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Comparison of physicochemical and sorption properties of activated carbons prepared by physical and chemical activation of cherry stones

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ABSTRACT

Cherry stones were used as a precursor for the preparation of activated carbons by physical and chemical activation with CO_2 and KOH, respectively. The effect of pyrolysis temperature (500 and 800 °C) and activation method on the acid–base character of the surface, textural parameters as well as sorption properties of adsorbents prepared toward gas and liquid impurities was tested. Depending on the method of preparation, the final products were microporous activated carbons of surface area ranging from 361 to 1173 m^2/g and pore volume from 0.21 to 0.74 cm^3/g, with very diverse acid–base character of the surface. The results obtained in our study proved that a proper choice of cherry stone pyrolysis and activation procedure can produce adsorbents with high capacity for nitrogen dioxide as well as different contaminants from the liquid phase.

1. Introduction

Because of their unique porous structure, easy availability and neutral effect on the natural environment, activated carbons have found a wide range of applications. Therefore, no wonder that their global production continuously increases. The countries using the greatest amounts of activated carbons are Japan and the USA [1], while the least demand for them shows as yet the African countries. The rapid increase in the significance of activated carbons is a result of increasing demand for these materials in all branches of industry in economically developed countries, following from the development of new technologies based on the use of porous materials. What is also important the activated carbons are low-toxic, cheap in production and easily utilised.

Production of activated carbons is based mainly on the natural organic substrates, mainly hard coal [2], brown coal [3,4], wood [5], sawdust [6], local waste products, for example nut shells [7,8] or fruit stones [9–11]. An attractive but much more expensive precursor of activated carbons are synthetic polymers, e.g. waste phenolic resins [12], phenol-formaldehyde resins [13] or urea-formaldehyde resins [14], polyurethane [15] and ethylene polyterephthalate [16].

Pyrolysis products of these precursors developed to a different degree surface area 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 physical or chemical activation [17–20]. In this process the amorphous carbon is removed and the crystallites are exposed to the activating agent, which leads to expansion of the microporous structure. The porous structure can be additionally developed by enlargement of the existing pores and formation of greater pores by burning of walls between neighbouring pores. This results in an increase in meso- and macroporosity and a decrease in the micropore volume [21]. The products obtained in this way are characterised by large specific surface area [22–25].

Difficult pollutants in wastewater and sewage are, among others, heavy metals, dyes and pigments. They come mainly from all kinds of industrial activity, including textile, paint, tanning, paper and cosmetic industries. In technological processes of wastewater and sewage purification, four main types of methods are applied; chemical, biological, physicochemical and mechanical. One of the most effective methods for the removal of heavy metals and dyes from water solutions is adsorption by carbon sorbents. Adsorption processes are particularly attractive because of their high effectiveness and the possibility of use in a wide range of pollutant concentrations. From among different sorbents, much attention is put on activated carbons as they offer high selectivity in ion exchange, e.g. in exchange of heavy metal ions, in the presence of other natural ions present in drinking water. That is why the use of activated carbons for removal of heavy metals, dyes and pigments is widely studied. The adsorbents are subjected to modification, for improvement of their sorption properties, by covering their surface with deposited gold [26–28], tin sulphide [29], silver and palladium nanoparticles [30]. Recently, carbon nanotubes [31] or new complexing lipophilic materials [32] have been increasingly used.

Another problem related to the use of activated carbon adsorbents is growing emission of nitrogen, sulphur and carbon oxides and volatile

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Table 1
Elemental analysis of the cherry stones, chars and activated carbons obtained and the yield of pyrolysis and activation processes (wt.%).

Sample	Ash	VM[a]	C^{daf}[b]	H^{daf}	N^{daf}	S^{daf}	O^{daf}[c]	Yield
CS	0.2	80.7	48.6	6.1	0.2	–	45.1	–
CS5	1.1	22.9	84.5	3.1	0.5	–	11.9	30.5
CS8	1.3	5.5	85.9	1.1	0.7	–	12.3	25.5
CS5PA	0.1	–	94.5	0.8	0.5	–	4.2	86.4
CS8PA	1.9	–	96.0	0.6	0.5	–	2.9	97.1
CS5CA	0.8	–	89.4	1.0	0.2	–	9.4	46.5
CS8CA	0.3	–	90.4	0.5	0.2	–	8.9	62.3

[a] Volatile matter.
[b] Dry-ash-free basis.
[c] Determined by difference.

organic compounds with car exhaust gases. Activated carbon has been found very effective in purification of gases as they show high sorption capacities towards nitrogen oxides and hydrogen sulphide in a wide range of their concentrations. However, the used bed of activated carbon becomes a secondary pollution.

In this work we report on the preparation of activated carbons by chemical and physical activation of cherry stones and test their ability to adsorb gas and liquid impurities. The effects of different preparation variables on the properties of the activation products were studied to find the optimum conditions for making activated carbons with a high surface area and well-developed porosity. Moreover, the activated carbons thus produced were tested for adsorption of NO_2 and H_2S from a gas steam as well as for removal of methylene blue and iodine from the liquid phase.

2. Materials and methods

2.1. Preparation of activated carbons

In the first step, cherry stones were air-dried at 110 °C, kernels were separated, shells were crushed and sieved to a particle size between 1.6 and 2.5 mm. Then the raw material (CS) was subjected to pyrolysis. This process was carried out in a horizontal furnace equipped with quartz tube under a stream of argon (Linde Gas, Poland) at a flow rate of 0.170 L/min. Fifteen grams of stones were heated (10 °C/min) from room temperature to the final pyrolysis temperature of 500 (CS5) and 800 °C (CS8), respectively. In the final pyrolysis temperature, the samples were maintained for 60 min and then cooled down in argon (Linde Gas) atmosphere. The products of pyrolysis were next subjected to physical (PA) or chemical activation (CA). Physical activation was carried out at temperature of 800 °C, under a stream of carbon dioxide (Linde Gas) at a flow rate of 0.250 L/min, for 30 min. Chemical activation by KOH obtained from Avantor Performance Materials Poland S.A. (Gliwice, Poland), was carried out for 30 min at temperature of 700 °C and performed with an alkali/char weight ratio of 2/1, in argon atmosphere (flow rate 0.330 L/min).

2.2. Nitrogen dioxide and hydrogen sulphide adsorption

The activated carbons obtained were tested as adsorbents against hydrogen sulphide and nitrogen dioxide (Linde Gas). The tests were performed in dry (D) and wet (M) conditions (70% humidity) at room temperature (22 ± 2 °C). Moreover, additional variant of H_2S adsorption was used — the activated carbon's bed was wetted by the air of 70% humidity for 30 min and then the sorption tests were performed either in dry (MD) or in wet (MW) conditions.

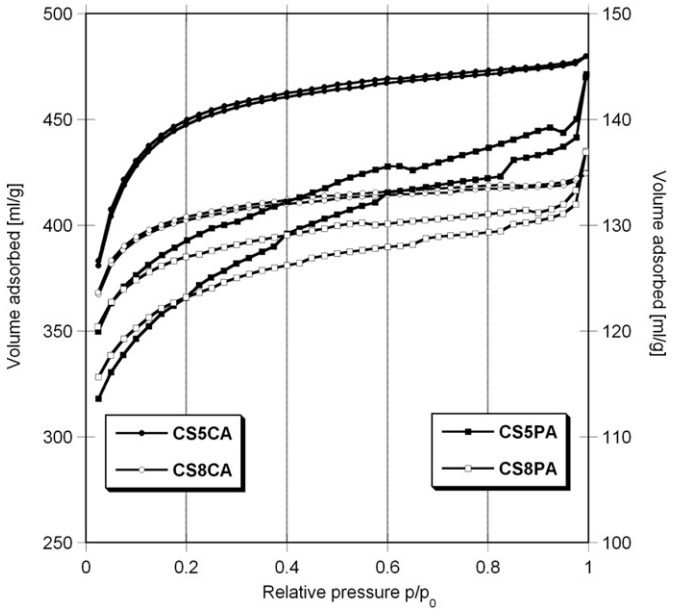

Fig. 1. Nitrogen adsorption isotherm of the activated carbons obtained.

The samples sieved to a particle size between 0.75 and 1.5 mm were packed into a glass column (internal diameter 9 mm, bed volume 3 cm^3). Dry or moist air with 0.1% of NO_2 or H_2S was passed through the dry bed of the adsorbent at 0.450 L/min. The breakthrough of H_2S or NO_2 was monitored using Q-RAE PLUS PGM-2000/2020 with electrochemical sensors. The tests were stopped at the breakthrough concentration of 100 ppm (in case of H_2S) or 20 ppm (for NO_2) because of the electrochemical sensor limits. The interaction capacities of each sorbent in terms of milligram of H_2S or NO_2 per gram of adsorbent were calculated according to the procedure described earlier [33,34]. To check the NO_2 reduction, as a result of its reaction with carbonaceous material surface, the concentration of NO in the system was also monitored.

2.3. Adsorption from the liquid phase

The iodine (Avantor Performance Materials Poland S.A.) sorption ability of the adsorbents was determined according to the ASTM D4607-94(2006) standard. Determination of the methylene blue (Avantor Performance Materials Poland S.A.) adsorption was performed using the following procedure: samples of the prepared activated carbons of equal portion of 0.2 g were added to 100 mL of the methylene blue pH = 6 solution with initial concentrations of 1000 mg/L and the suspension was stirred for 24 h to reach equilibrium. The concentrations of methylene blue in the solution after adsorption were determined using a double beam UV–Visible spectrophotometer (Cary Bio 100, Varian) at a wavelength of 660 nm.

Table 2
Textural parameters of activated carbons obtained.

Sample	Surface area [m^2/g]		External area [m^2/g]	Pore volume [cm^3/g]		V_{mic}/V_t	Average pore diameter [nm]
	Total surface area (BET)	Micropore area		Total pore volume	Micropore volume		
CS5PA	367	354	13.1	0.22	0.19	0.86	2.44
CS8PA	361	353	7.6	0.21	0.19	0.90	2.35
CS5CA	1324	1301	22.7	0.74	0.71	0.96	2.25
CS8CA	1173	1159	14.4	0.66	0.63	0.95	2.24