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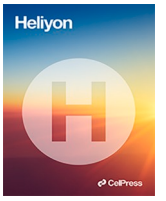

Research article

Activated carbons from open air and microwave-assisted impregnation of cotton and neem husks efficiently decolorize neutral cotton oil

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ABSTRACT

The decolorization of cottonseed oil with activated carbons (ACs) from neem and cotton husks has a dual interest: elimination of undesirable pigments in oil and valorization of the husks; by-products of neem and cottonseed processing, which would otherwise be dumped along river-banks and farms causing environmental pollution. ACs were produced from neem and cottonseed husks after acid impregnation assisted by microwave heating and in ambient air for the decolorization of neutral cottonseed oil. The experimental data were analyzed by the intraparticle diffusion and the pseudo-second-order kinetic models as well as the Langmuir and Freundlich isotherm models. The method of impregnation and carbonization time had dramatic effects on the specific surface area (800–1500 g/m^2), the quantity of burn-off (50–70 %), and methylene blue index (300–5000 mg/g) values which indicated the potential of the prepared activated carbons in the bleaching of vegetable oil and in other applications such as environmental clean-up and in agriculture. Pigment adsorption increased with temperature for all ACs indicating that the decolorization process was endothermic. The quantity of adsorbent equally had a significant effect on the pigment adsorption process for all ACs. All the activated carbons prepared in this work were 30–80 % more efficient in pigment adsorption than bleaching earth that is normally used in decolorizing neutral cotton seed oil in industries. All tested models are adequate to describe pigment adsorption by the ACs. Both methods of preparation of ACs were effective for oil decolorization, but microwave impregnation is more appealing because it requires only 1 h compared to 6 h for ambient air. Optimum decolorization conditions were 90 °C for 40min and adsorbent concentration of 2 %.

1. Introduction

Activated carbon (AC) is a carbonaceous material prepared from both synthetic and biomass sources that plays an important role as an adsorbent in many processes [1–3]. Activated carbons from biomass have recently gained more attention as adsorbents compared to those obtained from other resources. This is driven by the need to tackle environmental pollution and food safety using biodegradable adsorbents with interesting porous structures [4,5]. Much research has been done on the preparation and application of activated carbon from organic sources; it is used for deodorization and purification of water and air [4,5]. It is also used as an adsorbent to purify

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and detoxify pharmaceutical and food products [6,7]. In addition to these multiple advantages in de-pollution, activated carbon is also used as a catalyst and catalyst support in purification systems [8,9].

Vegetable oils contain undesirable pigments and free fatty acids which reduce the quality and shelf-life of the oil [10,11]. In industry, bleaching or decolorization is one of the several unit operations involved in the refining of crude oil into edible oil. It is a critical step because it is responsible for removing the undesirable pigments and free fatty acids of the oil and consequently reducing the color of the oil to acceptable levels. This step significantly improves the quality of the oil produced [12,13]. Usually, after the processing of neem and cotton seeds into the oil, the husks are disposed of in an unsustainable manner as waste, or a small quantity is removed and used as animal feed or as combustion fuels. This contributes to environmental pollution by blocking water runways or ends up polluting nearby waters.

Currently, in most tropical countries, the decolorization of cottonseed oil is done using imported bleaching earth. Importing this material is expensive and adds significantly to the overall cost of producing vegetable oil [14–16]. It would therefore be interesting to look for potential sources of bleaching agents capable of carrying out the decolorization of vegetable oils at a reduced overall cost, and which are renewable and biodegradable.

Recently, microwave heating technology has received considerable attention in different fields, with successful results and useful potential applications for different processes in the indicated industries. The literature indicates that the main advantages of microwave heating include the drastic reduction in processing times and heat requirements, as well as the preservation of the quality of the obtained products [17,18]. More specifically, microwave irradiation has been proven to significantly improve the activated carbon parameters from agricultural waste such as BET surface area, yield, porosity, etc which improves the adsorption capacities of the prepared activated carbons [19–23]. References [21,22] recommend that more research should be carried out on the use of microwave heating in the production of activated carbons from agricultural waste to further understand and enhance its use in different processes.

In our previous work, we demonstrated that activated carbons prepared from neem and cotton husks using conventional activation methods have a porosity that allows to carry out the decolorization of neutral cotton oil [24]. However, activation time and chemical requirements as well as energy for the conventional process remain high. Hence, the need to explore microwave activation to limit or eliminate these disadvantages and optimize the operating conditions for obtaining activated carbons with high decolorizing power for cottonseed oil.

The aim of this study was to optimize the operating conditions for obtaining activated carbons from neem and cotton seed husks with high decolorizing power for cottonseed oil using microwave and conventional activation methods.

2. Material and methods

2.1. Material

The materials used in this work were neem and cotton husks, neutral cottonseed oil, phosphoric acid, bleaching earth, methylene blue, potassium iodide, sodium thiosulphate, and ethanol. All chemicals were supplied by Fisher Bioblock Scientific and used without further purification.

2.2. Preparation of activated carbon

Activated carbons were prepared using neem and cotton husks. The neem husks were supplied by women who process neem fruits into oil in the Mora locality (1°02'45″ North, 14°08'24″ East), while cotton husks were supplied by Societé de Développement du Cotton (SODECOTON), an oil processing factory in Maroua town, both situated in the Far North Region of Cameroon. The pods were packaged in polyethylene plastics and transported to the Chemistry Laboratory of the University of Maroua. The neem and cotton husks were thoroughly washed with water, dried, and crushed using a mortar. The obtained powder was then sieved to obtain a particle size less than 50 μm. Activated carbons were produced by carbonizing 50g of the sieved powder in a muffle furnace (NABERTHERM GmbH, USA) at 600 °C for 3h. The charred samples were then treated with 14 N and 15 N phosphoric acid for 2, 6, 12, and 24h at room temperature (conventional activation) and 15, 30, 45, 60, 90, and 120 min in a microwave (microwave activation) respectively. The resulting activated carbons (ACs) were thoroughly cleaned with distilled water to remove residual acid and dried at 105 °C for 24h using an oven. To select the most efficient activated carbon for cotton seed oil decolorization, preliminary bleaching experiments were conducted with the ACs at 80 °C for 20 min.

2.3. Physicochemical characterization of the prepared activated carbons

The quantity of burn-off, methylene blue, iodine value, specific surface areas, and the concentrations of surface groups of the ACs were carried out as described in our previous study [24].

2.4. Adsorption experiments of cottonseed oil pigments

2.4.1. Decolorization procedure

The evaluation of the adsorption capacity of pigments was carried out by UV–visible spectroscopy. The spectra of decolorized vegetable oils are generally characterized by low or no absorbance in the visible region (350–750 nm). Refining is therefore considered effective when the optical density of the treated oil is as low as possible in this region or lower than that of the untreated oil. The

decolorization of oil was carried out with 27 mL (15 mg) of neutral cotton seed oil at temperatures of 70, 80, and 90 °C and a contact time ranging from 5 to 40 min with continuous stirring using the ACs produced. The mass ratios of 1, 2, and 3 % were used to evaluate the effect of concentration of activated carbon during the decolorization process. After each run, the oil was filtered through a Whatman filter N°1, and the absorbance of the filtered oil was then measured using a UV spectrophotometer at 664 nm. The efficiency of decolorization using the activated carbons was calculated using **Eq.** 1:

$$E = \frac{(A_0 - A) \times 100}{A_0} \tag{1}$$

Where E = % efficiency of decolorization, A_0 = absorbance of the neutral oil, and A is the absorbance of the decolorized oil.

2.4.2. Modelling of the bleaching process

The relative amount of pigments adsorbed per gram of adsorbent ($\frac{X}{m}$) and the relative amount of residual pigments at the adsorption equilibrium (q_e) are obtained from **Eq.**s 2 and 3:

$$q_t = \frac{X}{m} = \frac{(A_0 - A)}{A_0 m} \tag{2}$$

$$q_e = \frac{A}{A_0} \tag{3}$$

where A_o is the absorbance of neutral cottonseed oil, A the absorbance of decolorized cottonseed oil, and m is the mass of activated carbon.

2.4.2.1. Adsorption kinetics. The intra-particle diffusion **(Eq. (4))** and the pseudo-second **(Eq. (5))** models were used to model the kinetics of the adsorption process.

$$q_t = kt^{0.5} + C \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

To determine the constants of the kinetic model of intra-particle diffusion, the quantity of pigment adsorbed q_t was represented as a function of the square root of time *t,* and k and C were determined from the plot. Similarly, the constants of the pseudo-second-order model, k_2 and q_e were determined from the plot of $\frac{t}{q_t}$ versus time t.

2.4.3. Adsorption isotherms of pigments

Two equations were applied to study the decolorization mechanism of the pigments of the cottonseed oil at 70, 80, and 90 °C up to 45 min of contact time.

The experimental results of the adsorption isotherms of the cottonseed oil pigments were compared with the theoretical models of Langmuir and Freundlich which are presented in their linearized forms in **Eq. (6)** and **Eq. (7)** respectively.

$$\frac{X_e m}{X} = \frac{1}{aK_L} + \frac{X_e}{a} \tag{6}$$

$$\text{Log}\left(\frac{X}{m}\right) = Log(K_F) + \frac{1}{n} Log(X_e) \tag{7}$$

A graph of $\left(\frac{X_e m}{X}\right)$ as a function of X_e allows us to determine the coefficients a and K_L from the Langmuir isotherm, while K_F and n of the Freundlich isotherm were determined from a plot of Log $\left(\frac{X}{m}\right)$ versus $Log(X_e)$. X_e is the relative amount of pigment remaining at the adsorption equilibrium, $\left(\frac{X}{m}\right)$ is the relative amount of pigment adsorbed per gram of adsorbent, a is the amount adsorbed to the monolayer and K_L is the adsorption equilibrium constant. K_F and n are the constants reflecting the adsorption capacity measurement and adsorbent-adsorbate interaction respectively.

3. Results and discussion

Initially, 8 activated carbons (ACs) were prepared by both microwave and conventional activation. Considering the activation time, and degree of decolorization of the oil, the following ACs were selected for the continuation of the work. AC1: Activated carbon from 6-h conventional activation of cotton husks, AC2: Activated carbon from 30-min microwave activation of cotton husks, AC3: Activated carbon from 6-h conventional activation of neem husks, AC4: Activated carbon from 30-min microwave activation of neem husks.

3.1. Characterization of adsorbents

3.1.1. Amount of burn-off

Table 1 presents the burn-off results of the prepared ACs. According to Lua and Gu [25], ACs are qualified as microporous when the degree of burn-off is less than 50 % and as microporous when it is greater than 75 %. When the degree of burn-off is between 50 and 75 %, the adsorbents have a mixed porous structure containing all the types of pores. For the four ACs, the degree of burn-off was between 50 and 75 %, i.e., 67.63 % and 71.33 % (Table 1) for the cotton husks and 69.87 and 50.83 % for neem husks. Hence, the ACs produced had mixed porous structures, (micropores, mesopores, and macropores). The significant difference observed in the amount of burn-off suggests that the three types of pores present in its structure may not be distributed in the same way. In Ref. [24] it was demonstrated that ACs produced from cotton and neem husk by conventional activation had mixed pores.

3.1.2. Liquid phase adsorption test: iodine number and methylene blue index

The liquid phase adsorption test (iodine index, and methylene blue index) is very important for the characterization of activated carbons. The iodine index gives important information on the microporosity of ACs, and the MB index on the mesoporosity; the latter is synonymous with a strong adsorption capacity for large molecules. The average iodine indices of AC1, AC2, AC3, and AC4, were 711.2; 812.8; 1117.6, and 914.4 mg/mL (Table 1) respectively which corresponded to values of 843.32; 1002.92; 1481.72, and 1162.52 m^2/gin terms of the specific surface areas of the ACs. These values show that these samples have a high adsorption capacity with respect to ACs produced from organic sources. The presence of micropores in the samples as suggested by the values of the specific surface areas can be linked to the method of preparation and the nature of the starting material. The adsorption capacity of the prepared ACs from neem husks (AC3 and AC4) is significantly higher than that of cotton, indicating that microporosity was more developed for the sample prepared from neem husks. Generally, the adsorption capacities increase with an increase in specific surface area. Activated carbons, with specific surface areas varying between 500 and 1500 m^2/g have shown good absorption capacities according to De Gisi [26] suggesting that those reported here will also have good adsorption capacities. The adsorption of methylene blue is used to assess the performance of activated carbon before its use in a water purification or vegetable oil decolorization installation [27]. Table 1 represents the methylene blue index of the different activated carbon samples. The results obtained by adsorption of methylene blue have made it possible to verify the effectiveness and importance of activated carbons for the elimination of large molecules, in particular carotenoids contained in vegetable oils. When an adsorbent adsorbs methylene blue, a meso and/or macroporous structure can be formed; the macropores generally serve as an access route to the mesopores. The indices of methylene blue were 5369.58; 307.12; 7309.33 and 1232.91 mg/g respectively for samples AC1, AC2, AC3, and AC4 (Table 1). These high values suggest the presence of macropores indicating that the samples have high efficiency for the decolorization of cottonseed oil. This corroborates with reports of reference [14] who indicated that AC properties such as specific surface area, number of micropores and mesopores, and pore volume are strongly dependent on the method of preparation, activation agent, activation conditions, and source of raw material used in preparation. The results of the iodine and the MB indices show that the ACs prepared might have the ability to adsorb micro and macro-molecules which is in line with the Burn-Off results which show that the ACs have mixed structures. Table 2 shows that the different functional groups at the surface of the ACs are dependent on the starting material but not on the impregnation method used during activation. The occurrence of these groups at the surface could significantly influence the oil decolorization process.

3.2. Kinetic study of the adsorption of cottonseed oil pigments by activated carbon

The performance of the prepared ACs was tested in the decolorization of neutral cotton seed oils. To do this, the kinetics of decolorization of the oil was carried out in a batch system to determine the optimum temperature, adsorbent quantity, and the contact time necessary to reach the pigment adsorption equilibrium for the ACs in comparison to commercial bleaching earth, habitually used in the industrial decolorization of the oil.

3.2.1. Effect of source of AC and preparation method on decolorization

Fig. 1 shows the results of the kinetic study of the adsorption of cottonseed oil pigments by activated carbon prepared from neem and cotton husks in comparison with bleaching earth.

It can be observed in Fig. 1(a) that the relative quantities of cottonseed oil pigments adsorbed per gram of activated carbon increased progressively with contact time and then stabilized after a certain time. At 70 °C, adsorption equilibrium is reached after 40min. AC from neem (AC3) prepared by conventional activation adsorbed more pigments compared to others. Recall that AC3 had the highest specific surface area of adsorption which explained its high adsorption. Microwave heating did not significantly influence the pigment adsorption process at 70 °C. Bleaching earth and microwave-prepared samples adsorbed significantly lower amounts of

Table 1
Iodine Index (II), Methylene Blue Index (MBI), and Burn-Off of the different activated carbons.

K	II_2 (mg/mL)	MBI (mg/g)	Burn-off (%)
AC1	711.20	5369.58	67.63
AC2	812.80	307.13	71.33
AC3	1117.60	7309.33	69.87
AC4	914.40	1232.92	50.83

Table 2
Surface functional groups of the different ACs.

Samples	Carboxylic	Lactone	Phenolic	Acid	Basic
AC1	0.0114 ± 0.01	0.0052 ± 0.1	0.0080 ± 0.04	0.0246 ± 0.1	0.0662 ± 0.1
AC2	0.0113 ± 0.02	0.0047 ± 0.1	0.0078 ± 0.02	0.0239 ± 0.3	0.0612 ± 0.2
AC3	0.0171 ± 0.01	0.0078 ± 0.3	0.0120 ± 0.03	0.0369 ± 0.2	0.0497 ± 0.1
AC4	0.0169 ± 0.03	0.0076 ± 0.2	0.0119 ± 0.01	0.0358 ± 0.1	0.0477 ± 0.2

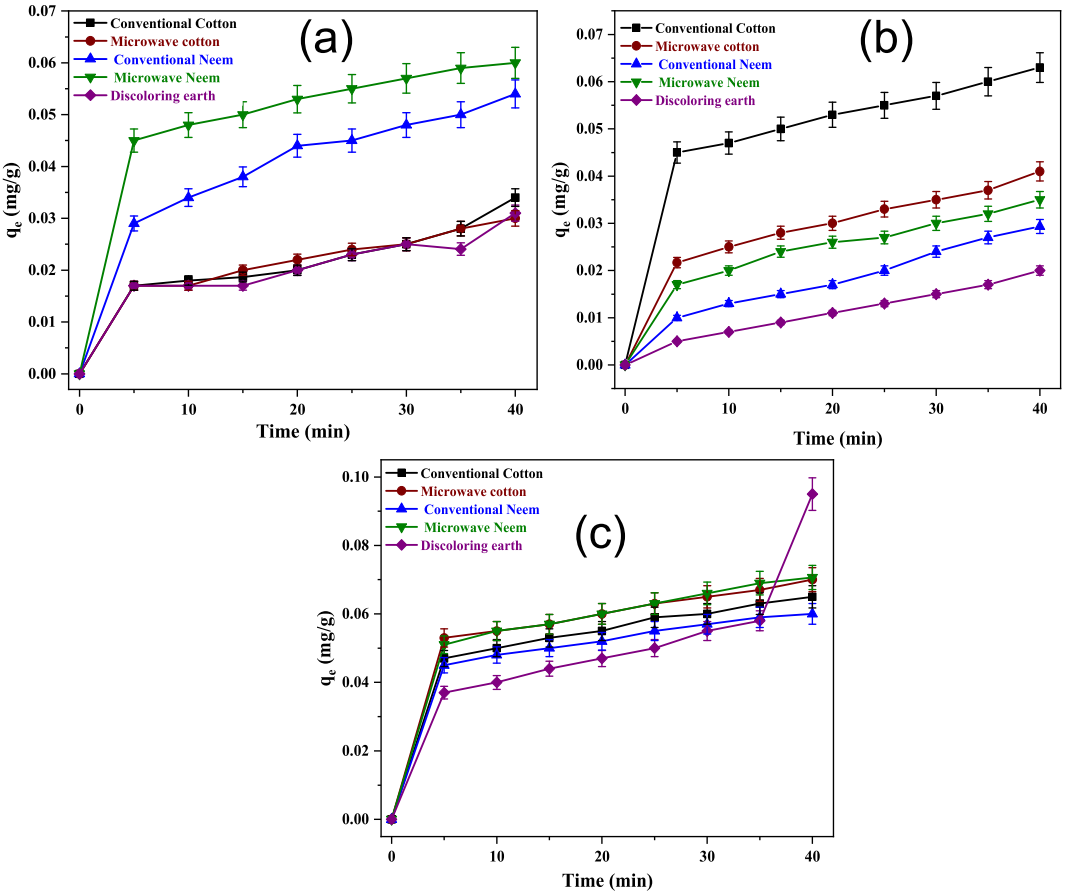

Fig. 1. Effect of activated carbon treatment on the discoloration of neutral cottonseed oil at 70 (a) 80 (b) and 90 °C (c).

pigments compared to conventional samples at 70 °C. At a temperature of 80 °C, it is observed in Fig. 1(b) that the relative quantities of pigments adsorbed per gram of activated carbon were significantly higher for the microwave ACs compared to the conventional ACs and bleaching earth. Microwave heating played an important role in the activation process of the husks at 80 °C. Microwave pretreatment has the potential to induce stress responses in biological systems. The use of microwave irradiation in the activation process may therefore cause an increase in mass transfer coefficients and consequently lead to cell membrane rupture due to localized microwave heating [28,29]. This effect results in the formation of permanent pores, allowing the pigments to adhere to the pores that have been created resulting in increased decolorization. It is possible that at 70 °C the adsorbates are not completely excited to occupy the pores created by the microwave irradiation but with the increase in temperature, the particles are excited and can better adhere to the pores created, thus explaining the weak adsorption on ACs activated by the microwave method at 70 °C. At 90 °C, ACs prepared from Neem (AC3 and AC4) were significantly more efficient in the bleaching process compared to ACs from cotton as shown in Fig. 1 (c). It seems that at 90 °C the decolorization process is more dependent on the pore structure because AC3 and AC4 which had the highest methylene blue values and specific surface areas showed the strongest adsorption. Fig. 1 shows that the AC source and the activation techniques (conventional or microwave) significantly influenced the quality of the decolorization process. These differences may be related to the iodine and methylene blue indices and to the different groups present at the surface of ACs as presented in Table 2. At all bleaching temperatures, the prepared ACs showed significant bleaching efficiencies which were better than the one of bleaching earth used in the industrial bleaching process. These results indicate that ACs from neem and cotton husks can be used in the bleaching of neutral cottonseed oil.

Table 3
Parameters of the pseudo-second order kinetic and intraparticle diffusion models for the adsorption of cottonseed oil pigments in the batch system.

	Intraparticle diffusion model														
Adsorbents/Temp (°C)	AC1			AC2			AC3			AC4			BE		
Constants	C	Kps	R^2	C	Kps	R^2	C	Kps	R^2	C	Kps	R^2	C	Kps	R^2
70	16.25	6.31	0.9897	6.05	3.98	0.8256	37.9	4.01	0.9948	8.15	3.49	0.9468	7.6	3.36	0.8092
80	−2.59	5.05	0.958	35.66	4.58	0.9789	7.35	4.48	0.9856	11.27	4.76	0.9825	−4.42	3.77	0.9692
90	37.74	4.02	0.9901	38.02	4.71	0.9876	41.14	5.17	0.9859	44.21	4.45	0.9729	19.48	6.26	0.9675
	Pseudo-second order model														
Adsorbents/Temp (°C)	**AC1**			**AC2**			**AC3**			**AC4**			**BE**		
Constants	**q_e**	**Ki**	**R^2**	**q_e**	**Ki**	**R^2**	**q_e**	**Ki**	**R^2**	**q_e**	**ki**	**R^2**	**q_e**	**ki**	**R^2**
70	58.82	0.0038	0.9717	34.48	0.0042	0.8828	64.52	0.0077	0.9932	32.47	0.0058	0.9493	31.35	0.0055	0.9092
80	34.84	0.0025	0.8222	66.67	0.006	0.9879	38.17	0.0047	0.9525	44.05	0.0046	0.9595	25.13	0.0024	0.7305
90	64.52	0.0075	0.9925	69.44	0.0062	0.99	75.76	0.0055	0.9893	74.07	0.0065	0.9911	62.5	0.0036	0.9625

Notes: AC1: Activated carbon from 6-h conventional activation of cotton husks, AC2: Activated carbon from 30-min microwave activation of cotton husks, AC3: Activated carbon from 6-h conventional activation of neem husks, AC4: Activated carbon from 30-min microwave activation of neem husks.

3.2.2. Effect of temperature on the decolorization of neutral cotton oil

The influence of temperature on the bleaching of neutral cottonseed oil for the different prepared ACs as well as the bleaching earth (BE) were investigated. For all treatments and at a given temperature, the adsorbed bleaching quantity increases with the bleaching time until saturation as shown earlier in Fig. 1. This observation was also reported by Hameed and Ahmad, (2009) [30] on the adsorption of methylene blue using AC produced from tea leaf waste, and by Al-Qahtani, (2016) [31] on the adsorption of heavy metals using cotton and neem fruit cortex and husk waste. Saturation is reached under given conditions (time, temperature, concentration, pH, etc.) when the adsorbent pores are filled with adsorbate molecules and have witnessed stability, as shown on the adsorption curves. Temperature has a significant effect ($p < 0.05$) on the bleaching process for ACs and bleaching earth. For a given bleaching time, the percentage of pigment removal increases with temperature as expected. At 70 °C, the decolorization rate was generally less than 30 %, but increased to more than 70 %, especially at 90 °C for the prepared ACs from neem husks.

The increase in pigment removal with an increase in temperature can be attributed to the activation of more adsorption sites on the adsorbents at higher temperatures [32]. According to the gas adsorption theory, the quantity of pigments adsorbed physically decreases while that adsorbed chemically increases with increasing temperature [33]. The increase in the amount adsorbed with temperature, therefore, suggests that the adsorption process is chemical and endothermic in nature [33]. Moreover, it is well known that the viscosity of oils decreases with increasing temperature, thus promoting the diffusion of adsorbate molecules and the observed increased in adsorption with temperature. The effect of increased adsorption rate with temperature has been demonstrated by Rahman [34].

3.2.3. Effect of AC concentration on the bleaching of neutral cottonseed oil

The effect of adsorbent dose on the decolorization of neutral cottonseed oil using microwave-activated ACs from neem and cotton at 80 °C was studied. Whatever the adsorbent dose used, the rate of adsorption becomes constant after 20 min of the reaction. For neem AC prepared by microwave and bleaching earth, it is observed that there is no significant difference between adsorption by 2 and 3 % of the adsorbent concentration. These are however significantly ($p < 0.05$) higher than those of 1 %. It is possible that as the dose of adsorbent increases, the total amount of pores and therefore surface area available for adsorption will increase thereby allowing more pigments to be removed. However, there was no significant difference between the different concentrations of the conventional AC from cotton samples in the bleaching process. These results are similar to those reported by Refs. [27,34].

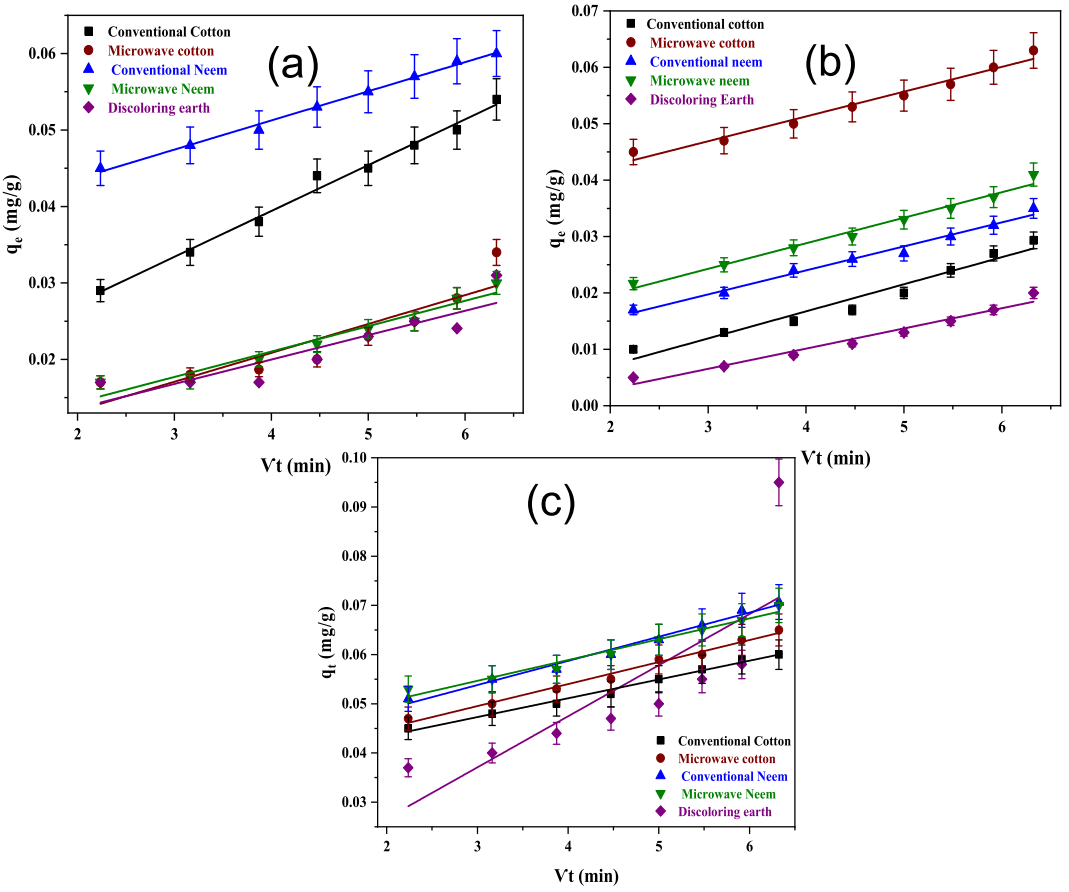

Fig. 2. Intraparticle Diffusion Kinetic plots for the decolorization of cottonseed oil at 70 (a) 80 (b) and 90 °C (c).

3.3. Modeling of pigment adsorption kinetics and isotherms

Four models grouped in two were used to describe the decolorization process: Kinetic models (intraparticle diffusion and pseudo-second-order) and isotherm models (Langmuir and Freundlich).

3.3.1. Kinetic models

3.3.1.1. Kinetic model of intra-particle diffusion. Table 3 shows the intraparticle diffusion constants obtained for the adsorption of cottonseed oil pigments, as well as the related regression coefficients. The R^2 values for all the adsorbents are greater than 0.90 indicating that the model describes the phenomenon of adsorption of oil pigments from neutral cottonseed oil in a batch system satisfactorily. The kinetic model of intra-particle diffusion gives an idea of the adsorption mechanism. Fig. 2(a-c) shows that the adsorption of cottonseed oil pigments generally takes place in one phase. It can also be observed that, for all adsorbents, no regression line passes through the origin; this result suggests that the adsorption of the pigments of this vegetable oil involves intraparticle diffusion but this step would not be the only factor controlling the reaction rate [24–27]. This may be an indication that the diffusion of the pigments into the solution is a limiting step in the adsorption process.

3.3.1.2. The pseudo-second-order kinetic model. Pseudo-second-order kinetic model constants were determined from plots of t/q_t versus t as shown in Fig. 3(a–c), where q_t is the relative amount of pigments adsorbed at equilibrium and at time t, k is the pseudo-second-order rate constant. The R^2 values, the quantities of pigments adsorbed at equilibrium, and the other constants of the model are presented in Table 3. It can be observed that the R^2 coefficients for the pseudo-second-order kinetic model are very close to unity; These results show that the pseudo-second-order kinetic model applies to the adsorption of cottonseed oil pigments on the various activated carbons. The adsorption mechanism of these pigments would therefore be based on the hypothesis of the second-order kinetic model. This kinetic model has been widely used to describe the adsorption of solutes in the liquid phase [30,35–37]. The calculated amounts of pigments adsorbed at equilibrium increase with temperature and vary depending on the type of activated carbon considered. It can be

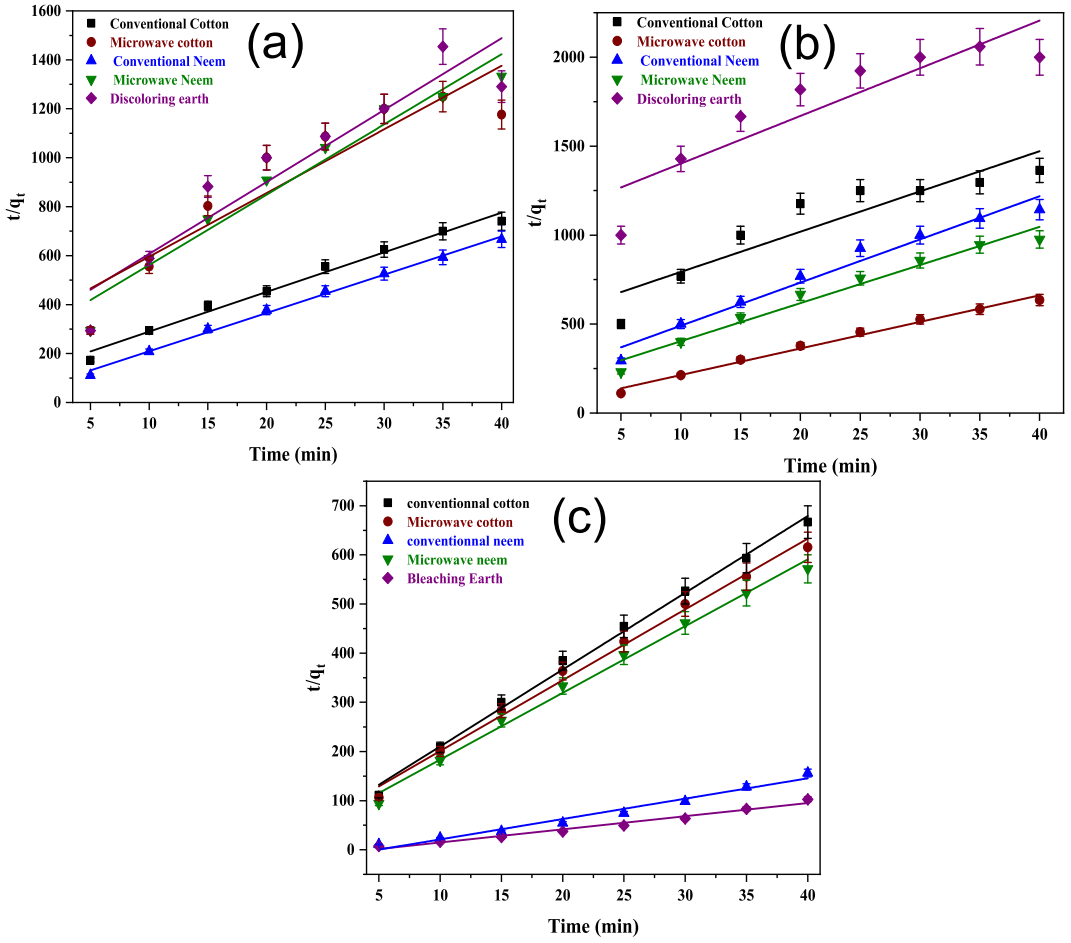

Fig. 3. Pseudo second order Kinetic plots of for the decolorization of cottonseed oil at 70 (a) 80 (b) and 90 °C (c).

Table 4
Langmuir and Freundlich model parameters for the adsorption of cottonseed oil pigments in the batch system.

Langmuir															
Temperature (°C)/Adsorbent	AC1			AC2			AC3			AC4			BE		
Constant		K_L	R^2	a_L	K_L	R^2	a_L	K_L	R^2	a_L	K_L	R^2	a_L	K_L	R^2
70	1.798	−0.293	0.979	0.682	−0.894	0.991	0.306	−1912	0.932	0.35	−1605	0.91	−0.682	−0.894	0.991
80	1.434	−0.468	0.98	0.449	−1553	0.937	0.327	−2157	0.975	0.042	−18.58	0.92	1146	−5142	0.912
90	2.801	−0.084	0.968	1779	7472	0.978	3	−0.074	0.96	3	−0.047	0.958	1236	−0.214	0.976
Freundlich															
Constant	**AC1**			**AC2**			**AC3**			**AC4**			**BE**		
	N	**K_F**	**R^2**	**N**	**K_F**	**R^2**	**N**	**K_F**	**R^2**	**N**	**K_F**	**R^2**	**n**	**K_F**	**R^2**
70	0.263	−5055	0.935	0.148	−95.35	0.915	0.158	−84.95	0.982	0.922	−160.8	0.933	0.567	−2.595	0.988
80	0.988	0.005	0.959	0.788	0.12	0.904	0.688	0.222	0.985	0.726	0.614	0 .964	0.279	1196	0.902
90	1	0.004	0.959	0.846	0.956	0.987	0.53	0.713	0.993	0.984	0.764	0.98	0.848	0.965	0.99

noted that at low temperatures, the amounts of pigments adsorbed are lower than the amounts of pigments adsorbed at high temperatures. Similarly, AC3-activated carbon presents the largest amounts of adsorbed pigments followed respectively by AC4, AC1, AC2, and bleaching earth (BE). This evolution is proportional to the value of the specific surface areas of the ACs earlier reported. For the same adsorbent, the rate constants K_S increased with an increase in temperature. For different adsorbents at the same temperature, the rate constants K_S decreased in the order AC1, AC2, AC3, AC4, and BE. The increase in adsorption rate with increasing temperature (Fig. 3(a-c)) is probably due to the rapid diffusion of adsorbate molecules to the surface of the activated carbon. This diffusion is in fact facilitated by the increase in the fluidity of the oil analyzed under the effect of temperature as earlier adduced [38,39].

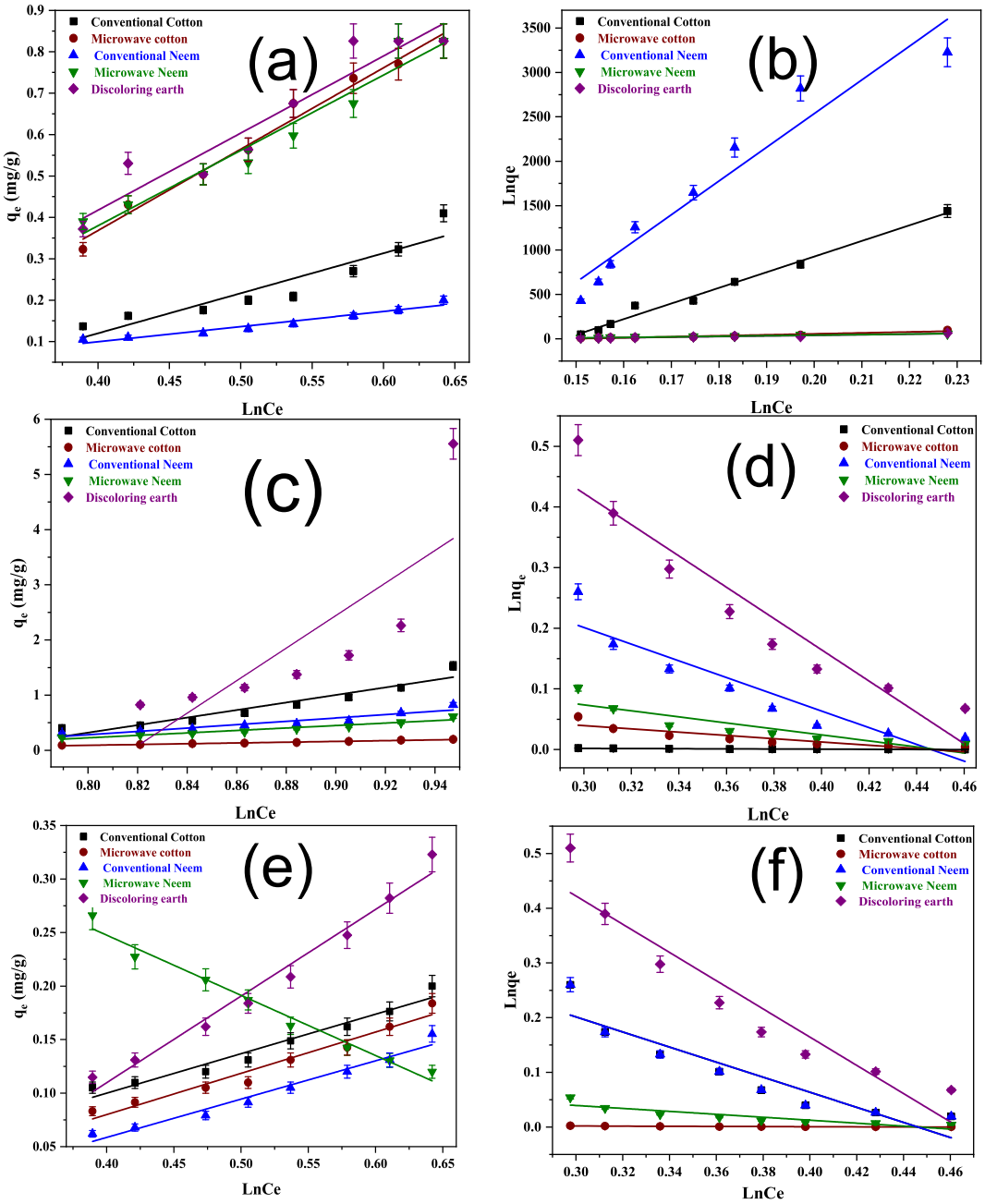

Fig. 4. Langmuir (a, c and e) and Freundlich (b, d and f) isotherms plots for the decolorization of cottonseed oil at 70, 80, and 90 °C respectively. Notes: AC1: Activated carbon from 6-h conventional activation of cotton husks, AC2: Activated carbon from 30-min microwave activation of cotton husks, AC3: Activated carbon from 6-h conventional activation of neem husks, AC4: Activated carbon from 30-min microwave activation of neem husks.

3.3.2. Models for adsorption isotherms

3.3.2.1. Langmuir and Freundlich models. Table 4 shows that the R^2 coefficients for the Langmuir and Freundlich models were generally greater than 0.91 at the three temperatures studied. The results presented in Fig. 4 a, c, e (Langmuir) and Fig. 4 b, d, f (Freundlich) also indicate that the two models fit the experimental data well. This is an indication that the adsorption of pigments and free fatty acids from cottonseed oil on activated carbons also involves a physical process. The values of the constant *n* of the Freundlich model are less than 1, which translates the fact that the pigments and the adsorbents (ACs) are bonded by weak forces [40]. The adequate description of the adsorption of pigments from neutral cottonseed oil by the Langmuir and Freundlich models at all temperatures also shows that the process is governed by the monolayer and multilayer adsorption mechanisms. Validation of Freundlich isotherms further shows that the adsorption was not at a uniform site [40]. Hence, validation of kinetic and isotherm models points to the fact that the adsorption of the pigments is made up of both physical and chemical adsorption types which indicates that decolorization would not be reversible.

4. Conclusion

Activated carbons (ACs) were prepared from neem and cottonseed husks by open air (conventional) and microwave-assisted impregnation in an acid medium and tested towards the decolorization of neutral cottonseed oil. Specific surface area and methylene blue index values of the ACs indicated that they have the potential to decolorize neutral cottonseed oil. Both the starting material and method of preparing the activated carbon had significant effects on the decolorization of neutral cotton seed oil. The prepared ACs were 30–80 % more efficient compared to bleaching earth normally used in industries for the decolorization of cottonseed oil. The process was successfully modelled by the intra-particle, pseudo-second-order models, and the Langmuir and Freundlich isotherms. Pigment adsorption from the oil by the ACs is endothermic and the adsorption type is a mix of physical and chemical adsorptions. Both methods of preparation of the ACs are effective in oil decolorization but microwave impregnation is more appealing because it requires only 1 h compared to 6 h for ambient air. Optimum decolorization conditions are a temperature of 90 °C, a time of 40 min, and a concentration of adsorbent at 2 %. The prepared activated carbons have great potential to replace bleaching earth currently used in the cotton oil industry and should be tested in column reactors and on a pilot scale to ascertain these results. The quality of the decolorized oil with these ACs should also be investigated.

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Data availability

Additional data that supports this research is available upon request from the corresponding author.

CRediT authorship contribution statement

Abba Chetima: Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **Divine Nde Bup:** Writing – review & editing, Supervision, Methodology, Data curation, Conceptualization. **Fannyuy Kewir:** Writing – review & editing, Writing – original draft, Formal analysis. **Abdoul Wahaboua:** Supervision, Methodology, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] D.P. Yang, Z. Li, M. Liu, X. Zhang, Y. Chen, H. Xue, R. Luque, Biomass-derived carbonaceous materials: recent progress in synthetic approaches, advantages, and applications, ACS Sustain. Chem. Eng. 7 (5) (2019) 4564–4585.
[2] S. Nethaji, A. Sivasamy, A.B. Mandal, Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass, Int. J. Environ. Sci. Technol. 10 (2013) 231–242.
[3] A.E. Ogungbenro, D.V. Quang, K.A. Al-Ali, L.F. Vega, M.R. Abu-Zahra, Synthesis and characterization of activated carbon from biomass date seeds for carbon dioxide adsorption, J. Environ. Chem. Eng. 8 (5) (2020) 104257.
[4] A.T. Hoang, S. Kumar, E. Lichtfouse, C.K. Cheng, R.S. Varma, N. Senthilkumar, X.P. Nguyen, Remediation of heavy metal polluted waters using activated carbon from lignocellulosic biomass: an update of recent trends, Chemosphere (2022) 134825.
[5] Z. Jiang, S.H. Ho, X. Wang, Y. Li, C. Wang, Application of biodegradable cellulose-based biomass materials in wastewater treatment, Environ. Pollut. 290 (2021) 118087.

[6] P. Ziarati, M. Mokhtarzadeh, V. Vambol, S. Vambol, B. Sawicka, A.E.D. Mahmoud, N.A. Khan, Bioremediation of pharmaceutical effluent by food industry and agricultural waste biomass, Hospital Wastewater Treatment 53 (2022).
[7] S. Arabian, P. Ziarati, B. Sawicka, Waste herbal and black tea as a novel adsorbent for detoxification of pharmaceutical effluent, J Med Discov 5 (3) (2020) 1–15.
[8] B. Narowska, M. Kułażyński, M. Łukaszewicz, E. Burchacka, Use of activated carbons as catalyst supports for biodiesel production, Renew. Energy 135 (2019) 176–185.
[9] I. Sanchis, J.J. Rodriguez, A.F. Mohedano, E. Diaz, N-doped activated carbon as support of Pd-Sn bimetallic catalysts for nitrate catalytic reduction, Catal. Today 423 (2023) 1–11.
[10] L. Piergiovanni, S. Limbo, 17 packaging and the shelf life of vegetable oils, Food Packag. Shelf Life (2010) 317.
[11] C. Vaisali, S. Charanyaa, P.D. Belur, I. Regupathi, Refining of edible oils: a critical appraisal of current and potential technologies, Int. J. Food Sci. Technol. 50 (1) (2015) 13–23.
[12] S. Manjula, R. Subramanian, Membrane technology in degumming, dewaxing, deacidifying, and decolorizing edible oils, Crit. Rev. Food Sci. Nutr. 46 (7) (2006) 569–592.
[13] S. Gharby, Refining vegetable oils: chemical and physical refining, Sci. World J. 2022 (2022) 1–10.
[14] M.R. Sabour, M. Shahi, Spent bleaching earth recovery of used motor-oil refinery, Civil Engineering Journal 4 (3) (2018) 572–584.
[15] W.F. De Greyt, Current and future technologies for the sustainable and cost-efficient production of high quality food oils, Eur. J. Lipid Sci. Technol. 114 (10) (2012) 1126–1139.
[16] G. Kılınççeker, M.K. Sangün, S. Çelik, U. Arslan, F. Zarifi, Evaluation of reusability of bleaching earth in vegetable oil refining, Pigment Resin Technol. 49 (5) (2020) 393–399.
[17] D.B. Nde, P.D. Muley, C.M. Sabliov, S.E. Nokes, D. Boldor, Microwave assisted pyrolysis of Kraft lignin in single mode high-Q resonant cavities: degradation kinetics, product chemical composition, and numerical modeling, Energy Convers. Manag. 230 (2021) 113754.
[18] D.B. Nde, M. Barekati-Goudarzi, P.D. Muley, L. Khachatryan, D. Boldor, Microwave-assisted lignin liquefaction in hydrazine and ethylene glycol: reaction pathways via response surface methodology, Sustainable Materials and Technologies 27 (2021) e00245.
[19] E. Yagmur, S. Turkoglu, A. Banford, Z. Aktas, The relative performance of microwave regenerated activated carbons on the removal of phenolic pollutants, J. Clean. Prod. 149 (2017) 1109–1117.
[20] E. Yagmur, M. Ozmak, Z. Aktas, A novel method for production of activated carbon from waste tea by chemical activation with microwave energy, Fuel 87 (15–16) (2008) 3278–3285.
[21] R.H. Hesas, W.M.A.W. Daud, J.N. Sahu, A. Arami-Niya, The effects of microwave heating method on the production of activated carbon from agricultural waste: a review, J. Anal. Appl. Pyrol. 100 (2013) 1–11.
[22] F.K. Yuen, B.H. Hameed, Recent developments in the preparation and regeneration of activated carbons by microwaves, Adv. Colloid Interface Sci. 149 (1–2) (2009) 19–27.
[23] S.S. Lam, R.K. Liew, Y.M. Wong, P.N.Y. Yek, N.L. Ma, C.L. Lee, H.A. Chase, Microwave-assisted pyrolysis with chemical activation, an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent, J. Clean. Prod. 162 (2017) 1376–1387.
[24] A. Chetima, A. Wahabou, G. Zomegni, A.N. Rahman, D.B. Nde, Bleaching of neutral cotton seed oil using organic activated carbon in a batch system: kinetics and adsorption isotherms, Processes 6 (3) (2018), https://doi.org/10.3390/pr6030022.
[25] A.C. Lua, J. Guo, Activated carbon prepared from oil palm stone by one-step CO2 activation for gaseous pollutant removal, Carbon 38 (7) (2000) 1089–1097.
[26] S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review, Sustainable Materials and Technologies 9 (2016) 10–40, https://doi.org/10.1016/j.susmat.2016.06.002. Elsevier B.V.
[27] J.B.B. Mbah, R. Kamga, J.P. Nguetnkam, J. Fanni, Adsorption of pigments and free fatty acids from shea butter on activated Cameroonian clays, Eur. J. Lipid Sci. Technol. 107 (6) (2005) 387–394, https://doi.org/10.1002/ejlt.200501149.
[28] V. Balasubramanian, et al., Holographic thermalization, Phys. Rev. D: Part., Fields, Gravitation, Cosmol. 84 (2) (2011), https://doi.org/10.1103/PhysRevD.84.026010.
[29] D. Boldor, A. Kanitkar, B.G. Terigar, C. Leonardi, M. Lima, G.A. Breitenbeck, Microwave assisted extraction of biodiesel feedstock from the seeds of invasive Chinese tallow tree, Environ. Sci. Technol. 44 (10) (2010) 4019–4025, https://doi.org/10.1021/es100143z.
[30] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard Mater. 164 (2–3) (2009) 870–875, https://doi.org/10.1016/j.jhazmat.2008.08.084.
[31] K.M. Al-Qahtani, Water purification using different waste fruit cortexes for the removal of heavy metals, J. Taibah Univ. Sci. 10 (5) (2016) 700–708, https://doi.org/10.1016/j.jtusci.2015.09.001.
[32] E.C. Achife, J.A. Ibemesi, Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils, J. Am. Oil Chem. Soc. 66 (2) (1989) 247–252, https://doi.org/10.1007/BF02546069.
[33] W. Schirmer, Physical Chemistry of surfaces, Z. Phys. Chem. 210 (1) (1999) 134–135, https://doi.org/10.1524/zpch.1999.210.part_1.134.
[34] A. Rahman, Modified composite activated carbon derived from post-consumer plastics and lignocellulosic materials, Am. Chem. Sci. J. 3 (1) (2013) 24–33, https://doi.org/10.9734/acsj/2013/2210.
[35] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, J. Hazard Mater. 141 (3) (2007) 819–825, https://doi.org/10.1016/j.jhazmat.2006.07.049.
[36] A. De Juan, M. Maeder, M. Martínez, R. Tauler, Combining hard- and soft-modelling to solve kinetic problems, Chemometr. Intell. Lab. Syst. 54 (2) (2000) 123–141, https://doi.org/10.1016/S0169-7439(00)00112-X.
[37] H. Zheng, D. Liu, Y. Zheng, S. Liang, Z. Liu, Sorption isotherm and kinetic modeling of aniline on Cr-bentonite, J. Hazard Mater. 167 (1–3) (2009) 141–147, https://doi.org/10.1016/j.jhazmat.2008.12.093.
[38] T. Langmaack, R. Eggers, On the bleaching kinetics of vegetable oils - experimental study and mass transfer-based interpretation, Eur. J. Lipid Sci. Technol. 104 (2) (2002) 98–109, https://doi.org/10.1002/1438-9312(200202)104:2<98::AID-EJLT98>3.0.CO;2-E.
[39] B.H. Hameed, M.I. El-Khaiary, Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K2CO3 activation and subsequent gasification with CO2, J. Hazard Mater. 157 (2–3) (2008) 344–351, https://doi.org/10.1016/j.jhazmat.2007.12.105.
[40] A.A. Inyinbor, F.A. Adekola, G.A. Olatunji, Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphia hookerie fruit epicarp, Water Resour. Ind. 15 (2016) 14–27, https://doi.org/10.1016/j.wri.2016.06.001.