

New carbon from low cost vegetal precursors: acorn and cypress cone

Research Article

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Abstract: Thermal-treated carbons from acorn and cypress cone were prepared and characterized. The uptakes of heavy metal ions (Ag^+ , Cd^{2+} and Cr^{+3}) and organics (phenol, methylene blue and sodium dodecylbenzenesulfonate) from aqueous solution have been studied. Effects of activation by HCl and HNO_3 acids on the sorption properties of these carbons were investigated by mass titration, sorption isotherms, IRS, SEM and XRS. The models of Langmuir and Freundlich do not represent our sorption data very well. An earlier proposed empirical correlation is applied successfully to carry out a parameter of comparison between the studied carbons. The acidic treatment changes the surface chemical properties of the two thermal-treated carbons lowering their sorption performances. The carbons show good capacities to uptake metals, phenol and methylene blue, but sodium dodecylbenzenesulfonate is removed from its solutions to minor extent. The up-taking properties are found similar to those of two worldwide used commercial grade carbons.

Keywords: Low-cost sorbent • Acorn • Cypress cone • Heavy metals • Organics

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1. Introduction

Activated carbon (AC) is widely used in various industrial, environmental, domestic appliances due to its high sorption capacity and selectivity for particular pollutants. Particularly, ACs are used in water and air purification, solvent and metal recovery, odours removal, decolorizing process, general home applications [1].

The world market for the activated carbon is 1.2 million metric tons and it is forecast to expand over the years, mostly driven by environmental considerations such as the lowering of the concentration limits of pollutants in drinking water, in industrial discharges and emissions, etc. [2].

Coconut shells, lignite and bituminous coals are usually the starting raw materials. Recently ACs obtained from raw vegetable materials or waste of little or negligible value is of widespread interest: eucalyptus wood, spruce, oak, peach stone, apricot stone, walnut shell, palm shell they are alone some of the materials lately used. These new sorbents have high qualities relating with their porosity, surface area, sorption capacity, hardness, and also lower prices [3-7].

In addition, the low cost of production does not require regeneration of the exhausted material but it allows a more convenient direct discharge.

The sorption properties of low cost ACs are influenced by the treatments of charcoal production and subsequent activation, both developed and controlled to produce carbon for special applications (gaseous or liquid phase treatment, organic or inorganic removal, industrial or domestic use, general or specific application); wide-ranging methods for the modification of ACs are possible such as an acidic treatment, base treatment, impregnation of foreign material, functionalization of graphite layers with ligands, microwave treatment, ozone and plasma treatment [8,9].

In this study, the use of acorn and cypress cone as raw vegetable material for AC production is investigated. The effect of an acid treatment coupled to thermal activation to change the sorption performances of the carbon is also studied.

Sorption selectivity of these carbons has been evaluated for some heavy metal ions and organic molecules such as phenol, methylene blue and sodium dodecylbenzenesulfonate (Fig. 1).

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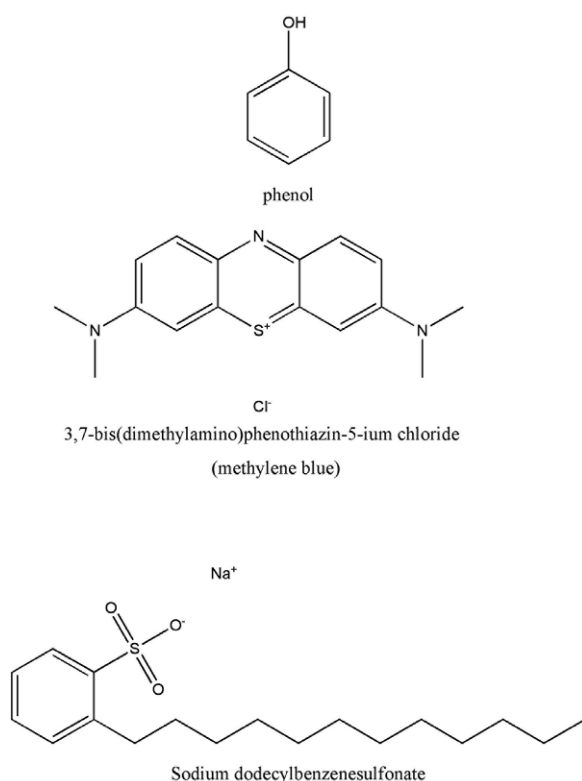


Figure 1. Testing organic molecules: a) phenol (Ph), b) Methylene blue (MB), c) Sodium dodecylbenzenesulfonate (BDSNa).

Table 1. Structural analysis and elementary composition (% w/w).

Components	Acorn	Cypress cone
Structural analysis		
Cellulose	29.3	27.5
Hemicelluloses	24.6	26.2
Lignin	40.7	43.2
Elementary composition		
Ash	1.4	1.2
Carbon	46.8	47.1
Oxygen	44.9	44.8
Hydrogen	5.5	5.7
Nitrogen	1.4	1.5

Silver, Cadmium and Chromium were selected as heavy metals with well-documented detrimental effects to biological systems and environment. The phenol and the methylene blue are molecules used in a large amount of studies in order to estimate the adsorption capacity of AC; the results on phenol adsorption, in particular, were used for introducing the different mechanisms of adsorption of organics on to AC, as the π - π dispersion interaction mechanism, the hydrogen bonding formation

mechanism, and the electron donor-acceptor complex formation mechanism [10-12]. The Methylene Blue is commonly used in adsorption tests to evaluate the adsorption capacity of an activated carbon for molecules having similar dimension to methylene blue and in order to obtain information on porous structure with particular attention to the mesoporous sites of adsorption. The sodium dodecylbenzenesulfonate was selected as anionic surfactant both for its enough stability, and is large use [13,14].

Sorption properties of these new carbons are compared with those of two worldwide used commercial carbons, namely Filtrasorb 200 (Calgon, USA) and Charcoal 6/14 AC (Fisherbrand, UK) made respectively by bituminous and coconut precursors.

In general, the results indicate that ACs obtained from acorn and cypress cone have suitable adsorption capacities for removal heavy metals, phenol and methylene blue from aqueous solutions likewise than commercial carbons.

2. Experimental procedure

2.1. Starting vegetable materials

Mature cones of *Cupressus sempervirens* pyramidalis (spherical or nearly so, ~5 cm long) and mature acorns from *Quercus pubescens* were collected in the region of Mt. Etna volcano (Sicily) in September 2009. The voucher specimens are deposited in the Department of Scienze Chimiche of University of Messina (Italy).

The raw samples were cleaned with deionized water, dried at $105 \pm 1.0^\circ\text{C}$ in ventilated oven, then ground by a roller mill into 2 – 3 mm particles. Table 1 shows structural analysis and elementary composition of these two precursors. Carbon and oxygen result the principal components of the raw materials used as typical for the lignocellulosic materials. The high content of lignin (more than 40%) found in the starting material suggests the probability to get an AC of good quality with elevated microporosity and suitable surface area [15].

2.2. Thermal carbonization of Acorn and Cypressus cones (TA and TC carbons)

The two granular materials have been carbonized separately; the carbonization method was done in a horizontal tubular furnace CTF 12/65/550 by Carbolite (England). Samples of granular material of about 25 g, under nitrogen atmosphere (99.99 %), were heated until 700°C with a temperature rate of 5°C min^{-1} and subsequently maintained at 700°C for 2 h. Charcoal from acorn is referred as TA and that from cypress cone as TC.

2.3. Carbons activated by chemical treatment (TA-HCl, TC-HCl, TA-HNO₃, TC-HNO₃ carbons)

The two thermal-treated carbons have been washed with deionized water, dried at 105±1.0°C and then chemically activated by means of treatment with two different acids, HCl or HNO₃. To prepare the two series, samples of TC and TA charcoal have been suspended separately into the respective 2 N acidic solutions (ratio 1:1 of carbon: solution, w/w) overnight (14 hours) at room temperature under mechanical agitation. After acid treatment the samples were washed with deionized water to remove the residual acids and then dehydrated at 105±1.0°C for 3 h. The activated carbons from hydrochloric and nitric acid treatment are referred as TA-HCl, TC-HCl, TA-HNO₃ and TC-HNO₃ respectively.

After cooling, the activated carbons were sieved to desired particle sizes (25-35 U.S. mesh) and kept in vacuum desiccator for further use.

Table 2. Characterization of thermal-activated carbons from acorn (TA) and cypress cone (TC).

Parameter	Unit	TA	TC
Yield	% (w/w)	33.7	35.9
Total ash	% (w/w)	5.38	5.17
Total carbon	% (w/w)	74.4	79.6
Total sulphur	% (w/w)	0.17	0.14
pH	-	9.77	9.58
PZC	-	9.74	9.51
Bulk density	% (w/v)	0.74	0.75
Loss in water	% (w/w)	2.15	2.18
Loss in HCl	% (w/w)	2.86	2.94
Ball pan hardness	% (w/w)	96	98
BET surface area	m ² g ⁻¹	400	390

Table 3. Characterization of TA and TC carbons activated by acidic treatments.

Parameter	Unit	TA-HCl	TA-HNO ₃	TC-HCl	TC-HNO ₃
Yield	% (w/w)	29.5	29.6	31.1	31.8
Total ash	% (w/w)	2.39	2.24	1.98	1.81
Total carbon	% (w/w)	76.7	75.8	84.5	80.1
Total sulfur	% (w/w)	0.04	0.05	0.05	0.05
pH	-	3.87	3.01	3.81	2.98
PZC	-	3.70	3.04	3.79	3.05
Loss in HCl	% (w/w)	0.12	0.10	0.08	0.09
Ballpan hardness	% (w/w)	95	95	97	97
BET Surface area	m ² g ⁻¹	560	440	510	420

2.4. Characterization of the carbons

The carbons have been characterized to determine various parameters such as bulk density, total ash, total carbon, total sulfur, pH of aqueous slurry (1:10 carbon:water ratio), point of zero charge (PZC), loss in water, loss in HCl solution, ball pan hardness. The yield of final product has been also determined. The results are reported in Tables 2 and 3.

The specific surface area of the ACs were measured by N₂ gas adsorption at -196°C (Micromeritics Autochem II 2920). The PZC, which is pH at which that surface has a net neutral charge, were calculated by the mass fraction method proposed from Wang and Lu [16]. Different initial pH solutions were prepared using HNO₃ (0.1 M) and NaOH (0.1 M) and the equilibrium pH was measured after 24 h. The plot of pH versus mass fraction shows a plateau and the PZC is identified as the point at which the change of pH is zero. The PZC calculated results from the average of the three asymptotic pH values.

The loss in water and in acid was determined by suspending 1 g of carbon respectively into 10 mL of deionized water and 10 mL of 0.25 N HCl solution for 24 h at controlled temperature (20±0.5°C), and then drying in an air oven at 105±1.0°C to constant mass. Ball pan hardness parameter has been determined according to ASTM D3802-10 standard test method.

2.5. Analytical methods

A GF-AAS Spectra 55A (Varian, USA) was used for metal determination. The concentration of phenol was measured using a AVDP10 HPLC chromatograph (Shimadzu, Japan). Methylene blue (MB) was determined by the sorption capacity observed at 20±1°C suspending each carbon (1 g) into 100 mL of a 2 g L⁻¹ MB solution. The absorbency of MB solutions was determined at 653 nm wavelength using a UV-vis spectrophotometer (Cary UV50, Varian, USA). Sodium dodecylbenzenesulfonate (DBSNa) anionic surfactant

was measured spectrophotometrically after reacting with MB and extracting by chloroform of the resulting ion pair.

Each carbon surface has been analysed by Scanning Electronic Microscopy (SEM) and Energy-Dispersive X-ray Spectrometry (EDXS) using a LEO S420 SEM instrument (Leica–Cambridge Instruments, MA-US).

To obtain the infrared spectra, the carbons were ground to a very fine powder in an agate mortar, dried at $105 \pm 1.0^\circ\text{C}$ for 1 h, diluted and homogenized to 0.05% (w/w) with KBr and then analyzed using a Genesis II FTIR spectrophotometer (Thermo Nicolet Scientific, MA-USA).

2.6. Sorption properties

Sorption capacity of each AC has been measured by the sorbed amount of each metal ion (Ag^+ , Cd^{2+} and Cr^{3+}) and organic molecule.

During the experiments at controlled temperature ($20 \pm 0.5^\circ\text{C}$), aqueous slurries of 4 g L^{-1} of activated carbon were used. The initial concentration (C_i) of each solute was ranging in a range of 0 – 1.6 mM. The initial pH of 6.5 as varying over ± 0.2 units was adjusted (pH_{adj}) by small addition of HCl or NaOH 0.01 M solution.

All experiments were performed according to the standard methodology of batch equilibrium test described elsewhere [17]. Our sorption kinetics have been conducted at both pH ~ 6.5 and low metal initial concentration, to ensure that the removal of Ag^+ , Cd^{2+} and Cr^{3+} ions could be attributed mainly to sorption excluding precipitation.

Reaction mixture, after the required time, was filtered through $0.45 \mu\text{m}$ Millipore membrane and the filtrate was analyzed for the studied chemicals.

Equilibrium in the system was achieved when the solute concentration into solution (C_e) varied under 2% per half an hour. Experiments were triplicates and the results averaged. The percent standard deviation of the sorption parameters was under 1.0%.

2.7. Chemicals

Chemicals of analytical grade from Fluka Ltd (Switzerland) have been used. Deionized water at $18.2 \text{ M}\Omega \text{ cm}^{-1}$ from a Milli-Q Millipore apparatus (MA - USA) was used for each experiment. Metal standards were prepared by the dissolution of metal nitrate in deionized water.

2.8. Commercial carbons

Two commercial carbons, Charcoal 6/14 AC (CC) and Filtrasorb 200 AWD-LF 12x40 (F200) purchased respectively from Fisherbrand (UK) and Calgon Carbon Corporation (PA – USA), have been used.

3. Results and discussion

3.1. Surface chemistry of carbons

Both the starting raw materials had similar characteristics, judging by their elementary and structural composition (Table 1).

The two thermally activated carbons showed a good predominance of carbon, very low sulfur, moderate presence of ash, low solubility in water and acid (Table 2). The subsequent treatment with HCl and HNO_3 changes clearly the values of some parameters but equally for both TA and TC carbons. The acid washing reduced the total ash content and made acidic the surface of carbons (Table 3). Our thermal-treated carbons show basic values of pH and PZC (~ 9.6) while their acidic derivatives are found with acidic pH and PZC values, more acidic those treated with HNO_3 . These findings were due respectively to removal of inorganic oxides and salts and to protonation of basic sites on carbon surface (ether, ester, lactone and carbonyl groups). Particularly, the HNO_3 treatment contributed also to destroy micropores and to make them selectively accessible [18].

3.2. Physical characterization

EDX spectra of the developed carbons (TA, CA and acidic derivatives) showed no peak, indicating their amorphous nature.

The IR spectrum of each carbon showed peaks in the region of $3853\text{--}453 \text{ cm}^{-1}$ but they have not been assigned. The IR spectra of all TA and TC carbons are analogous (Fig. 2) and they have prominent bands in the $3853\text{--}3245 \text{ cm}^{-1}$ range that may be associated to the presence of OH groups then the bands in the range $1800\text{--}1540 \text{ cm}^{-1}$ they can be related to carbonyl groups. The band at 1590 cm^{-1} can also be related to structures containing oxygen [19].

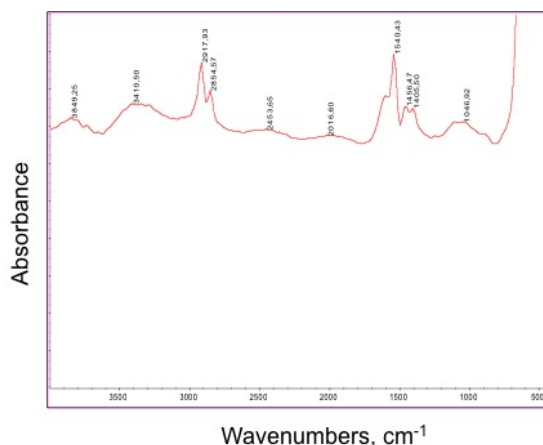


Figure 2. FT-IR spectrum of TA carbon.

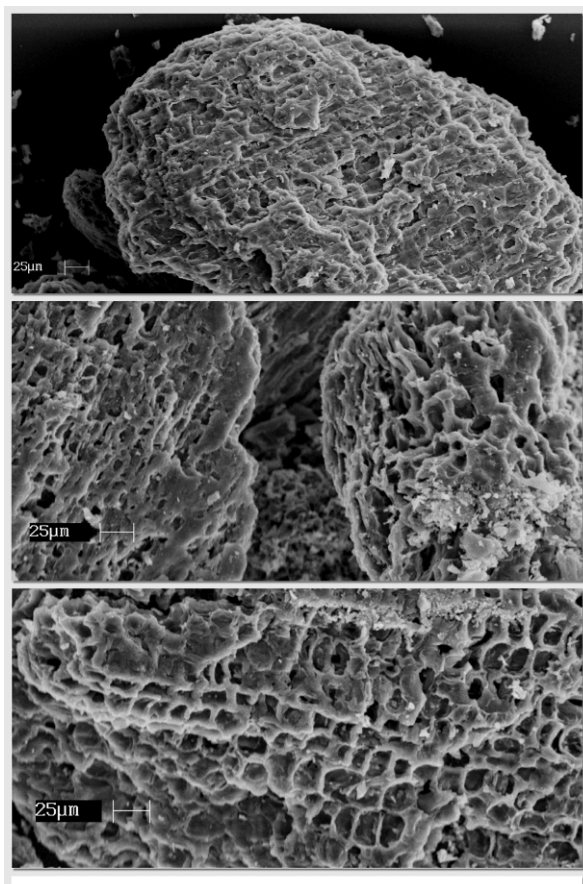


Figure 3. SEM images (400x) of carbons: a) TA acorn, b) TA-HCl acorn, c) TA-HNO₃.

Scanning electron images of TA, TC and their acid-derivatives are shown on Figs. 3 and 4. The different skeleton of the two vegetal precursors is distinctly perceptible. The carbons after the acidic treatment show fragmented and pitted surface, more structure like canals, pores of different size and shape. This finding is most clearly evident on the surface of the acorn carbons.

3.3. Equilibrium condition

To evaluate the time needed to get equilibrium conditions in the sorption, kinetic tests have been performed. In Figs. 5 and 6 kinetic trends of sorption on TA-HCl and TC-HCl carbons are shown as an example because all the developed carbons exhibit the same behavior. The kinetic curves are smooth and continuous, steep initially and then tend to flatten leading to saturation in short time for all metals and organics in this study.

The rate of metal sorption reaches the plateau on average within 30 minutes while organic solutes needed more time to reach the equilibrium (~2 hours). This different behavior confirms the hypothesis of a different mechanism of sorption process for the various solutes.

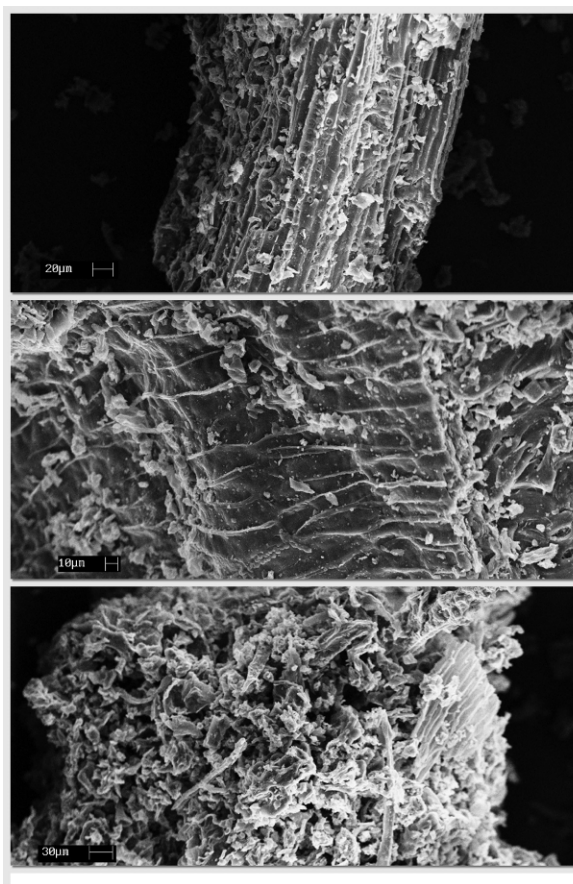


Figure 4. SEM images (400x) of carbons: a) TC cypress cone, b) TC-HCl cypress cone, c) TC-HNO₃ cypress cone.

Kinetic tests have been performed at different initial concentrations of solute (C_i). The equilibrium data reveal that at increasing C_i values the time needed to get sorption equilibrium remains almost constant, the amount adsorbed by sorbent unit mass increases and the percent sorption decreases. This last could be because at lower C_i values the ratio between initial amount of solute and the number of surface active sites is low and then the sorption process becomes independent of C_i . Instead at high initial concentration the available active sites become fewer and less accessible and then the percentage removal of solute is decreased. For even higher initial concentrations, the number of active sites is insufficient compared to the solute concentration and the process is heading towards saturation.

3.4. Sorption isotherms

Both Langmuir and Freundlich isotherms have been tested as sorption model. Data fitting are unsatisfactory with the Langmuir equation; the data fitting with the Freundlich equation is better but not fully acceptable, confirming the heterogeneous nature of the surface of

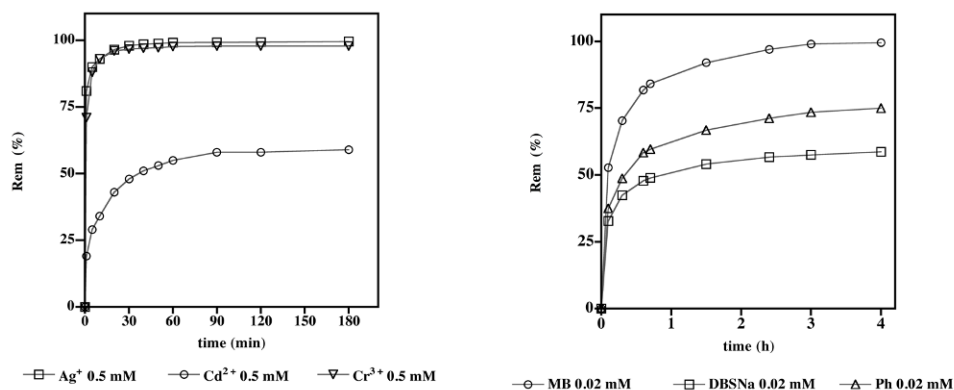


Figure 5. Effect of contact time on sorption of different sorbates on TA-HCl carbon.

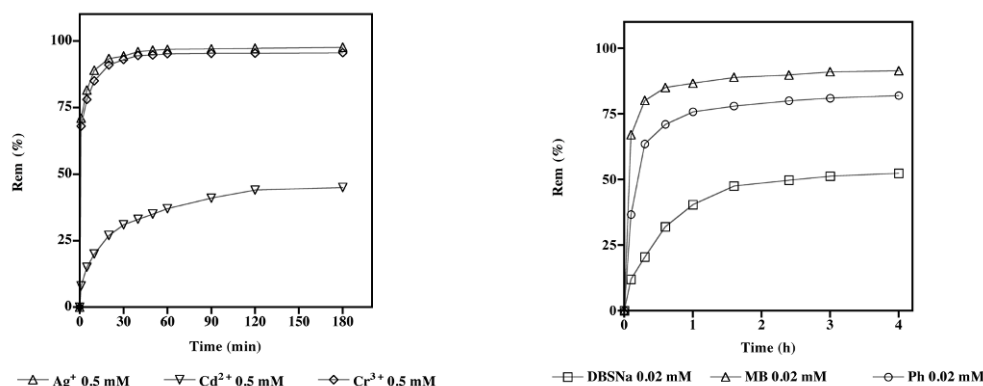


Figure 6. Effect of contact time on sorption of different sorbates on TC-HCl carbon.

all the developed carbons. In Figs. 7 and 8 a linearized Freundlich isotherm for metals and organics on TA-HCl and TC-HCl are shown: C_e (mg L^{-1}) is the equilibrium concentration and Q_e is the amount adsorbed at equilibrium (mg g^{-1}).

Freundlich experimental parameters of the various carbons are shown in Tables 4 and 5, where K_F ($\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$) indicates the sorption capacity and n is related to the sorption intensity. The results show that the sorption performance of thermal-treated carbons varies for metals in the order $\text{Ag}^+ > \text{Cr}^{3+} > \text{Cd}^{2+}$ and for organics in the order $\text{Ph} > \text{MB} \gg \text{DBSNa}$. The acid-treated carbons show K_F values significantly lower than thermal-treated carbons, for all the tested solutes excluding the DBSNa anionic surfactant.

The n values of our carbons are greater than one, indicating both heterogeneity of the sorbents and energetically favorable sorption conditions [20].

3.5. K_{sa} parameter from experimental linear relation

From analysis of experimental data a good linear correlation between initial concentration of solute (C_i) and amount of sorbate on unit sorbent mass at

equilibrium (C_s) was observed. For all our carbons, C_s (mg g^{-1}) and C_i (mg L^{-1}) parameters show a linear fitting up to the following maximum values of C_i : 1.4 mM for metal cations and 0.5 mM for organics.

We have observed earlier similar trends proposing a model that allows comparing the sorption performance of different materials [21].

In fact, within the concentration range of the observed linear trend, is verifying the Eq. 1

$$I_s = 100 C_s/C_i \quad (1)$$

where I_s (index of sorption) represents the amount (mg) of solute uptaken by 100 g of carbon from a solution at unit initial concentration (mg L^{-1}). Comparing two different carbons, the higher I_s value indicates a greater sorption capacity with regard to the considered solute.

Tables 6 and 7 shows I_s and R^2 (linear correlation coefficient) values of all carbons here studied and Table 8 lists the same parameters observed for two commercial carbons.

The findings confirmed the previous results obtained by Freundlich model but experimental data show better linear fitting. Overall the new carbons showed a better

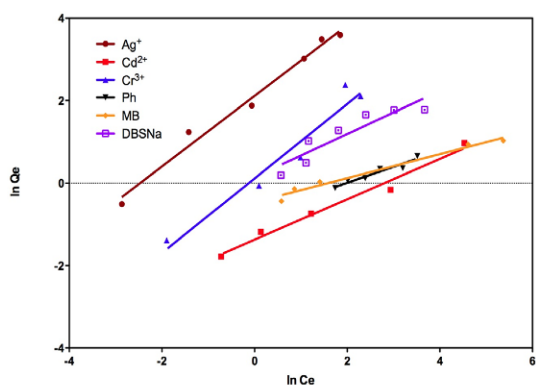


Figure 7. Freundlich plot for the adsorption of metals and organics on TA-HCl carbon.

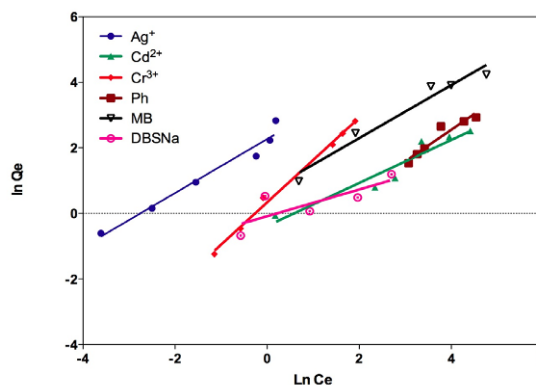


Figure 8. Freundlich plot for the adsorption of metals and organics on TC-HCl carbon.

Table 4. Freundlich parameters and linear regression coefficient for acorn carbons.

Sorbate	TA			TA-HCl			TA-HNO ₃		
	KF	n	R ²	KF	n	R ²	KF	n	R ²
Metals									
Ag ⁺	24.1	1.79	0.8561	8.83	1.12	0.8838	0.83	1.13	0.8694
Cd ²⁺	0.59	1.80	0.8132	0.31	1.07	0.8077	0.22	1.12	0.8653
Cr ³⁺	3.19	1.76	0.8261	0.88	1.09	0.8309	0.61	1.14	0.8405
Organics									
Ph	2.29	1.95	0.8664	0.85	1.78	0.8964	0.93	1.62	0.8989
MB	2.05	1.78	0.8512	0.69	1.57	0.8311	0.81	1.89	0.8111
DBSNa	0.15	1.18	0.8115	18.1	1.45	0.8234	18.8	1.32	0.8127

Table 5. Freundlich parameters and linear regression coefficient for cypressus cone carbons.

Sorbate	TC			TC-HCl			TC-HNO ₃		
	KF	n	R ²	KF	n	R ²	KF	n	R ²
Metals									
Ag ⁺	15.5	1.68	0.9768	5.15	1.18	0.8351	1.33	1.12	0.8158
Cd ²⁺	0.67	1.56	0.9614	0.44	1.13	0.8011	0.22	1.14	0.8356
Cr ³⁺	4.49	1.30	0.9686	0.65	1.12	0.8108	0.51	1.18	0.8361
Organics									
Ph	2.72	1.54	0.9770	0.95	1.53	0.8233	0.63	1.53	0.8511
MB	2.04	1.77	0.9636	0.58	1.81	0.8251	0.41	1.58	0.8326
DBSNa	0.20	1.51	0.9741	15.3	1.25	0.8147	15.7	1.28	0.8223

ability to remove metal cations, Ph and MB from aqueous solutions than DBSNa. An acid treatment does not improve the sorption performance of the thermal-treated carbons with exception of the nitric acid treatment that enhances the uptake of DBSNa. The sorption efficacy of TA and TC carbons is comparable to that of both F200 and CC commercial carbons, regarding all solutes excluding the DBSNa anionic surfactant.

3.6. Effects of acid treatments

Some simplify the mechanisms of sorption process in two types: the first involving electrostatic interactions between carbon surface active sites and solute, the second referring to the intra-particle diffusion promoted by interactions between the π-electrons of both the graphene layers into the carbon pores and the molecules of solute (aromatic rings, C = C or N = N or C = N bonds)

Table 6. Sorption index (I_s) of cypressus cone carbons for various solutes.

Substrate	TA		TA-HCl		TA-HNO ₃	
	I_s	R ²	I_s	R ²	I_s	R ²
Metals						
Ag ⁺	25	1.0000	19	0.9993	22	0.9994
Cd ²⁺	15	0.9994	10	0.9998	11	0.9991
Cr ³⁺	24	0.9991	19	0.9995	20	0.9997
Organics						
Ph	21	0.9998	11	0.9991	14	0.9997
MB	19	0.9990	15	0.9996	16	0.9993
DBSNa	9	0.9995	9	0.999	15	0.9998

Table 7. Sorption index (I_s) of acorn carbons for various solutes.

Substrate	TC		TC-HCl		TC-HNO ₃	
	I_s	R ²	I_s	R ²	I_s	R ²
Metals						
Ag ⁺	24	0.9993	18	0.9997	17	0.9991
Cd ²⁺	14	0.9989	9	0.9991	8	0.9994
Cr ³⁺	23	0.9998	17	0.9997	18	0.9997
Organics						
Ph	20	0.9989	14	0.9991	18	0.9990
MB	19	0.9995	15	0.9989	16	0.9955
DBSNa	9	0.9989	8	0.9997	14	0.9998

Table 8. Sorption affinity (I_s) of F200 and CC commercial carbons for various solutes.

Substrate	F200		CC	
	I_s	R ²	I_s	R ²
Metals				
Ag ⁺	25	0.9999	24	0.9999
Cd ²⁺	13	0.9935	14	0.9979
Cr ³⁺	25	0.9999	23	0.9998
Organics				
Ph	22	0.9984	21	0.9997
MB	25	0.9999	25	0.9999
DBSNa	22	0.9997	17	0.9845

[22]. The predominance of one over the other is depending on factors related to both experimental conditions (pH of the medium, PZC of carbon, contact time, solute concentration) and characteristics of the solute-sorbent system (structural and surface characteristics of the carbon, dominant electrostatic charges, electron-donor or electron-acceptor capacity, the spatial size of the solute, rigidity of the water coordination sphere).

Sorption is a complex process and this makes it critical to design models giving a correct and universal

explanation of its running. In the literature various models proposed, some have a theoretical foundation and some being of empirical nature. Unfortunately, its application is limited (gases, vapors, liquids) and failing to give a complete understanding of the process (full range of relative pressures, simultaneous sorption of two or more components...). In addition, unexpected and sometimes opposite behaviors of similar solute-sorbent systems are observed and then new concepts are suggested.

Some of these mechanistic models appear valid and interesting such as the hard and soft acids and bases (HSAB) theory that allows predicting the potential sites of sorption on the carbon surface as a function of the hardness of metal ion [23].

Others propose the concept of the size and rigidity of molecules or hydrated ions that make them difficult to enter into the inner carbon pores. Others still suggest models of surface complex formation (SCF) between solutes in the aqueous solution and carbon surface groups (carboxylic, anhydride, lactone, phenolic, carbonyl, quinone, ether) [24-26].

Our carbons show sorption behavior opposite to that based on electrostatic interaction between solute

and sorbent. Also in previous studies we found this unexpected behavior [21].

Since thermal-treated carbons (TA and TC) are basic (PZC \approx 9) it is to assume that at the pH conditions of our experiments ($\text{pH}_{\text{adj}} \approx 6.5$) the acidic carbon surface should repel the cationic solutes (metal cations and MB) and attract the anionic solutes (Ph and DBSNa) in solution.

Instead, Tables 4-7 show that thermal-treated carbons (TA and TC) exhibit sorption affinity high for Ag^+ , Cr^{3+} and Phenol, medium for Cd^{2+} and MB, low for DBSNa.

Just to improve the sorption properties, activation of TA and TC carbons by treatment with hydrochloric acid was been performed to remove the oxides that block the pores, to increase number and density of active sites, to decrease the energetic heterogeneity of carbon. The treatment with nitric acid had also to change the surface complexes on the carbon producing more acidic groups (such as carboxyl, lactone, ether) and to increase the number of mesopores [27,28].

Since the surface chemistry of new acid-treated carbons was acidic (PZC \approx 3) lower uptake for the anions (Ph and DBSNa) and higher performance for cationic solutes (metal cations and MB) were expected at our experimental pH conditions. Instead, our data shows acid-treated carbons have similar or sometimes lower performance than thermal-treated carbons, with exception of TA- HNO_3 and TC- HNO_3 that enhanced the uptake of DBSNa.

Compared to Ph, the DBSNa anionic surfactant has an anomalous behavior showing lower uptake. Principally this is due to greater size of DBSNa molecule that undergoes steric hindrance. In addition, Ph may behave as a weak base that interacts with the

acidic surface of thermal-treated carbons by electron dispersion or donor-acceptor interaction while with acid-treated carbons it benefits from electrostatic attraction of the basic surface.

In conclusion, under our conditions the sorption is occurring due not only to electrostatic interactions between carbon surface and cations or anions but also to physical-chemical interactions (electron dispersion, donor-acceptor interaction, formation of dominant complexes, steric hindrance) with enough energy to overcome the above mentioned electrostatic forces.

4. Conclusions

Carbons prepared by thermal treatments of acorn (TA) and cypress cone (TC) exhibit satisfactory sorption capacity for metal ions (Ag^+ , Cd^{2+} and Cr^{3+}) and organic compounds (Ph, MB and DBSNa). For sorption of metal cations and Ph the new carbons show uptake capacity comparable to that of worldwide used commercial carbons such as F200 and CC.

Treatments with HCl and HNO_3 acids influence surface properties of TA and TC basic carbons lowering the uptake of metal cations and organic molecules.

Overall, this study shows that acorn and cypress cone, today regarded as waste and low-cost material, can be converted to sorbents effective in removing metal and organic pollutants from industry aqueous effluents. Its low cost of production would also allow the convenient direct discharge of the exhausted material.

At present, studies are in progress to test new activation treatments in order to improve property and selectivity of these low cost carbons and to test application fields.

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