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Characterization and utilization of activated carbons prepared from coffee residue for adsorptive removal of salicylic acid and phenol: Kinetic and isotherm study

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ABSTRACT

In this work, coffee residue was used as source material to prepare activated carbons by chemical activation with zinc chloride. The influence of impregnation ratio (Zinc chloride/coffee residue) on the physical and chemical properties of prepared carbons is studied in order to optimize this parameter. Texture properties of these carbons were determined by measuring the adsorption of nitrogen at 77 K. The nitrogen adsorption isotherms were interpreted by BET and Dubinin-Radushkevick (D-R) equations. The nature of carbon surface functionalities was studied by Boehm titration method. Phenol and salicylic acid removal from aqueous solutions by adsorption onto the prepared activated carbons was investigated. The effect of parameters such as pH, agitation time, initial phenol and salicylic acid concentrations, temperature, adsorbent dosage and particle size on phenol and salicylic acid removal were observed. In addition, adsorption kinetics and adsorption isotherms study were realized. Maximum phenol removal was obtained at pH 3 and 20°C, while for salicylic acid it was obtained at pH 3 and 25°C. In the isotherm studies, Langmuir and Freundlich isotherm models were applied and it was observed that the phenol experimental data were perfectly described by the Langmuir model while the salicylic acid experimental data were correctly fitted by both Langmuir and Freundlich equations. Batch adsorbent capacity (q_m) was calculated as 55 mg/g for phenol and 128 mg/g for salicylic acid. The rates of adsorption were found to conform to pseudo-second-order kinetics with good correlation.

Keywords: Coffee residue; Activated carbon; Salicylic acid; Phenol; Adsorption; Isotherm; Kinetic; Modelling

1. Introduction

The compounds that contain phenolic group are significant water contaminants. Their presence, even at low concentrations in water could be an obstacle to the use and the reuse of this resource. These pollutants appear in the water as a consequence of degradation of the phenolic compounds which are used in the synthesis of pesticides, insecticides, drugs, etc. [1,2]. Several methods are used to decontaminate the wastewater such as reverse osmosis, adsorption, solvent extraction and ion exchange. Among all the methods, adsorption is highly effective and economical. The use of commercial activated carbon is a well-known adsorbent for the removal of organic compounds from water and wastewater but the high cost of activated carbon limits its use as an adsorbent in developing countries [3]. Consequently, many investigators have studied the feasibility of various low cost and abundantly available substances for removal of organic compounds from wastewaters [4,5].

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Many domestic and economic activities generate a large quantity of residues, such as coffee residue. Algeria annually consumes between 100 000 and 110 000 tons of coffee and all of these quantities end up in the form of coffee grounds in discharges. This one could be recovered and used to produce activated carbon with good physical and chemical characteristics and low cost, it is an alternative route for the exploitation of this dust.

The physicochemical properties of activated carbons are dependent on the method of activation and the precursor nature.

Various methods of activation have been used to obtain activated carbons from waste products. The so-called chemical activation refers to carbonisation of precursor after addition of substances such as zinc chloride, phosphoric acid, aluminium chloride, magnesium chloride, potassium hydroxide, etc [6] and the commonly used is Zinc chloride. Several authors reported that the main degradation of the lignocellulosic materials takes place in the 200–350°C temperature range. Distillation of heavier hydrocarbons (tar) takes place in the range 350–500°C, and above 500°C, there is little weight loss, thus indicating that the basic structure is already formed. Consequently, if chemical activation is used, one could expect that the activity of the reagent is almost complete at this temperature, this being the main reason why chemical activation is commonly carried out at 450–600°C. The chemical incorporated to the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed. A carbonized product with well-developed porosity may be obtained after appropriate washing [7]. The activation process promotes the formation of the carbon porosity: conversion of already existing micropores to the mesopores as well as formation of new micropores [8].

In general, the adsorption capacity of activated carbon is related to the pore structure, the surface area and the surface chemistry. In the liquid–phase adsorption, the capacity of activated carbon to uptake the aromatic compounds depends on a several factors, these include the intrinsic properties of the solute (polarity, solubility, molecular size, functional groups …), the intrinsic properties of the adsorbent (such as pore structure, functional groups, ash content ….), the temperature of the system and the solution properties (such as pH, initial concentration of the solute) [9,10].

Several organic compounds are frequently found in contaminated water. Among these, phenol and molecules that contain phenolic group, such as salicylic acid are relatively common as contaminants. In wastewaters, it is unusual to find only one pollutant. The multicomponent nature of the mixture presents supplementary complications which involve many factors to be taken into account like interaction between the different adsorbate molecules, both into the water and on the surface [10].

The main objectives of this paper are

- to determine the physico-chemical characteristics of activated carbons prepared from coffee residue such as surface area, pore size distribution, surface functional groups;
- to study the feasibility of activated carbons prepared as an adsorbent for the removals of phenol and salicylic acid
- to study the effect of several parameters such as the contact time, temperature, initial concentration, initial pH, adsorbent dose and particle size on the adsorption efficiency of phenol and salicylic acid on the prepared activated carbon;
- to determine the best-fit kinetic and isotherm model for experimental data by using error analysis.

2. Experimental procedures

2.1. Adsorbent preparation

Coffee residues were provided by coffee houses and households. Zinc chloride of 95% purity was available at the laboratory. Nitrogen gas was industrial grade of 99% purity.

To obtain an activated carbon, the precursor had undergone several treatments as follows and the general schematic diagram for the preparation has been given in Fig. 1.

The waste was washed to remove any impurities and dried. The residue has undergone a chemical activation using Zinc chloride in different activating ratios: 0, 25%, 50%, 75% and 100%. The reagent has been dissolved in 500 mL hot water (85°C) and then mixed with 400 g of coffee residue. The mixture was put in the oven at 85°C and kept during 7 h in order to facilitate the hydratation of the precursor and the swelling of the interior channels of lignocellulosic structure allowing for a better access of the Zinc chloride into the interior of the particles. The temperature was raised to 110°C and the mixture was kept 24 h under this temperature to cause complete evaporation of the water which will force the incorporation of Zinc chloride to the interior of the particles.

The precursor was subjected to the carbonisation at heating rate 10°C/min under nitrogen flow and held at 600°C for 1 h. Resulting carbon was treated with HCl solution (10%) to remove the impregnation salt following by washing with hot distilled water (65°C) to remove the acidity of the carbon and chlorides. The washing operation

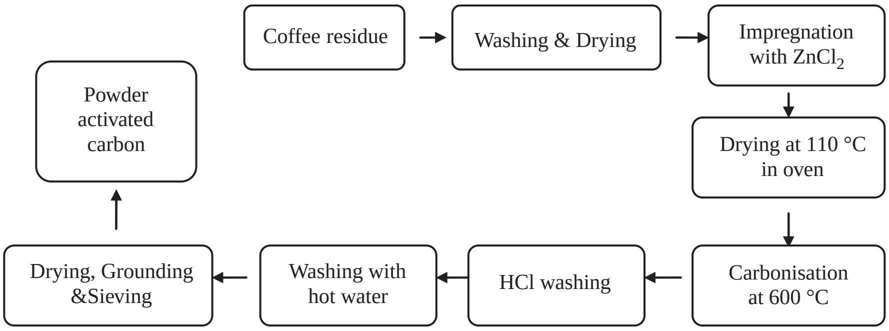

Fig. 1. Schematic presentation for preparation of activated carbon from coffee residue.

is stopped when the conductivity of the washing water reached the conductivity value of the distilled water used (≈7 µs). The resultant activated carbon was dried and ground to particles having an average size of 63 µm.

2.2. Adsorbent characterization

The textural heterogeneity of the prepared carbons was characterized by N_2 adsorption-desorption isotherms measurements at liquid nitrogen temperature (77 K) using Quantachrome Novawin2 Analyser in order to determine the specific surface area and pore volume of the samples (coffee residue and five activated carbons with different impregnation ratios, i.e. 0; 25; 50; 75 and 100%). The surface areas (S_{BET}) were calculated by BET method assuming that the surface area occupied by nitrogen molecule was 0.162 nm^2. The total pore volumes were estimated on the basis of the liquid volume of nitrogen adsorbed at a relative pressure of 0.98. The microporous volumes (pores < 2 nm) (IUPAC, 1985) were determined according to the Dubinin-Radushkevich equation (D-R plots) [12,13]. The microporous volume (V_{micro}) and the external surface (S_{ext}) were obtained by *t*-plots method. The microporous surface area (S_{micro}) was calculated by subtracting the external surface area from the BET surface area [12,13]. The mesoporous volume (V_{mes}) was obtained by deducing the microporous volume from the total pore volume.

2.3. Evaluation of surface chemistry

Two hundred gram of activated carbon (AC) sample were immersed in 250 mL Erlenmeyer flasks containing 50 mL of NaOH and HCl solutions at a concentration of 0.1 N aqueous solutions. The glass vessel containing the solution and the sample was sealed and then shaken for 48 h at 150 rpm. Then, after filtration of the solutions, excess base and acid of the filtered solutions (10 mL) were titrated with HCl and NaOH, respectively. The number of acidic sites (acidic functions) and the number of basic sites (basic functions) were calculated from the amount of HCl and NaOH consumed by the titration, respectively [14].

2.4. pH point of zero charge (pHPZC) measurements

The point of zero charge of the activated carbon was determined by using the method reported by Rivera-Utrilla et al. [15].

The point of zero charge was determined from acid–base titration. Aliquots with 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH was adjusted with addition of 0.01 M solutions of NaOH or HCl. When the pH value was constant, 0.15 g of carbon sample was added to each flask and it was shaken for 24 h. Blank tests were also made without sample to eliminate the influence of CO_2 on pH. The pH_{pzc} value is the point where the curve pH_{final} versus $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

2.5. Chemicals

All the chemicals used were of analytical reagent grade. Stock salicylic acid and phenolic solutions were prepared by dissolving 0.72 g/L and 5 g/L respectively in 1000 mL of distilled water. Working standard solutions of initial concentrations ranging between 10 and 110 mg/L were prepared by progressive dilution of stock salicylic acid (SA) and phenolic solutions. The pH of the tested solutions was adjusted to the required value with 2 N H_2SO_4 or 1 N NaOH solutions before the experiments.

2.6. Batch experiments

To study the effect of important parameters like Zinc chloride/coffee residue weight ratio, pH, contact time, initial concentration of phenol or salicylic acid 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 (1 L) 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. The residual phenol or salicylic acid concentration in the filtrate was determined by finding out the absorbance at the characteristic wavelength using UV/vis spectrophotometer (model JENWAY 6305 UV/vis.). A standard solution of phenol or salicylic acid 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}) was determined from this plot. The λ_{max} for phenol and salicylic acid were found to be 270 and 303 nm, respectively. These wavelengths were used for preparing the calibration curves between absorbance and the concentration of the phenol or salicylic solution.

The percentage removal of phenol and equilibrium adsorption uptake q_e (mg/g) was calculated using the following relationships:

$$\%removal = 100\frac{(C_0 - C_e)}{C_0}$$

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

where C_0 is the initial sorbate concentration (mg/L), C_e the equilibrium sorbate concentration (mg/L), V the volume of the solution (L) and m is the mass of the adsorbent (g).

2.7. Adsorption isotherms and modelling-theoretical background

Several models have been used in the literature [16] to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models.

2.7.1. Langmuir isotherms

The Langmuir (1918) suggested a theory to describe the monolayer coverage of adsorbate over a homogeneous adsorbent surface. The basic assumption is that sorption takes at specific homogeneous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place at that site. Thus, an equilibrium value can be reached and the saturated monolayer curve can be expressed as [17,18]:

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

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $q_m$is the maximum adsorption capacity (mg/g), b is the Langmuir constant and C_e is the equilibrium concentration of the solute in the bulk solution (mg/L).

Equation (3) can be linearized as shown in follow [17]:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right)C_e + \frac{1}{bq_m} \tag{4}$$

where b and q_m are calculated by plotting C_e/q_e versus C_e.

The isotherm shape may be considered with a view to predict if an adsorption system is favourable or unfavourable. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless constant R_L [19]:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where R_L is the equilibrium parameter which is a direct function of the Langmuir constant b. The parameter RL indicates the shape of the isotherm accordingly:

$R_L > 1$, unfavourable;
$R_L = 1$, linear;
$0 < R_L < 1$, favourable;
$R_L = 0$, irreversible.

2.7.2. Freundlich isotherm

Freundlich isotherm was also applied for phenol and salicylic adsorption on activated carbon. Freundlich isotherm model is given by the following equation [17]:

$$q_e = K_F C_e^{1/n}, \tag{6}$$

where K_F and n are Freundlich isotherm parameters indicating the adsorption capacity and adsorption intensity, respectively. They were determined by plotting ln q_e versus ln C_e which is given as follow:

$$\ln q_e = \ln K_F + (1/n)\ln(C_e) \tag{7}$$

3. Results and discussion

3.1. Characterization of the Activated Carbons

The N_2 adsorption—desorption isotherms by swinging N_2 pressure at 77 K of activated carbons obtained

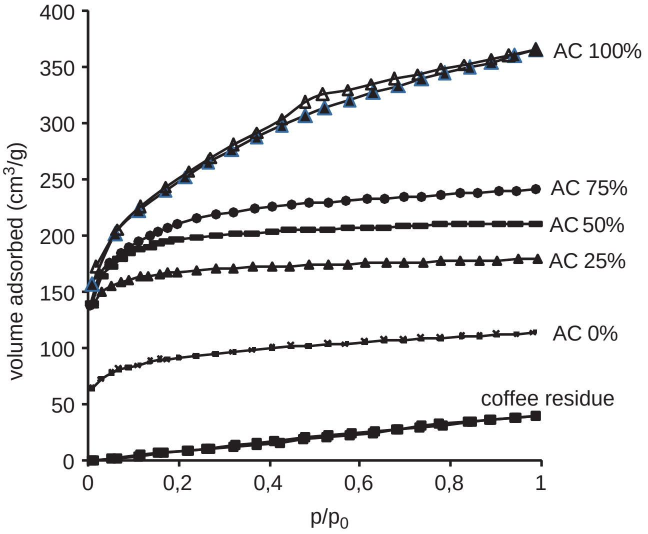

Fig. 2. Adsorption and desorption isotherms of nitrogen at 77 K for prepared carbons (PAC).

from various zinc chloride/coffee residue ratios are show in Fig. 2. According to the IUPAC classification, coffee residue exhibits adsorption isotherm of type III corresponding to macroporous sorbent with strong adsorbate-adsorbent interactions. Carbons prepared with zinc chloride/coffee residue ratios varying from 0% to 75% exhibit steep type I isotherms. Adsorption curve rose sharply at relative pressure P/P_0 less than 0.10 and then approached plateau with increasing of relative pressure. When the zinc chloride/coffee residue ratio increased up to 100% a gradual increase in isotherm slope at relative pressure higher than 0.1 and an hysteresis loop at a high relative pressure indicating the existence of mesopores, were observed [13,20].

The BET surface area (S_{BET}), external surface area (S_{ext}) and microporous surface area (S_{micro}), total pore volume ($V_{0.98}$), mesoporous volume (V_{mes}) and microporous volume (V_{micro}) results obtained by applying the BET equation to nitrogen adsorption at 77 K and D-R equation are listed in Table1.

It appears that the activated carbons include micropores and mesopores, but the percentage of micropores is greater than that of the mesopores according to the results given in Table 1, so, they are principally microporous carbons.

Table 2 presents the amounts of acidic, basic and the ratio of the numbers of acidic to basic groups. It can be observed that all the prepared carbons have acidic character and the carbon prepared with ratio equal to 25% has the lower one.

3.2. *Effect of the activating ratio*

The efficiency of the prepared carbons has been tested by subjecting them to adsorption of molecules of phenol and salicylic acid in the following conditions: $C_0 = 30$ mg/L, pH 3 at room temperature ($T = 25°C$) and in the presence of 1 g of carbon. The results are reported in table 3.

Table 1
Porous structure parameters of the activated carbons.

Carbons	$V_{0.98}$ (cm^3/g)	V_{micro} (D-R) (cm^3/g)	Microporosity ($V_{micro}/V_{0.98}$)(%)	V_{mes} (cm^3/g)	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{micro} (m^2/g)
Non-activated (0%)	0.18	0.13	75	0.04	298	1	248
AC 25	0.28	0.27	96	0.01	520	6	514
AC 50	0.33	0.30	92	0.023	617	5	612
AC 75	0.37	0.31	82	0.07	680	12	668
AC 100	0.48	0.34	70	0.15	810	17	793

Table 2
Surface groups of activated carbons.

Carbon	Acidic functions (mmol/g)	Basic functions (mmol/g)	Acid functions/Basic functions
Non-activated (0%)	4.3	0.4	10.8
(AC) 25	3.3	1.7	1.9
(AC) 50	3.4	1.4	2.5
(AC) 75	3.7	1.0	3.8
(AC) 100	3.6	0.3	11.2

Table 3
Phenol and Salicylic acid (SA) adsorption tests onto prepared carbons (C_0 = 30 mg/L, T= 25°C, pH 3 and 1 g/L of carbon).

Carbon	(%) phenol removal	(%) SA removal	Microporosity (V_{micro}/V_{tot})(%)	Acidic func/Basic func
Non-activated (0%)	42	66	75	10.6
AC 25	68	97	96	1.9
AC 50	59	94	92	2.5
AC 75	58	95	82	3.8
AC 100	58	95	70	11.2

These values show that the activated carbon prepared with an activation ratio of 25% is the most successful compared to the other carbons, which can be explained by the presence of a large microporosity (96%) in addition to the smaller ratio of the numbers of acidic to basic groups (ratio = 1.9). This result is in agreement with those of Koganovski [21] who reported that the adsorption of phenol at low equilibrium concentrations on an activated carbon is not only depending on the pore volume of the activated carbon, but also on the ratio of the numbers of acidic to basic groups. The larger is this ratio, the lower is the adsorption.

Consequently, the activated carbon prepared with an activation ratio of 25% was used in all the following study. It will be designated as PAC.

3.3. Phenol and salicylic acid adsorption

3.3.1. Effect of contact time and initial concentration on adsorption of salicylic acid and phenol individually

The effect of contact time on removal of phenol and salicylic acid by carbon developed from coffee residue (PAC) can be seen in Figs. 3 and 4, respectively. Since all curves corresponding to the phenol and salicylic adsorption onto the PAC present the same shape, we present then figures corresponding to 25°C.

Experimental studies were carried out at 20, 25, 30, 35 and 40°C with varying initial concentrations of salicylic acid and phenol from 10 to 110 mg/L using 0.5 g/L of adsorbent dose at pH 3. Equilibrium adsorption was established within 10 min for both molecules and a larger amount of both phenol and salicylic acid was removed in the first 5 min of contact time for all adsorption systems. This result is important because equilibrium time is one of the parameters for economical wastewater treatment plant application. According to these results, the agitation time was field at 60 min for all experiments to make sure that equilibrium was attained.

Figs. 3 and 4 show that the initial phenol and salicylic acid concentration provides an important driving force to overcome all mass transfer limitations of the solutes between the aqueous and solid phase. According to the precedent figures, it was indicated that q_e value increased with increasing initial concentration.

It was also observed that a much higher amount of salicylic acid than phenol was adsorbed at equilibrium onto prepared activated carbon for the same initial

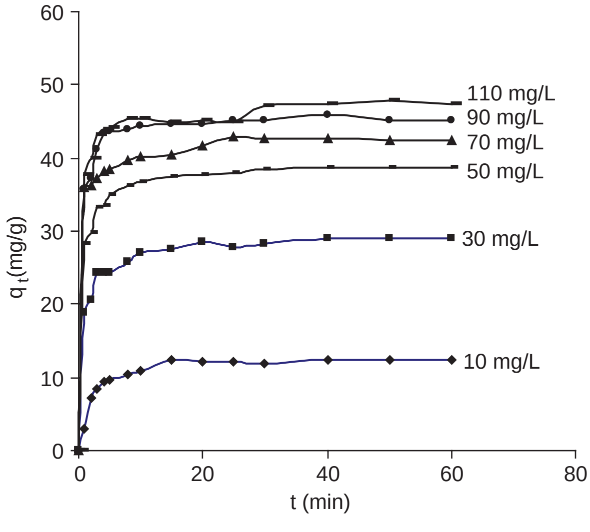

Fig. 3. Effect of contact time and initial concentration on phenol adsorption.

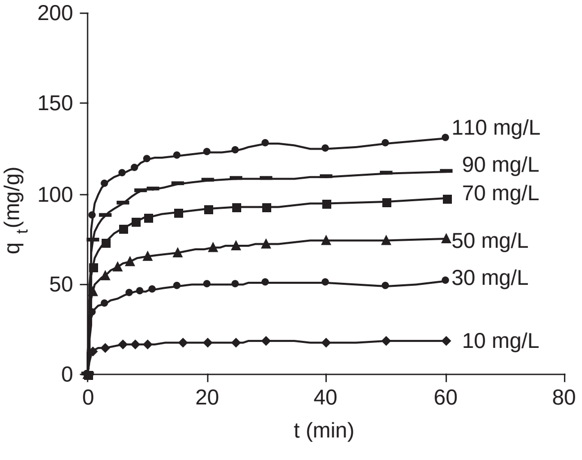

Fig. 4. Effect of contact time and initial concentration on salicylic acid adsorption.

concentration. This indicates that salicylic acid presents more affinity than phenol toward the carbon because of the difference in the solubility value, since phenol solubility (83.5 g/L at 20°C in water) [22] is greater than salicylic acid one's (2 g/L at 20°C in water) [23].

3.3.2. Effect of temperature

A temperature has an effect on the adsorption capacity of the adsorbent since the sorption capacity decrease when the temperature increases (see Figs. 8 and 9). Therefore, the process is exothermic and so, the adsorption is physic [24]. Moreover, the temperature effect was more marked when the adsorbate was phenol.

3.3.3. Effect of carbon dose

The experimental results revealed that salicylic acid or phenol removal efficiency increases up to the optimum dosage, beyond which the elimination efficiency does not change with the adsorbent dosage (Fig. 5). As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial salicylic acid or phenol concentration, because for a fixed initial solute concentration, adsorbent dose provide a greater surface area or more adsorption sites. It is evident that for a quantitative removal of salicylic acid (98%), 1 g/L of activated carbon is required and for a quantitative removal of phenol (84%), 1.5 g/L of activated carbon is required.

3.3.4. Effect of particle size

The influence of adsorbent particle size was investigated at pH 3, salicylic acid or phenol initial concentration of 30 mg/L, adsorbent concentration of 1 g/L and 25°C by using five selected particle sizes (Fig. 6). The results show that the amount of acid adsorbed increases from 21.46 to 29.03 mg/g and from 15.34 to 20.89 mg/g for phenol when the adsorbent particle size decreases from 200 to 63 µm. This behaviour can be assigned to the fact that specific surface area for adsorption increases with decreasing particle size [25]. In the following text, all sorption experiments are conducted with activated carbon prepared from coffee residue with 63 µm particle size.

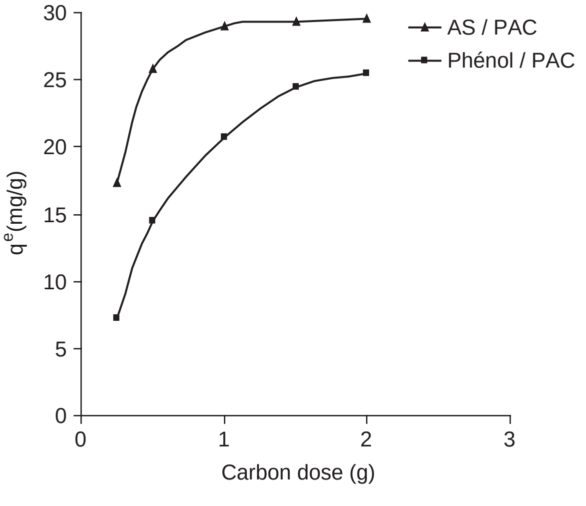

Fig. 5. Effect of carbon dosage on the salicylic acid and phenol adsorption.

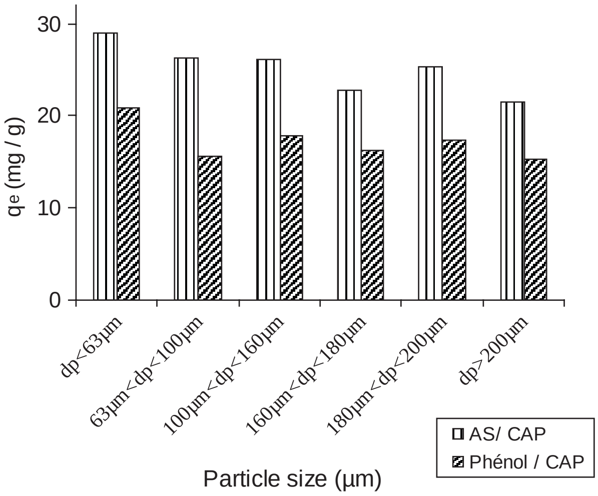

Fig. 6. Effect of particle size of carbon onto the removal of salicylic acid or phenol by PAC.

3.3.5. Effect of initial pH

In general, solution pH not only influences the properties of the adsorbent surface, but also affects the adsorbate speciation of different compounds in solution .The change in pH affects the adsorptive process through dissociation of functional groups on the solid surface active sites. Therefore, this leads to a change in reaction kinetics and equilibrium characteristics of adsorption process. It is observed that the surface adsorbs anions favourably at lower pH due to presence of H^+ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions [27].

The possible interactions between the carbon surface and the aromatics (SA, phenol) are: dispersion effect between the π-electrons in phenolic compounds and π-electrons in carbon structure; electron donor-acceptor interaction between the aromatic ring and the basic surface sites and electrostatic attraction and repulsion when ions are present in the medium.

To study the influence of pH on the adsorption capacity of prepared activated carbon for phenol and salicylic acid, experiments were performed at initial

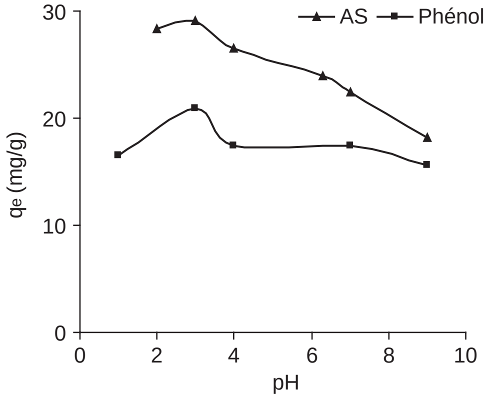

Fig. 7. Effect of pH onto the removal of salicylic acid and phenol by PAC.

concentration of 30 mg/L using different solutions pH values changing from 1 to 9 (Fig. 7). It is seem from this figure that adsorption for both SA and phenol involve an optimum corresponding to pH 3 and it is noted that the uptake decreases at lower (pH < 3) as well as higher pH values (pH > 3). At lower pH ($pH < pH_{PZC} = 4.47$), the activated carbon surface is positively charged. SA is being as mixtures of two forms in water due to partial ionization ($pKa_1 = 2.97$) [28] but phenol ($pK_a = 9.89$) is in neutral form [27]. SA possessing very low water solubility is adsorbed on the activated carbon to a greater extent than phenol. SA uptake is due to dispersion interaction which predominated and electrostatic attraction between the carbon surface positively charged and the salicylate ions. Phenol interacts with carbon surface according to dispersion interaction between the π-electrons in phenol and π-electrons in carbon structure or electron donor–acceptor interaction between the aromatic ring and the basic surface sites [27].

At pH equal to $pH_{PZC} = 4.47$, the carbon surface is almost neutral. SA is still in the two forms: anionic and neutral states, having an —OH substituent (in ortho position to carboxylate) that possesses two lone pairs of electrons on O atom, shows the highest rate of adsorption via dispersion and hydrogen bonding interactions. However, an intramolecular hydrogen bonding is also expected in SA [28]. Phenol still in neutral state interacts according to dispersion interaction between the aromatic ring and the electrons of the carbon structure and hydrogen bonding interactions [27].

At higher pH ($pH_{PZC} = 4.47 < pH < pH9$), the carbon surface is negatively charged and SA is mainly in anionic state. So, the electrostatic repulsion between like charges lowers the adsorption capacity [28]. In the same range of pH, phenol still in neutral form interacts with the carbon surface via dispersion interaction, consequently, the rate of adsorption remain unchanged. At pH close to 9.89, carbon surface is charged negatively and some of phenol molecules may exist in anionic form so, electrostatic repulsion is resulting and the decrease of the rate of adsorption is observed. V. C. Srivastava et al. [26] reported that competitive adsorption of water molecules must also be considered.

Subsequent studies are conducted at pH 3.

3.4. *Kinetics of salicylic acid and phenol adsorption*

Adsorption process depends on contact time between absorbent and adsorbate. The study of the effect of contact time onto the adsorbed quantity (phenol, SA) shows that this later increases with the contact time. Phenol and Salicylic acid adsorbed by PAC increased linearly with time in the beginning and then slowly until reaching equilibrium. To analyse the adsorption kinetics of the two molecules, correlations between adsorbed amounts and time were looked for through the testing of mathematical expressions corresponding to pseudo-first-order (Lagergren's equation) and pseudo-second-order models [5,18,28].

3.4.1 Pseudo first-order model or Lagergren's equation

This model is widely used for adsorption in liquid phase [5,28]. Once rearranged and linearised, it presents as follow:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303} t, \tag{8}$$

where q_e (mg/g) and q_t (mg/g) are the quantities of the adsorbed substance at equilibrium and at time t, respectively and k_1 (min^{-1}) is the rate constant. Plot of log ($q_e - q_t$) (Eq.8) versus t don't give a straight line consequently; this results show that the adsorption of both salicylic acid and phenol onto PAC don't fit the pseudo-first-order model.

3.4.2. Pseudo second-order model

This model [5,18,28] is represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where q_t (mg/g) and q_e (mg/g) represent the amounts of adsorbed substance at time t and at equilibrium respectively, and k_2 is the corresponding kinetic constant (g/mg.min). The applicability of this model can be examined by linear plot of t/q_t (Eq. 9) versus t (not shown). Our results (Table 4) showed high correlation coefficients (R^2) and similarity between the experimental capacities

Table 4
Pseudo second-order rate constant k_2, the correlation coefficient R^2 and uptake at equilibrium q_e, experimental and calculated using the model.

Molecule	T (°C)	C_0 (mg/L)	k_2 (g/mg min)	q_e(cal) (mg/g)	q_e(exp) (mg/g)	R^2
–	–	10	0,069	18,48	18,14	0,999
–	–	30	0,022	51,55	51,58	0,999
SA	–	50	0,011	75,76	74,90	0,999
–	25	70	0,012	98,04	97,08	0,999
–	–	90	0,019	112,35	112,10	1
–	–	110	0,017	126,58	127,57	0,999
–	–	10	0,063	14,65	13,41	0,999
–	–	30	0,051	31,45	29,86	0,999
Phenol	–	50	0,050	38,02	39,04	1
–	20	70	0,051	44,05	44,25	0,999
–	–	90	0,078	48,78	48,50	0,999
–	–	110	0,081	48,78	48,50	0,999

at equilibrium (q_e (exp)) and the predicted from the model q_e (cal)) for both salicylic acid and phenol. These results suggest that the pseudo-second-order model fits better the experimental data ($R^2 \geq 0.999$).

3.5. Adsorption isotherms – Modelling of the adsorption isotherms

The adsorption studies were carried out at 20, 25, 30, 35 and 40°C to determine the adsorption isotherms. The isotherms for the adsorption of phenol and salicylic acid on the prepared activated carbon at optimum pH and different temperatures are shown in Figs. 8 and 9, respectively. The adsorption of both the adsorbates on the activated carbon used decreases with an increase in the temperature reflecting the exothermic nature of the reaction. According to Giles' classification [29] the isotherms may be classified as L-type. The L-type isotherms suggest the completion of monolayer on the surface of adsorbent.

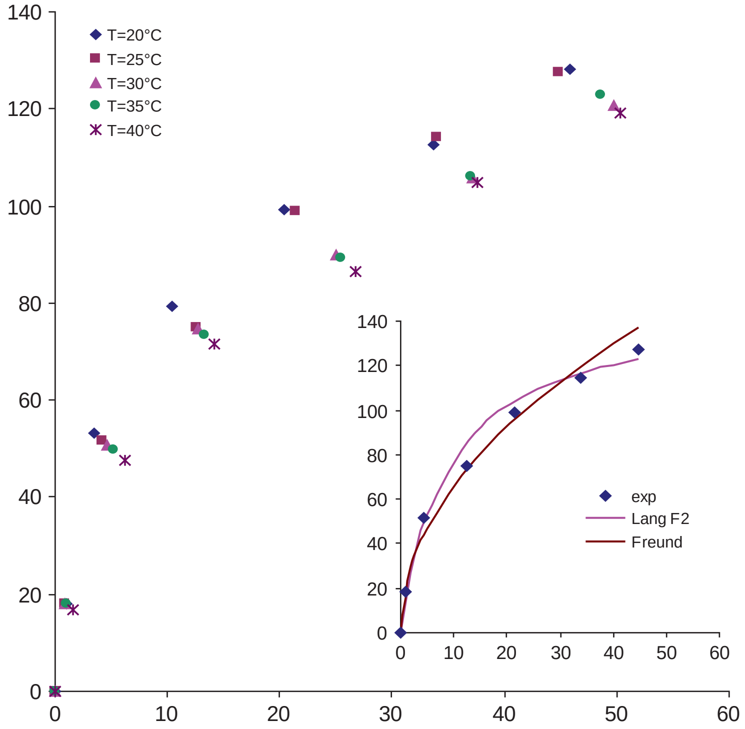

Fig. 8. Experimental adsorption isotherms of SA onto PAC and comparison of experimental and predicted adsorption isotherms according to Langmuir and Freundlich models.

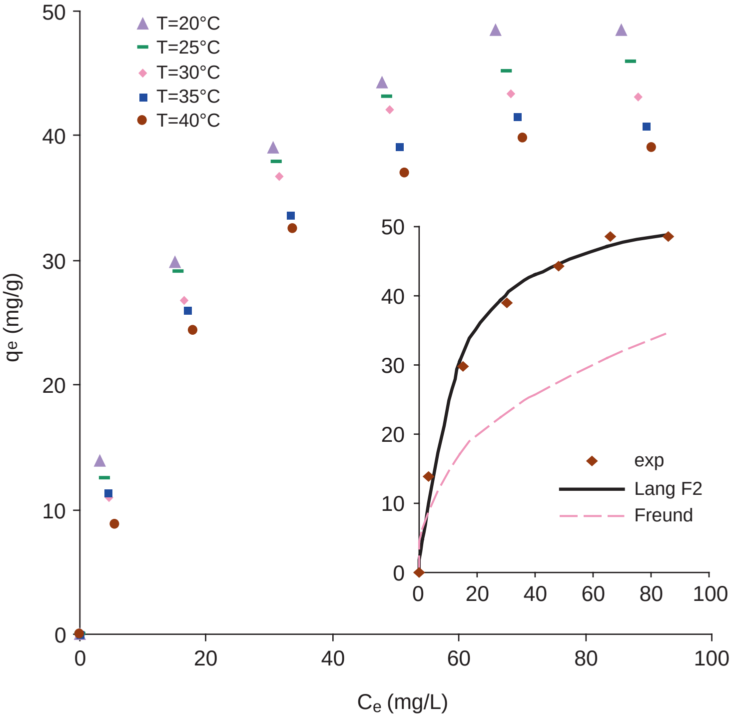

Fig. 9. Experimental adsorption isotherms of phenol onto PAC and comparison of experimental and predicted adsorption isotherms according to Langmuir and Freundlich models.

3.5.1. Langmuir isotherm

Values of Langmuir constants (Eq. 4) are presented in Table 5 for the adsorption of phenol and salicylic acid on prepared activated carbon.

In order to check the validity of the model, it is interesting and essential to recalculate the adsorbed amount using the calculated constant parameters determined using the linearized form and the average percentage error (P (%)):

$$P(\%) = \left(\frac{100}{N}\right)\sum\left(\frac{\left|q_e^{exp} - q_e^{pred}\right|}{q_e^{exp}}\right) \tag{10}$$

where q_e^{exp} and q_e^{pred} are the experimental and predicted adsorption amounts of the studied substances at any time t and N is the number of data points: the lower is the value of P (%), the better is the fit.

The average percentage error (Eq.10) and the simulated curve at optimal temperature determined using Langmuir model are given in Table 5 and Figs. 8 and 9. The points represent experimental data and the line represent Langmuir isotherm model. It is clear from the average percentage error shown in table 5 that the isotherm data fits the Langmuir equation well (Figs. 8, 9). Hamdaoui et al. [17] reported that linear correlation coefficient showed the fit between experimental data and linearized form of isotherm equation while the average percentage error (P(%)) (Eq.10) indicated the fit between the experimental q_e^{exp} and predicted q_e^{pred} values of sorption capacity used for plotting isotherm curves. It is not appropriate to use the coefficient of correlation of linear regression method for comparing the best-fitting isotherms.

Table 5
Constants of Langmuir and Freundlich isotherms for the adsorption of salicylic acid and phenol.

Modèle/Paramètres	Phenol	Salicylic acid
	20°C	25°C
q_e (exp)	48,50	127,57
Langmuir		
b (L/mg)	0.089	0.112
q_m (mg/g)	55.248	147.059
R^2	0.997	0.984
R_L	0,097–0,540	0,075–0,472
P (%)	12.585	14.089
Freundlich		
K_F	0.147	21.223
n	2.575	2.038
R^2	0.974	0.978
P (%)	27.392	15.206

Calculated R_L value (Table 5) according to Eq. (5) indicated that adsorption of phenol and salicylic acid on prepared activated carbon was favourable at all initial concentrations used.

3.5.2. Freundlich isotherm

The calculated Freundlich isotherm constants obtained from Eq. (7) and the corresponding coefficient of correlation and the average percentage errors values were shown in Table 5. In spite of the higher coefficients of correlation (R^2) obtained using Freundlich model, this model does not describe perfectly the equilibrium data of phenol (Fig. 8) because of the higher values of average percentage error. The salicylic acid experimental data can be simulated by the Freundlich equation (Fig. 9) since the value of average percentage error calculated for this one is close to those obtained for Langmuir one (Table 5).

We can conclude that the Langmuir model describes perfectly the sorption isotherms of phenol whereas the salicylic acid experimental data are correctly fitted by both Langmuir and Freundlich models but the Langmuir equation seems slightly better than that of Freundlich.

3.6 Adsorption competition between phenol and salicylic acid

When more than one organic compound is present in solution, they may compete with each other for adsorption sites.

In order to examine the influence of salicylic acid presence in solution, on the efficiency of phenol uptake an adsorption test was realised in the following conditions: initial concentration of phenol (C_{0ph} =10 mg/L), initial concentration of salicylic acid (C_{0SA} = 30 mg/L), pH 3, T = 25°C and 1 g of activated carbon per litre of solution.

The simultaneous analysis of binary mixture was achieved spectroscopically by recording the total absorbances at two wavelengths, 270 and 303 nm, the former being the absorption maximum of phenol (A_{ph}) and the later being the absorption maximum of salicylic acid (A_{SA}).

The mixture absorbance at 270 nm A^{270}_{mix} can be given by

$$A^{270}_{mix} = \varepsilon^{270}_{SA}.C_{SA} + \varepsilon^{270}_{ph}.C_{ph}$$

And that at 303 nm A^{303}_{mix}, , can be given by

$$A^{303}_{mix} = \varepsilon^{303}_{SA}.C_{SA} + \varepsilon^{303}_{ph}.C_{ph}$$

As phenol does not absorb at 303 nm, then

$$C_{SA} = A^{303}_{mix}/\varepsilon^{303}_{AS}$$

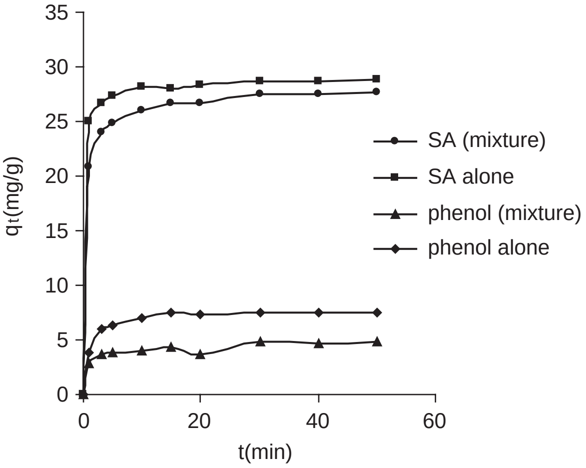

Fig. 10. Adsorption of phenol and salicylic acid onto PAC from the binary and single systems.

$$C_{ph} = (A^{270}_{mix}/\varepsilon^{270}_{ph}) - (A^{303}_{SA}\varepsilon^{270}_{SA}/\varepsilon^{270}_{ph}\varepsilon^{303}_{SA}).$$

The evolution of the concentrations of the two species with time was checked and the plot of the variation of the adsorbed quantity of each molecule in the mixture with time was done and was compared with those obtained when each molecule was alone. Results from competition experiment in this study are shown in Fig. 10. The phenol and salicylic acid adsorption onto prepared activated carbon are about 30% and 5% respectively, higher than that obtained in case of mixtures. One type of the molecule present interfered with the uptake of another one in the system and the adsorbate uptake was lower than that in the single system. It is indicated that the functional groups on the surface of prepared activated carbon had a relatively stronger affinity for salicylic acid than phenol. This behaviour is attributed to the difference in acid and phenol affinity towards the activated carbon

4. Conclusion

The results of the present study show that activated carbon prepared from coffee residue is an effective adsorbent for the elimination of organic compounds such as salicylic acid and phenol from aqueous solutions. The salicylic acid and phenol uptake depend not only on the physics characteristics of the adsorbent (micropore volume) but also on the chemical properties of the carbon (the ratio of acid to basic groups).

The effect of different parameters related to the adsorbent characteristics and to properties of the adsorbed molecules as well as the operative conditions corresponding to salicylic acid and phenol adsorption onto activated carbon prepared from coffee residue was investigated. The obtained results showed that adsorption capacity of the prepared carbon was considerably affected by the initial phenol and salicylic acid concentration, initial pH and the carbon dose. The size of particle affected the phenol and acid adsorption in the selected particle sizes. It was also observed that the phenol and salicylic acid adsorption decrease with the temperature which indicates that the process is exothermic and then, the adsorption is physic.

The adsorption capacity of prepared activated carbon for phenol (at 20°C) and for salicylic acid (at 25°C) were 55 mg/g and 128 mg/g, respectively

The adsorption kinetics could be very adequately fitted by a pseudo second-order equation. The phenol and salicylic acid adsorption isotherms could be correctly adjusted by Langmuir's model.

Sorption in single system is more effective than the one in binary system. It may be concluded that activated carbon prepared from coffee residue may be used for the individual and simultaneous removal of phenol and salicylic acid from phenolic contaminant effluents.

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