

Contents lists available at [ScienceDirect](#)

Chemical Engineering Research and Design

journal homepage: [www.elsevier.com/locate/cherd](http://www.elsevier.com/locate/cherd)

IChemE

## Comparison of the effects of different chemical activation methods on properties of carbonaceous adsorbents obtained from cherry stones

Robert Pietrzak<sup>a,\*</sup>, Piotr Nowicki<sup>a</sup>, Justyna Kaźmierczak<sup>a</sup>,  
Izabela Kuszyńska<sup>a</sup>, Joanna Goscińska<sup>a</sup>, Jacek Przepiórski<sup>b</sup>

<sup>a</sup> Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland

<sup>b</sup> West Pomeranian University of Technology, Pułaskiego 10, 70-322 Szczecin, Poland

### A B S T R A C T

A method for obtaining activated carbons from cherry stones by chemical activation with NaOH is described. Carbonaceous adsorbents were obtained by two methods of activation (physical mixing and impregnation) and two variants of thermal treatment (at a constant or increasing temperature). Cherry stones were proved to be effective cheap precursors of carbon adsorbents, characterised by large pore volume (ranging from 0.22 to 0.47 cm<sup>3</sup>/g) and good sorption abilities (iodine number from 343 to 996 mg/g). The activated carbons obtained usually have strongly microporous structure and acidic surface character. The best physicochemical properties and adsorption properties towards iodine were found to be shown by the carbon samples obtained by physical mixing of the precursor or char with the activating agent followed by activation at 600 °C.

© 2013 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

**Keywords:** Cherry stones; Chemical activation; Physical mixing; Impregnation; Physicochemical properties

### 1. Introduction

Activated carbon can be obtained from different materials of organic origin, ranging from wood to fossil coal (Nowicki and Pietrzak, 2010; Pietrzak, 2009). In view of increasing demand for activated carbon, which is related to development of many branches of industry and increasingly restrictive regulations related to protection of the natural environment, much attention is paid to the search for new precursors and new technologies of activated carbon production. Economically and ecologically attractive is the use of vegetation origin waste products. The materials that have already been applied for this purpose include nut shells or fruit stones (Nowicki et al., 2010a,b; Poinern et al., 2011; Chen et al., 2002; Soleimani and Kaghazchi, 2008; Uçar et al., 2009). The use of cheap and commonly available substrates permits obtaining activated carbon of new properties and applicability, being on the other hand a new method of dealing with waste. Of importance is

also the fact that activated carbons are nontoxic and can be regenerated after contamination.

Pyrolysis products of these precursors show surface area developed to a different degree, whose character depends on the nature of the initial material and pyrolysis conditions. Unfortunately, the porosity of chars is insufficient for the majority of applications, so they are subjected to a process of activation.

Many methods of obtaining activated carbons have been proposed but all of them are based on one of the two activation mechanisms; physical activation known also as thermal activation or chemical activation. Physical activation is usually performed using steam of carbon dioxide (Rodriguez-Reinoso et al., 1995; Molina-Sabio et al., 1996; Arenas and Chejne, 2004), while chemical one – with the use of KOH, NaOH, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, MgCl<sub>2</sub>, AlCl<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, etc. (Nowicki et al., 2008; Lozano-Castello et al., 2001; Hsu and Teng, 2000; Hayashi et al., 2002).

\* Corresponding author. Tel.: +48 618291581; fax: +48 618291555.

E-mail address: [pietrob@amu.edu.pl](mailto:pietrob@amu.edu.pl) (R. Pietrzak).

Received 28 March 2013; Received in revised form 20 August 2013; Accepted 6 October 2013

0263-8762/\$ – see front matter © 2013 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

<http://dx.doi.org/10.1016/j.cherd.2013.10.005>

Much better textural parameters, mainly 2–3 times larger specific surface area and pore volume as well as much better sorption capacity, show carbons obtained by chemical activation. Depending on the type of precursor and the activating agent, precursor/activator ratio, thermal conditions and activation time, the method permit obtaining a wide gamut of products of much diverse physicochemical properties and thus a wide range of possible applications. So far the process of chemical activation with the use of  $\text{ZnCl}_2$  or  $\text{H}_3\text{PO}_4$  has been most often applied and enjoyed the greatest interest, unfortunately it is unfavourable from the ecological point of view as it generates considerable amounts of harmful waste. That is why the studies of preparation of activated carbons should concern the easiest available and the cheapest precursors as well as the most environmental friendly technological processes of their production.

According to our earlier results (Nowicki and Pietrzak, 2010; Nowicki et al., 2010a,c) the activated carbons obtained from sawdust, plum stones or walnut shells often show better sorption properties than those obtained from fossil fuels. These results suggest that after optimisation of the technology of their production, they could be used in practice.

In view of the above, the main aim of the paper was to obtain cheap activated carbons as a result of chemical activation of cherry stones, conducted in different variants and to characterise their physicochemical and sorption properties.

## 2. Experimental

### 2.1. Materials and preparation of activated carbons

The initial sample of raw cherry stones (CS;  $W^a = 6.8 \text{ wt.}\%$ ;  $\text{Ash}^d = 0.3 \text{ wt.}\%$ ;  $\text{VM}^{\text{daf}} = 82.3 \text{ wt.}\%$ ) was dried in a drier, crushed and sieved to collect the grain size fraction of 2–4 mm. The material obtained was divided into two parts and then subjected to modification.

The pyrolysis (P) was carried out in a horizontal furnace under a stream of argon at the flow rate of  $170 \text{ mL min}^{-1}$ . The sample was heated ( $5 \text{ }^\circ\text{C min}^{-1}$ ) from room temperature to the final pyrolysis temperature of  $400 \text{ }^\circ\text{C}$ . In the final temperature, the sample was kept for 15 min and then it was cooled in inert atmosphere.

The activation was performed in a horizontal pipe reactor heated by a resistance furnace, at  $600 \text{ }^\circ\text{C}$  (increasing rate of  $10 \text{ }^\circ\text{C min}^{-1}$ ) for 20 min in an argon atmosphere supplied at the flow rate of  $170 \text{ mL min}^{-1}$ . The activating agent was sodium hydroxide. The activation process was realised in two variants:

Method I (A) – by physical mixing of the precursor or char with refined activating agent at the 2:1 weight ratio of NaOH/precursor (CSAX and CSPAX respectively, when  $X = 1$  or 2 depending on variant of thermal treatment).

Method II (IA) – by impregnation of the precursor or char with a solution of NaOH. keeping the 2:1 weight ratio of NaOH/precursor (CSIAX and CSPIAX respectively, when  $X = 1$  or 2 depending on variant of thermal treatment). The precursor or char was mixed with a water solution of NaOH by a magnetic stirrer and then the mixture was dried at  $105 \text{ }^\circ\text{C}$  for 24 h to a constant mass.

For each method of activation two variants of thermal treatment were applied:

Variant I (1) – a boat with the sample was placed in a furnace heated to  $600 \text{ }^\circ\text{C}$ , to rest till stabilisation of temperature. Thermal activation was performed for 20 min, counted from the moment the furnace temperature reached  $600 \text{ }^\circ\text{C}$ .

Variant II (2) – the sample was heated from room temperature to the final temperature of  $600 \text{ }^\circ\text{C}$  increasing at the rate  $10 \text{ }^\circ\text{C min}^{-1}$ . After reaching  $600 \text{ }^\circ\text{C}$  the sample was kept at this temperature for 20 min.

The precursor CS was activated according to variant I (samples CSA1, CSIA1) and II (samples CSA2 and CSIA2), while the char CSP only according to variant I (samples CSP1 and CSPI1). The activated carbons obtained were washed with a 5% HCl solution to remove the excess of NaOH, and then with hot distilled water to remove chlorides, and dried at  $105 \text{ }^\circ\text{C}$ .

### 2.2. Analytical procedures

Elemental analyses of the materials under investigation were performed on an elemental analyzer CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany). The content of ash was performed according to the Data National Standards ISO 1171:2002.

Characterisation of the pore structure of obtained materials was performed on the grounds of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micromeritics Instrument Corp. (USA). Prior to the isotherm measurements, the samples were outgassed at  $150 \text{ }^\circ\text{C}$  for 10 h. Surface area was calculated by BET (Brunauer–Emmett–Teller) method based on the evaluation of the monolayer capacity – the number of adsorbed molecules in the monolayer on the surface of a material and BJH (Barrett–Joyner–Halenda) methods, respectively (Choma and Jaroniec, 2006). Total pore volume and average pore diameter were determined as well. Micropore volume and micropore area were calculated using the t-plot method.

The surface properties were evaluated using potentiometric titration experiments using 809 Titrand equipment manufactured by Metrohm. The instrument was set at the mode when the equilibrium pH was collected. Materials studied of about 0.100 g in 50 mL 0.01 M  $\text{NaNO}_3$  were placed in a container thermostated at  $25 \text{ }^\circ\text{C}$  and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric  $\text{CO}_2$ , the suspension was continuously saturated with  $\text{N}_2$ . The carbon suspension was stirred throughout the measurements. Volumetric standard NaOH (0.1 M) or HCl (0.1 M) were used as the titrants.

The iodine sorption ability of the activated carbon samples, expressed as the efficiency of adsorption of molecular iodine from a water solution, was determined according to the ASTM Standard [ASTM D4607-94 (2006)]. This method permits estimation of the ability of the adsorbents obtained to remove substances whose molecules have the size close to that of iodine molecules, so of diameters close to 1 nm, from the liquid phase. To measure the adsorption capacity of the materials in a powdered form, the granular samples were pulverised manually in a mortar.

## 3. Results and discussion

Elemental analysis of the char obtained as a result of pyrolysis of raw cherry stones at  $400 \text{ }^\circ\text{C}$ , see Table 1, prove a significant increase in carbon and a decrease in the content of hydrogen and oxygen. These changes are caused by evolution of

Download English Version:

<https://daneshyari.com/en/article/620721>

Download Persian Version:

<https://daneshyari.com/article/620721>

[Daneshyari.com](https://daneshyari.com)