C$  - mass of dry sorbent g.

Specific adsorption values calculated according to (1) were used to plot the sorption isotherms shown in Figures 3 to 6. The vertical axis in these drawings presents the adsorption of mg of dye per g of sorbent sample, while the vertical axis determine the equilibrium concentration of the dye solution sorbed by the tested material. The trend lines shown in these figures, however mathematically calculated, have no physical meaning. It indicates only the expected course of the sorption isotherm based on the obtained set of points.

Methyl orange sorption isotherm on coconut shell AC1 (Figure 3) shows a fairly normal Langmuir isotherm.

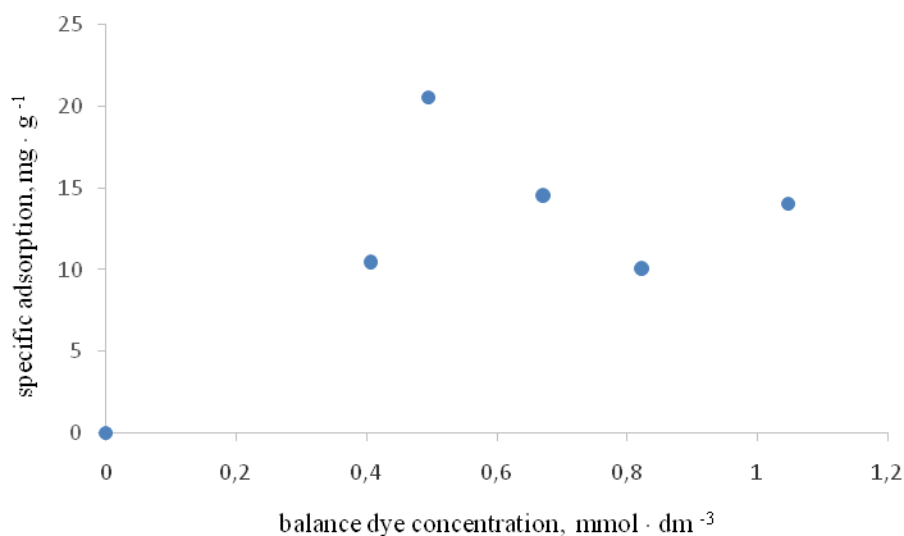


**Figure 3.** Adsorption of methyl orange on the active carbon AC1.



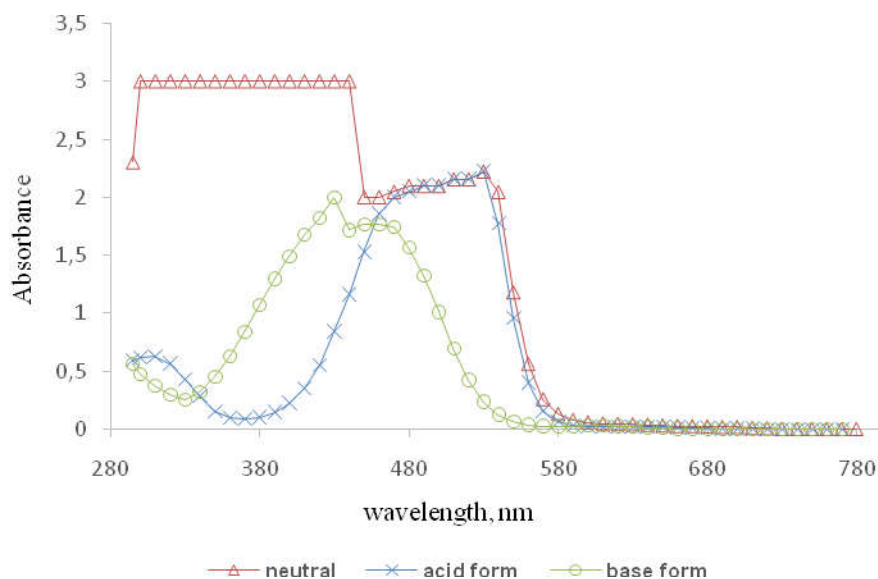
**Figure 4.** Sorption of methyl orange on the biosorbent from orange peel.

Isotherm of sorption of methylorange on biosorbent - orange peel does not show regular character (Figure 4). In this case, the trend line is not added because of irregular location of experimental points. Difficulties with the determination of equilibrium concentration and sorption are probably due to the presence another dye with colour like the methyl orange. Probably this dye was able to pass into the solution and despite the homogenization of the grains after milling and sieve segregation, could pass differently to the solution for the individual samples, thus distorting the absorbance/transmittance readings in the colorimeter for the specified wavelength. This fact is also confirmed in the observation of the partial decomposition of the biosorbent during the adsorption of the dye.



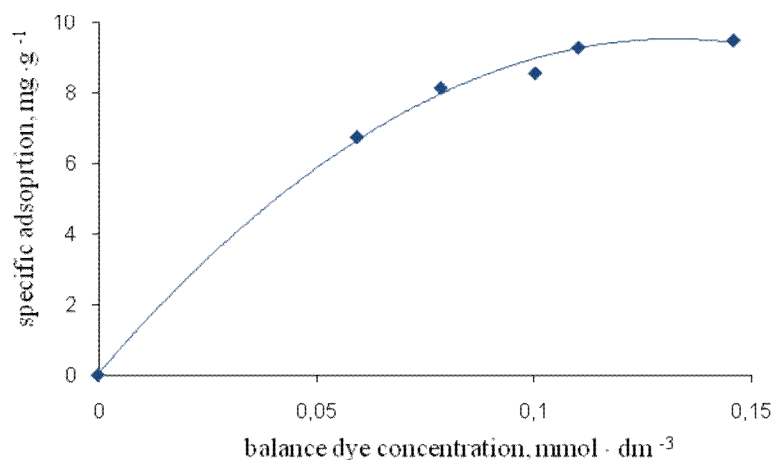
**Figure 5.** Sorption of methyl orange on the lignite Be

Sorption measurement of the methyl orange on the Be lignite is not regular (Figure 5) - big deviation from regular trend are stated. Possible cause of this situation could be an imperfect homogenisation of the probe of the lignite before dividing to small samples.



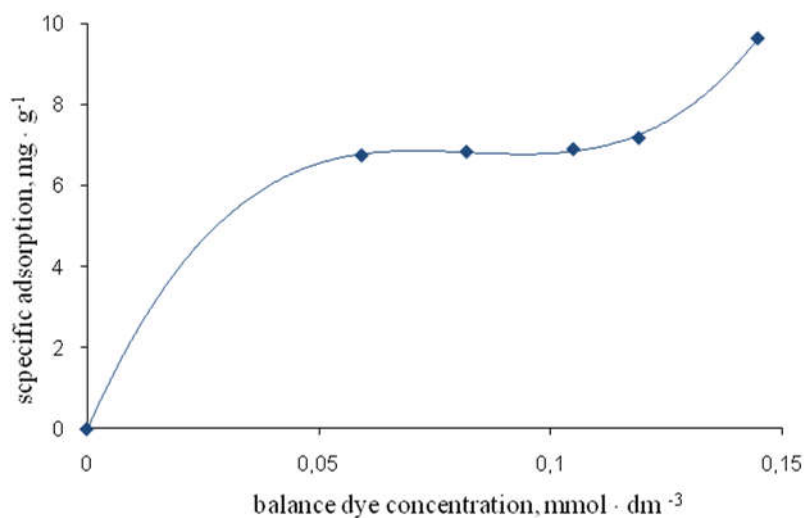
**Figure 6.** The spectrum of methyl orange absorbance.

Great uncertainty of the measured data for methyl orange causes the necessity of the control of the wavelength for spectrophotometric measurement. In the aim of checking of the selectivity of the colorimeter measurement the spectrum of methyl orange was measured for different form of the dye. Result of this measurement is presented on the Figure 6, it approves the right choice of the wavelength as 550 nm because with this value one could observe the peak on the spectrum for acidic form (pH=5.5) of methyl orange. In the case of base form (pH=10) peak position is different, about 400 nm and neutral form shows wide range of big absorbance.



**Figure 7.** Adsorption of bromocresol green on the active carbon AC1.

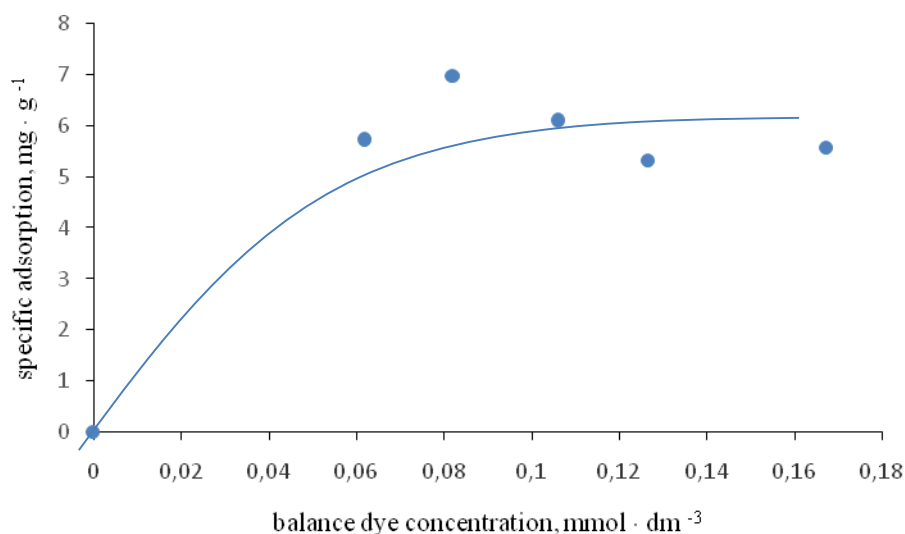
The bromocresol bromide adsorption isotherm on coconut shell AC1 (Figure 7) shows the nature of the BET type I isotherm as in the case of methylorange (Langmuir isotherm - the best mathematical fitting of the trend line).



**Figure 8.** Sorption of bromocresol green on the biosorbent from orange peel.



The isotherm of sorption of bromocresol green on the orange peel biosorbent (Figure 8) is more regular than that of methyl orange, what supports the thesis that a part of the natural dye from the orange peel is passed to the solution. The trend line indicates the sigmoidal type of isotherm (type II of BET isotherm characteristic for microporous sorbents). It represents the mono-polylayer sorption on the sorbent, hence limitation of the range of data taken for further calculations and it can be considered that for the initial range of isotherms represents mono-layer adsorption and Langmuir equation can be used for analysis. Isotherm of bromocresol sorption on lignite Be (Figure 9) is rather Langmuir type and could be approximate by Langmuir equations directly.



**Figure 9.** Sorption of bromocresol green on the lignite Be.

#### 4. Results analysis

Adsorption isotherms were estimated by approximating the linear form of the Langmuir equation on measured data [20]:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{1}{b \cdot a_m} \cdot \frac{1}{C_b} \quad (2)$$

where:  $a$  - adsorption,  $a_m$  - maximal adsorption in monolayer,  $b$  - physicochemical parameter describing sorption balance of the sorption system in the measurement temperature,  $C_b$  - balance dye concentration.

Equation (2) lets one to estimate of the  $a_m$  parameter characterizing the maximum monolayer sorbent capacity of the given sorbent-sorbate (in this case dye) system. The obtained parameters are shown in Table 3. Parameter  $b$  does not have a strictly physical meaning. Moreover the maximum coverage of the monolayer is not achieved. Therefore, the surface coverage ratio is additionally calculated using the formula (3) [21]:

$$\theta = b \cdot C_b / (1 + b \cdot C_b) \quad (3)$$

where:  $b$  - parameter of Langmuir equation,  $C_0$  - starting concentration of dye solution.

Based on the Langmuir equation, it can also be stated that in a given system, adsorption is the preferred mechanism for location of the dye molecules on the adsorbent surface. For this purpose, the parameter called the separation factor ( $Sr$ ) is calculated (equation 4) [21]:

$$Sr = 1 / (1 + b \cdot C_0) \quad (4)$$

Parameter  $S_r$  depicts the adsorption process:

$S_r > 1$  - adsorption is not preferred mechanism of sorbent surface covering by the dye molecules (probably condensation appears);

$S_r = 1$  - isotherm of adsorption has a linear character;

$0 < S_r < 1$  - adsorption is a preferred mechanism of the sorbent surface covering by the dye molecules.

All calculated parameters of studied sorption systems are resented in the Table 3.

**Table 3.** Parameters describing sorption according to the Langmuir theory.

parameter	methyl orange			bromocresol green		
	AC1	biosorbent	Be	AC1	biosorbent	Be
$a_m$ [mmol·g <sup>-1</sup> ]	0.2061	0.0136	0.0399	0.0199	0.0209	0.0767
$b$	2035	469	835333	16490	21638	130300
$\theta$	0.7095	0.3606	0.9990	0.7673	0.8123	0.9962
$S_r$	0.2905	0.6394	0.00098	0.2327	0.1877	0.0038

The  $S_r$  parameter indicates that adsorption is the preferred mechanism for settling dye particles on the adsorbent surface for all sorption systems. Whereas, isotherm of the adsorption of methyl orange on the biosorbent is most similar to the linear character, with the lowest degree of surface coverage  $\theta$ . In other cases the surface coverage has not reached its maximum value. Surprisingly, the biosorbent proved to be a better sorbent for bromocresol green than active carbon because it attained higher monolayer loading ( $a_m$ ) and achieved a higher degree of coverage for the examined dye concentration range. In the case of the sorption of methyl orange the situation is reversed - the sorption of the dye on the biosorbent is of a magnitude lower than the adsorption on the activated carbon. This may be due to problems with measuring the equilibrium concentration of the dye using a spectrophotometer. The high values of factor  $b$  for bromocresol green for both adsorbents may be indicative of the high energy of adsorption for this dye. The coverage parameter of lignite BE by both dyes is very big (nearly 100%) what suggests the full usage of the sorbent surface.

## 5. Results discussion

The results obtained in this stage of experiment shows good decoloring properties vs, bromocresol green and completely lack of relevancy to methyl orange. Surface coverage factor  $\theta$  is over twice greater for bromocresol than for methyl orange. It indicates the less applicability of this biosorbent to adsorption of second dye.

Biosorbent produced in these conditions is cheap substitute for active carbon in the case of first dye. Further treatment e.g. oxidization could increase the adsorption capacity of biosorbent and it could reach even 25-40 times bigger capacity i.e. about 0.5 mmol·g<sup>-1</sup> [22]. This literature result is relevant to the mixture of dyes. Another idea on increasing of adsorption capacity of the biosorbent is hydrothermal treatment at 180°C with OH<sup>-</sup> ion exchange and Fe(II)/Fe(III) ions soaking [23] what increase the adsorption capacity of Arsenic ion As(V) to about 1 mmol·g<sup>-1</sup> in comparison to our procedure it results in 80 times bigger adsorption. This last result suggests the way of further investigation to introduce the polar surface group to the surface of biosorbent. Additional treatment increases the cost of adsorbent and is not the purpose of experiments presented in this paper.

## 6. Conclusion/summary

The adsorption capacity of the dyes depends on the concentration of dye in the solution. In the case of methyl orange, the orange peel biosorbent was not a competitive material for AC1 active carbon, since adsorption capacity on this first sorbent was about 15 times lower. In the case of bromocresol green, the adsorption value is comparable for both adsorbents, so the biosorbent from orange peel can be a cheap substitute of AC1 active carbon. Some interpretative difficulties in the case of methyl orange may be a result of the occurrence of a natural dye in the orange peel, which may enter the solution

during adsorption and distort the absorbance reading in the spectrophotometer. This problem could be solved by the use of another research technique to determine the balance concentration of the dye solution after adsorption. Another way for increase of the biosorbent applicability in the case of methyl orange is using of further treatment of dried material, e.g. fast carbonisation in the purpose of natural dye immobilization.

The approximation of the Langmuir equation to the measured data shows that the orange peel biosorbent is a very good substitute for active carbon with respect to bromocresol green. At the same time, method of its manufacture is much cheaper than the production of activated carbon. On the other hand, methyl orange sorption studies on biosorbent failed due to decay of the sorbent and transport of natural dye to solution. This phenomenon further hindered separation of the purified liquid from the biosorbent. The solution to this problem may be a change in the way of biosorbent preparation (e.g. additional carbonization), but this would increase the cost of its production.

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