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Short communication

Production of activated carbon from a new precursor molasses by activation with sulphuric acid

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Abstract

Activated carbon has been prepared from molasses, a natural precursor of vegetable origin resulting from the sugar industry in Morocco. The preparation of the activated carbon from the molasses has been carried out by impregnation of the precursor with sulphuric acid, followed by carbonisation at varying conditions (temperature and gas coverage) in order to optimize preparation parameters. The influence of activation conditions was investigated by determination of adsorption capacity of methylene blue and iodine, the BET surface area, and the pore volume of the activated carbon were determined while the micropore volume was determined by the Dubinin–Radushkevich (DR) equation. The activated materials are mainly microporous and reveal the type I isotherm of the Brunauer classification for nitrogen adsorption. The activated carbons properties in this study were found for activation of the mixture (molasses/sulphuric acid) in steam at 750 °C. The samples obtained in this condition were highly microporous, with high surface area ($\geq$1200 m^2/g) and the maximum adsorption capacity of methylene blue and iodine were 435 and 1430 mg/g, respectively.

Keywords: Activated carbon; Molasses; Sulphuric acid; Adsorption; Microporosity

1. Introduction

Activated carbons are the oldest industrially-manufactured adsorbents. They are used in drinking water production and waste water treatment. Currently, activated carbons have are of significant interest and intervene in many applications, such as air treatment and adsorption of organic materials. They have also proven to be very effective for the removal of a wide range of pesticides, dissolved organic compounds from water and waste water [1–3], and elimination of heavy metals [4].

The adsorbent properties of activated carbons are essentially attributed to their large surface area, a well-developed porous structure, and a favorable pore size distribution which make the internal surface accessible and enhance the adsorption rate [5].

The control of pore size distribution in activated carbon depends upon the type of the raw materials and the method of activation. The preparation of activated carbon by physical or chemical activation is very important from the industrial point of view [6,7].

Since commercial activated carbon is relatively expensive, it is seldom possible to use it in the treatment process and operation of contaminated air and water in developing countries. However, previous research works have demonstrated

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that activated carbons can be produced from agricultural waste products (fruit stones, coconut shells, etc.). Various raw materials have been used for the production of low-cost adsorptive material, for example, olives wastes [8,9], apricot stones [10,11], ears of palm tree [12] and peach stones [13].

For this reason, we have investigated whether it is possible to produce of activated carbon from a new precursor, molasses abundant waste materials from the production of sugar, by chemical activation.

The activating agent used was sulphuric acid and conditioning variables examined were temperature and time of heating and atmospheric gas. The change in the microtexture of the raw material and produced activated carbon was examined by determination of the maximal adsorption capacity of methylene blue and iodine, the BET surface and the pore volume.

2. Materials and methods

2.1. Preparation of activated carbon

In the present investigation molasses was treated with sulphuric acid (37N) in proportion 1:1 (w/w). The sample is placed in cylindrical reactor. The heating is carried out at a rate of 10 °C/min until desirable temperatures at different atmospheric gas and heating times. After several experiments of activation and preliminary tests of adsorption of methylene blue and iodine, the best adsorbents properties were observed for particular combination of the experimental parameters.

Two products were obtained by carbonisation of the mixture (molasses/sulphuric acid) in different atmospheric gas. The first, referred MS, was prepared in air at 120 °C. For the second sample, the temperature and time of heating were fixed respectively, at 550 °C and 2 h, the gas vector being nitrogen (N_2), this process yielded a product called MS550N. Another simple product, referred by MS750V, was obtained by activation of the mixture in water steam, at 750 °C during 1 h.

2.2. Characterisation of activated carbon

2.2.1. Nitrogen adsorption isotherms and their analysis

Nitrogen adsorption isotherms were obtained, at 77 K, with the help of a conventional volumetric apparatus. The equivalent surface area was obtained from the linear BET plots (S_{BET}) [14], the total pore volume estimated from the liquid held at saturation (V_p) and the mean pore radius from $\bar{r} = 2V_p/S_{BET}$.

The micropore volume can be determined according to the Dubinin–Radushkevich equation (DR plot) [15,16]:

$$\log_{10} V_p = \log_{10} V_{mic} - D(\log_{10}(P_o/P))^2$$

where P_o is the saturation pressure, D a constant, and V_{mic} is the total micropore volume according to the DR equation.

The complete exploitation of the isotherms of adsorption and desorption of nitrogen makes it possible to define the texture of the porous solids, i.e. their specific surface, their porous volume, the shape of their pores as well as the distribution of their surface or volume according to dimensions of the pores. This method proves particularly interesting to analyze and determine the surface properties of the solids; it makes it possible to give a rather complete image of the evolution of the porous texture of a solid during a thermal processing by varying several parameters.

2.2.2. Adsorption tests

The adsorption tests for determination of maximum adsorption capacity of methylene blue and iodine, were carried out by the batch wise adsorption method. Different amounts (50 at 180 mg/l) of adsorbent were added aqueous solutions (250 ml) containing C_o of adsorbed molecule equal 50 and 200 mg/l for methylene blue and iodine, respectively, in 500 ml flasks. The flasks were agitated at room temperature for 20 h (time fixed by kinetics tests). When the equilibrium was reached, the residual concentration C of adsorbed molecules was measured. The adsorbed concentration (C_{ad}) is calculated according to the relation:

$$C_{ad} = C_o - C$$

Pertinent data were determined by application of Langmuir model in its linearized form [17].

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC}$$

where q_e is the adsorption capacity (mg/g or mol/g), Q_o the maximal adsorption capacity (mg/g or mol/g), C the residual concentration (mg/l or mol/l) and b is the thermodynamic adsorption constant (l/mg or mol/l).

3. Results and discussion

3.1. Determination of the isotherms of adsorption and desorption

The adsorption isotherms (Fig. 1) indicate a typical type I curve of BDDT classification of physisorption isotherms [18]. These are characteristic of microporous solids having a small external surface area, the limiting uptake being governed by the internal surface area. According to the isotherms of adsorption we notice that the mesopore contribution is more significant for MS750V activated in steam than for the other samples because the increase in the quantities of nitrogen adsorbed according to the partial pressure is faster with sample MS750V.

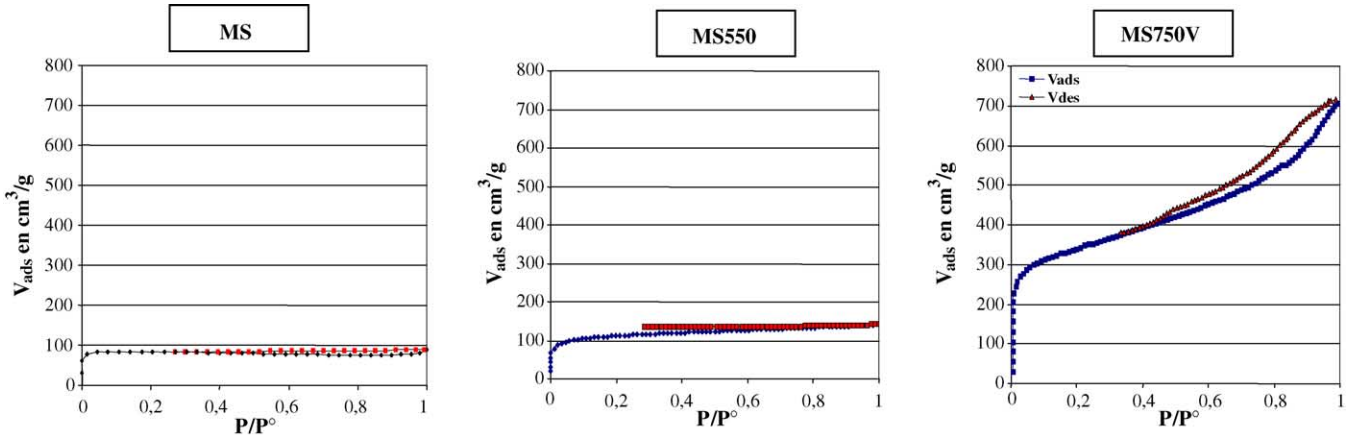

Fig. 1. Adsorption isotherms of nitrogen for adsorbents MS, MS550N and MS750V.

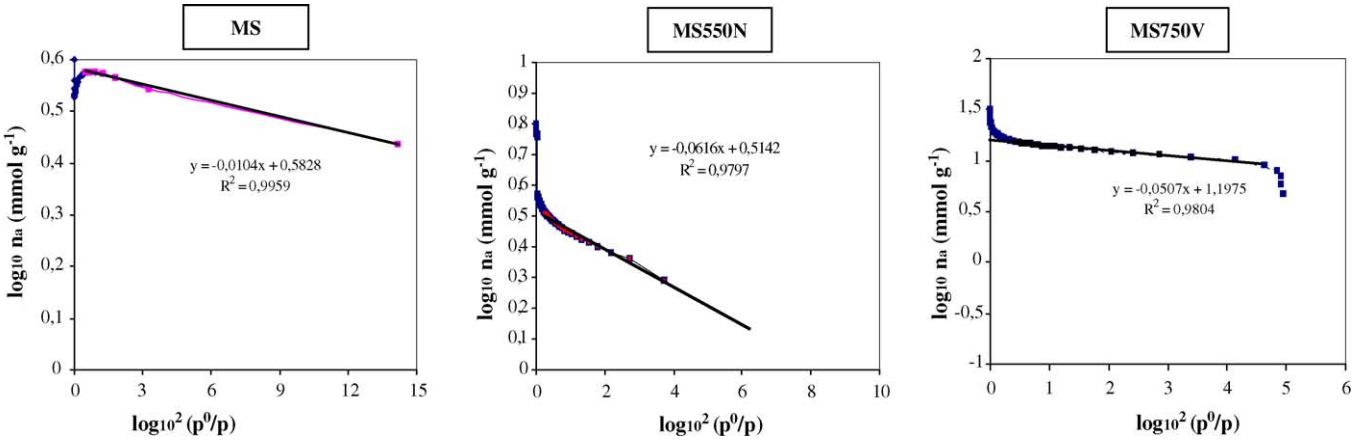

Fig. 2. Logarithm plot of N_2 uptake according to the DR equation.

3.2. Determination of microporous volume by the method of Dubinin–Radushkevich

As indicated previously, the experimental points relating to each sample are placed on a line whose ordinate in the beginning defines the value of the volume of nitrogen adsorbed in the micropores.

The Dubinin–Radushkevich plots for the adsorption of nitrogen are shown in Fig. 2 and the corresponding parameters of the specific surfaces, DR equation, such as micropores volume are recorded in Table 1.

This table reveals a good agreement between the various values of specific surface and porous volume. It also shows important effects of activation with steam. Values of pores volume obtained by the method Dubinin–Radushkevich indicate that the major part of pores volume consists of the micropores, but there are pores of greater dimensions. If we compare specific surfaces obtained, it is noticed that the specific surfaces of the sample MS750V activated under water vapor is higher than that of samples MS550N treated under nitrogen.

3.3. Distribution of porous volume according to the sizes of the pores

The volume distribution determined by the method of Barret, Joyner and Halenda (BJH) [19] according to dimensions of the pores for the various examined samples are shown

Table 1
The BET surface area, total pore volume, V_{mic} and the mean pore radius

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	V_{mic} (cm^3/g)	$r_p = 2V_p/S$ (nm)
MS	343 ± 8	0.140 ± 0.002	0.133 ± 0.003	1.63 ± 0.02
MS550N	402 ± 8	0.220 ± 0.002	0.113 ± 0.002	1.10 ± 0.03
MS750V	1214 ± 14	1.093 ± 0.003	0.547 ± 0.002	1.80 ± 0.01

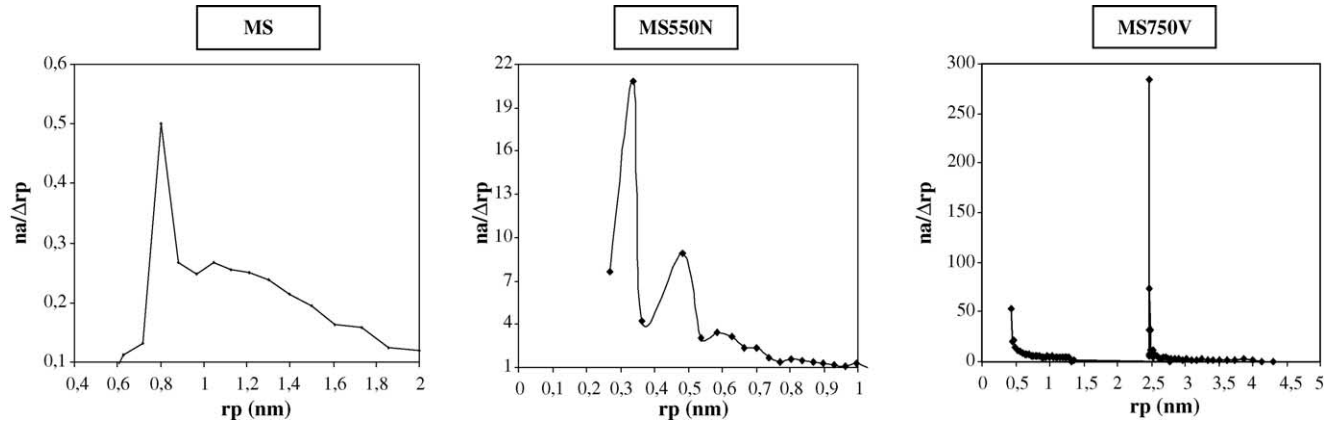

Fig. 3. Distribution of porous volume according to the sizes of the pores.

in Fig. 3, the differential curves highlight the existence of only one family of pores for samples MS and MS550N. This family is composed of pores whose size lies between 1 and 10 Å. On the other hand, this distribution widens when the crude MS750V is activated in steam. For MS750V activated in steam, one notices the existence of micropores and supermicropores (pores of sizes ranging between 14 and 32 Å). These results indicate that steam activation of the activated carbon produced a widening of the microporosity and an important development of the mesoporosity. Which is in agreement with that found by other authors with activated carbons obtained from different precursors and steam activated.

3.4. Adsorption tests

The performance of activated carbon is always tested using methylene blue and iodine molecules adsorption. The results of adsorption methylene blue and iodine molecules on different samples in the form of Langmuir's adsorption isotherm, will demonstrate the efficiency of the prepared carbon.

Table 2 shows the values of maximum adsorption capacity Q_o.

The results of the adsorption on different types of carbon, show that the MS750V has a high adsorption capacity. Methylene blue and iodine values increases gradually as the change in vector gas, the value is higher of the activation in steam. In addition, these results are in accordance with the various volume of specific surface and porous volume.

Table 2
Maximal adsorption capacity Q_o (mg/g) of methylene blue and iodine in different samples

Samples	Maximal adsorption capacity Q_o (mg/g)	
	Methylene blue	Iodine
MS	280	850
MS550N	320	975
MS750V	435	1430

4. Conclusions

In this study, the molasses can be used as a raw material for the preparation of activated carbon by chemical activation with sulphuric acid.

The adsorption tests and the results of characterisation of the obtained products are conclusive. These results have shown that it possible to produce high quality activated carbon from molasses. The highest surface area (1214 m^2/g) and the important maximum adsorption capacity of methylene blue (435 mg/g) and iodine (1430 mg/g) were found by activation of mixture (molasses/sulphuric acid) in steam at 750 °C.

The furthermore, the utilization of molasses, waste product of industry, as a raw material for production of activated carbon has the advantage of being expected to provoke a significant economical benefit.

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