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Effect of Texture and Surface Chemistry of Palm Nut Hull Activated Carbon on the Adsorption of Pigments and Free Fatty Acids from Vegetable Oils

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Abstract: Activated carbons were produced from palm nut hull, which is a waste material of palm oil extraction industries. Activated carbons having various pore size distributions and surface composition were obtained by conventional carbonization method via the sulphuric acid solution pre-treatment method. The surface areas, mesopore volume and -OH groups of activated carbons increase with the increases of sulphuric acid solution concentration. The activated carbons obtained were tested for the adsorption of pigments and free fatty acids from palm oil and shea butter. It comes out from this study that the amount of adsorbate (i.e. pigments and free fatty acids) fixed increases with the increase of the adsorption temperature and with the increases of mesopore volume. Intraparticle diffusion, pseudo-first-order and pseudo-second-order kinetics models were used to analyze the kinetics data obtained at different temperatures (temperature range 60 °C to 90 °C). Among the kinetics models used, the pseudo-second order was the best applicable model to describe the adsorption of oil pigments and free fatty acid onto activated carbons. The activation energies obtained by applying the Arrhenius equation for the adsorption of pigments were low (i.e. less than 40 $kJ\cdot mol^{-1}$ for the both vegetables oils), indicating that the adsorption could be assigned to physisorption.

Key words: Palm nut hull, activated carbon, pores size distribution, surface composition, vegetable oil decolourisation.

1. Introduction

Crude vegetables oils possess minor components which among them are phospholipids, hydroperoxides, free fatty acids and pigments (carotenoids, chlorophyll, gossypol and related compound). Colour and free fatty acid content are important quality parameters of edible oil. They are used as basis for its acceptability or rejection in trading. Furthermore, lighter coloured oils are preferred by consumers because they believe that these oils have fewer negative effects on the organoleptic characteristics of the food which they are preparing [1].

The refining process involved the removal of colouring pigments. The removal is achieved by adsorption of oil pigments onto an adsorbent. Many types of adsorbents have been tested for the removal of pigments from vegetables oils [2-6]. However, the most effective adsorbents for pigments adsorption from vegetables oils are montmorillonite based activated clay [7-9], but activated carbon has also been tested [4, 10]. Vegetables oil extraction and refining factories are the main industries in Cameroon, but they cover their need for adsorbent by the import of activated clay. Those industries also produced a

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large number of cellulosic by-products, which can be transformed into activated carbon [11-14]. Palm nut hull is one of those cellulosic by-products. Up to now, this palm nut hull is used as fuel or waste in the field. But it will be more appropriate to transform this cellulosic substance to activated carbon which is a more valuable material.

It has been reported that texture and surface chemistry of activated carbon significantly influence the adsorption capacity of organic matters from solution [15-18]. However this has not been tested for the adsorption of pigments and other unwanted compounds from crude vegetable oil. Several researchers have pointed out that texture (i.e., surface area and pore size distribution) and surface chemistry of activated carbons depend strongly on the starting material and on the pre-treatment method [11, 13, 15, 18, 19]. In this work the effects of acid treatment of the palm nut hull, on the composition, texture and surface chemistry of activated carbons are examined, and the influences of those properties on the adsorption characteristics of pigments and free fatty acids of shea butter and palm oil are investigated. The scope of this work encompasses the valorisation of cellulosic by-product as well as the improvement of the quality of local produced vegetable.

2. Materials and Methods

2.1 Materials

Vegetables oils used in this work were shea butter and the olein portion of fractioned palm oil. The olein portion of fractioned palm oil was provided by SOCAPALM Co. (Cameroon). The shea butter used was extracted at the laboratory by the Soxhlet method. The solvent used was cyclohexane. The samples of shea fruit used for this purpose were obtained from Tchabal, a village located at 30 km from the town of Ngaoundéré in the Adamawa region of Cameroon (North latitude 07°33.953′, West longitude 13°33.804′).

The adsorbents used in the present study were palm nut hull activated carbons. The palm nut hull was a gift of SOCAPALM Co. (Cameroun). The palm nut hull samples were washed several times with pure water (MiliQ ultra filtration), dried in open air and then ground. The obtained powder was sieved over a 50 µm mesh sieve. Before carbonisation, samples of the powdered palm nut hull (PCP) were pre-treated with solutions of sulphuric acid. This pre-treatment was carried out by mixing the solid material with solutions of sulphuric acid in the mass to volume ratio of 20 g/100 mL. The resulting slurry was introduced in a 250 mL round bottle flask and heated under reflux for two hours. After cooling at room temperature, suspensions were filtered and the collected solid phases were washed several times with pure water (MiliQ ultra filtration) until the silver nitrate test for sulphate ion was negative. Three different solutions of sulphuric acid were used and the activated carbons obtained were labelled accordingly. That is CA1N, CA2N and CA3N when the original palm nut hullpowder was pre-treated with sulphuric acid solutions of concentration 1 N, 2 N and 3 N respectively. The untreated sample was labelled CA0N.

All the chemicals used herein, namely sulphuric acid, glacial acetic acid, cyclohexane, diethylether, ethanol, chloroform, potassium iodide, potassium hydroxide and sodium sulphide were analytical grade reagents purchased from Prolabo (Rumania).

2.2 Methods

The carbonisation was carried out by heating palm nut powder hull under a stream (5 mL/s) of ultra pure (99.999%) argon gas in a horizontal tubular furnace. The temperature of the furnace was kept at 750 °C and the heating period was two hours. The furnace was left to cool to room temperature under the argon stream. The obtained material was washed with 100 mL of hydrochloric acid solution 0.27 N. Thereafter the activated carbons were washed several times with pure water (MiliQ ultra filtration) until the silver nitrate test for chloride ion was negative. The resulting suspension was dried in the oven at 105 °C until the complete evaporation of water. The dry activated carbons were kept in a close glass bottle flask before use.

The adsorption of pigments and free fatty acids from vegetable oil onto activated carbons was performed using bath experiments. An amount of 10 g of vegetable oil was placed in a 100 mL conical flask. The flask was stoppered and then placed in a shaken (80 cycles/min.) water bath thermostated at the predetermined temperature, that is 60 ± 1 °C, 70 ± 1 °C, 80 ± 1 °C or 90 ± 1 °C. When the content of the flask had reached the required temperature, usually not more than 15 min, a known amount of adsorbent was added to the flask which was then shaken for the desired time. Thereafter, the content of the flask was filtered through Whatman No. 1 filter paper and the concentration of pigment and free fatty acids in the filtrate were determined as described below. The amount of pigment and free fatty acids adsorbed was determined by difference between the initial and the final concentration. The adsorbent was pre-dried overnight at 105 °C before use.

The evaluation of the amount of pigment removed was made by UV-visible spectroscopy. The samples were diluted in cyclohexane. For this purpose 0.05 g of shea butter was diluted in 5 mL of solvent, while for palm oil 0.10 g of oil was diluted in 5 mL of cyclohexane. The absorbance of the diluted sample was determined at the maximum absorption wave length using cyclohexane as reference. The UV-visible absorption spectra of vegetable oil were first recorded. The maximum absorption bands were 297.0 nm and 472.5 nm for shea butter and palm oil respectively. The relative amounts of pigment adsorbed per gram of adsorbent were calculated according to the following equation:

$$X = \frac{A_0 - A}{A_0 m} \tag{1}$$

where A_0 and A are the absorbance of the crude and decolourised oil respectively and m is the mass of adsorbent used.

Acid value is usually used in the assessment of the quality of vegetable oil. Indeed a high acid value is an indication of the poor quality of a vegetable oil sample. Therefore the acid values were determined for crude oil and decolourised according to the AFNOR methods [20].

The chemical composition of the superficial layer of adsorbent particles was determined by X-ray photoelectron spectroscopy (XPS). The analysis was carried out in a differentially pumped load-lock rapid sample entry ultra-high vacuum analysis chamber. The residual pressure was 10-100 torr.

The X-ray diffraction spectra were recorded on disoriented samples at the rate of 0.02° 2θ/s.

Nitrogen adsorption and desorption isotherms were determined at -195 °C with ASAP 2010 from a Micromeritics Instrument. Prior to adsorption, samples were out gassed overnight at 120 °C and under a residual pressure of 0.01 Pa. The specific surface area was calculated by applying the BET equation to the adsorption isotherm. The pore size distribution was calculated on the desorption branch using the numerical integration method of Barrett-Joyner-Halenda (BJH) [21], assuming a cylindrical pore shape.

Infrared spectra were recorded using Perkin Elmer 2000 Fourier Transform IR spectrometer equipped with an MCT detector (6,000-600 cm^{-1}) cooled at 77 K and in diffuse reflectance mode. The activated carbon was diluted in a KBr matrix.

3. Results and Discussion

3.1 Adsorbents Characteristics

The adsorbents characteristics are depicted in Table 1. It is observed that the palm nut hull powder (PCP) has the highest pH whereas the activated carbon CA3N has the lowest pH value. There is a steady but progressive acidification of the activated carbon as the concentration of the acid solution used for the

Table 1 Characteristics of adsorbents.

	Adsorbent				
	PCP	CA0N	CA1N	CA2N	CA3N
pH	7.39	7.45	6.94	6.78	6.64
Ash content (%)	21.12	4.00	5.82	6.12	6.52
Moisture content (%)	18.05	8.04	7.25	7.11	7.05
Zeta potential	nd*	12.42	-17.15	-20.04	-24.12
C (%)	69.13	88.25	87.31	85.68	85.02
O (%)	3.51	4.73	5.51	8.61	11.23
H (%)*	0.56	0.72	1.04	1.58	1.87
N (%)	1.02	0.51	0.41	0.35	< 0.20
BET surface area (m²/g)	60	670	750	948	1,103
BET constant C'	458	842	648	512	387
BJH cumulative surface area (m²/g)	56	667	787	954	1,099
Mean pore diameter (nm)	2.61	4.50	4.76	4.78	5.48
Differential main pore diameter (nm)	nd*	2.0	3.0	4.0	4.8

nd: non determined.

The chemical composition was obtained by XPS, hydrogen contain was determined by ICP.

* obtained by ICP.

pre-treatment increases. The zeta potential of the activated carbons decreases with the increase of the concentration of acid solution. While the zeta potential of the non treated active carbon is positive those of the pre-treated sample are highly negative. The pH and the zeta potential results indicated that the activated carbons have Brönsted acidity. Since the pH of the activated carbons is slightly lower than 7, this shows that the functional groups at the surface of this material are a phenolic or alcoholic group. A carboxylic group would lead to much more lower pH value. The ash content of activated carbons increases with the increase of the acid solution used for the pre-treatment. This is due to a progressive mineralisation of the palm nut hull powder during the pre-treatment process.

The elementary composition of the absorbents is also shown in Table 1. The amount of carbon in the raw material, PCP is high (69.13%). This shows that this material is suitable for the production of activated carbon [11, 13, 22]. The activated carbons have higher carbon content than the starting material. However, as the concentration of the acid solution used for the pre-treatment increases the carbon content of the activated carbons decreases, meanwhile the oxygen content and hydrogen content increases with the increase of acid solution concentration. It is obvious therefore that the formations of hydroxide or carboxylic group at the surface of activated carbon occur during the carbonization when the PCP is pre-treated with mineral acid.

The infrared spectrums of raw material and of the activated carbon are presented in Fig. 1. The main bands of the palm nut hull are attributed as follows: 3,342 cm^{-1}, -OH vibration of alcohol or of phenol; 2,922.5 cm^{-1}, -CH_2 and -CH_3 vibrations of alkyl; 1,543.7 cm^{-1} and 1,506.8 cm^{-1} aromatic group's vibrations. The organic compounds are almost completely destroyed during carbonization as CA0N exhibited no well defined transmission band. Fourier transform IR spectrums of CA1N, CA2N and CA3N confirmed was already stated that acid pre-treatment induced the oxidation of the carbon with the formation alcoholic groups. There is no band in the spectrum of activated carbons at 3,200 cm^{-1} region. Thus, there is no phenolic compound at the surface of activated carbon.

X-ray diffraction patterns of the raw palm nut hull and of the activated carbons are presented in Fig. 2. The main peak of the activated carbons (band range

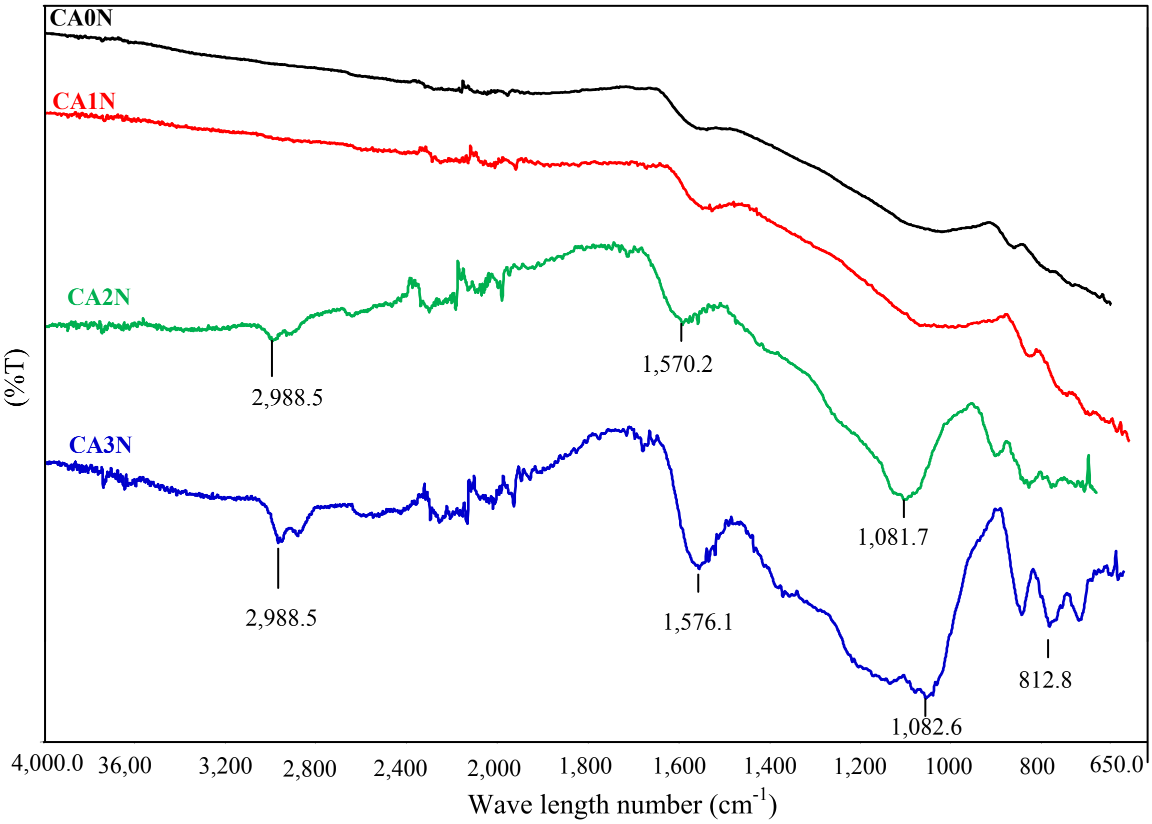

Fig. 1 FTIR spectra of activated carbons, black: non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

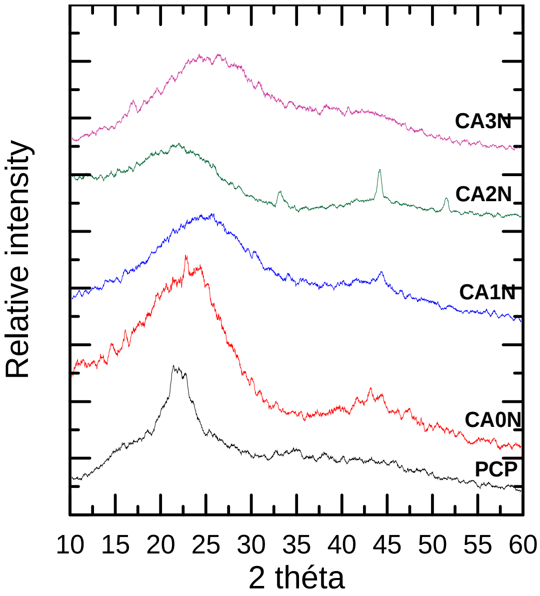

Fig. 2 X-ray diffraction patterns of the raw powder palm nut hull (PCP) and of the activated carbons, non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

between 17.5° and 30° (2θ)) correspond to that of α-cristobalite. α-Cristobalite was also found in rice hull ash by Protor [23]. This band broadening as the concentration of sulphuric acid solution increases. This is an indication of the formation of an amorphous phase.

Nitrogen adsorption-desorption isotherms obtained from raw material PCP are of type I of IUPAC classification, with no hysteresis (result not shown). This suggests that PCP contained mainly micropores. Nitrogen adsorption-desorption isotherms obtained on activation carbons display similar shapes of type IV isotherm of IUPAC classification. However the hysteresis loop increases as the concentration of the sulphuric acid solution used for treatment increases (result not shown).

Fig. 3 shows the differential pore volume distribution of the activated carbons. It is noticed that the pore diameter increases with the increase of sulphuric acid solution concentrations. The main pore diameters are 2 nm, 3 nm, 4 nm and 4.8 nm for CA0N, CA1N, CA2N and CA3N respectively. Those main pores are surrounded by increasing number of mesopore as the concentration of sulphuric acid solutions used for pre-treatment increases.

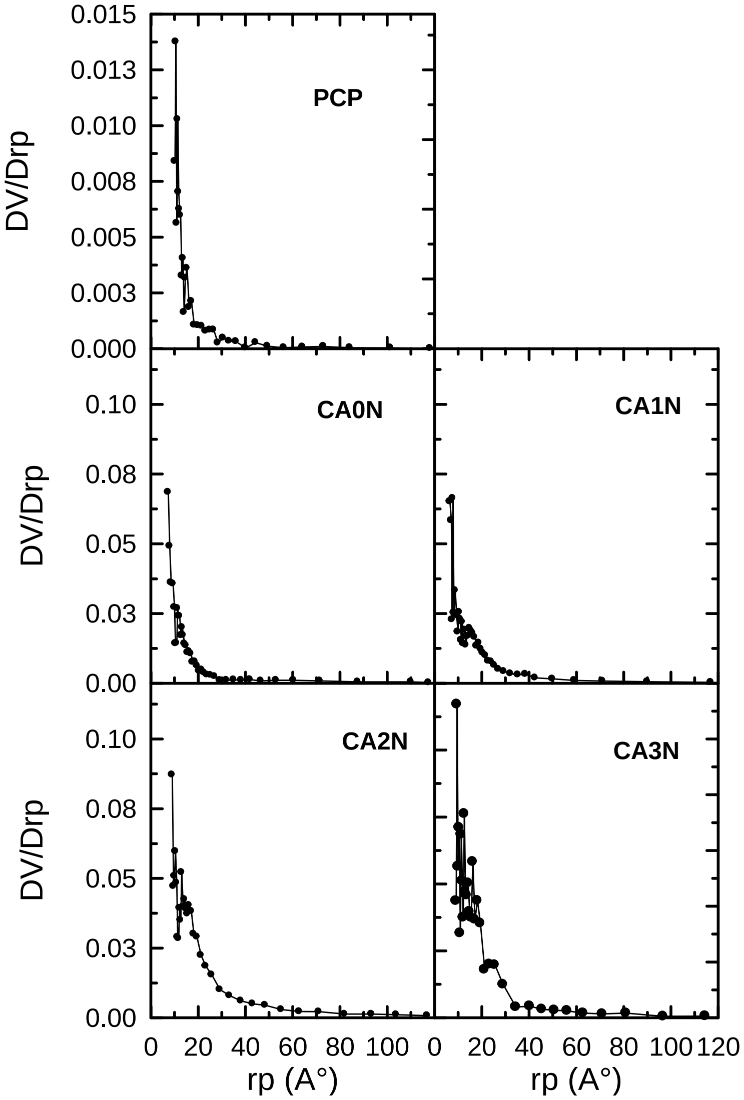

Fig. 3 Differential pore volume distribution of the raw powder palm nut hull (PCP) and of the activated carbons, for non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

Numerical values deduced from N_2 adsorption-desorption isotherm are given in Table 1. There is a good agreement between the BET specific surface area and the inner pore surface area determined by the BJH method. The mean pore diameter of the adsorbent is greater than the main pore diameter shown by the differential pore volume plot. This is due to the fact that the mean pore diameter is the diameter of a hypothetical pore whose volume is the cumulative pore volume and the surface area is the cumulative surface area. Then the mean pore diameter is a rough representation of the mesopores volume, while the differential pore volume plot, represents the actual pore volume distribution of the solid material. The decrease of the C constant is an indication of low energy surface of activated carbons when the PCP was pre-treated with sulphuric acid solution of increasing concentration before carbonisation.

3.2 Kinetics of the Adsorption of Pigments

The kinetic studies were carried out at 60 °C, 70 °C, 80 °C and 90 °C with adsorbent oil ratio of 3%. The adsorbents used for kinetic studies are the palm nut hull powder and activated carbons obtained from palm nut hull carbonization. The results obtained are reported in Figs. 4 and 5. For shea butter pigment adsorption (Fig. 4), it can be observed that the time required for reaching the adsorption equilibrium decreases when the temperature increases independently of the absorbent used. Indeed, the time of contact required to reach the equilibrium at 60 °C is 135 min; this time is reduced to 100 min at 70 °C and to 90 min at 80 °C and 90 °C. The activated carbon CA3N has the greatest adsorption effectiveness, followed by the CA2N and then by CA1N and CA0N. The amount of pigments adsorbed by PCP was too low and was not reported.

The adsorption of palm oil pigments by the activated (Fig. 5) carbons has the same feature as the adsorption of shea butter pigments. However, the time required to reach the adsorption equilibrium is shorter for palm oil pigments adsorption than the time required for shea butter pigments adsorption at the same temperature. The efficiency of activated carbons

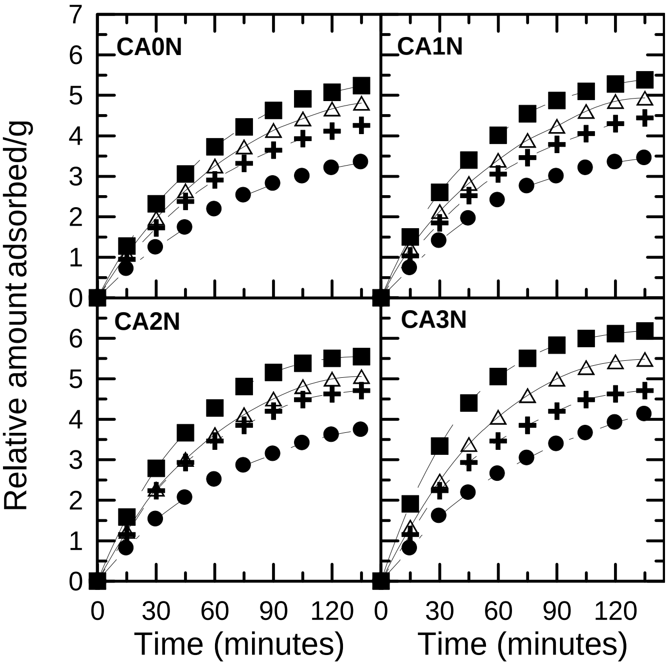

Fig. 4 Kinetics of the adsorption of the shea butter pigments onto activated carbons, at (●) 60 °C, (✚) 70 °C, (Δ) 80 °C, (■) 90 °C for non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

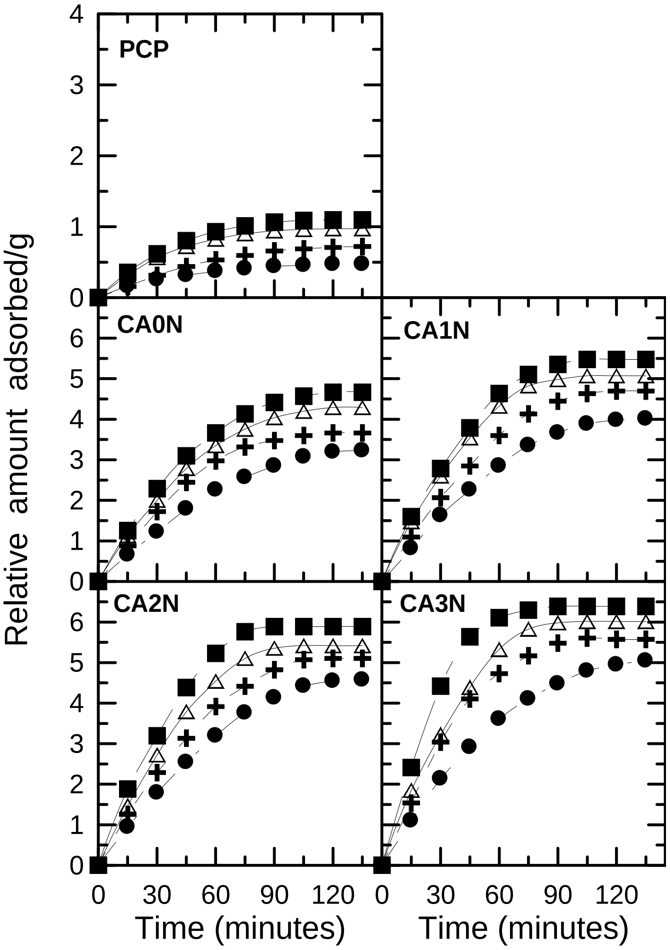

Fig. 5 Kinetics of the adsorption of the palm oil pigments onto different adsorbents, at (●) 60 °C, (✚) 70 °C, (Δ) 80 °C, (■) 90 °C powder palm nut hull (PCP) of the activated carbons, for non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

for palm oil pigment adsorption increases in the order CA0N, CA1N, CA2N and CA3N. The amount of pigment adsorbed by PCP was too low compared to that adsorbed by any activated carbon.

The differences in the decolourisation efficiency of activated carbons can be attributed to their surface composition and to their texture. Indeed the increasing order of efficiency of activated carbons is the same as the increasing number of mesopores of these materials. Other researchers have shown that the presence of mesopores in activated carbons enhances their adsorption capacities when they are used for the adsorption of large molecules from solution [11, 13, 15-17]. The amount of -OH groups at the surface of activated carbon also increases with the increase of sulphuric acid solution. Therefore, they are probably the preferable sites of the adsorption of pigment.

3.3 Kinetics of the Adsorption of Free Fatty Acids

The effect of contact time on the adsorption of free fatty acid during the adsorption experiment has been carried out at 90 °C. Fig. 6 presents the variation of the relative amounts of free fatty acids adsorbed with time from shea butter (Fig. 6a) and from palm oil (Fig. 6b).

The time required for the free fatty acids adsorption equilibrium to be achieved is 100 min independently of adsorbent and of vegetable oil. The efficiency of the adsorbents for free fatty acids adsorption increases with the increase of sulphuric acid concentration. The adsorption of free fatty acids during vegetable oil decolourisation was previously observed by Bike Mbah

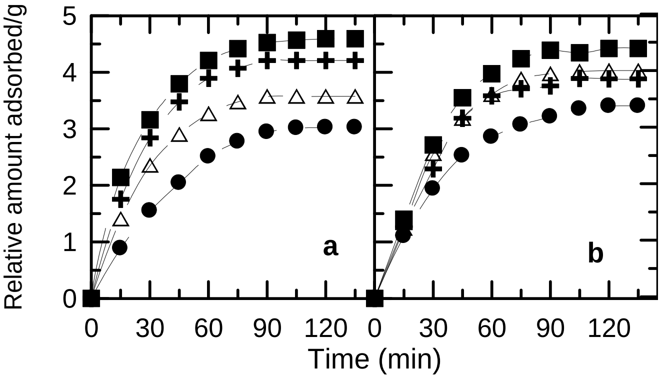

Fig. 6 Kinetics of the adsorption at 90 °C of shea butter (a) and palm oil (b) free fatty acids onto the activated carbons. (●) CA0N, (Δ) CA1N, (✚) CA2N, (■) CA3N.

et al. [24], while Nguetkam et al. [25] show that the increase or decrease of free fatty acids content of the oil during the decolourisation of vegetable oils depends on the adsorbent, its amount and on the type of oil. Topalar and Bayrak [26] found that rice hull ash is effective for the adsorption of myristic, palmitic and stearic acid.

3.4 Kinetic Modelling

A number of models are available for the kinetics of adsorption process. These models describe the sorption rate equation as the rate of solutes transferring from liquid suspension to the surface of the sorbent [1, 27-29]. These models are normally used in order to determine the existence of particular mechanism for the sorption process, i.e. chemical or physical adsorption. In this study intraparticle diffusion, pseudo-first-order and pseudo-second-order models have been tested.

3.4.1 Intraparticle Diffusion Study

The intraparticle diffusion model is usually represented by the equation:

$$q_t = k_{\mathrm{int}}\sqrt{t} + C \tag{2}$$

where q_t is the amount of solute adsorbed at time t, C is the constant and k_{int} is the intraparticle diffusion rate constant. The diffusion of the solute from solution to the surface of the adsorbent may occur in several steps. i.e.: external diffusion, pore diffusion and surface diffusion. Each step is represented by a particular diffusion equation. Figs. 7 and 8 present the linear regression of the amount of pigment adsorbed per gram of adsorbent versus $t^{1/2}$, for shea butter and palm oil. It came out from those figures that the adsorption of pigment from vegetable oil proceeds in two steps. Furthermore, none of the regression passes through the origin, suggesting that adsorption involves intraparticle diffusion, but that was not the only rate controlling step [11]. It should also be noticed that the slope of the first portion increases as the temperature increases independently of the adsorbent and of the vegetable oil. On the contrary, the slope of second portion decreases as the temperature decreases. This is a strong indication that film diffusion, is one of the limiting steps of the adsorption process. It is a well known phenomenon that, the viscosity of oil decreases as the temperature increases, and the diffusion of adsorbate is favored. Table 2 reported the k_{int} and D constant for the adsorbent used herein, for the first step of the adsorption process.

3.4.2 Pseudo-First-Order Model

The pseudo-first-order model rate equation has long been widely used as kinetic model for liquid phase adsorption [27, 28]. The pseudo-first-order equation is generally expressed in the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2{,}303}t \tag{3}$$

where q_e and q_t are the amount of solute adsorbed per unit mass of adsorbent at equilibrium and at time t, respectively and k_1 is the pseudo-first-order rate

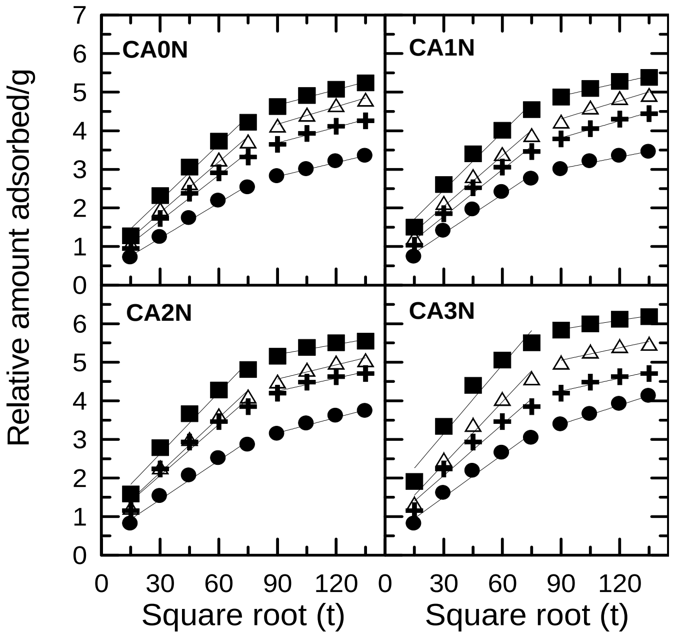

Fig. 7 Intraparticle diffusion plots of the asdorption of shea butter pigments onto different adsorbents, at different temperature: (●) 60 °C, (✚) 70 °C, (Δ) 80 °C, (■) 90 °C, for non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

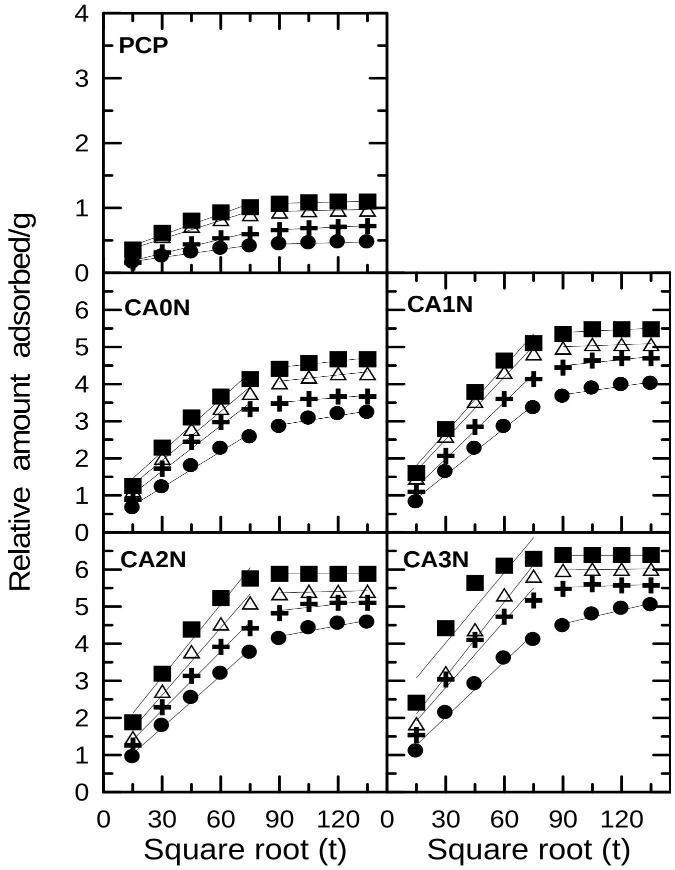

Fig. 8 Intraparticle diffusion plots of the asdorption of palm oil pigments onto different adsorbents. (●) 60 °C, (✚) 70 °C, (Δ) 80 °C, (■) 90 °C, for non pre-treated sample (CA0N), 1 N sulphuric acid pre-treated sample (CA1N), 2 N sulphuric acid pre-treated sample (CA2N), 3 N sulphuric acid pre-treated sample (CA3N).

Table 2 Intraparticle diffusion model and Pseudo-second-order model constants.

	Activated carbon	Intraparticle diffusion model			Pseudo-second-order model	
		T (°C)	k_{int} (μmol/mg·min$^{1/2}$)	R^2_1	k_2 (μmol/mg·min)	R^2
Shea butter	CA3N	60	0.465	0.999	0.0010	0.989
		70	0.564	0.993	0.0018	0.987
		80	0.684	0.998	0.0014	0.981
		90	0.761	0.988	0.0026	0.989
	CA2N	60	0.429	0.999	0.0014	0.994
		70	0.564	0.993	0.0018	0.987
		80	0.602	0.999	0.0016	0.990
		90	0.675	0.996	0.0019	0.994
	CA1N	60	0.426	1.000	0.0015	0.975
		70	0.513	0.999	0.0014	0.996
		80	0.556	1.000	0.0014	0.997
		90	0.635	0.999	0.0020	0.994
	CA0N	60	0.384	0.997	0.0013	0.992
		70	0.500	0.999	0.0013	0.992
		80	0.557	1.000	0.0011	0.994
		90	0.617	0.999	0.0014	0.992
Palm oil	CA3N	60	0.633	0.999	0.0011	0.988
		70	0.767	0.984	0.0025	0.990
		80	0.853	0.995	0.0028	0.979
		90	0.823	0.932	0.0058	0.987
	CA2N	60	0.592	0.998	0.0009	0.987
		70	0.671	0.999	0.0015	0.974
		80	0.770	0.997	0.0022	0.979
		90	0.831	0.996	0.0031	0.979
	CA1N	60	0.530	0.999	0.0011	0.957
		70	0.641	0.999	0.0015	0.957
		80	0.713	0.998	0.0027	0.961
		90	0.751	0.997	0.0024	0.987
	CA0N	60	0.409	0.997	0.0012	0.987
		70	0.521	0.996	0.0024	0.988
		80	0.559	0.998	0.0022	0.990
		90	0.606	0.997	0.0023	0.993
	PCP	60	0.053	0.997	0.0296	0.987
		70	0.093	0.996	0.0087	0.958
		80	0.123	0.985	0.0198	0.985
		90	0.138	0.989	0.0170	0.985

constant.

The linear regression plots of $\log(q_e - q_t)$ versus t for shea butter and palm oil pigment were carried out in this study. The obtained correlation coefficients (R^2) values were less than 0.76. These poor values of R^2 suggested that adsorption of shea butter and palm oil pigment on activated carbon is not pseudo-first-order process.

3.4.3 Pseudo-Second-Order Model

The pseudo-second-order model equation has the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

where q_e and q_t are the amount of solute adsorbed at equilibrium and at time t, respectively and k_2 is the pseudo-second-order rate constant.

The fit of the pseudo-second-order model with our experimental data was checked by the linear plot of $\frac{t}{q_t}$ versus t (figure not shown). The relevant q_e and k_2 values and the corresponding R^2 are reported in Table 3. The R^2 values are nearly unity for pseudo-second-order kinetic model, indicating that the pseudo-second-order adsorption mechanism was predominant for the adsorption of shea butter and palm oil pigments on palm nut hull activated carbons.

3.5 Validity of Kinetic Modelling of Pigment Adsorption

The intraparticle diffusion model constants and the pseudo-second-order model parameters as well as and the R^2 values for all the two kinetic models for the four adsorbents and for the two vegetable oils are reported in Table 2. The experimental data best fit the intraparticle diffusion and the pseudo-second-order models. However the intraparticle model is applicable only to portion of the adsorption process while the pseudo-second-order model explains the overall adsorption process. This is not surprising since the pseudo-second-order model seems to be nowadays the more appropriate method to describe adsorption of solutes from solutions onto solid adsorbents [1, 27, 28]. The parameters obtained from pseudo-second-order model were used for the determination of the activated energy.

3.6 Determination of the Activation Energy

Arrhenius relationship was used to evaluate the activation energy of adsorption of pigment. The pseudo-second-order rate constant was used for this purpose. The Arrhenius equation is commonly expressed in its logarithm form:

$$\ln k_2 = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T} \qquad (5)$$

when $\ln k_2$ is plotted against $\frac{1}{T}$, a straight line with slope $-\frac{E_a}{R}$ is obtained. Table 3 presents the result of fitting experimental data with the Arrhenius model. The high correlation coefficients of determination obtained indicate that the oil pigments sorption on activated clay fits the Arrhenius model.

The high correlation coefficients of determination obtained indicate that the oil pigments sorption on activated clay fits the Arrhenius model. The magnitude of activation energy gives a type of adsorption, which is mainly physical or chemical. The range of 5-40 kJ·mol^{-1} of activation energies indicates a physisorption mechanism while the range of 40-80 kJ/mol suggests a chemisorption mechanism [30]. The activation energy obtained in this study varied between 4.29 and 29.98 kJ·mol^{-1} for shea butter pigments adsorption and between 17.92 and 37.46 kJ·mol^{-1} for palm oil pigment adsorption, indicating that the adsorption could be assigned to physisorption.

3.7 Kinetic Models for Free Fatty Acids Adsorption

The pseudo-first-order and pseudo-second-order models were also tested for the adsorption of free fatty acids from both the shea butter and palm oil, on activated carbons. The correlation coefficients for pseudo-first-order were very low, i.e. less than 0.70 for both vegetable oils. This model is therefore not suitable to describe the adsorption of free fatty acids from vegetable oil.

Table 3 Activation energies for the adsorption of vegetable oil pigments.

Activated carbon	Shea butter		Palm oil	
	E_a (kJ·mol^{-1})	R^2	E_a (kJ·mol^{-1})	R^2
CA0N	4.29 ± 0.01	0.981	17.92 ± 0.09	0.985
CA1N	7.69 ± 0.10	0.990	30.37 ± 0.14	0.987
CA2N	9.71 ± 0.03	0.989	33.44 ± 0.06	0.991
CA3N	29.98 ± 0.13	0.994	37.46 ± 0.02	0.992

Table 4 Pseudo-second order model kinetics constants for the adsorption of free fatty acids.

Activated carbon	Shea butter			Palm oil		
	q_e (μmol/mg)	k_2	R^2	q_e (μmol/mg)	k_2	R^2
CA0N	4.4248	0.0043	0.974	4.5662	0.0059	0.989
CA1N	4.3860	0.0101	0.988	5.0761	0.0059	0.971
CA2N	5.0761	0.0089	0.991	5.3191	0.0054	0.969
CA3N	5.4054	0.0095	0.996	5.7803	0.0051	0.972

The free fatty acid pseudo-second-order rate constant k_2, the amount adsorbed at equilibrium q_e and the related correlation coefficients R^2 are reported in Table 4. The high values of R^2 suggest that the free fatty acids adsorption on activated carbon is a pseudo-second-order process. The q_e values show that the efficiency of the adsorbent for free fatty acid increases as the concentration of the sulphuric acid used for pre-treatment increases.

4. Conclusion

Treatments of palm nut hull with sulphuric acid solutions before carbonization lead to the formation of activated carbon which possesses Brönsted acid sites at the surface. Those acidic sites are probably the -OH groups of alcohol compound. When the concentration of sulphuric acid solutions increases the number of -OH sites on the activated carbon increases. The number of mesopore of activated carbon also increases upon treatment of palm nut hull with sulphuric acid solution of increasing concentration. When the activated carbons were used for the sorption of pigment and of free fatty acids from shea butter or palm oil their efficiency increases with the concentration of the sulphuric acid solution used for the pre-treatment. Therefore, it is obvious that the factors that favor the adsorption of pigment and free fatty acids are the presence of Brönsted acid sites and the presence of large mesospores. Pigment adsorption and free fatty acids adsorption are both a pseudo-second-order kinetic process. The pigment adsorption activation energy derived from the pseudo-second-order rate constant shows that the adsorption of pigment is probably a physisorption process.

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