Open Chem., 2015; 13: 1150–1156
DE GRUYTER OPEN

Research Article
Open Access

Hanna Fałtynowicz*, Jan Kaczmarczyk, Marek Kułażyński

Preparation and characterization of activated carbons from biomass material – giant knotweed (*Reynoutria sachalinensis*)

DOI: 10.1515/chem-2015-0128
received February 13, 2015; accepted June 24, 2015.

Abstract: Activated carbons from biomass material of giant knotweed *Reynoutria sachalinensis* (F. Schmidt ex Maxim.) Nakai were obtained. Use of this plant for manufacturing activated carbon has not been studied yet. Therefore, the first activated carbons of giant knotweed origin are described. Both physicochemical (by steam and CO_2) and chemical (by KOH) activation methods were applied. Influences of temperature (500, 600, 700 and 800°C), burn-off [10, 25 and 50 wt. % (daf)] and KOH concentration on pores surface area and volume distribution of the obtained activated carbons were explored. Porosity of the elaborated sorbents was determined by benzene and carbon dioxide sorption measurements. Sorbents obtained by steam activation were micro- and mesoporous with surface area and volume of pores increasing with temperature and burn-off to $V = 0.351\ cm^3\ g^{-1}$ and $S = 768\ m^2\ g^{-1}$ at 800°C at 50% burn-off. Carbon dioxide activation resulted with notably microporous activated carbons with porous texture parameters also increasing with burn-off to $V = 0.286\ cm^3\ g^{-1}$ and $S = 724\ m^2\ g^{-1}$ at 50% burn-off. The highest BET surface area of $2541\ m^2\ g^{-1}$ was achieved when chemical (KOH) activation was performed using KOH to char ratio 4:1.

Keywords: biomass, activated carbon, chemical activation, steam activation, carbon dioxide activation, benzene and carbon dioxide sorption, sorption properties

1 Introduction

Activated carbons are highly porous materials commonly used as catalysts [1], capacitor components [2] and drugs [3] as well as for storage, separation and purification of gases [4] and liquids [5,6]. For their preparation, materials with high carbon and low ash contents can be used [7]. Among them, the widest commercial application is found with coal, wood and coconut shells. To make activated carbon production more environmentally friendly, waste materials are used as sources. These can be industrial wastes, such as by-products of the petroleum industry [8], used tires [9] and polymer resins [10,11]; biomass waste, *i.e.* agricultural residues [13-15], cones [16,17], bamboo waste [18-20], saw dust [21]; or food-processing wastes, such as sugarcane bagasse [22]. Such approaches improve the utilization, recovery and reuse of waste and reduce the cost of the final product [23].

During our study on activated carbons from biomass, we prepared and characterized carbon sorbents from giant knotweed *Reynoutria sachalinensis* (F. Schmidt ex Maxim.) Nakai. This is the first report of activated carbons prepared from giant knotweed biomass. This herbaceous perennial plant from *Polygonaceae* family can reach up to 2–4 m height and originated in northeast Asia. It was introduced to Europe in the middle of 18th century as an ornamental plant. Additionally, it serves also as a honey and energy crop [24]. However, it rapidly has spread into the natural environment and proved to be one of the most invasive species in Europe [25], which harms biodiversity and leads to economic and agricultural losses. Importation, cultivation and sale of giant knotweed in Poland requires permission [26,27]. Moreover, its removal from protected areas is recommended. Biomass of this plant is usually used as an energy source. In this paper we evaluated the usefulness of ligneous stems of giant knotweed as raw material for manufacturing activated carbons.

***Corresponding author: Hanna Fałtynowicz:** Division of Chemistry and Technology of Fuels, Faculty of Chemistry, Wrocław University of Technology, Wrocław 50-344, Poland, E-mail: hanna.faltynowicz@pwr.edu.pl
Jan Kaczmarczyk, Marek Kułażyński: Division of Chemistry and Technology of Fuels, Faculty of Chemistry, Wrocław University of Technology, Wrocław 50-344, Poland

2 Experimental procedure

Raw material characterization

Giant knotweed pellets of 10 mm diameter (Fig. 1) used as raw material for activated carbon manufacturing were obtained from plantation in Russia.

Pellets were standardized to constant mass. Air-dried raw material was characterized by technical analysis in compliance with Polish Standard (PN – 80/G – 04511, 04512, 04516), elemental (Elementar VarioEl) and thermogravimetric analysis (TG). The TG measurements were performed under an argon atmosphere, at 25-900°C with a heating rate of 5°C min^{-1}.

Chars preparation

The raw material was first carbonized in the Fischer-Schrader retort at temperature of 500°C. Technical analysis was conducted for the obtained low-temperature char. After grinding to grains of less than 3.15 mm, it was subjected to further carbonization in the thermogravimetric furnace with heating rate of 10°C min^{-1} under an argon atmosphere and held at final temperatures of 500, 600, 700, 800 and 900°C for 30 min. The final carbonizates were designated as C500, C600, C700, C800 and C900, respectively.

Activated carbons preparation

The resulting chars were subjected to physicochemical activation by steam and carbon dioxide in the thermogravimetric furnace. First, the impact of the activation temperature on the porous texture of the activated carbons was evaluated. For that purpose, chars C500–C800 were steam activated to 50% wt. burn-off (daf) at the same temperatures as the final charring temperatures of the respective carbonizates, meaning C500 was activated at 500°C, C600 at 600°C, *etc*. The four steam activated carbons that resulted were designated as AH500-50, AH600-50, AH700-50 and AH800-50. The development of the porosity of the activated carbons was also investigated as a function of burn-off. Char C700 was physicochemically activated under isothermal conditions at 700°C to 10%, 25% and 50% wt. burn-off (daf). Activated carbons obtained by carbon dioxide activation were assigned AC700-10, AC700-25 and AC700-50, while those obtained by steam activation were called AH700-10, AH700-25 and AH700-50. The activated carbon AH700-50 present in both series was the same sample.

Additionally, low-temperature char obtained initially was subjected to chemical activation with solid potassium hydroxide purchased from POCH (AR quality). We assessed how the resultant pores size and volume depend on the weight of KOH to weight of char ratio, here termed the 'weight ratio'. KOH was physically mixed and homogenized with char in weight ratios of 1:1, 2:1, 3:1 and 4:1. Obtained activated carbons were marked as KOH1, KOH2, KOH3 and KOH4, respectively. Activation process was conducted in a vertical tube furnace for chemical activation made by Czylok Company (Poland) at 25–700°C under nitrogen atmosphere (flow: 30 dm^3 h^{-1}). A heating rate of 5°C min^{-1} was applied until the final activation temperature was reached and then maintained for 1h. After activation, products were heated in a beaker with the addition of 3 M HCl for 30 min to remove reaction by-products. Hot distilled water was used successively until chloride ions were washed out. The obtained activated materials were dried in a dryer at 110°C to constant mass.

Figure 1: Giant knotweed pellets used as a raw material for activated carbons preparation.

The percent of char burn-off after activation was calculated from equation (1) as the ratio of dry ash-free carbon weight loss during process (Δm^{daf}) to initial dry ash-free carbon mass (m^{daf}).

$$\% \text{ burn-off} = [\Delta m^{daf} \times (m^{daf})^{-1}] \times 100\% \quad (1)$$

Determination of porous texture parameters

Porosity of raw material, chars and activated carbons were characterized using sorption measurements in a gravimetric apparatus of the McBain–Bakr type [28,29]. The surface areas and volumes of micro- and mesopores, average mesopores widths and specific surface areas (BET) were calculated based on the adsorption isotherm of CO_2 and adsorption/desorption isotherm of benzene (25°C) (see the supplementary materials for a detailed description of the calculations).

3 Results and discussion

3.1 Giant knotweed pellets characterization

Raw material in the form of pellets used for preparation of the activated carbons contained 11.23% of moisture, 4.91% of ash (dry state) and 79.47% volatile fraction (dry ash-free state – daf). The elemental composition was as follows (%): C, 50.0; O, 42.0; H, 5.51; N, 2.12, S, 0.01 (daf). The characteristics of giant knotweed pellets were similar to that of the other biomass materials [30]. Thermogravimetric analysis (Fig. 2) revealed that thermal decomposition of the analyzed pellets occurred in three main phases. The first phase (50–200°C) is associated with moisture release (9.4% weight loss). The most intensive decomposition of an organic matter occurred in the range of 225–375°C (additional 49.7% weight loss). According to literature, cellulose and hemicelluloses undergo decomposition in this temperature interval giving a volatile fraction of biomass [31]. Above that temperature, rate of the decomposition process decreased and further weight loss was small, which was due to formation of char structural units more resistant to thermal decomposition. Compounds with higher thermal stability decompose in this phase, *e.g.* lignin [31]. At the final temperature of 900°C total weight loss was 74% (daf). A carbonization yield of 26% (daf) at 900°C is comparable to that obtained for other materials of plant origin, such as palm shell (24% yield) [32].

Sorption measurements revealed that the giant knotweed biomass did not have a developed porous texture. Volume of micro- and mesopores (V) did not exceed 0.034 cm^3 g^{-1} (Fig. 3A). The porous structure of the raw material consisted mainly of submicropores (pores of width below 0.4 nm) which constituted 92% of a total micro- and mesopores surface area (S). Therefore S (77 m^2 g^{-1}), the surface area of meso- and micropores (including submicropores), was significantly higher than BET surface area (S_{BET}) (2 m^2 g^{-1}) (Fig. 4A). The latter was calculated from an adsorption isotherm of benzene. Submicropores are micropores inaccessible to benzene molecules, so BET surface area does not include the surface area of submicropores. Therefore, in the case of notably submicroporous materials, like the giant knotweed pellets, S_{BET} values are significantly lower than S values.

In spite of the poorly developed porous texture of the raw material, high carbon and low ash contents make it suitable for preparation of activated carbons.

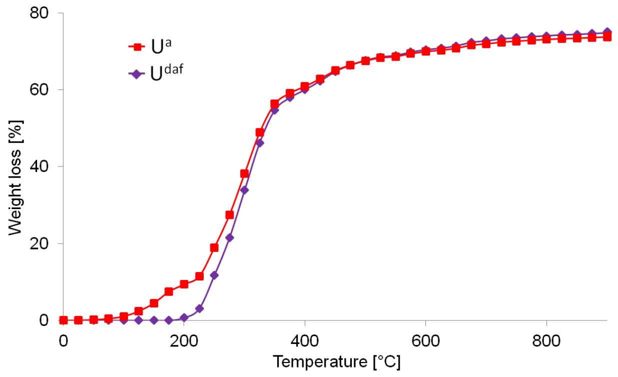

Figure 2: Thermogravimetric analysis of giant knotweed pellets in analytical state (U^a) and dry ash-free state (U^{daf}).

3.2 Chars characterization

Charring of the raw material gave low-temperature char with 34% yield. It contained 0.99% moisture, 10.75% ash (dry state) and 26.64% volatile fraction (daf state). Further carbonization to higher temperature causes significantly lower weight loss, and gave chars C500–C900 with 71–84% yields of the low-temperature char weight. The porous texture of the chars was much more developed. Volume of micro- and mesopores (V) ranged from 0.125 to 0.168 cm^3 g^{-1} depending on the temperature applied (Fig. 3B and Table S1), so it was three times greater than that in the raw material. Also, their S values increased and were in the range of 310–415 m^2 g^{-1}, compared to S_{BET} – 13–46 m^2 g^{-1} (Fig. 4B and Table S2). It was likewise observed for the raw material, with the chars S_{BET} considerably smaller than S. The difference is associated with the predominance of submicropores in their porous texture, which accounted for 61–88% of the total adsorption pores volume. The higher the carbonization temperature, the bigger values of above mentioned parameters. The same trend has been observed for coconut shell chars [33]. However, when temperature exceeded 800°C, total pore volume and surface area decreased. The biggest decrease of these parameters values was observed for micropores (0.4–2 nm width). This can be explained by progressive partial blockage of these pores by deposited carbonization by-products, mainly condensed tars, or by rearrangement of the char structure [34].

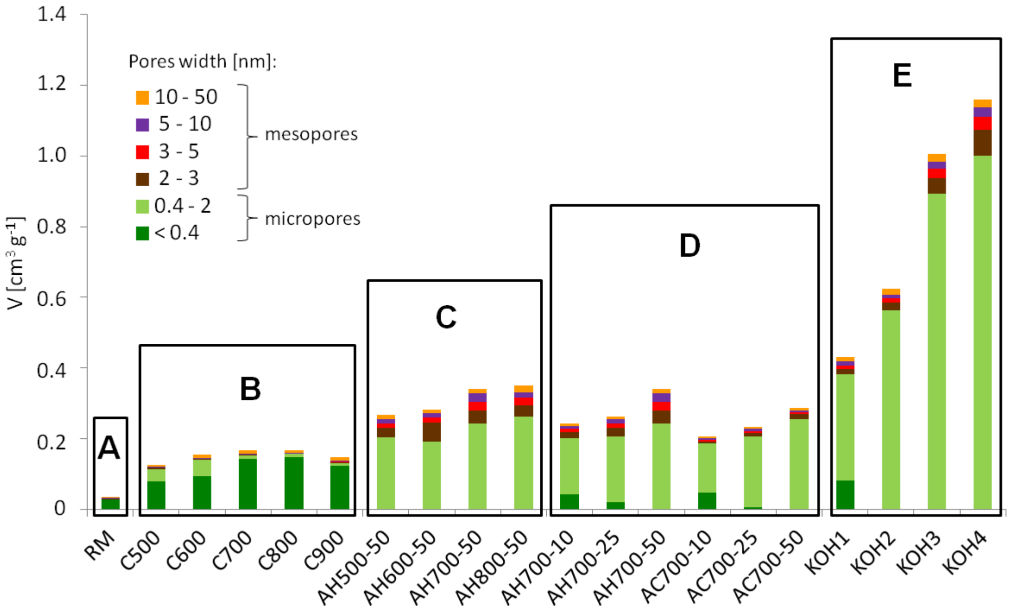

Figure 3: Distribution of micro- and mesopores volume according to pore size in raw material (A), chars (B) and activated carbons obtained by steam activation at different temperatures (C), steam and carbon dioxide activation to different burn-off (D) and chemical (KOH) activation (E).

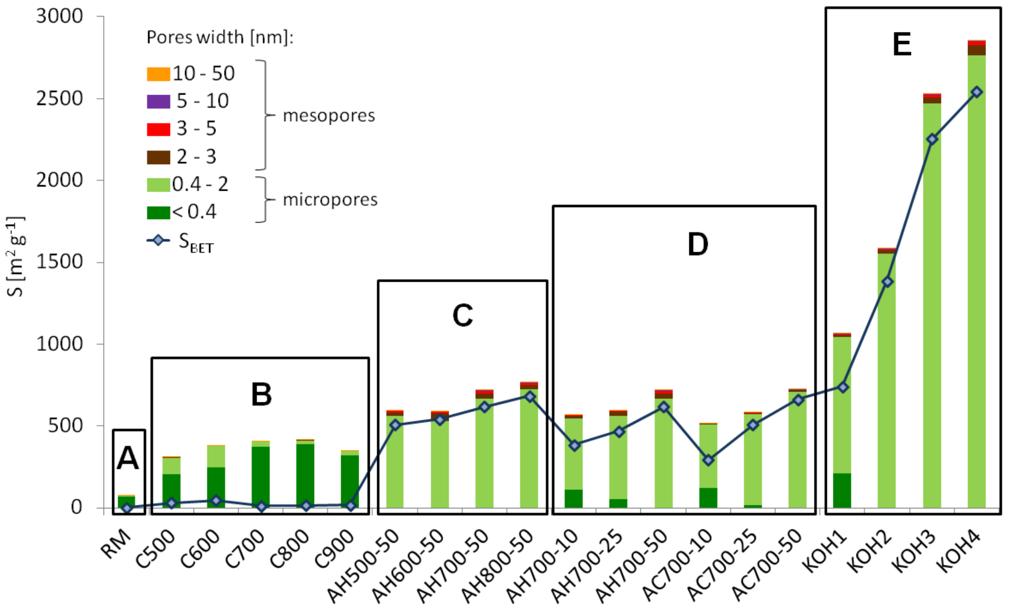

Figure 4: Distribution of micro- and mesopores surface area according to pore size and BET surface area in raw material (A), chars (B) and activated carbons obtained by steam activation at different temperature (C), steam and carbon dioxide activation to different burn-off (D) and chemical (KOH) activation (E).

3.3 Steam activation – activation temperature effect

Chars C500–C800 were used for steam activation. The duration of this process was decreased when temperature was increased from 878 to 45 min. In the course of activation process, all submicropores, which dominated in the chars, were widened to micropores range (Figs. 3C and 4C). The resulting activated carbons were micro- and mesoporous materials in which micropores accounted for 68–76% of total adsorption pores volume and mesopores (2–50 nm width) – for 24–32%. Volume and surface area of micro- and mesopores also increased with temperature of the activation process in the range of 0.266–0.351 cm^3 g^1

and 596–768 m^2 g^{-1}, respectively (Figs. 3C, 4C and Tables S1, S2). These values were approximately twice those of corresponding chars. BET surface area also rose from 508 to 685 m^2 g^{-1} (Tab. S2). The increase of the parameters' values was associated with the pores' enlargement caused by reaction of carbon with an oxidizing agent.

3.4 Physicochemical activation – burn-off and activating agent effect

We compared the impact of two activating agents, steam and carbon dioxide, used for physicochemical activation on porous texture of obtained sorbents. First, we checked their reactivity towards char during reaction. Average reactivity (R_{av}^{daf}) was calculated from Eq. 2, as dry ash-free char weight loss during carbon reaction with steam or carbon dioxide (Δm^{daf}) divided by total reaction time (t) and initial dry ash-free char mass (m^{daf}).

$$R^{daf} = \Delta m^{daf} \times (m^{daf} \times t)^{-1} \qquad [h^{-1}] \qquad (2)$$

Average reactivity with steam varied between 0.21–0.28 h^{-1}, whereas with carbon dioxide it was between 0.035–0.042 h^{-1}. Thus, steam was over six times more reactive than carbon dioxide. Experimental data shows that weight loss is nearly linear with time for reactions both with steam and carbon dioxide (R^2 = 0.992 and 0.995, respectively) (Fig. 5).

Carbon dioxide activated sorbents were mostly microporous (~90% of total adsorption pores volume in all samples), while steam activated chars had a higher contribution of the mesopores (up to 29% of total adsorption pores volume in AH700-50). This is due to the different activity of both oxidizing agents during activation. Less reactive carbon dioxide more deeply penetrates the pores' structure and widens submicro- and micropores. The much higher reaction rate of the steam causes the reaction to proceed more closely to the pores' exteriors. Gaseous products of the reaction impede steam's migration deep into the pores. This results in widening of micro- and mesopores of the char [35]. Generally, at the same burn-off, similar pore volumes and surface areas were achieved for both activating agents, but slightly bigger after steam activation. Pores widened and porosity developed with increasing burn-off, which agrees with the previous studies of burn-off impact on the development of activated carbon porous texture [36]. This means that the volumes and surface areas of submicropores decreased, and in the samples AH700-50 and AC700-50, the narrowest pores utterly disappeared, while those of micropores and mesopores increased and the highest values were observed at 50% wt. burn-off (daf). Overall adsorption pore volume and surface area also increased with burn-off, reaching 0.340 cm^3 g^{-1} and 720 m^2 g^{-1} for AH700-50 and 0.286 cm^3 g^{-1} and 724 m^2 g^{-1} for AC700-50 (Figs. 3D, 4D and Tables S1, S2). The highest BET surface area of 664 m^2 g^{-1} was obtained for AH700-50 (Table S2). Generally, the values of the porous texture parameters suggest that these activated carbons are sorbents of an average quality.

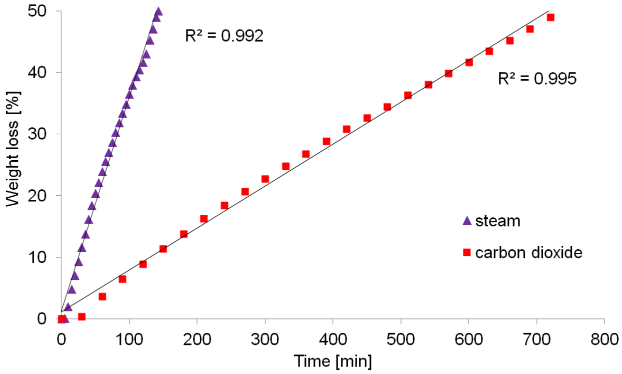

Figure 5: Weight loss of C700 as a function of reaction time during steam and carbon dioxide activation to 50% wt. burn-off (daf) at 700°C.

3.5. Chemical activation – KOH concentration effect

Through chemical activation, we obtained four activated carbons with yields ranging from 38% (KOH4) to 60% (KOH1). A higher concentration of potassium hydroxide resulted in a the lower yield of the reaction product. The resulting sorbents were highly microporous (86–93% of total adsorption pores volume). Volume and surface area of micropores and mesopores increased with increasing KOH-to-char weight ratio. Submicropores were absent in all samples except KOH1. Total micro- and mesopores volume and surface area also increased from 0.431 to 1.161 cm^3 g^{-1} and from 1065 to 2856 m^2 g^{-1} (BET surface area: 741–2541 m^2 g^{-1}) (Figs. 3E, 4E and Tables S1, S2). The same trend was observed for chemical activation by solid KOH of bituminous coal when the KOH-to-char ratio was increased from 2:1 to 4:1 [37]. The parameter values obtained for KOH1 were similar to those for activated carbon made from another lignoceous biomass, namely bamboo waste. As a result of chemical activation with NaOH impregnation at 950°C, the authors obtained porous sorbents with total pore volume of 0.42 cm^3 g^{-1} and specific surface area of 985 m^2 g^{-1} [38]. The most significant developement of porous texture of the activated carbons was observed when KOH-to-char weight ratio rose from 2:1 to 3:1; further increase in the KOH-to-char ratio did not have as noticeable impact. Activated carbons obtained by chemical (KOH) activation are characterized by far more developed porous texture compared to those activated physicochemically described earlier.

4 Conclusions

As a result of the study, we obtained activated carbons from biomass material – giant knotweed pellets – which so far has not been used for activated carbon preparation. We applied various activation techniques: physicochemical activation by steam and carbon dioxide and chemical activation with solid KOH as an activating agent. The activated carbons obtained from steam activation were micro- and mesoporous, with 20–30% mesopores contribution to the total adsorption pores volume. Those activated carbons obtained by carbon dioxide and KOH activation were notably microporous with ~90% proportion of micropores in the total adsorption pores volume. Physicochemical activation of chars resulted in sorbents with BET surface area no higher than 700 m^2 g^{-1}. This value is not attractive for commercial application if we consider microporous sorbents. However, activated carbons obtained by steam activation are more mesoporous and therefore could serve as potentially good materials for adsorption from solutions of bigger size molecules, *e.g.* organic dyes or biosurfactants. Chemical activation allowed the production of materials with much more developed porous textures. In all samples, irrespective of KOH-to-char weight ratio, BET surface area was higher than in any sample from physicochemical activation. Activated carbon with the highest BET surface area of 2541 m^2 g^{-1} was obtained by this method. Predominantly microporous structure makes these materials suitable for gas storage, purification and separation. In addition to the impact of the chosen method on porous texture of received sorbents, we also examined how temperature, burn-off and KOH-to-char weight ratio affect porosity of the obtained products. Activation at higher temperature allows production of sorbents with higher pore volumes and surface areas. Conducting physicochemical activation for longer periods of time to higher burn-off also resulted in materials with more developed porous texture. During chemical activation, the higher concentration of KOH, the more microporous products were obtained with better developed porosity. Activated carbon manufacturing is an interesting alternative to the current application of giant knotweed pellets, which are used mainly for co-firing in energetic boilers.

Acknowledgements: Edition of the publication was financed with funds of Leading National Research Center (KNOW) for the years 2014-2018 for Faculty of Chemistry Wroclaw University of Technology as a member of the consortium of Wrocław Center for Biotechnology.

References

[1] Trawczyński J., Kułażyński M., Active carbon monoliths as catalyst supports for scr (selective catalytic reduction) of NO_x with ammonia, Coal Science and Technology, 1995, 24, 1803-1806.

[2] Lee H.-C., Byamba-Ochir N., Shim W.-G., Balathanigaimani M. S., Moon H., High-performance super capacitors based on activated anthracite with controlled porosity, J. Power Sources, 2015, 275, 668-674.

[3] Wu M., Guo Q., Fu G., Preparation and characteristics of medicinal activated carbon powders by CO_2 activation of peanut shells, Powder Technology, 2013, 247, 188-196.

[4] Sroka Z. J., Kułażyński M., Kaczmarczyk J., Michałowski R., Application of carbon adsorbent to methane storage in fuel tanks of vehicles, Pol. J. Environ. Stud., 2009, 18, 211-215.

[5] Dabioch M., Skorek R., Kita A., Janoska P., Pytlakowska K., Zerzucha P. et al., A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification, Open Chem., 2013, 11, 742-753.

[6] Bratek K., Bratek W., Kułażyński M., The utilization of sorbents obtained from miscanthus using steam as the activation agent for wastewaters treatment, Pol. J. Chem. Technol., 2007, 9, 102-105.

[7] Bansal R. C., Goyal M., Activated carbon adsorption, CRC Press, New York, 2005.

[8] He X., Li R., Qiu J., Xie K., Ling P., Yu M. et al., Synthesis of mesoporous carbons for supercapacitors from coal tar pitch by coupling microwave-assisted KOH activation with a MgO template, Carbon, 2012, 50, 4911–4921.

[9] Zhi M., Yang F., Meng F., Li M., Manivannan A., Wu N., Effects of pore structure on performance of an activated-carbon supercapacitor electrode recycled from scrap waste tires, ACS Sustainable Chem. Eng., 2014, 2, 1592–1598.

[10] Tseng R.-L., Wu F.-C., Juang R.-S., Adsorption of CO_2 at atmospheric pressure on activated carbons prepared from melamine-modified phenol-formaldehyde resins, Sep. Purif. Technol., 2015, 140, 53-60.

[11] Bratek K., Bratek W., Kułażyński M., Carbon adsorbents from waste ion-exchange resin, Carbon, 2002, 40, 2213-2220.

[12] Ali I., Asim M., Khan T. A., Low cost adsorbents for the removal of organic pollutants from wastewater, J. Environ. Manage., 2012, 113, 170-183.

[13] Ioannidou O., Zabaniotou A., Agricultural residues as precursors for activated carbon production - a review, Renew. Sust. Energ. Rev. 2007, 11, 1966-2005.

[14] Vargas D. P., Giraldo L., Moreno-Piraján J. C., Calorimetric study of activated carbons impregnated with $CaCl_2$, Open Chem., 2015, 13, 683-688.

[15] Bratek K., Bratek W., Kaczmarczyk J., Kułażyński M., Activated carbons prepared by corn cobs activation in water purification, Pol. J. Environ. Stud., 2005, 14, 115-118.

[16] Nowicki P., Kuszyńska I., Przepiórski J., Pietrzak R., The effect of chemical activation method on properties of activated carbons obtained from pine cones, Cent. Eur. J. Chem., 2013, 11, 78-85.

[17] Toscano G., Cimino G., New carbon from low cost vegetal precursors: acorn and cypress cone, Cent. Eur. J. Chem.,2013, 11, 2012-2021.

[18] Li D., Ma X., Liu X., Yu L., Preparation and characterization of nano-TiO_2 loaded bamboo-based activated carbon fibers by H_2O activation, BioResources, 2014, 9, 602-612.

[19] Zhang Y.-J., Xing Z.-J., Duan Z.-K., Li M., Wang Y., Effects of steam activation on the pore structure and surface chemistry of activated carbon derived from bamboo waste, Appl. Surf. Sci., 2014, 315, 279-286.

[20] González P. G., Hernández-Quiroz T., García-González L., The use of experimental design and response surface methodologies for the synthesis of chemically activated carbons produced from bamboo, Fuel Process. Technol., 2014, 127, 133-139.

[21] Banerjee S., Chattopadhyaya M. C., Srivastava V., Sharma Y. C., Adsorption studies of methylene blue onto activated saw dust: kinetics, equilibrium, and thermodynamic studies, Environ. Prog. Sustainable Energy, 2014, 33, 790-799.

[22] Mohan D., Singh K. P., Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse - an agricultural waste, Water Research, 2002, 36, 2304–2318.

[23] Patteson J. W., Industrial wastes reduction, Environ. Sci. Technol., 1989, 23,1032-1038.

[24] Nowakowski T., Rośliny energetyczne, In: Lisowski A. (Ed.), Technologie zbioru roślin energetycznych, Wydawnictwo SGGW, Warszawa, 2010 (in Polish).

[25] Delivering Alien Invasive Species Inventories for Europe (DAISIE) project, http://www.europe-aliens.org/speciesFactsheet.do?speciesId=8170# (access: 12.02.2015).

[26] The Nature Conservation Act of 16 April 2004 (in Polish).

[27] Regulation of the Minister for the Environment of 9 September 2011 on the List of alien plant and animal species, which if realesed into the environment could threaten native species (in Polish).

[28] McBain J. W., Theories of adsorption and the technique of its measurement, Nature, 1926, 117, 550-551.

[29] McBain J. W. , Bakr A. M., A new sorption balance, JACS, 1926, 48, 690-695.

[30] Skoulou V., Zabaniotou A., Investigation of agricultural and animal wastes in Greece and their allocation to potential application for energy production, Renew. Sust. Energ. Rev., 2007, 11, 1698-1719.

[31] Mohamed A. R., Mohammadi M., Darzi G. N., Preparation of carbon molecular sieve from lignocellulosic biomass: a review, Renew. Sust. Energ. Rev., 2010, 14, 1591-1599.

[32] Daud W., Ali W., Sulaiman M., Effect of carbonization temperature on the yield and porosity of char produced from palm shell, J. Chem. Technol. Biotechnol., 2001, 76, 1281-1285.

[33] Li W., Yang K., Peng J., Zhang L., Guo S., Xia H., Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars, Ind. Crops Prod., 2008, 28, 190-198.

[34] Arriagada R., Bello G., Garcia R., Rodriguez-Reinoso F., Sepulveda-Escribano A., Carbon molecular sieves from hardwood carbon pellets. The influence of carbonization temperature in gas separation properties, Micropor. Mesopor. Mater., 2005, 81, 161-167.

[35] Molina-Sabio M., Gonzalez M., Rodriguez-Reinoso F., Sepulveda-Escribano A., Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon, Carbon, 1996, 34, 505–509.

[36] Rodriguez-Reinso F., Lopez-Gonzalez J. de D., Berenguer C., Activated carbons from almond shell - I. Preparation and characterization by nitrogen adsorption, Carbon, 1982, 20, 513-518.

[37] Labus K., Gryglewicz S., Machnikowski J., Granular KOH-activated carbons from coal-based cokes and their CO_2 adsorption capacity, Fuel, 2014, 118, 9-15.

[38] Moreno-Piraján J. C., Giraldo J., Activated carbon from bamboo waste modified with iron and its application in the study of the adsorption of arsenite and arsenate, Cent. Eur. J. Chem., 2013, 11, 160-170.