A LJEST

Adsorption of phenol onto activated carbon prepared from coffee extract residue chemically activated using ZnCl$_2$

L. Yahia cherif*, F Aissani-Benissad

Laboratoire de Génie de l'Environnement,
Faculté de Technologie, Université A/ Mira de Bejaia, Algérie.

*Corresponding author: lamia.yc@gmail.com   ; Tel.: +213550094930

ARTICLE INFO

ABSTRACT/RESUME

Abstract: In this work, coffee residue, a natural precursor of vegetal origin was used as a source material to prepare activated carbons by chemical activation with zinc chloride. The effects of differences found in the surface functional groups and textural characteristics of five activated carbons prepared with different impregnation ratios (activating agent/precursor) on their capacity to retain phenol from aqueous solutions are reported. Batch experiments were conducted to study the main parameters such as initial adsorbate concentration, contact time, pH solution, temperature and adsorbent concentration.
It was found that retention of phenol is less in acidic carbons than in basic nature carbons. Activated carbon prepared with 25 % impregnation ratio showed best adsorption capacity and waschosen for further studies. Optimum conditions for phenol removal were found to be pH = 3, adsorbent concentration = 2 g/L and equilibrium time = 20 min. Under optimised conditions, the prepared activated carbon showed 85 % removal efficiency for a solution concentration of 30 mg/L. The experimental data were analysed by the Langmuir and Freundlich isotherm models. The results clearly showed that the adsorption data of phenol onto activated carbon fit perfectly to the Langmuir model with correlation coefficient higher than 0.99 at all temperatures. The surface chemistry of activated carbon affects the adsorption capacity significantly while the texture characteristics of surface area and pore volume play a minor role in phenol adsorption. Therefore, the surface chemistry must be taken into account in the decision-making process of choosing an adsorbent for phenol removal.

I. Introduction

Increasing population and industrializationhave led to increasing environmental problems. This has caused catastrophes which destroyed the ecological system. The presence of organic compounds in aquatic environment has been of great concern to scientists because oftheir increasing discharge and their non-biodegradability. Phenolic compounds are considered to be highly toxic and difficult to degrade biologically. The major sources containing phenols are the wastewater from processing manufacturing industries such as those from oil refineries, petrochemical production, coal tar processing, pharmaceutical industry, textile processing, leather processing, and insecticide production [1]. Symptoms of phenols toxicity reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances [2-7]. Because of their toxicity, the US Environmental Protection Agency (EPA) and the European Union have designed phenols as priority pollutants. Therefore, removal of phenolic

compound before disposal of wastewater is necessary.

Among various treatment technologies, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodology [8] but commercially available carbons in market are expensive, so there is a need to produce low cost and disposable activated carbons that can be applied to remove pollutants from wastewater. In recent years, numerous studies on carbons preparation from solid wastes for organic or metallic compounds removal have been reported in the literature [2, 9 - 16]. The development of methods to re-use waste materials is greatly desired and the production of activated carbons from wastes offers promising future. Any inexpensive material with high carbon content can be used as a raw material for the production of activated carbon. The preparation method involve either thermal treatment in the presence of chemical agent (chemical method) or activation of carbonizates through controlled gasification (physical method). Donni Adinata et al. [16] reported that chemical activation is an efficient method to obtain carbons with high surface area and narrow micropore distribution. K. Mohanty [10] reported two important advantages of chemical activation: the lower temperature in which the process is accomplished and the other is that, the global yield of chemical activation, which tends to be greater since burn-off char is not required.

The adsorption process depends on several factors which include the nature of the adsorbent, adsorbate, and adsorption conditions. Adsorbent characteristics include surface area, pore size distribution, hydrophobicity, and the concentration of functional groups present on the surface of carbons. The surface chemistry of the carbon is a result of the existence of heteroatoms such as oxygen, nitrogen, hydrogen and phosphorus [17]. The content of heteroatoms depends on the origin of the carbon and the method of activation and their presence can determine the acidity or basicity of the activated carbon [18, 19].

The objective of this study is to screen activated carbon prepared from coffee residue for potential application for removal of phenol from wastewater. In this work we are reporting the results obtained from the preparation of activated carbons from coffee residue an inexpensive precursor with zinc chloride activation and their ability to remove phenol from aqueous solutions. Different weight ratios (ZnCl$_2$/ coffee residue) were studied to prepare a well efficient activated carbon for phenol removal. The influence of several operating parameters, such as pH, temperature, adsorbent dosage, contact time, and initial concentration on the adsorption capacity were investigated. The equilibrium adsorption data were evaluated by Langmuir and Freundlich models and kinetic

models were also used to identify the possible mechanisms of adsorption process.

II. Materials and Methods

II.1. Adsorbent preparation

The adsorbent was prepared from coffee-residue, whichwas collected from local coffee-stalls. The material was first washed with water to remove water-soluble impurities and then dried at 60°C to remove moisture and other volatile impurities. Chemical activation of powdered precursor was done with ZnCl$_2$. 200 g of dried precursor material was well mixed with ZnCl$_2$, at ZnCl$_2$/coffee residue weight ratios of 1:4, 1:2 and 3:4 and in separate jars and the mixtures were then kneaded by adding distilled water. The mixtures were then dried in an oven at 85 °C for 7 hours. Portions of the impregnated coffee-grounds were taken on silica crucibles and heated up to activation temperature under nitrogen flow (100 mL/min) at a rate of 10 °C/min and held at the activation temperature (600 °C) for 1 hour. After the activation process, the samples were cooled under nitrogen (N$_2$) flow to room temperature. The ZnCl$_2$ –impregnated activated carbons were washed with distilled water, and treated with HCl solution (10 % mass) to remove impregnating salts, and then washed with hot distilled water to remove chlorides and acidity. This operation was repeated until the disappearance of chloride reaction with AgNO$_3$. The washed samples were dried at 110 °C, crushed and then sieved to particle size diameter of less than 63 μm.

II.2. Physical characterization

Physical characteristics of the samples were determined by nitrogen adsorption-desorption isotherms measured by Gaz Sorption Analyzer (Quantachrome NOVA Win 2, version 9.0). Prior to each measurement, carbon samples were outgased at 200 °C under nitrogen flow for 3 h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K). The specific surface areas were calculated from the BET equation. All surface areas were calculated from the nitrogen adsorption isotherms by assuming the projected areas of a nitrogen molecule to be 0.162 nm².

II.3. Adsorbate and analytical measurements

An accurately weighed quantity of phenol was dissolved in distilled water to prepare stock solution (5000 mg/L). Experimental solutions of desired concentrations were obtained by successive dilutions with distilled water adjusted to desired pH. Concentrations of phenol were controlled by finding out the absorbance at the characteristic wavelength using UV/vis. Spectrophotometer model IC 6305. A standard solution of the phenol was taken and the absorbance was determined at different wavelengths to obtain a

plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) as determined from this plot was 270 nm. This wavelength was used to prepare calibration curves of absorbance versus phenol solution concentration. This plot showed a linear variation of concentration up To 110 mg/L.

II.4. Surface chemistry – Boehm titration

The oxygenated surface groups on surface of prepared carbons were determined according to Boehm titration [20, 21]. Amounts of various acidic functional groups can be measured by selective neutralization using 0.1 M $NaHCO_3$, Na_2CO_3, HCl, NaOH aqueous solutions and 0.1 M C_2H_5ONa solution, respectively. A 0.5 g carbon sample was placed into each of the above solution (100 mL) and the mixtures were sealed and shaken for 3 days at room temperature. The suspensions were then separated by filtration and excessive base or acid in the filtrate was titrated with HCl or NaOH depending on the original solution used. The moles of acidic sites of activated carbons was determined based on the assumptions that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na_2CO_3 neutralizes carbonylic and lactonic groups, $NaHCO_3$ neutralizes only carboxylic groups and C_2H_5ONa neutralizes all acidic functional groups including carbonylic groups. The moles of surface basic sites were calculated from the amount of HCl that reacted with the carbon.

II.5. Batch adsorption procedure

To study the effect of important parameters like $ZnCl_2$/coffee residue weight ratio, pH, contact time, initial concentration of phenol and adsorbent dose, batch experiments were conducted in 5-L glass vessel. The vessel was submerged in a water bath controlled at a predetermined constant temperature (precision: ± 0.1 °C). When the temperature of the adsorbate solution was stabilized at a desired level, a known weight of activated carbon was left in contact with agitated phenol solution (stirring speed: 160 rpm). This was considered as initial time for the kinetic experiment. Small volume liquid samples were withdrawn at different time intervals. Samples were filtered through glass filter paper to remove adsorbent particles. Before filtrate samples were taken for analysis, one millilitre of the sample was filtered and discarded. The residual phenol concentration in the filtrate was determined by UV/Vis. spectrophotometer at 270 nm wavelength. In order to obtain the sorption capacity, the amount of adsorbed phenol per mass unit of activated carbon (q_e in milligram of phenol per gram of adsorbent) was determined based on the phenol concentration measured after and before

equilibration. The amount of adsorption at equilibrium, q_e (mg g^{-1}) was obtained as follows:

$$q_{e} = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

C_0 being the initial phenol concentration (mg/L), C_e the equilibrium phenol concentration (mg/L), V the volume of the aqueous phase (L) and m is the weight of activated carbon used (g). The percentage adsorption (% removal) of phenol from aqueous solution was computed as follows:

$$\text{Removal}(\%) = 100 \frac{(c_0 - c_e)}{c_0} \qquad (2)$$

Adsorption isotherm studies at different temperatures were carried out with six different initial concentrations of phenol from 10 to 110 mg/L at fixed adsorbent dose (0.5 g/L) and at an optimal pH (pH=3).

III. Results and discussion

III.1 Effect of impregnation ratio

Activated carbon can be represented by a model of a twisted network of defective hexagonal carbon layer planes which are cross-linked by aliphatic bridging groups. Heteroatoms are incorporated into the network and are also bound to the periphery of the planes. The heteroatoms bound to the surfaces assume the character of functional groups typically found in aromatic compounds and react in similar ways with many reagents. The results of the physical properties and the chemical surface groups of the prepared activated carbons are presented in Table 1. The physical characteristics of the carbon samplesused in this study are obtained from the interpretation of nitrogen isotherms. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the pores may be subdivided in broad terms according to diameter (d) into a tortuous network of macropores (d › 50 nm), mesopores (2 ‹ d ‹ 50 nm) and micropores (d ‹ 2 nm) [22]. As shown in Table 1, it can be seen that the average pore diameter (d = $4V_p$ /S_{BET}) of activated carbon samples are approximately the same for all samples. All activated carbon (except 0%) may be classified into mesoporous carbon. The same results were reported by Hu et al. [23] but Q. Quian et al. [24] reported that the average pore diameter decreased when the ratio $ZnCl_2$ to precursor increased from 25% to 100%.

The titration results of the chemical surface groups (Table 1) reveals that all the carbons possess oxygen functionalities. The concentration of acidic

groups (total) in non-activated carbon obtained from heat treatment alone (0% sample) is significantly higher when compared to those obtained from ZnCl$_2$ activation. The total concentration of these groups increases with the increase of the ZnCl$_2$ /coffee residue ratio used in the activation method. For all the investigated activated carbons, except 0% sample, the ratio of the numbers of acidic to basic groups was always higher than 1 and increases with increasing the ZnCl$_2$/coffee residue ratio. Activated carbon prepared with 25% of ZnCl$_2$ exhibits the lower acid / basic ratio.

Phenol adsorption data have been expressed in term of efficiency (phenol removal by adsorption / phenol in the initial solution). The experiments were performed with an adsorbent dose of 0.5 g/L at pH 3, initial concentration of 30 mg/L and 20°C. Experimental results show that the uptake of phenol depends on the surface chemistry of activated carbons and increasing impregnation ratio decreases the removal percentage of activated carbons. Chemical ratio of 25% was found to be the optimum.

Table 1. *Physical and chemical characteristics of the studied activated carbons*

Characteristics	Impregnation ratio				
	0%	25%	50%	75%	100%
BET surface area: S$_{BET}$ (m²/g)	297	520	617	680	810
Miropore surface area: S$_{mic}$ (m²/g)	283	379	390	392	413
Total pore volume :V$_p$ (cm³/g)	0.178	0.279	0.326	0.374	0.484
Pore diameter: d = 4V$_p$/S$_{BET}$ (nm)	2.39	2.14	2.12	2.20	2.39
Carboxylic groups (mmol/g)	1.5	1.09	1.20	1.38	0.71
Carbonylic groups (mmol/g)	0.90	0.71	0.84	1.07	0.44
Phenolic groups (mmol/g)	0.20	0.60	0.40	1.34	0.91
Lactonic groups (mmol/g)	1.10	1.04	1.10	0.04	1.54
Total acidity (mmol/g)	4.30	3.44	3.54	3.83	3.59
Total basicity (mmol/g)	0.40	1.70	1.40	0.99	0.73
Acidic/basic ratio	0.449	2.030	2.538	3.788	4.930
Removal (%)	42.04	73.56	60.56	58.70	58.33

The adsorption capacity of the activated carbon was markedly greater than that of the non-activated one [25, 26]. This increased adsorption can beattributed to the increase of the basic surface groups created during the activation. Singh et al. [19] reported that basic functional groups on the carbon surface increase π electron density on the graphene layers of activated carbon, and thus dispersive interactions between π-π electrons are stronger. We can conclude that the adsorption of phenol is better onto the activated carbons containing basic surface groups. This result is in agreement with those reported by Ania et al. [28]. Based on the values of the surface concentration of the titrated basic groups and the maximum surface oncentration

of adsorbed molecules, adsorption can occurs only at the titrated functional basic groups because the surface concentration of the titrated groups is found to be significantly higher to the surface concentration of the adsorbed molecules.This result is not in agreement with those reported by O. Hamdaoui [29]. All adsorption experimentsin the following textwere conducted with activated carbon prepared from coffee residue with 25 % impregnation ratio.

III.2 Effect of solution pH

The influence of initial pH of phenolic solution on the adsorption of phenol is shown in Figure 2. The experiments were performed for an initial

concentration of 30 mg/L, 0.5 g/L adsorbent dose and ambienttemperature (20°C). It is clear that prepared activated carbon iseffective for the quantitative removal of phenol at pH 3. Above and below this pH, there is adecrease in theadsorption capacity of the prepared carbon.

The solution pH is an important parameter affecting adsorption of organic compounds [24]. The adsorption of weak electrolyte such as phenol on the surface of an activated carbon depends, mainly on two important factors: the degree of dissociation of the electrolyte and the dominant charge on the surface of the solid. The first factor can be qualitatively predicted by pKa of phenol (pKa = 9.89). The second factor is more difficult to ascertain. The cell wall of the activated carbon contains a large number of surface functional groups and facilitates adsorption.

The pH dependence of phenol adsorption can largely be related to type and ionic state of these functional groups and also to the chemistry of the phenol in solution. Low pH values (pH ⟨ 3) lead to an increase in H^+ ion concentration in the system and the surface of activated carbon acquires positive charge by adsorbing H^+ ions. As the pH of the system decreases, the number of positively charged surface of activated carbon does not favour the adsorption of phenol molecules due to the competitive adsorption between H^+ ions and phenol molecules. From Figure 1, the maximum removal of phenol is observed at pH 3. The presence of an adsorption maximum at this pH could be explained by the high concentration of basic functional groups within the activated carbon (Table 1). Laszlo et al. [21] reported that both the functional groups on thecarbon surfaceand the phenolic compounds are in protonated form, that is, the groups are either neutral or positively charged.

The interaction between the carbon surface and the phenol is weaker and can be predominantly attributed to the dispersion effect and the electron donor-acceptor interaction. Between pH 4 and pH 7, phenol uptake appears as a plateau. This case results from a competitive adsorption between phenol and water molecules. Above pH 7, the uptake of phenol is considerably reduced. As the pH of the system increases, the number of negatively charged sites increases due to the excess of OH^- ions. A negatively charged surface sites on the carbon does not favour the adsorption of phenol molecules.

Subsequent studies were conducted at pH 3.
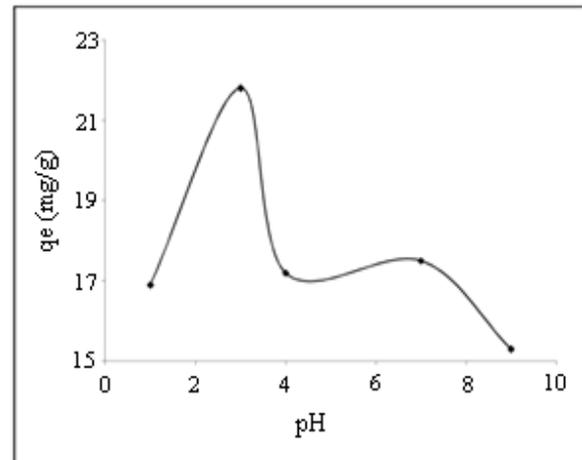
Figure 1. *Effect of system pH on the phenol removal by activated carbon.Experimental conditions – temperature: 20°C, carbon concentration: 0.5 g/L, contact time: 60 min.*

III.3 Effect of contact time and initial concentration of phenol

The effect of agitation time and initial concentration on the removal of phenol by coffee residue carbon is shown in Figure 2. All the other parameters like (pH 3), carbon dosage (0.5g/L), stirring speed (160 rpm) and temperature (20 °C) were kept constant. All of the curves in Figure 2 have a similar shape; they only differ in the adsorbed amount. This figure shows an increase in the amountof removed phenol with increasing agitation time. This may be due to the concentration gradient between the solution and the solid phases. Extend of uptake of phenol reaches a maximum value indicated by a plateau. The time corresponding to maximum adsorption is around 20 min for lower initial concentration (10 mg/L) and less than 15 min for other initial concentrations. It can be concluded that the adsorption rate of phenol on coffee residue carbon is fast and equilibrium state is established very quickly.

III.4 Effect of adsorbent dose

The removal percentage of phenol as a function of adsorbent dosage is presented in Table 2. The results showed that an increase in adsorbent dosage increases the removal percentage due to the increase in number of adsorption sites. The maximum removal of 85 % was observed at dosage of 2 g/L and pH 3 for an initial phenol concentration of 30 mg/L.
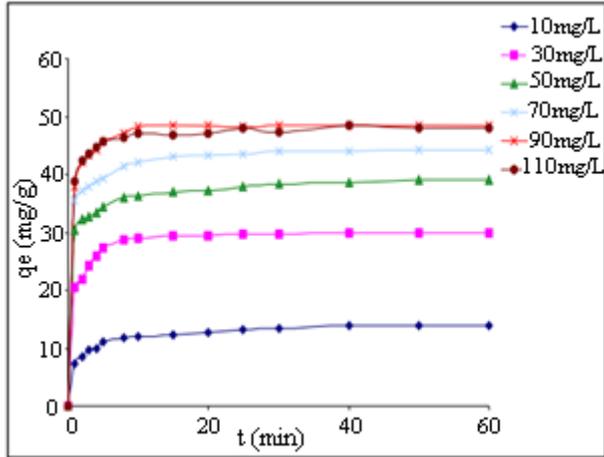
Figure 2. Effect of initial concentration on the phenol adsorption onto activated carbon as function of adsorption time. Experimental conditions – temperature: 25 °C, pH: 3, carbon concentration: 0.5 g/L.

Table 2. The phenol removal percentage as a function of adsorbent dosage

Adsorbent dose (g/L)	0.25	0.50	1.00	1.50	2.00
% Removal	24.43	48.41	69.63	81.50	84.93

III.5 Adsorption isotherms- the Langmuir and Freundlich equations

Figure3 shows the adsorption isotherms of adsorbed phenol by coffee residue carbon at different temperatures. These curves are obtained by measuring the maximum capacity of phenol adsorption in the saturated condition as a function of the concentration of phenol in the liquid phase. According to their shapes, it is obvious that the adsorption isotherms are all likely to be a typical Langmuir type. As seen from Figure 3, the adsorption decreases with increasing temperature.

The results were analysed using the Langmuir and the Freundlich models. The Langmuir model assumes that the phenol adsorption occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules of phenol. The theoretical Langmuir isotherm equation can be written as follows:

$$q_e = q_{mon} \frac{K_L C_e}{1 + K_L C_e} \qquad (3)$$

The linear form of this equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{mon} K_L} + \frac{1}{q_{mon}} C_e \qquad (4)$$

Where C_e (mg/L) and q_e(mg/g) are the adsorbate equilibrium concentrations in the liquid and solid phases, q_{mon} and $K_L$are the Langmuir constants related to the adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively. q_{mon} (mg/g) and K_L were evaluated from the slope and the intercept of the linear plots of C_e/ q_e versus C_e (Table 2).

The Freundlich adsorption isotherm model [29, 31] was also applied to describe the adsorption of phenol by coffee residue carbon. This fairly satisfactory empirical isotherm can be used for non-ideal adsorption that involves heterogeneous surface energy systems and it is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

The linear form of this equation can be written as:

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \qquad (6)$$

Where K_F is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. In general, as the K_F value decreases the adsorption capacity of the adsorbent for a given adsorbate decrease and the magnitude of $1/n$ give an indication of the favourability of adsorption. The values of n between 1 and 10 imply favourable adsorption condition [32]. Values of K_F and n are calculated from the intercepts and slopes of theplots and are listed in Table 2. The results suggest that phenol is favourably adsorbed by activated carbon prepared from coffee residue. The correlation coefficient (R^2) of linear regression is high, ranging between 0.992 and 0.999 for the Langmuir equation and between 0.948 and 0.995 for the Freundlich equation. Based on the regression coefficients, the Langmuir and the Freundlich isotherms describe quite well the adsorption of phenol on activated carbon tested in this work. Linear regression was the frequently used method to determine the most fitted isotherms, but non-linear method would be a better way to model the experimental isotherms. The parameters for each model at different temperatures were calculated from the isotherms experimentally determined (Table 3). Figure 3shows the experimental and the predicted isotherms by non-linear method for the adsorption of phenol onto coffee residue carbon. As can be seen, the Langmuir adsorption isotherms provide the best fit because this model similarly represents the experimental data. The Freundlich isotherms predict that the equilibrium removal of phenol would keep increasing progressively with increasing equilibrium concentration in the liquid phase.

Table 3. *Langmuir and Freundlich constants of the phenol adsorption on coffee residue carbon at different temperatures*

T (°C)	Langmuir			Freundlich		
	q_{mon} (mg/g)	K_L	R^2	K_F	n	R^2
20	58.139	0.069	0.997	12.393	3.236	0.993
25	55.045	0.072	0.999	12.768	3.049	0.975
30	56.818	0.054	0.992	10.435	2.865	0.948
35	51.813	0.059	0.997	9.984	2.915	0.988
40	47.846	0.062	0.995	9.687	2.985	0.995
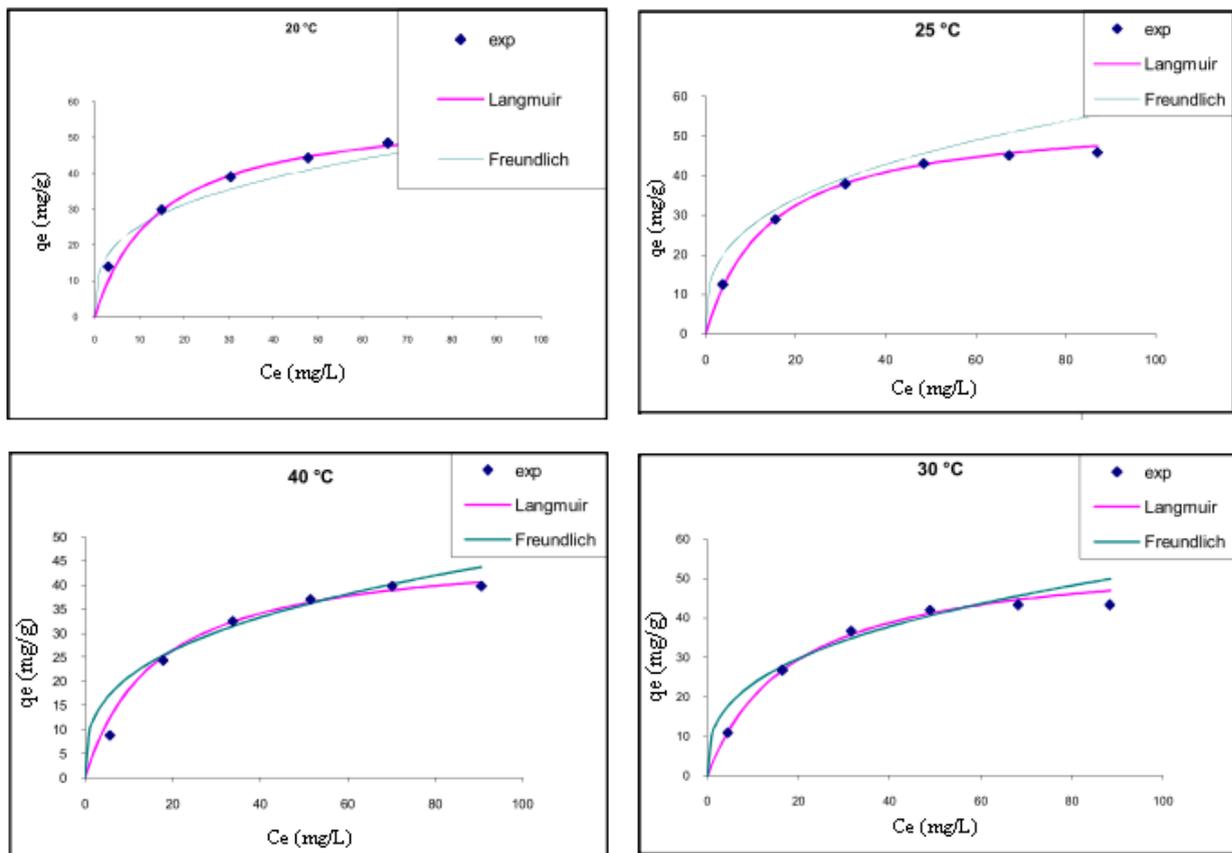
Figure 3. *Equilibrium isotherms of the phenol removal by coffee residue carbon at different temperatures.*

III.6 Adsorption kinetics

To investigate the adsorption process of phenol on coffee residue carbon, the experimental data were applied to select adsorption kinetics models namely pseudo-first-order[1, 33], pseudo-second-order [33, 34] and intraparticle diffusion models [33, 35].

Pseudo-first-order model

The first-order equation also called Lagergren equation can be written as follows:

$$\log(q_{e\,(exp)} - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (7)$$

Where $q_{e(exp)}$, q_t, q_e and k_1 are the amounts of phenol adsorbed (mg/g) at equilibrium-experimental data, at time t (min), at equilibrium-calculated data and equilibrium rate constant (min^{-1}), respectively. The values of q_e and k_1 were calculated from the intercepts and slopes of the plots of $\log (q_{e(exp)} - q_t)$ versus t and are shown in Table 3. The correlation coefficient values (R^2) of the pseudo-first-order kinetic are found to be lower than 0.955 and the calculated equilibrium adsorption capacities do not agree with experimental values. Then the adsorption data do not fit the pseudo-first-order equation.

Pseudo-second-order model

Kinetic data are treated with the pseudo-second-order model rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (8)$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1}min^{-1}) and q_e the amount of phenol adsorbed (mg/g) at equilibrium-calculated data. The equilibrium adsorption capacities (q_e), the second-order rate constants (k_2), were calculated from the intercept and the slope of the linear plots of t/q_t versus t. The results are given in Table 4. The correlation coefficients (R^2) for the second-order equation are higher than 0.917 ranging from 0.917 to 0.992 but the experimental $q_{e(exp)}$ values do not agree with the calculated ones as can be seen in Table 4. Thus, the adsorption data do not fit the pseudo-second-order equation [36].

Table 4. Pseudo-first and pseudo-second-order adsorption rate constants, experimental and predicted values at equilibrium time, pH 3, initial concentration: 30 mg/g and stirring speed: 160 rpm.

T (°C)	$q_{e(exp)}$ (mg/g)	Langmuir			Freundlich		
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_1 (min^{-1})	q_e (mg/g)	R^2
20	13.841	0.0071	20.914	0.917	0.0010	36.496	0.967
30	26.849	0.0068	16.545	0.848	0.0011	29.154	0.992
40	24.301	0.0101	15.159	0.955	0.0033	31.660	0.917

Intraparticle diffusion model

The adsorbate transport from the solution phase to the surface of coffee residue carbon particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or combination of more than one step [37]. The intraparticle diffusion model proposed by Weber and Morris is applied when intraparticle diffusion is considered as a rate-limiting step. This model is described by:

$$q_t = k_{id}t^{1/2}$$
(9)

Where q_t and k_{id} are the amount adsorbed at time t (mg/g) and intraparticle rate constant (mg g^{-1} min$^{-1/2}$), respectively. The applicability of the Weber–Morris model can be examined by linear plot of q_t versus $t^{1/2}$. If the Weber – Morris plot gives a straight line, then the sorption process is controlled by intraparticle diffusion. However, if the data

exhibit multi-linear plots, then two or more steps influence the sorption process.

Figure 4 presents the plots of phenol adsorbed versus $t^{1/2}$ for different initial phenol concentrations at 20 °C. It can be seen from the figure that data points are linked by two straight lines. Hsieh et al. [38] and Srivastava et al. [37] reported that the first straight portion depicts macropore diffusion and the second represents the micropore diffusion. Similar patterns are obtained at 25, 30, 35 and 40 °C, the k_{id} values at different initial phenol concentrations and different temperatures are summarised in Table 5. The deviation of the first linear portion of the plot from the origin or near saturation may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. Furthermore, such deviation from the origin indicates that the pore diffusion is not the only rate controlling step[2].

The values of k_{id} were calculated from the slopes of later portion of the plots (Figure 4). This was further supported by calculating the intraparticle diffusion coefficient D_{ip}(cm^{2}s^{-1}) using

Bhattacharya and Venkobachar equation reported by Singh et al. [39]:

$$D_{ip} = \frac{0.03\, r^2}{t_{1/2}}$$

(10)

Where r (cm) is the average radius of the adsorbent particle and $t_{1/2}$ (min) is the time for half adsorption.

In this investigation, the values of D_{ip} were about 10^{-7}. According to these values, it may be concluded that intraparticle diffusion was not the only rate controlling step because Michelsen et al. reported a D_{ip} value of about 10^{-11} when the intraparticle diffusion is the rate determining step [40].
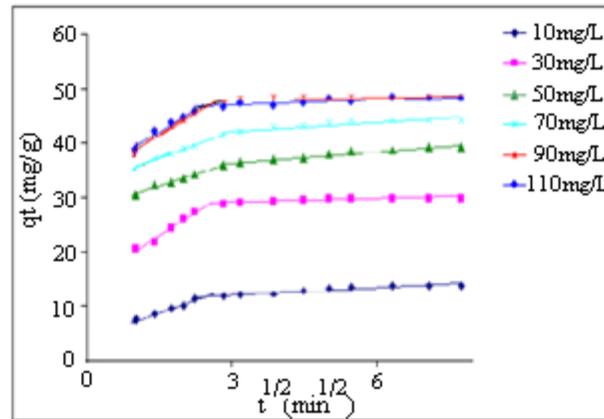
Figure 4. Intraparticle diffusion plots of the phenol adsorption on activated carbon at different temperatures. Experimental conditions – initial phenol concentration: 30 mg/L, pH: 3, carbon concentration: 0.5 g/L.

Table 5. Kinetic parameters of the phenol removal by prepared activated carbon at 20 °C and for different initial concentrations

C_0 (mg/L)	K_{id} (mg g^{-1}min$^{-1/2}$)	D_{id} (cm^2 s^{-1})
10	0.472	$2.52\ 10^{-7}$
30	0.227	$4.25\ 10^{-7}$
50	0.664	$5.04\ 10^{-7}$
70	0.536	$5.04\ 10^{-7}$
90	0.142	$5.04\ 10^{-7}$
110	0.334	$5.04\ 10^{-7}$

IV Conclusions

The activated carbon prepared from coffee residue, which is an inexpensive precursor could be used as a potential adsorbent for the removal of phenol from aqueous solution. From the results of phenol removal percentage by activated carbons prepared with different chemical ratios, it was found that the increase of impregnation ratio up to 25 % decreases the removal percentage because of the increase of acidic surface group concentration. Uptake of phenol is better onto activated carbon of higher basic groups concentration. The surface chemistry of activated carbon affects the adsorption capacity significantly while thetexture characteristics ofsurface areaand pore volume play a minor role in phenol adsorption. Impregnation ratio of 25 % was found to be the optimum.

In batch mode studies, the adsorption of phenol onto activated carbon prepared with an optimal impregnation ratio was dependent on solution pH, contact time, initial phenol concentration, adsorbent dose and temperature. The maximum adsorption uptake was achieved at pH 3 and the

results showed that the capacity of adsorption increases with a rise in initial concentration of phenol in solution at any temperature and with the increasing powdered activated carbon dosage. The time corresponding to maximum adsorption is less than 20 min for all initial phenol concentrations.

The equilibrium data fit perfectly the Langmuir model of adsorption, showing monolayer coverage of phenol molecules. The value for maximum adsorption, q mon is 58 mg/g. The kinetic of phenol adsorption onto activated carbon coffee residue follows the intraparticle diffusion model and the data linked by two straight lines indicated that the intraparticle diffusion was not the only rate-controlling step.

V.References

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Please cite this Article as:
Yahia cherif L., Aissani-Benissad F., *Adsorption of phenol onto activated carbon prepared from coffee extract residue chemically activated using Zn*Cl$_2$, **Algerian J. Env. Sc. Technology**, **2**:**1 (2016) 22-32**