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CHARACTERIZATION OF ACTIVATED CARBON PREPARED FROM A NEW RAW LIGNOCELLULOSIC MATERIAL: *ZIZIPHUS SPINA-CHRISTI* SEEDS

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ABSTRACT: The objective of this study is the characterization of activated carbon prepared from a lignocellulosic natural residue which is a vegetation waste "seeds of *Ziziphus spina-christi*" of the central of Tunisia. The activated carbon was prepared by these conditions as follows: 3/4/1 (w/w) a water/KOH/coal ratio, 700 °C carbonization temperature and 120 min activation time. Characterization of the activated carbon obtained was performed by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and specific surface. The adsorption properties of samples of carbons were studied from their adsorption isotherm of copper from aqueous solutions at 25°C. This study has resulted that the adsorption obeys the Langmuir isotherm as well the Freundlich isotherm with maximum adsorption capacity of about 104 mg /g.

Keywords: *Ziziphus spina-christi* seeds; activated carbon; Characterization; Adsorption.

RÉSUMÉ: L’objectif de cette étude, est la caractérisation d’un résidu naturel ligno-cellulosique en charbon actif préparé à base de déchets végétaux "noyaux de *Ziziphus spina-christi*" du Centre Tunisien. Le charbon actif a été obtenu dans les conditions : un rapport eau / KOH / charbon de 3/4/1 (w/w), une température de carbonisation de 700 °C et un temps d'activation de 120 min. La caractérisation du charbon actif obtenu a été réalisée en utilisant la microscopie électronique à balayage (MEB), la diffraction des rayons X (XRD), la spectroscopie infrarouge à transformée de Fourier (FT-IR) et la surface spécifique. Les propriétés adsorbantes des échantillons de charbons préparés ont été étudiées à partir de l’établissement de l’isotherme d’adsorption de cuivre en solution aqueuse à 25°C. Les résultats ont permis de montrer que l’adsorption peut être modélisée par les modèles de Langmuir et de Freundlich avec une capacité maximale d’adsorption de l’ordre de 104 mg/g.

Mots-clés : noyaux de *Ziziphus spina-christi*, charbon actif, caractérisation, adsorption.

INTRODUCTION

Activated carbon is a carbonaceous material possessing a higher porosity due to which it is commonly used in variety of applications, concerned principally with the removal of chemical species by adsorption from the liquid or gas phase [1]. The high adsorptive capacity of Activated carbon is associated with its internal porosity and other properties such as surface area, pore volume and pore size distribution [2]. These properties have been determined not only by the physical properties and the chemical composition of the precursor, but also by the activation process of lignocellulosic precursors [3]. Activated carbons can be produced by both physical and chemical means. Physical activation involves using gases such as carbon dioxide, steam or their mixtures [4]. Chemical activation is performed by carbonization or using such chemical agents as hydroxides, salts and acids. A large amount of studies have reported that coal-based materials could be activated by KOH to prepare activated carbons [5,6,7,8,9,10]. The most precursors used for the production of activated carbons are organic materials that are rich in carbon [11]. Agricultural wastes are the one,

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which considered being a very important feed stock for activated carbon preparation because there are renewable sources and low-cost materials. With many earlier studies, an agricultural wastes such as corn cob[12], coconut shell [13], palm shell [14], grain sorghum [15], pistachio nut shell [16], olive stones and walnut shell [17], cherry stones [18], rice bran[19], jackfruit shell waste[11] and oil palm shell [20] have been found to be suitable precursors owing to their high carbon and low ash contents.

Ziziphus spina-christi is a plant species that has edible fruits and a number of other beneficial applications that include the use of leaves as fodder, branches for fencing, wood as fuel, for construction and furniture making, and the utilization of different parts e.g. Fruits, leaves, roots and bark in folk medicine. This plant is a species that is highly adapted to the dry and hot conditions which prevail in North Africa. In this work, our studies were directed towards use a new raw material, Zizyphus spina-christi seeds, for preparation of the activated carbons. These adsorbents were used for the removal of toxic heavy metals such as copper that is largely released into the environment from various types of industries such as electronics, metal plating, automotive, battery, etc.

The aim of the present work was to prepare and characterize a new activated carbon from Zizyphus spina-christi seeds (ZSAC) chemically activated with potassium hydroxide. Surface area, Crystallinity structure, Boehm titration, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis, adsorptive capacity in removing copper from aqueous solution and scanning electron microscopy (SEM) were used to investigate the obtained activated carbons.

MATERIALS AND EXPERIMENTAL PROCEDURE

1. Preparation of the activated carbon

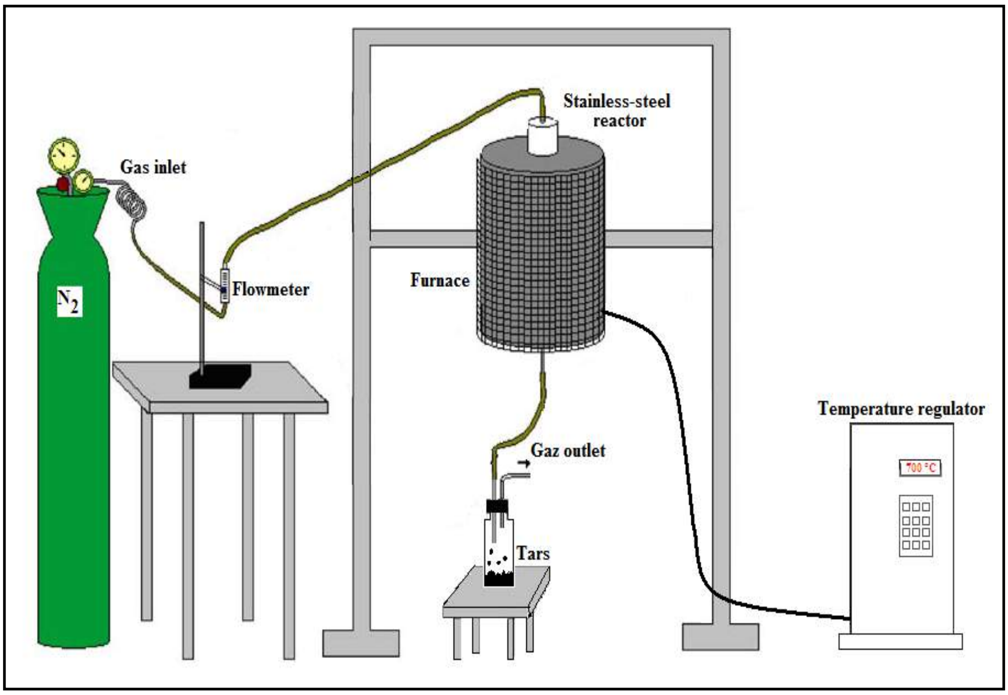

Figure 1: Activated carbon preparation apparatus.

1.1. Preparation of raw coal of *Ziziphus spina-christi* seeds

Ziziphus spina-christi seeds for the preparation of coal were collected from trees (*Ziziphus spina-christi*) located in the region of Sidi Bouzid City, Tunisia. The material was first washed to remove dirt from its surface and was then dried overnight in an oven at 110 °C. The dried stones were crushed and sieved to desired mesh size (1-2 mm) and loaded in a vertical stainless-steel reactor (length 170 mm, interior diameter 22 mm) which was inserted into an cylindrical electric furnace Nabertherm connected to a temperature regulator (Figure 1). Carbonization of the precursor was carried out by ramping the temperature from room temperature to 600 °C with heating rate of 10 °C/min and hold for 90 min. Throughout the carbonization process, purified nitrogen (99.99%) was flown through at flow rate of 150 cm^3/min. Coal obtained is stored safe from moisture.

1.2. Activation of the raw coal of *Ziziphus spina-christi* seeds by KOH

The coal produced was mixed with water and KOH with the weight ratio of water/KOH/coal equal to 3/4/1, with constant mechanical stirring for 6 h and a temperature of 85°C. The impregnated coal was dried overnight at 120 °C and then placed in the furnace under continuous nitrogen flow (200 cm^3/min), heated at a rate of 10 °C/min to 700 °C, and kept at this temperature for 2 h. All the activated samples were washed with water and were poured into 0.1 mol/L HCl and stirred for 1 h to eliminate the residual alkali [21]. Then, the samples were washed with hot distilled water, until the pH of the filtrating solution was neutral [22]. The produced activated carbon was then dried at 105 °C overnight, ground and sifted to obtain a powder with a particle size smaller than 45 µm, and finally kept in hermetic bottle for subsequent uses.

2. Characterization of the prepared activated carbon

2.1. Textural properties

The specific surface (S_{BET}) is determined by a Micrometrics apparatus (ASAP 2010) by adsorption of nitrogen at 77 K according to the traditional method of Brunauer Emmet and Teller or BET [23]. Porous volume (Vp) is deduced from the adsorption isotherm of nitrogen in the zone of capillary condensation. The bulk density was determined according to procedure followed by Ahmedna et al. [24]. Moisture content was determined using oven drying method [25]. Ash content was determined by standard method [26]. The qualitative elemental analysis of the prepared activated carbon was determinate by an analyzer EDAX (Energy Dispersive Analysis of X Rays) and the activated carbon yield was calculated based on Eq. (1)

$$Yield\,(\%) = \frac{W_c}{W_0} \times 100 \qquad (1)$$

Where W_c is the dry weight (g) of final activated carbon and W_0 is the dry weight (g) of precursor.

2.2. Boehm titration

The well-known Boehm's method allows modeling the principal acidic oxygenated functions of the activated carbon such as carboxylic acids, lactones and phenols using bases of increasing strength as $NaHCO_3$, Na_2CO_3 and NaOH, respectively. Then, the total basicity is given by titration by HCl. More details are given in Refs. [27].

2.3. pH determination

The pH of the prepared adsorbent was determined as follows: 5.0 g of carbon is weighed into a 250 ml beaker and 100 mL of water is added. The beaker is heated to boiling temperature for 5 min. The decanted portion is cooled to room temperature and pH value is measured.

2.4. Iodine and methylene blue number

The iodine number of activated carbon was obtained on the basis of the Standard Test Method, ASTM Designation D4607- 86 by titration with sodium thiosulphate (ASTM, D 4607-86). The concentration of iodine solution was thus calculated from total volume of sodium thiosulphate used and volume dilution factor. Methylene blue adsorption was conducted by mixing 0.2 g of the prepared activated carbon with 100 mL of 1000 mg/L methylene blue solution [28]. After agitation during 24 h, the suspension was filtered and the methylene blue residual concentration was measured at 660 nm, using an UV/vis spectrophotometer

(Visible spectrophotometer 1011, CECIL). A previously established linear Beer-Lambert relationship was used for the concentration determination.

2.5. FTIR and SEM analyses

The functional groups on the surface of the carbon were determined by FTIR spectroscopy. The spectra were recorded using a NICOET spectrophotometer. The spectrum was obtained over the range of 500-4000 cm^{-1}. The microstructure of the activated carbon was evaluated by means of scanning electron microscope (Philips XL30 microscope).

3.6. XRD and TG/DTG analysis

X-ray powder diffraction analysis of the adsorbent was carried out using a Philips® PW 1710 diffractometer (Cu Kα, 40 kV/40 mA, scanning rate of 2θ per min). Thermogravimetric analysis of the activated carbon was performed in a Perkin-Elmer TG/DTA apparatus at a nitrogen flow rate of 100 ml/min and a heating rate of 10 °C/min up to 600 °C.

3.7. Copper adsorption

In batch adsorption experiments 100 mg ZSAC (adsorbent) was thoroughly mixed with the 200 mL aqueous solutions having the copper ion concentrations of 10, 20, 30, 50, 80,100, 125, 150 and 200 mg/L and was agitated in a thermostated rotary shaker for a contact time fixed of 120 min at a speed of 300 rpm at 25°C. The solutions were prepared by diluting the stock solution having the copper concentration of 1000 mg/L. The stock solution was prepared by dissolving $CuSO_4.5H_2O$ in distilled water. The pH of the solutions was adjusted with value 5 based to research works of Moreno-Piraján et al. [29]. After adsorption process the adsorbent separated from the samples by filtering and the filtrate was analyzed for copper (II) using a flame atomic absorption spectrophotometer (ZEENIT). The adsorption capacity (q_e) was determined by the following equation:

$$q_e = \frac{(C_0 - C_e)\cdot V}{W} \tag{2}$$

Where C_0 and C_e are the initial and equilibrium Cu(II) concentrations (mg/L), respectively, V is volume of solution (L), and W is the mass of adsorbent (g).
Copper uptake was estimated by the Langmuir [30] and Freundlich [31] models given respectively by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \tag{4}$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the metal uptake (mg copper/ g of adsorbent), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_F and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively.

RESULTS AND DISCUSSION

1. Proximate analysis and ultimate analysis

The granular ZSAS prepared on the condition mentioned above was black and inodorous with the final yield of 27.85 wt.%. The results of proximate analysis and ultimate analysis for ZSAC are listed in table I. The activated carbon prepared has a high carbon content. That was attributed to activating agent serving as dehydrating agents who influenced the pyrolytic decomposition and inhibited the formation of ash, thus enhancing the carbon yield. Other elements (N, S and O content) were various, which might result in chemical characteristic of the activated carbon by forming various functional groups. We also note the presence of potassium from the treatment with potassium hydroxide comes into play during the activation step.

Table I: Results of proximate analysis and ultimate analysis of the ZSAC

Characteristics	**%**
Moisture	11.98
Ash	6.61
Yield	27.85
C	73.398
O	8.823
N	14.011
K	3.420
S	0.347

2. Characteristics of the porous structure

The surface area, pore structure, iodine and methylene blue number of porous materials are extremely important when they are applied in sorption processes since this is where chemisorption and/or physisorption occurs. Table II shows the characteristics of the porous structure of produced sample. The ZSAC prepared has the following textural characteristics: a BET surface area of 914.23 m^2/g, a total pore volume of 0.731 cm^3/g and micro-pore volume of 0.528 cm^3/g. This value of micro-pore volume indicated that the ASC was in the micro-porous region. The surface area was much higher than conventional activated carbons that is, hazelnut shell activated carbon (441 m^2/g) [32] and Ceiba pentandra hulls activated carbon (521 m^2/g) [33].

Table II: Characteristics of the porous structure of ZSAC.

Parameters	**Value**
BET surface area, S_{BET} (m^2/g)	914.23
Total pore volume (cm^3/g)	0.731
Micropore volume (cm^3/g)	0.528
Bulk density (g/cm)	0.493
I_2 (mg/g)	797
BM (mg/g)	264

3. Oxygen functional groups

The identification and quantification of the surface oxygen groups in the prepared carbon was done by means of the point of zero charge and Boehm titration. The results are shown in table III. Acidic surface groups consist of temperature sensitive and temperature insensitive types. Temperature sensitive types of acidic surface groups can decompose at high temperature. Hence, activated carbons produced by KOH activation are basic character. For this reason, the activated carbon prepared has predominantly basic surface groups. On the other hand, the carbon also possesses high ash content; therefore the basic nature might also be associated to the mineral matter of the carbon (Lewis basic structures). The pH of the activated carbon was measured as 9.36. This result confirmed the Boehm analysis.

Table III: Chemical parameters of the ZSAC obtained from Boehm method and pH.

Chemical parameters			**Values**
Total of acid functions (mequiv/g)			1.766
	Carboxylic	(-COOH)	0.302
	Lactones	(-COO-)	1.103
	Phenol	(-OH)	0.361
Total of basic functions (mequiv/g)			3.581
pH			9.36

4. SEM observation

SEM image of the ZSAC is shown in Figure 2. The external surfaces of these ZSAC show large cavities and are very irregular, indicating that the porosity of the material was produced by aggressive attack of the reagent (KOH) during activation. Activation at 700 °C with KOH resulted in the creation of more pores and a substantial removal of volatiles [34]. Large and well-developed pores were clearly found on the surface of the activated carbon. Pore development in the ZSAC during pyrolysis was also important as this would enhance the surface area and pore volume of the activated carbon by promoting the diffusion of KOH molecule into the pores and thereby increasing the KOH−carbon reaction, which would then create more pores in the activated carbon. Activation with KOH represents the intercalation of potassium between the layers of graphenes and the hydrogen formation which causes to minimize the quantity of surface oxygen catalytically active according to the following reaction [35].

$$6KOH + 2C \leftrightarrow 2K + 3H_2 + 2K_2CO_3 \qquad (5)$$

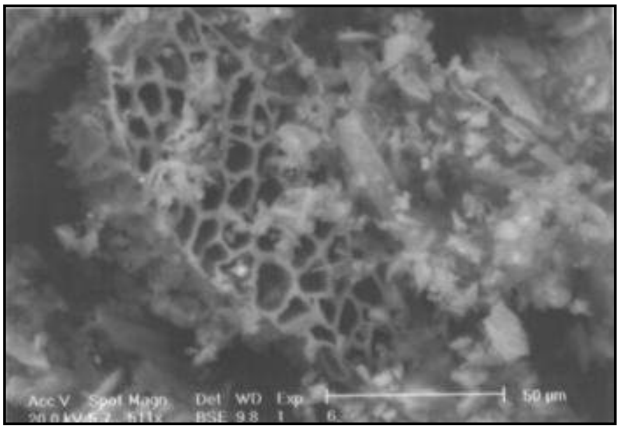

Figure 2: SEM image of ZSAC

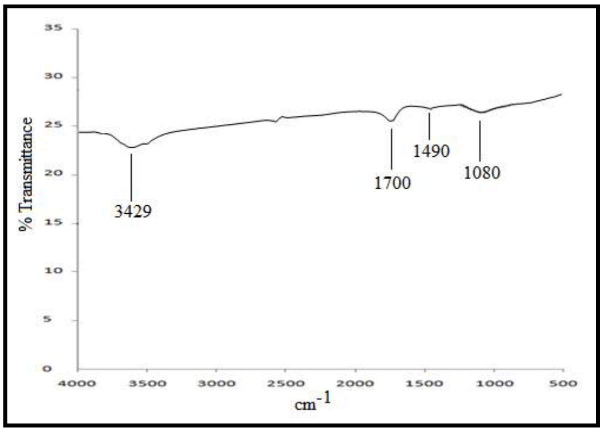

Figure 3: FTIR spectra of ZSAC.

5. FTIR analysis

The FT-IR spectra of the activated carbon prepared at 700 °C was shown in Figure. 3. The bands at 3429 and 1080 cm^{-1} were assigned to O-H bonds and C-OH stretching of phenolic groups, respectively [36]. According to Montes-Morán et al. [37], the bands observed in the region between 1700 cm-1 and 1490 cm-1 were attributed to C=C symmetrical stretching of pyrone groups and C=O of carboxylic groups. Moreover, Chiang et al. [38] noted that the alkaline treatment increased the amount of oxygen functional groups, especially, phenolic groups. In addition, carbon skeleton vibrations, which are characteristic in activated carbon, were observed.

6. XRD analysis

Figure 4 illustrates the X-ray diffraction profile of the ZSAC. This activated carbon exhibit very broad diffraction peaks and the absence of a sharp peak reveals a predominantly amorphous structure [39]. There are two broad diffraction peaks around 2θ = 24° and 43° in spectrum, corresponding to the diffraction of (0 0 2) and (1 0 0), respectively. The appearance of the peak at around 24° at activation temperature (700 °C) signifies an increasing regularity of crystalline structure, which will result in a better layer alignment [40].

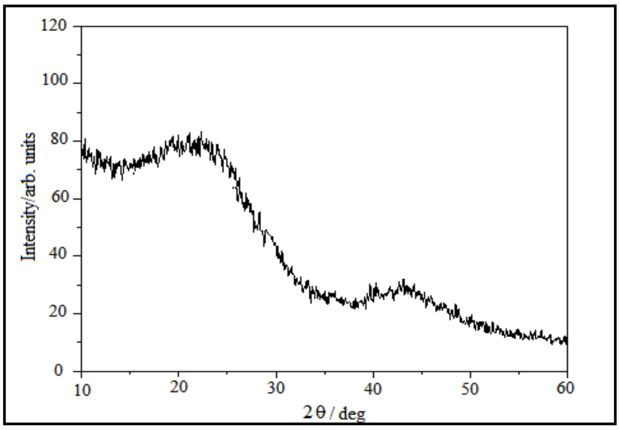

Figure 4: X-ray diffraction profile of ZSAC

7. Thermogravimetric analysis

The TG curves given in Figure. 5 show that at low temperatures (up to 120 °C), the raw material presents a slight mass loss (7%) due to the elimination of moisture. Then, up to approximately 230°C, the sample mass remains nearly constant, decreasing markedly between 250 and 410 °C due to the release of the volatile matter occurs from degradation of cellulose and hemicelluloses from the precursor (65% mass loss) [41, 42] . At 450 °C, the remaining material corresponds to 21% of the initial material. At higher temperatures, the sample mass decreases slightly up to 600 °C, remaining only 18 % of the initial mass indicating the decomposition of lignin, which was a structure with higher stability [43]. Moreover, the ZSAC thermogram showed a final average yield of 81% for heating up to 600 °C, indicating a high thermal resistance.

Figure. 6 shows the peaks derived from the thermogram. The peak observed between 60 and 120 °C for the ZSAC is due to moisture elimination.

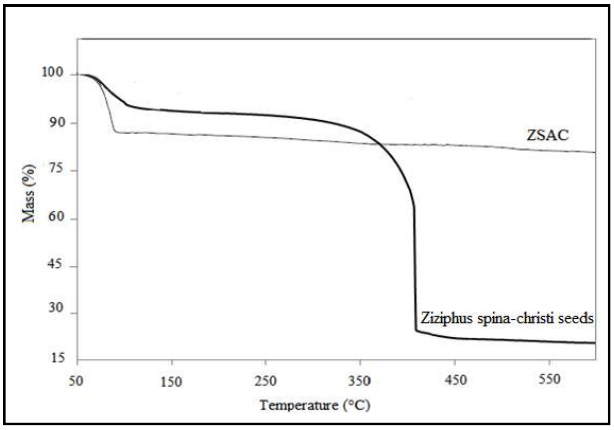

Figure 5: TG thermogram of *ziziphus spina-christi* seeds and ZSAC.

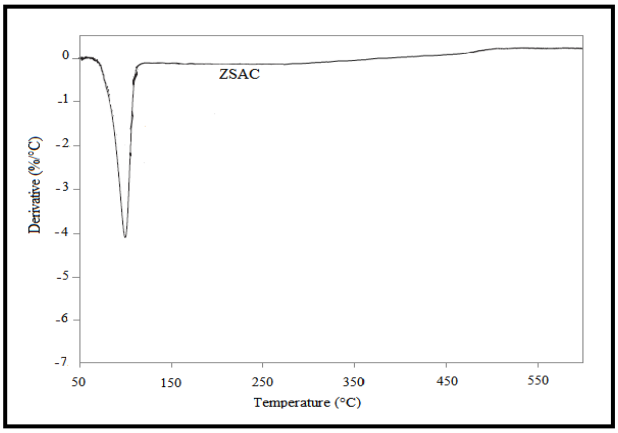

Figure 6: DTG thermogram of ZSAC.

8. Adsorption performances of copper

Experimental Cu(II) adsorption isotherm of activated carbon was shown in Fig. 7. The isotherm curve show typical type 1 shapes according to IUPAC classification. This higher sorption is probably due to the highly microporous structure of ZSAC. The linear plot of equation isotherm shows that the adsorption obeys the Langmuir model. This evidences a monolayer adsorption of Cu(II) ions. The calculated maximum capacity Q_0 value is 104.16 mg/g (table IV). Comparing the loading capacity with that reported in the literature for other materials, the biomass-(*ziziphus spina-christi* seeds) derived carbon outperforms other adsorbents. We give few examples of different adsorbents for comparison-maximum copper adsorption capacity of different activated carbons in table V.

Table IV: Langmuir and Freundlich isotherm constants for manganese adsorption on ZSAC

Langmuir			Freundlich		
R^2	Q_0 (mg/g)	b (l/mg)	R^2	K_F (mg/g(l/mg)$^{1/n}$)	1/n
0.991	104.166	0.064	0.969	14.521	0.404

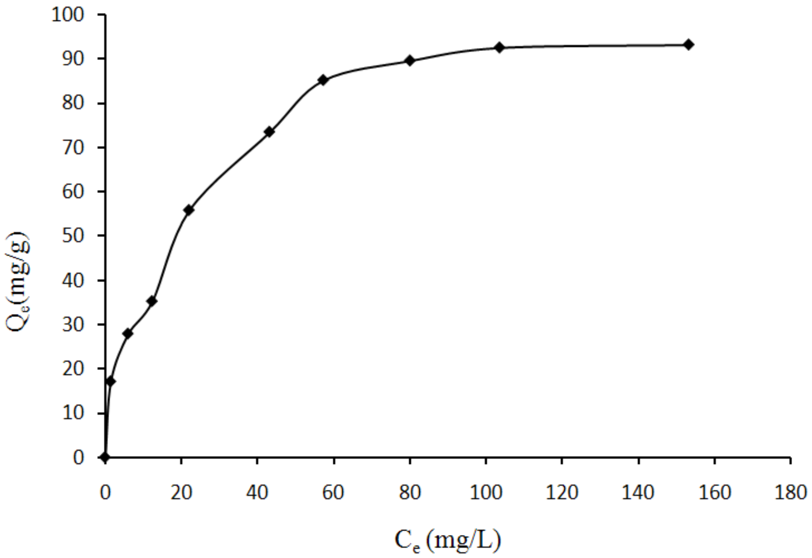

Figure 7: Equilibrium adsorption isotherm of copper on ZSAC.

Table V: Comparison of equilibrium adsorption capacities of ZSAC for copper with other adsorbents.

Adsorbent	S_{BET} (m^2/g)	Q_0(mg/g)	C_0 (mg/L)	Reference
hazelnut shell activated carbon	441	58.27	50-1000	[32]
Ceiba pentandra hulls activated carbon	521	20.78	40-240	[33]
Chestnut shell activated carbon	1319	100	1000	[44]
grapeseed activated carbon	916	48.78	1000	[44]
cassava peel activated carbon	1567	56.17	10-100	[45]
hazelnut husks activated carbon	1092	6.645	200	[46]
Ziziphus spina-christi seeds activated carbon	914	109.89	10-200	This study

CONCLUSION

The results of this work demonstrate that *ziziphus spina-christi* seeds are an attractive source of raw material for preparing high quality activated carbon by chemical activation with KOH. The activated carbon was obtained by using 3/4/1 impregnation ratio of water/KOH/coal (by weight) at

700 ºC carbonization temperature for 2 h of activation time. Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy investigations were evidenced the presence of a porous structure and different functionalities on the ZSAC surface. The results of liquid phase adsorption experiments revealed that the prepared activated carbon is a suitable adsorbent for copper from aqueous solutions.

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