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The utilization of sorbents obtained from miscanthus using steam as the activation agent for wastewaters treatment

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The possibility of obtaining sorbents with a good sorption capacity from miscanthus has been investigated. The chars and the activation products were obtained from the miscanthus in a rotary furnace. The activation process of miscanthus was carried out by water vapour at 700 – 800°C and at the activation time of 30 – 90 min. We found that the optimum conditions for the activation process were: the activation temperature of 750°C (activation time of 60 and 90 min) and 800°C (activation time of 45 or 60 min). For these conditions the sorbents with the best sorption capacity for p-chlorophenol, toluene, methylene blue and Congo red were obtained.

Keywords: agricultural waste, miscanthus, sorbents, wastewater treatment.

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INTRODUCTION

The most crop effective grasses and the most frequently cultivated plants are grasses named *Miscanthus* such as miscanthus giant – *Miscanthus sinensis giganteus* and sugar miscanthus – *Miscanthus chariflorus*. The naturally grown plants of miscanthus grasses are located in central and South-East Asia. The miscanthus grasses grow to the heights from 1 to 4 m. They do not require very good soils and can to grow on the soils of the V-th and VI-th class, waste lands, as well as on the soils contaminated with heavy metals. Miscanthus are perennial plants, their plantations can grow for 15 – 20 years. Their cultivation is very cheap and the high crop of biomass can be harvested. In Poland the sugar miscanthus is mainly cultivated. Their crops are usually in the range of 5 – 30 tones of dry mass per hectare and depend on the type of the soil and fertilization. The main components of miscanthus are: cellulose – 44 wt.%, hemicelluloses – 24 wt.%, lignin – 17 wt.% and other components 15 wt.%[1 – 3].

Miscanthus was considered as a raw material for obtaining active carbons, useful for the purification of aqueous solutions. Miscanthus is a cheap, easily available, homogeneous and renewable material. In the literature there was rather scanty information on the investigations of sorbents from these materials[4 – 5].

Active carbons prepared from miscanthus, using CO_2 as a gasifying agent, at the temperatures of 750, 800 and 850°C exhibited high iodine numbers (140 – 930 mg I_2/g) and methylene numbers (0 – 6 cm^3) and very effectively cleaned the concentrated solutions of toluene, p-chlorophenol, methylene blue and Congo red[5]. The char obtained from miscanthus showed high efficiency only in the removal of toluene from aqueous solutions.

A limited number of publications regarding the adsorbents prepared from miscanthus grass gave ground to our investigations on the possibility of the preparation of sorbents from this raw material in a one step activation process, using water vapour as a gasifying agent.

The applicability of active carbons obtained from miscanthus grass for the purification of aqueous solutions contaminated with toluene, p-chlorophenol, methylene blue and Congo red was examined.

EXPERIMENTAL

Samples preparation

The raw material (miscanthus grass) was used in the form of pellets.

A one-step carbonization and activation process was performed in the horizontal pipe rotating reactor introduced into the electrical furnace. Preliminary (the carbonization step) the sample (20 g) was heated in the nitrogen atmosphere with the heating rate of 10°C/min up to the final temperatures: 700, 750 and 800°C. The residence time at these temperatures was 15 min. Subsequently, the gasifying agent (steam) was introduced and the activation process was conducted at a proper final temperature. The activation time was changed in the range of 30 – 120 min. Since prior to the process of char activation the carbonization process was conducted, for the correct evaluation of the course of activation, the results were calculated for the out-gassed char (X_i^{ko}).

Experimental analysis

During the investigations the following determinations were performed: strength, iodine number, methylene number and the technical analysis of the raw material. The purification tests for the water contaminated by toluene (T), p-chlorophenol (PCP), methylene blue (MB) and Congo red (CR) were conducted, too.

Strength studies were carried out with a modified Marsh-Ragan's method, readjusted to the samples grain size. The apparatus for strength determination consisted of two stainless-steel cylinders (length 32 cm). Two grams of the sample (1.0 – 3.15 mm) were placed into the tube together with 12 balls, closed by caps and then rotated at a constant speed of 25 rpm for 2 min. The amount of breakage was determined by sieve analysis. The sample was mechanically shaken and the fractions > 1.0; 1.0 – 0.6 and < 0.6 mm were weighed. The weight percentage re-

maining on the 1.0 mm sieve was recorded as the strength (R_1) and the contribution of fraction < 0.6 mm was recorded as grindability (R_3).

Adsorption from solutions was investigated to assess the chars and the activation products capacity for removing different water contaminates. The water polluted with toluene and p-chlorophenol (500 mg/dm^3), Congo red (100 mg/dm^3) and methylene blue (200 mg/dm^3) was used as the model sewage. The stock solutions were prepared by dissolving contaminants in the deionized water.

In order to establish the equilibrium time, 0.1g of the dry (< 0.2 mm) sorbent was mixed with the sewage (50 cm^3) and agitated for different times. A blank sample was investigated under the same conditions. After stirring, shaking and the sorbent separation by centrifugation at 4000 rpm for 5 min, the oxygen demand (COD) originated from potassium dichromate required for the oxidation of the compounds found in the sewage with toluene, and p-chlorophenol was determined according to the ISO 6060 standard. In this method the sample is oxidized with a hot sulfuric solution of potassium dichromate, with silver sulfate as the catalyst. The concentration of the unconsumed yellow $Cr_2O_7^{-2}$ ions was determined before and after the treatment, photometrically at the wavelength of 449 nm.

The Congo red and methylene blue concentration was determined using a photometer Spectroquant NOVA 60 provided by Merck at the wavelength of 500 and 620 nm, respectively using silica cells of path length 1 cm. The adsorption yield (A_d) and the equilibrium substance concentration on the adsorbent (q_e) was determined. The experiments were carried out at room temperature 25±2 °C in duplicate and the mean values were reported. The maximum deviation was 2%.

RESULTS

The investigated miscanthus had 6.4 wt.% of moisture, 2.2 wt.% ash and 81.5 wt.% of the volatile matter. Miscanthus had the cells structure with a very well developed macropores system.

In the miscanthus carbonization process about 25 wt.% of the chars were obtained. The chars had a low iodine number (12 – 38 mg I_2/g). Chars had only the pores inaccessible to iodine < 0.8 nm.

The weight loss in the activation process of the miscanthus char using water vapour, the strength, iodine and methylene numbers of the chars and activation products are presented in Table 1. During the char treatment in water vapour significant quantities of the organic materials are liberated as volatiles. The role of water vapour is not limited only to the activation of the char to transform it into the activated carbon but also to the transport and the stabilization of volatile products.

The increase of the activation temperature (from 700°C up to 800°C) and the duration of water vapour activation (from 30 – 120 min.) results in the decrease of the yield and the increase of weight loss of the activation products as well as an improvement of iodine and methylene numbers.

Water cleaning by the obtained sorbents

Active carbon obtained at 750°C (AM750/45) was used for studying the influence of the shaking time on the effectiveness of the removal of the impurities (toluene, p-chlorophenol, methylene blue and Congo red) from the contamined water (Fig. 1a).

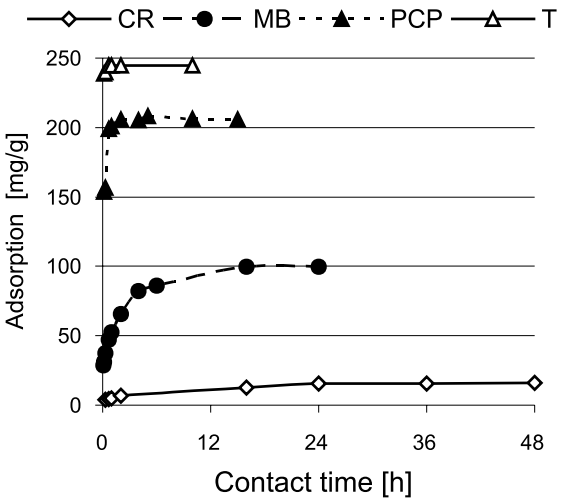
The equilibrium was established quickly within 1 h for toluene and 2 h for p-chlorophenol. For methylene blue (MB) and Congo red (CR) the equilibrium times were 16 h and 24 h, respectively. The equilibrium time is the time taken for the maximum adsorption of dye onto the adsorbent surface, above which the adsorption remains constant. Equilibrium time is a very important sorbents parameter for wastewater treatment applications.

The contact time required for the equilibrium of contaminants between the sorbent and the solution appeared to be dependent on the ratio of adsorption sites to the

Table 1. The properties of chars (CM) and the activation products (AM) from miscanthus

Sample			Weight loss X^{KO}_{A} [wt.%]	Strength R_1 [wt.%]	Grindability R_3 [wt.%]	Iodine number IN [mg I_2/g]	Methylene number MN [cm^3]
Char		CM					
700°C		CM700	–	61,3	11,3	25	0
750°C		CM750	–	62,6	11,9	12	0
800°C		CM800	–	70,6	9,4	38	0
Activation product			–				
Activation temperature [°C]	Activation time [min]	AM temp/time	–				
700	30	AM700/30	13,3	61,0	11,1	438	0
	60	AM700/60	20,3	56,0	12,0	526	1
	90	AM700/90	26,9	54,6	13,0	642	2
	120	AM700/120	31,1	52,1	13,9	714	3
750	30	AM750/30	17,5	62,4	11,1	579	1
	45	AM750/45	23,0	60,0	11,4	626	3
	60	AM750/60	28,6	54,6	14,2	696	5
	90	AM750/90	39,1	41,9	16,9	822	10
800	30	AM800/30	24,5	58,4	10,0	648	2
	45	AM800/45	36,7	57,5	14,2	768	11
	60	AM800/60	45,2	51,2	17,7	825	17

a)



b)

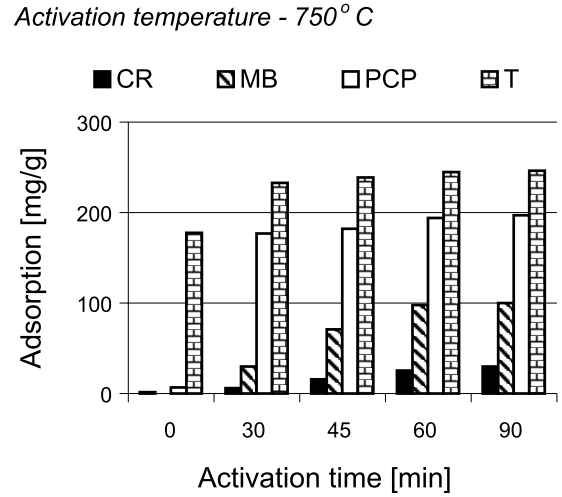


Figure 1. The effect of the contact time (a) and the activation time (b) on the amount of adsorbed substances

numbers of the contaminants particles that can be adsorbed. For our sorbents the initial sorption

of the investigated contaminants (T and PCP) occurs rapidly because large numbers of vacant surface sites are easily available for their adsorption.

The investigated activation product obtained at 750°C (AM750/60) was the most effective for the removal of the toluene and p-chlorophenol. Its removal efficiencies for methylene blue and Congo red are smaller than for toluene and p-chlorophenol (Fig 1b). The removal efficiencies for the activated products obtained at 750°C for the organic impurities from the model sewage is in the following order: toluene > p-chlorophenol > methylene blue > Congo red.

The efficiency of removing organic compounds from the model sewage by all the investigated samples at the equilibrium times is shown in Fig 2. The activation temperature and the time have a great effect on the activated carbons adsorption process. The amount of the adsorbed contaminants by sorbents increases with the activation temperature and time. The adsorption properties depend on the number of active sites where the adsorbate molecules are adsorbed.

Small pores in the sorbents obtained from miscanthus are not fully accessible to methylene blue and Congo red molecules, which are in the liquid phase. Carbons with the large pore diameter have a large adsorption capacity for methylene blue and Congo red. These sorbents have the highest iodine numbers and the internal surface area. These activation products obtained at different temperatures using different activation times from miscanthus show a similar cleaning efficiency for toluene and p-chlorophenol. Only the adsorptions of methylene blue and Congo red are strongly related to the sorbents degree of activation. Since only pores larger than the size of adsorbate molecules are accessible to the adsorbate it means that the availability of pores larger than methylene blue and Congo red molecule size increases with the activation temperature and time. The most effective sorbents for the removal of all the organic impurities are: AM750/60 and AM750/90, AM800/30 and AM800/45.

The removal efficiency for the investigated contaminants from the model sewage by the miscanthus chars (CM) are smaller than that for the activation products. Chars exhibited the porosity mostly limited to submicropores. The especially small removal efficiency is for p-chlorophenol (3%). Toluene and p-chlorophenol have similar particles sizes (d = 0.54 and 0.64 nm respectively), but toluene is removed with higher efficiency by miscanthus char (70 – 73%) that p-chlorophenol. This means that the groups with the basic character responsible for p-chlorophenol removal were not observed on the char surface. P-chlorophenol forms hydrogen bonds between the electron acceptor groups on the carbon surface and the hydrogen atom on phenolic group[6].

CONCLUSIONS

It was stated that miscanthus grasses are the suitable raw material for obtaining granular active carbons of high strength.

The chars prepared from miscanthus grass exhibited a relatively high strength. In their structure the ultramicropores were dominating. This is the reason of low iodine and methylene numbers observed. The chars were non-effective in water purification tests (only toluene was removed from the water solution by these chars).

The process of the activation of chars from miscanthus caused a growth of iodine and methylene numbers as well as the development of the pore system in the range of wider micropores and mesopores.

The efficiency of the purification of water solution from toluene, p-chlorophenol, methylene blue and Congo red by active carbons prepared from miscanthus grass was high and grows with the activation temperature and time.

Toluene was observed to be the most easily removed contaminant using all the active carbons prepared from the miscanthus grass biomass. Congo red was the most troublesome contaminant for the purification with the examined sorbents.

It seems that the optimal conditions for the miscanthus activation process were: the temperature of 750°C and the activation time of 60 – 90 min or the temperature of 800°C and the activation time 30 – 45 min. Under these conditions the sorbents with the best developed internal surface areas and the best sorption capacity were obtained.

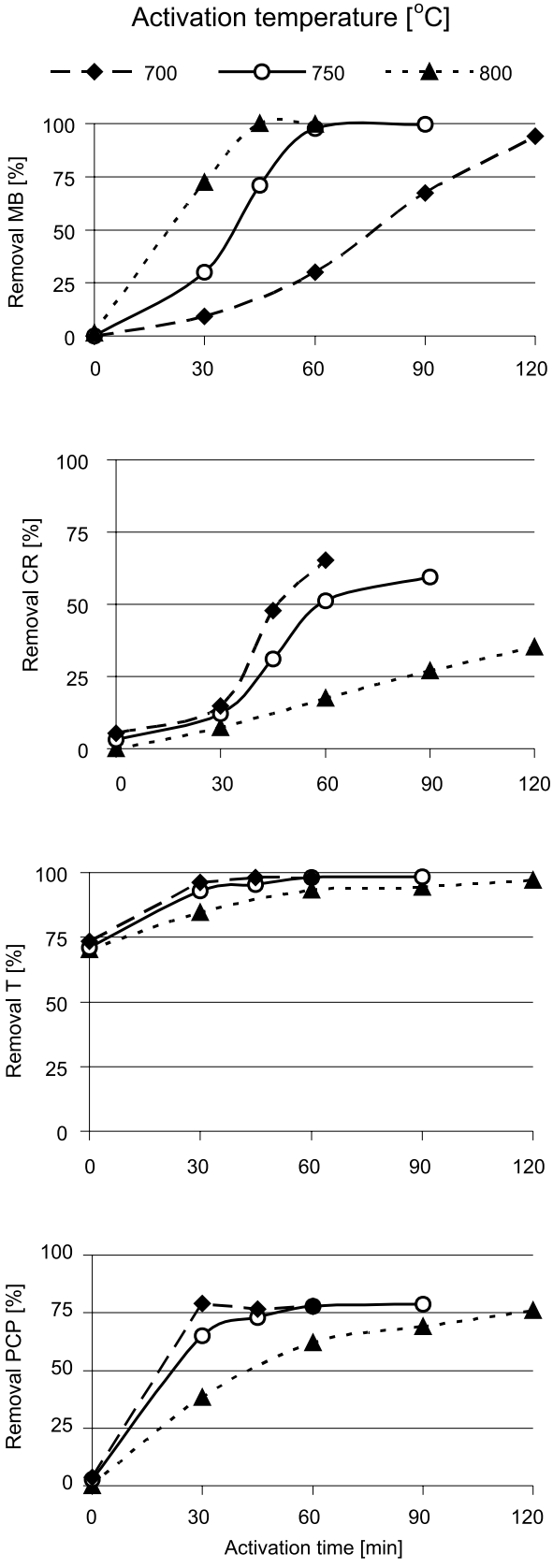


Figure 2. The efficiency of removing methylene blue (MB), Congo red (CR), toluene (T) and p-chlorophenol (PCP) from the aqueous solution by active carbons from miscanthus

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