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Characterization of Activated Carbon Synthesized from Coffee Hulls

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Abstract

Adsorption on commercial activated carbon (CAC) is a highly sought-after physical technique for the treatment of industrial effluents [1]. However, this adsorbent is expensive for developing countries where it is imported [2]. As a result, research is shifting towards local natural materials as alternatives to CAC because of their comparable efficiency, high availability and low cost [3]. This study aims to produce activated carbons with interesting structural and chemical characteristics from biomass. Thus, four coals of coffee shells three of which were activated by orthophosphoric acid (H_3PO_4) at different concentrations and a crude were developed. Characterization of these coals was done by different methods (Boehm, MEB-EDS, Methylene Blue adsorption and First bisector). The results showed that 60% activated charcoal of H_3PO_4 has an acidic character, a production yield of 43.72%, a carbon content of 69.67%, a developed porous structure and a surface area of 705 m^2. g^{-1}. The results indicate the high quality of the obtained active carbon. In perspective, the characterization by the use of the BET method (Brunauer-Emmett and Teller) for the determination of the specific surface and the porosity (pore volume) will be investigated and the capacity of this CA to treat the textiles effluents evaluated.

Keywords: Adsorbent, Biomass, Features, Hulls, Orthophosphoric Acid
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1. Introduction

The pollution of aquatic environments by industrial effluents is a major concern. Among the industries, the textile industry is positioned as one of the industries that generates large amounts of effluent highly rich in dye. Several biological, physical and chemical processes were applied for the treatment of these contaminated waters [4]. However, commercial activated carbon adsorption appears to be the most appropriate because of its proven efficacy for a wide variety of dyes in wastewater, its flexibility of operation, and the absence of generation of hazardous by-products [1]. However, because of the high cost of adsorbents [2], when there are imported, research in recent years had focused on development of the activated carbons from lignocellulosic residues such as agricultural waste. In Ivory Coast, agricultural waste is abundant and available. This is the case for coffee with an estimated production of 28 000 tons per year [8]. Indeed, the hulls of coffee deriving from the process of shelling of this material constitute garbage which requires a management plan. Nevertheless, the recovery of this waste as an active carbon for the treatment of textile effluents is judicious considering their efficiency comparable to that of commercial activated carbon [7].

The objective of this study is to propose efficient and economically accessible adsorbents made from local agricultural materials (coffee) to treat textile effluents.

2. Material and methods

2.1. Reagents and solvents

Orthophosphoric acid (H3PO4) (85%), sodium hydroxide (NaOH) (99%), sodium chloride (NaCl) (99%), sodium carbonate (Na2CO3) (99%), sodium thiosulfate (Na2S2O3) (85-100%), sodium hydrogen carbonate (NaHCO3) (99%) and hydrogen chloride (hydrochloric acid solution) (HCl) (37%) were supplied by Scharlab SL, Iodine (I2) (85%), potassium iodide (KI) (85%) and methylene blue (96%), supplied by Scharlab SL Distilled water was used to prepare solutions.

2.2. Sampling

2.2.1. Sampling site

The collar of the coffee hulls was carried out in two coffee-cocoa storage shops. These stores are members of the Cooperative Group of Agricultural Producers of Ivory Cost (CGAPIC). They are located in the town of Abobo (Abidjan) at the crossroads of the market. They source all parts of the western, eastern and southwestern parts of the country where coffee production is high.

2.2.2. Preparation of coals

The raw material had undergone preliminary treatment before activation. It was ground, sieved, washed and dried in an oven at 105 °C for 24 hours. The grain sizes used are greater than or equal to 1 mm and strictly less than 2 mm. Then solutions of orthophosphoric acid (H_3PO_4) of concentrations of 10%, 30% and 60% were prepared for 6 hours of impregnation time of the samples in a mass ratio of material to volume of the solution equal to 1/1. 24 hours of oven drying time (Memmert Basic) followed at 110 °C. After which they were calcined at 450 °C. for one hour in the oven (Nabertherm). The calcination of the raw biosorbents was carried out respecting the same temperature and the same time. Finally, thoroughly washed

with distilled water, each carbonisate was oven-dried at 110 °C. For 24 hours and packaged in Stomacher bags. The washing of the chemically activated coals was terminated at pH of the residual water of between 6.5 and 7.

2.3. Characterization methods for coals

3.1. Coal production yield and mass loss (Burn-off)-

Yield is a quantitative characteristic of activated carbon, the determination of which gives a precise idea of the mass lost during calcination. The synthesis yield of activated carbons was determined by equation **[1]**.

$$Yield\ (\%) = \frac{M_1}{M_0} \times 100 \qquad (1)$$

M_1: mass of coal obtained (g); M_0: mass of raw hulls (g)

The mass of coal obtained after calcination is always less than that of the starting material used for its preparation. This lost mass expresses the degree of activation (or activation rate) usually called burn-off [10]. This loss is deducted from the production yield and expressed as a percentage.

3.3.2. Specific surface

In a solution of 100 ml of methylene blue of mass concentration 2 mg.L^{-1}, 800 mg of activated charcoal or not activated. The mixture is stirred. Each 10 minutes a volume of at least 2 mL of the suspension is taken, centrifuged and then analyzed with visible UV spectrophotometer. The specific surface area of each coal is then determined by means of the residual concentration of the dye obtained at equilibrium [6]. The area expressed in m^2.g-1 is obtained by calculation according to relations 2 and 3.

$$Q_m = \frac{(C_0 - C_r) \times V}{m} \qquad (2)$$

Where

Q_m: maximum adsorption capacity of coal for methylene blue (mg.g^{-1});

C_0: initial concentration of methylene blue in the solution (mg.L^{-1});

C_r: concentration of equilibrium methylene blue in the solution (mg.L^{-1});

m: mass of coal in the solution (g);

V: volume of methylene blue solution (mL).

$$Surface\ spécifique\ (S_{SP}) = Q_m \times NA \times S \qquad (3)$$

S: Area occupied by a molecule of methylene blue = 175 Å^2

NA: Number of Avogadro = 6,02.10^{22}

2.3.3. Analysis of the morphology and elemental composition of coals

Principle

The Scanning Electron Microscopy (SEM) method is a technique with a principle based on electron-matter interactions, capable of producing high resolution images of the surface of a sample by microscopic observation. This technique thus gives information on the morphology of the grains and their arrangement. It also gives qualitative and quantitative information through X-ray microanalysis via the energy dispersive spectrometer (EDS) [11].

2.3.4. Analysis of surface functions

The acid-base measurement of the surface functions is carried out according to the protocol described by Boehm.

In 50 ml of a basic or acidic solution of normality 0.01N, 0.1 g of adsorbent is added. The whole is stirred with a magnetic stirrer for 24 hours. The excess of base or acid is titrated back on 10 ml of filtrate using a solution of HCl or NaOH concentration 0.01 N. The dosage is made in the presence of phenophthalein for use basic solutions such as sodium hydroxide (NaOH) and sodium ethanoate ($C_2H_3O_2Na$) and in the presence of helianthine for the other bases.

The acid functions are determined as follows:

GI = [$NaHCO_3$] = Concentration of strong carboxylic acids

GII = [Na_2CO_3] - [$NaHCO_3$] = Concentration of weak carboxylic groups and lactones

GIII = [NaOH] - [Na_2CO_3] = Concentration of phenolic groups

GIV = [$NaOC_2H_5$] - [NaOH] = Concentration of carbonyl groups

Acidité totale = GI + GII + GIII + GIV

The basic functions are determined as follows:

$$\boldsymbol{Total\ basicity = \frac{C_{NaOH} + V_{NaOH}}{m_{support}}}$$

2.3.5. First bisector method

A quick and easy way to determine the pHzc is to place 50 mL of the distilled water in closed vials and adjust the pH which is initially between 6.5 and 7 to values between 2 and 12, by adding NaOH or HCl (0.1 M). 0.15 g of material sample to be characterized is then added to each flask. The suspensions should be stirred at room temperature for 48 hours, and the final pH is then determined. We are dealing with a graph ΔpH = f (pHi) where ΔpH = (pHf-pHi). The intersection of this curve with the axis passing through zero gives the pH-zero charge **[12; 13]**.

3. Results and discussion

3.1. Production yield

Table 1 presents the values of the yield and the mass loss of the prepared active carbons.

Table (1): Production yield and burn-off mass loss of activated carbon

Coals type	Yield (%)	A loss of mass (%)
Raw coal (CA 0% H_3PO_4)	33,97	
Activated carbon (CA 10% H_3PO_4)	48,02	51,98
Activated carbon (CA 30% H_3PO_4)	45,60	54,4
Activated carbon (CA 60 % H_3PO_4)	43,72	56,28

10% of H_3PO_4 = 1,74 mol.L^{-1} ; 30% de H_3PO_4 = 5,23 mol.L^{-1} ; 60% de H_3PO_4 = 10,47 mol.L^{-1}

It can be seen from Table 1 that the yields obtained are 48.02%, 45.60% and 43.72% respectively for activated carbons with orthophosphoric acid at 10%, 30% and 60%.

The yields of chemically activated coals are higher than that of raw coal (CA 0%) which is 33.97%. This indicates that chemical activation limits mass loss (volatile matter). This remark is supported by the literature that showed that during treatment, orthophosphoric acid penetrates the interior of the particles and then restricts the formation of tar and other liquids such as acetic acid and methanol and then inhibits shrinkage of particles [14]. However, a slight decrease in the efficiency of the chemically activated coals is observed following the increase in the H_3PO_4 concentration while remaining higher than that of the raw coal. These results show that the decomposition of the coffee hulls is more pronounced when the H_3PO_4 impregnation ratio is high. The burn-off varies from 51.98% to 56.28% with a slight increase following the rise in the impregnation ratio. This loss of mass during the calcination of the coffee hulls as well as the yield of production are related to the number of carbon atoms having established bonds with the oxygen and hydrogen atoms. Indeed, during the heat treatment, these lignocellulosic materials are transformed into carbon with the departure in the form of gases (H_2O, CO, CO_2, CH_4, aldehydes, etc.) from a part of the atomic elements such as oxygen (O) and hydrogen (H); or purification in the form of heavier hydrocarbons (tars) [15; 16]. Also, the evolution of the mass loss of chemically activated carbon is not solely caused by the heat treatment temperature [15]. It appears then that the desiccant character of the orthophosphoric acid, its action and the temperature of the heat treatment are responsible for the slight decrease in the yield of the coals observed.

3.2. Specific surface area of coals

Table 2 presents the surface characteristics of of coals from coffee husks.

Table 2 shows the different specific surfaces of coals from coffee husks

	$CA_{0\%}$	$CA_{10\%}$	$CA_{30\%}$	$CA_{60\%}$
Specific surfaces ($m^2.g^{-1}$)	504	542	590	705

Raw coal: $CA_{0\%}$; Activated carbon with H_3P0_4: 10% ($CA_{10\%}$), 30% ($CA_{30\%}$) and 60% ($CA_{30\%}$).

Activated carbon with H_3P0_4: 10% ($CA_{10\%}$), 30% ($CA_{30\%}$) and 60% ($CA_{30\%}$).

The analysis in Table II reveals a large increase in specific surface area with the rise in the calcination temperature. This increase is even more pronounced with the increase in the concentration of activating agent. They are 504 $m^2.g^{-1}$, 542 $m^2.g^{-1}$, 590 $m^2.g^{-1}$ and 705 $m^2.g^{-1}$ respectively for coals, CA0%, CA10% CA30% and CA60%. The results are satisfactory and confirmed by data from the literature, which has shown that the larger the surface area, the greater the amount of pollutants adsorbed [17]. In addition, the values of these specific surfaces that are greater than 500 m2.g-1 fall within the range of specific surface values of commercial activated carbons located between 500 $m^2.g^{-1}$ and 1500 $m^2.g^{-1}$ [18].

3.3. Morphological structure of coals

Figures 1, 2 and 3 show the images obtained by scanning electron microscopy of the raw coals, activated at 10% and 60% of H_3PO_4. The size of the magnification is 400 x 20 µm x 10 mm.

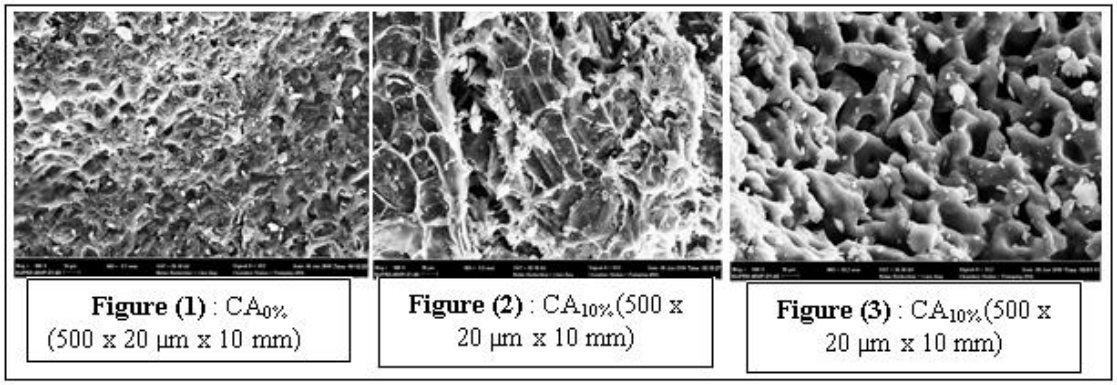

Figure (1) : $CA_{0\%}$ (500 x 20 µm x 10 mm)

Figure (2) : $CA_{10\%}$ (500 x 20 µm x 10 mm)

Figure (3) : $CA_{10\%}$ (500 x 20 µm x 10 mm)

These images obtained by MEB externalize the different specific surfaces by revealing that the pore size is governed by the increase in the concentration of the activating agent. Thus, the porosity is better and better developed with the increase of the concentration of the activating agent. This finding is supported by other studies whose results have shown that materials prepared at lower activation concentrations are essentially microporous [15].

3.4. Elementary composition

The chemical element contents of the various carbons activated at 10%, 30% and 60% with orthophosphoric acid are shown in Table 3.

Table (3): Elemental composition of activated carbon and that of raw material

Atomic element (%)	Types of activated carbon (CA)			
	Raw coffee hulls	CA H_3PO_4 10%	CA H_3PO_4 30%	CA H_3PO_4 60%
C	40,38	57,82	61,45	69,67
P	-	2,11	1,96	1,16
O	46,45	15,94	15,32	13,08

These results show that the concentration of H_3PO_4 for the impregnation of the biosorbent in the production of activated carbon has an influence on the content of the elements that make up the coal. Indeed, the activated carbons prepared consist essentially of carbon with a rate ranging from 57.82-69.67%. This content increases with the increase in the concentration of H_3PO_4 as opposed to oxygen (15.94-13.08%) and phosphorus (2.11-1.16%) also present in the coals. The high carbon content can be related to the conversion of organic matter to this element with a strong elimination of other compounds during pyrolysis [19]. In addition, the appearance of phosphorus can be attributed to treatment with orthophosphoric acid.

3.5. Functional groups

The contents of oxygenated functional groups obtained during the Boehm titration as well as the pH and pHzc measured are recorded in Table 4.

Table 4: Surface functions of activated carbon

Chemical functions ($mmol.g^{-1}$)	Activated carbon		
	CA10%	CA30%	CA60%
Strong carboxyl	0,54	0,46	0,33
lactones	0,19	0,19	0,23
phenolic	0,69	0,68	0,98
carbonyls	0,11	0,12	0,11
Total oxygenated group	1,55	1,46	1,65
Total basic functions	0,00	0,00	0,00
pH	4,1	3,9	3,9
pHzc	4,1	3,9	4,2

The Boehm titration results (Table 3) indicate zero basicity for all activated carbons at different concentrations of orthophosphoric acid and a relatively high acidity, greater than 1.4 $mmol.g^{-1}$ for all coals. This acidity of the surface of the coals is confirmed by the pH and pHzc values found. The values of these last parameters are equal or very close to each other for each coal. This strong presence of acidic oxygen functions could be a favorable asset for acid dye adsorption which is anionic in nature [21]. As for the zero-basicity observed, it can be explained by the fact that the coals have not been brought into contact with oxygen at temperatures below 200 °C or above 700 °C. They have not been cooled at room temperature either. However, it is at this stage that the basic functions in coal are introduced [22].

4. Conclusion

At the end of our study, it appears that orthophosphoric acid has had a qualitative and quantitative impact on the quality of coffee husks. Indeed, this activating agent has promoted the increase of the coal yield with the increase of its concentration. It has also improved the quality of the coal with the increase of its specific surface and the development of its porous structure. Otherwise, the surfaces of these coals show distinct and well-developed morphologies following the increase of the orthophosphoric acid content. In addition, these acidic coals are highly carbon-rich with increasing concentration of activating agent. On the other hand, for phosphorus, in addition to its low presence, its proportion decreases with the increase in the concentration of orthophosphoric acid. In perspective, considering the promising values of these characteristic parameters and the morphology of the specific surface of the coals, it will be necessary to test their capacity to treat the textile effluents.

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