

Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl_2 and H_3PO_4

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Abstract

In order to evaluate the adsorptive capacities of granular activated carbon produced from coffee grounds by chemical activation, the adsorption of different phenols and acid and basic dyes, has been carried out. The comparison with a commercial activated carbon has been made. Adsorption isotherms of phenols and dyes (acid and basic) onto produced and commercial granular activated carbons were experimentally determined by batch tests. Both Freundlich [1] and Langmuir [2] models are well suited to fit the adsorption isotherm data. As a result, the coffee grounds based activated carbon may be promising for phenol and dye removal from aqueous streams.

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1. Introduction

Water pollution is a very persistent problem, the intensive disposal of different toxic substances without control constitutes a real danger. Phenolic compounds are common contaminants in wastewater. They are widely used for commercial production of a wide variety of resins [3]. They are harmful at low concentrations, and US Environmental Protection Agency (EPA) call for a maximum phenol content in wastewater of than 1 mg/l [4].

Effluents from dyeing and finishing processes are generally highly coloured with a large amount of suspended organic solids. They are important sources of water pollution because dyes in wastewater undergo chemical as well as biological changes, consume dissolved oxygen, and destroy aquatic life. Therefore, it is necessary to treat textile effluents prior to their discharge into the receiving water. The removal of synthetic dyes (that are carcinogens), has become

an important aspect of textile wastewater treatment and many studies have been conducted on the toxicity of dyes and their impact on the ecosystem, as well as the environmental issues associated with the manufacture and subsequent usage of dyes [5].

To remove organic pollutants and/or dyes many treatments have been proposed, such as coagulation, sedimentation, filtration, oxidation (KMnO_4 , H_2O_2 , Cl_2 , O_3), adsorption [6–11]. Biological treatment processes are reported to be efficient in the reduction of organic pollutants concentration, but ineffective in removing colour [12,13]. Of these methods, adsorption has been found to be an efficient and economic process, and an effective and widely employed mean of water and wastewater treatment.

Despite its prolific use in water and wastewater treatment, commercial activated carbon remains a rather expensive material. This leads to a search for low cost materials as alternative adsorbents. Among these alternatives, agricultural and/or wood wastes such as, sawdust, maize cob, coconut husk fiber's, fruit kernel, and nut shells appear to be more economically attractive in certain countries because they are abundant [14–16].

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Algeria annually consumes an average of one hundred thousand tons of coffee [17]. Aside from some unimportant losses, all these quantities of coffee end up in the form of coffee grounds in the discharges. Hence, the interest is to recover and to develop them by transforming this material into activated carbon for need of the water treatment processes.

The aim of this paper is to investigate the feasibility of manufacturing carbonaceous adsorbents from coffee grounds. The goals are the reduction of the solid wastes and the production of materials that could be usable as adsorbents of pollutants and color substances.

2. Materials and methods

2.1. Production of activated carbon

Raw material for the preparation of activated carbon (ACP) is produced locally (coffee grounds). Dyes (acid blue 25, $C_{20}H_{13}N_2NaO_5S$ and basic yellow 2, $C_{17}H_{21}N_3HCl$) and other chemicals used in this study were reagent grade.

The experimental procedure used in the activation process is as follows: the carbonaceous material is washed in a first step with hot water to eliminate the impurities, dust and water-soluble substances, and in second one with distilled water, then it is oven dried for 24 h at 105 °C (*MEMMERT, DIN 40050-IP20*). After drying to constant weight, it undergoes a chemical activation step with ($ZnCl_2 + H_3PO_4$) as the activating agent. The activated sample is obtained by putting 50 g of coffee grounds in contact with the adequate volume of an aqueous equal-molecular solution of ($ZnCl_2 + H_3PO_4$) 1 mol/l for 24 h in a continuous reactor. The activated sample is subsequently oven dried at 100 °C for 1 h. The resulting sample is then carbonized for 45 min at 600 °C in a horizontal cylindrical furnace (*ProLabo, VOLCA MC18*). After cooling, the char is washed with diluted HCl (10% by weight) in order to eliminate the excess of dehydrating agents and the fraction of soluble ash, followed by distilled water to remove the residual organic and mineral matter. Washing with water easily removes most of the residues from activating agents. The completion of washing is done when the conductivity measurements become stable. It is then dried at 105 °C for 48 h. The carbon product is crushed and sieved to a uniform particle size (30 μm) and stored in closed bottles [18].

2.2. Characterization of the produced and the commercial activated carbons

Chemical and physical characterization of granular activated carbon produced from coffee grounds (ACP) and commercial activated carbon (ACC) has been made.

- A measurement of specific area has been made by nitrogen adsorption (at 77 K), with a discontinuous volumetric apparatus (Micrometrics model 2100) [19].

- For a better knowledge of the nature of the mineral components, a spectrographic analysis (spectrograph UEI No. ICA5) and by fluorescence (Fluorescence X sequential spectrometer, Phillips PW1480) have been done.
- To provide information on the chemical structure of the activated carbon, a study of the surface functional groups has been done by IR analysis (*NICOLET 560 FT-IR*).
- Zeta potential, which enables to quantify the electrical potential of the solid particle surface, was determined with a *Micrometrics Zêta Potential Analyzer*.
- The determination of acidic and basic surface functional groups of the activated carbon has been done according to the protocol established by Boehm et al. [20].
- The apparent density was calculated by filling a calibrated cylinder with a given activated carbon weight and tapping the cylinder until a minimum volume was recorded. This density is referred as tapping or bulk density of adsorbent. For the real density we used the pycnometer's method, which consisted of filling a pycnometer with the activated carbon, then added a solvent (methanol or an other solvent) to fill the void, at each step the weight is determined.
- The pore volume and the porosity were determined by using a volumetric method which consists in filling a calibrated cylinder with a V_1 volume of activated carbon (mass m_1) and solvent (methanol, CCl_4 , Benzene) until volume V_2 (total mass m_2) is reached. Knowing the density of solvent, porous volume and the porosity of the adsorbent are easily calculated.

2.3. Adsorption test

To characterize the adsorption capacity of an activated carbon, different adsorbates are commonly used. Iodine and methylene blue are among these and are frequently used to characterize activated carbons used in wastewater treatment.

The results from these (commercial) tests like the iodine, methylene blue or phenol indices give a technical estimate of the adsorption capability of a carbon but they do not provide any insight on the intrinsic properties of the material.

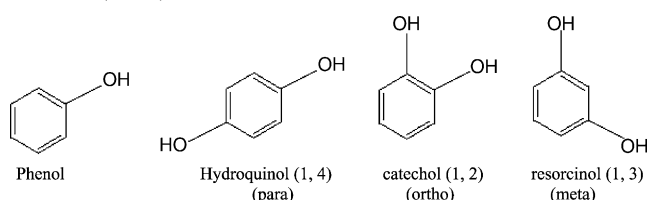
In general iodine number and the amount of methylene blue adsorbed are considered as a measure of adsorption capability of adsorbents for low and high molar mass solutes, respectively.

The iodine number corresponding to the produced adsorbent was determined according to the procedure established by the Standard Test Method (ASTM D4607-86) [21]. According to this test:

A mass of (0.1 g) of activated carbon was placed in a 250 cm^3 dry Erlenmeyer flask and fully wetted with 10 cm^3 of diluted HCl (5% by weight). 100 cm^3 of iodine solution (0.1 mol/l) was poured into the flask and the mixture was vigorously shaken for 30 s. After filtration, 50 cm^3 were titrated with 0.01 mol/l sodium thiosulfate. For the determination of the amount of methylene blue, the activated carbon (1 g) was added into a 100 cm^3 aqueous solution containing 0.5 g/l of methylene blue (Merck) and stirred for 5 days at 30 °C. After

filtration, the aqueous phase concentration of methylene blue was determined with a UV–vis spectrophotometer (Beckman DU-6) at wavelength of 663 nm.

The production of mesoporous carbons (with pores >50 nm) is extremely important in the field of bulk materials adsorption and separation. To characterize the adsorption ability of the produced activated carbon in wastewater treatment, adsorption tests were carried out. Two dyes (acid blue 25 and basic yellow 2,) and phenols were chosen as adsorbates. Phenol (C₆H₅OH) and di-substituted phenols (C₆H₄(OH)₂) (*para*, *ortho*, *meta*) were used to evaluate the produced adsorbent with respect to the size of adsorbate molecule, substitution position involving a steric effect and a preferential uptake caused by the inductive effect of the radicals (–OH).



We must have in mind, that in the physio-sorption, the only attraction between the adsorbed species and the surface arises from weak van der Waals forces. But the interaction of a molecule with a given surface will also depend upon the presence of any adsorbed species. The most common are hydrogen, oxygen, nitrogen, phosphorus, and sulfur present as heteroatoms or/and in the form of functional groups, it results in surface, chemical heterogeneity. During the approach of the molecule towards the adsorbent surface, the molecule energy and the electronic configuration change, including the angular orientation, changes in the internal bond angles, also change as well as the bond lengths, the position of the molecule to the surface and the distribution of electric charges.

The presence of (–OH) radicals involves a polarization of the bond (ϕ –OH), the radical phenyl ϕ (C₆H₅) is donor of electrons by delocalization of the π bonds, whereas the group hydroxyl (–OH) is acceptor of electrons. There would be an electric effect, Phenol:

ϕ –OH \Rightarrow $\phi^{\delta+}$ \rightarrow $\text{OH}^{\delta-}$, delocalization of the electric charges and creation of an electric dipole (δ^+ , δ^- the electric inductive charges) and hydroquinone: OH – ϕ – $\text{OH} \Rightarrow \text{OH}^{\delta'-}$ \rightarrow $\phi^{2\delta'+}$ \leftarrow $\text{OH}^{\delta'-}$.

The nature of the adsorbent surface directs the molecules (inductive effect) and lets them to adsorb, the group (–OH) ahead, if it is acid, in this, case, the cross-sectional area is the smaller one. As we mentioned it previously, the factor limiting adsorption is the size of the molecules, the effect of polarization involves a preferential position during the mechanism of adsorption. The positions of the radicals (–OH) for the catechol (1, 2) and resorcinol (1, 3) do not benefit from this privilege, these molecules having two radicals (–OH), in the final approach towards the adsorbent surface, they present the maximal cross sectional area which added to the steric effect, greatly disturb the adsorption.

Dyes (CI acid blue 25, and CI basic yellow 2) and phenols were prepared and diluted to the required initial concentration for adsorption experiments. The initial concentration was obtained by measuring the optical density (OD) or absorbance at wavelength corresponding to maximal absorbance for each chemical reagent considered. For this purpose, a UV–vis spectrophotometer was used (Beckman DU-6).

The maximal wavelengths were 597 nm, 406 nm for acid blue and basic yellow, respectively, and 315, 289, 271, and 269 nm, respectively, for catechol (1, 2), hydroquinone (1, 4), phenol and resorcinol (1, 3). All the tests were repeated with a commercial activated carbon (ACC), for the needs of comparison.

The amount of adsorption at time t was calculated by: $q_t = x/m = (C_0 - C_t)V/m$ where C_0 (mg/l) and C_t (mg/l) are the liquid-phase concentrations initially and at time t (min), V (l) the volume of solution and m (g) the mass of dry adsorbent.

Kinetic experiments were carried out in order to find out the adsorption equilibrium time. The aqueous solution of dyes or phenols was agitated at a stirring speed of 150 rpm.

At given intervals of time, samples were taken (5 cm³), filtered and the concentrations of dyes or phenols were spectrophotometrically determined. Each experiment was repeated at least once. The time needed for reaching a concentration value without further increase (equilibrium concentration) needs 60 min. For isotherm determinations, exactly 100 ml of solutions of known initial concentration were shaken at constant stirring speed (150 rpm) with a required dose of ACP (or ACC) during 60 min wherein more than 80% of the adsorption is achieved. Kinetic and equilibrium experiments were carried out at room temperature (25 ± 2 °C) under batch mode.

3. Results and discussion

The main physical properties of the activated carbons are listed in Table 1.

The results of spectrographic analysis indicates that the sample contains very small quantities of copper, zinc mag-

Table 1
Main characteristics of activated carbons

Characteristics	Values	
	ACP	ACC
Real density	1.56	1.48
Apparent density	0.72	0.73
Pore volume (cm ³ /g)	0.95	1.29
Specific surface area (m ² /g)	640	950
Porosity	0.48	0.64
Isoelectric point	5.80	4.35
Surface function	Weakly acid	Weakly acid
pH	6.35	5.70
Iodine number (mg/g)	440	590
Decolourisation of methylene blue (%)	>90	>90

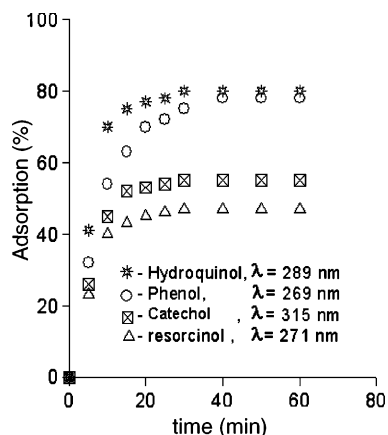


Fig. 1. Adsorption of different phenols onto ACP with time $C_0 = 20 \text{ mg/l}$; $T = 25^\circ\text{C}$ hydroquinol (1,4); phenol, catechol (1,2); resorcinol (1,3).

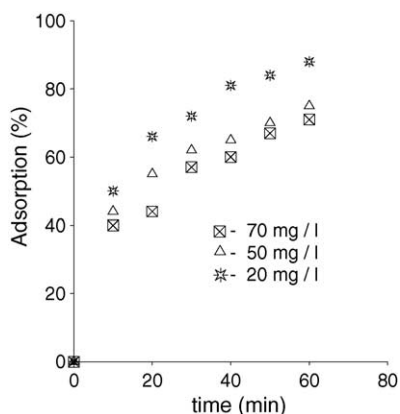


Fig. 2. Adsorption of Acid blue dye onto ACP at different concentrations, $T = 25^\circ\text{C}$.

nesium, nickel, cobalt, chromium, molybdenum, barium and tin (percentage by weight is in the order of 10^{-4} to 10^{-2}). Oxides of calcium, magnesium and iron, and the presence of phosphate were detected (percentage by weight is about a 10^{-1}). The results of the different adsorption tests are graphically represented in Figs. 1–3.

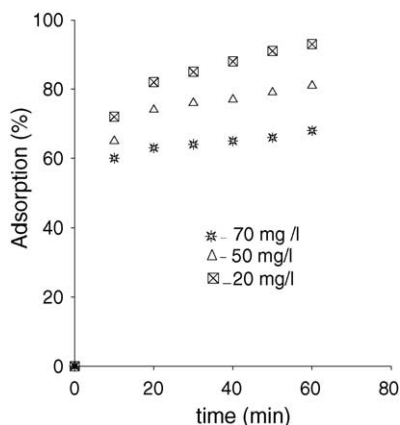


Fig. 3. Adsorption of Basic yellow dye onto ACP at different concentrations, $T = 25^\circ\text{C}$.

As can be seen, in so far as the phenols are concerned, equilibrium times are not dependent on the nature and the concentration of the adsorbates (Fig. 1). The quantity of solute adsorbed depends on the position of the hydroxyl radical ($-\text{OH}$). The highest percentage corresponds to hydroquinol, where the radicals ($-\text{OH}$) substituted in position para (1, 4) give the molecule a planar structure and a smaller cross-sectional area, easier to adsorb than the other structures more cumbersome. The attractive effect of functional surface groups (weakly acid: electrons acceptor) of the activated carbon is helping the molecule to move towards the surface, radical hydroxyl ($-\text{OH}$) ahead (electric attraction). For the phenol, the adsorption is facilitated by one substitution (the molecule is consequently smaller), but the random position of the molecule during its approach (more mobile than hydroquinol) make it less adsorbed, the radical ($-\text{OH}$) is not always present ahead of the molecule. The adsorption of both phenol and hydroquinol indicates a preferential orientation of the molecules and adsorption, the radical ($-\text{OH}$) ahead in the majority of the situations.

Naturally resorcinol is more adsorbed than catechol (the molecule being bulkier). The combined effect of the two mechanisms gives information on the form structure and the size of the pores. From adsorption of hydroquinol and phenol, we deduce that the form of the adsorbent pores is cylindrical, and from the resorcinol (1, 3) adsorption (the cumbersome molecule), to approximate the dimensions of the pores.

Basically, the structure of activated carbons containing pores are classified according to the International Union of Pure and Applied Chemistry (IUPAC classification) into three groups, micropores (pore size $< 2 \text{ nm}$), mesopores ($2\text{--}50 \text{ nm}$) and macropores ($> 50 \text{ nm}$) [22]. The comparison of the pores dimension of adsorbent with the cross sectional area of phenol in flat orientation calculated by Puri et al. [23], ($\sigma = 52.2 \text{ \AA}$), the study of percentages of covering surface in the case of the phenol adsorption onto various adsorbents [24], and the mechanism of adsorption outlined above, who shows a reducing of cross sectional area of the molecule lets suppose that the selected manufacturing process of activated carbon enabled to obtain an adsorbent presenting much more mesopores than macropores.

Concerning the dyes adsorption (Figs. 2 and 3), equilibrium times dependent on the nature of the adsorbates. The basic dye (yellow) is faster adsorbed than the acid one (blue). The van der Waals forces are usually predominant but the nature of adsorbent surface (weakly acid) and the molecular size of the adsorbate (yellow dye smaller than blue) supports its adsorption.

A comparative study involving the isotherms corresponding to the adsorbates removal from solutions by produced activated carbon (ACP) and commercial activated carbon (ACC) is illustrated in Figs. 4–6.

As can be seen, each compound adsorption data corresponds to isotherms of type 1 [19], i.e. convex upward curves, who are considered to be of a strong adsorption.

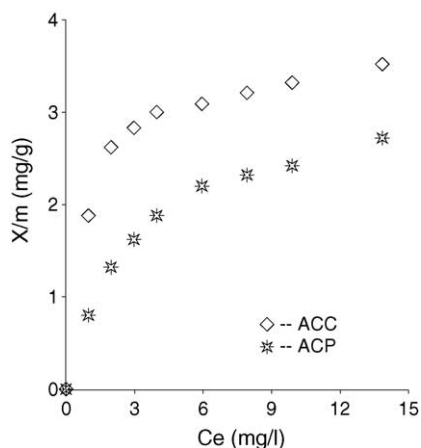


Fig. 4. Adsorption isotherms of phenol for both activated carbons. $C_0 = 20 \text{ mg/l}$; $T = 25^\circ\text{C}$.

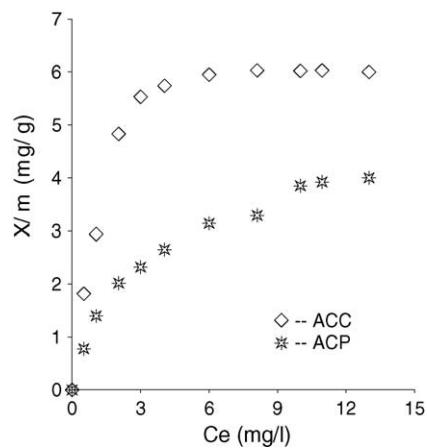


Fig. 6. Adsorption isotherms of Acid dye for both activated carbons. $C_0 = 20 \text{ mg/l}$; $T = 25^\circ\text{C}$.

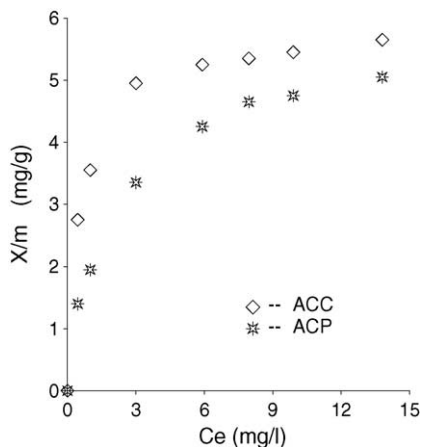


Fig. 5. Adsorption isotherms of basic dye for both activated carbons. $C_0 = 20 \text{ mg/l}$; $T = 25^\circ\text{C}$.

Results obtained for each adsorbate adsorption were fit to two adsorption isotherm models, those of Langmuir and Freundlich.

Langmuir equation is based on a theoretical model and assumes that the maximum adsorption corresponds to a monolayer saturated with adsorbate molecules on the adsorbent surface that is energetically homogeneous, $q_e = K_L q_m C_e / (1 + K_L C_e)$, where K_L is a parameter which

make reference to the adsorption energy and q_m is a constant relative to the maximum adsorption capacity.

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface, $q_e = K_F C_e^{1/n}$ where K_F is relative to the adsorption capacity and n refers to the process intensity. The coefficients of determination of the data fitting to each of the above models are shown in Table 2 together with the values of the characteristic parameters for each of the two models studied. According to the coefficient of determination (CD, or regression coefficient), both Langmuir and Freundlich models provided good fittings for the data of phenols and dyes adsorption.

A characteristic of the Langmuir isotherm is the definition of a dimensionless factor r defined as $r = (1 + K_L q_m)$ [25] and called separation factor.

Adsorption is considered favourable when $r < 1$ which is the case in all experiments. As for values obtained from the Freundlich model, the n value indicates a favourable adsorption when $1 < n < 10$, thus the adsorption is better when smaller values are obtained [26].

The study of the parameters obtained shows that the produced activated carbon has a better affinity for basic substances than the commercial activated carbon.

For dyes adsorption, the kinetic of basic yellow is faster, and has better uptake than acid blue.

Table 2
Results from fitting to Langmuir and Freundlich models

Adsorbate	Adsorbent	Langmuir model				Freundlich model		
		K_L	q_m	CD	r	K_F	n	CD
Phenol	ACP	0.33	3.22	0.998	0.48	1.07	2.70	0.964
	ACC	1.08	3.70	0.987	0.20	2.41	7.14	0.980
Acid blue	ACP	0.74	3.57	0.979	0.27	2.27	1.40	0.993
	ACC	0.57	8.33	0.991	0.17	2.27	2.89	0.900
Basic yellow	ACP	1.70	10	0.978	0.06	2.04	2.56	0.982
	ACC	1.32	4	0.989	0.16	3.49	4.76	0.931

4. Conclusion

Activated carbon produced from coffee grounds proved to be suitable for the removal of organic pollutants and dissolved dyes. In batch discontinuous tests, both adsorption kinetic studies and isotherms determination indicate that the adsorbents behaviour depends on the nature of the compound to be removed from the solution.

Adsorption of phenol and di-substitutes shows that the radical (–OH) radical (–OH) has a significant influence on the adsorption process.

The phenol adsorption and its substitutes makes possible it to have an idea on the shape of the pores, and gives an order of magnitude of their dimensions.

Freundlich and Langmuir equations appropriately fitted all isotherms adsorption data.

The removal by produced activated carbon is found to be favourable according to the separation factor related to the Langmuir isotherm model.

The produced activated carbon and a commercial product are quite comparable from adsorption capacity (Table 2), but the activated produced carbon appears to be better as for as the basic dye adsorption is concerned.

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