

# Adsorption of Tartrazine onto Activated Carbon Based Cola Nuts Shells: Equilibrium, Kinetics, and Thermodynamics Studies

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## Abstract

The uptake of tartrazine from its aqueous solution by powdered activated carbon prepared from cola nut shells chemically activated with potassium hydroxide (ACK) and phosphoric acid (ACP) has been investigated using kinetics models. Batch isotherm data were analysed with the pseudo-first order, pseudo-second order model as well as the intraparticle diffusion model. For structural elucidation, the materials were characterized using FTIR, XRD and SEM. These analyses revealed that the activated carbons (ACK and ACP) were predominantly mesoporous with several oxygen-containing functional groups dispersed on their surface. The reaction was systematically investigated under various experimental conditions such as contact time, adsorbent dose and pH. For the two adsorbents, the quantity adsorbed of 19.256 mg/g and 18.196 mg/g respectively for ACP and ACK at respective contact times of 5 and 10 min were obtained. The adsorption data were tested with the Langmuir, Freundlich models. Langmuir model was found to best describe the adsorption of tartrate ions with maximum monolayer adsorption capacities of 24.57 and 21.59 mg/g for ACP and ACK, respectively. Results analysis indicated clearly that the pseudo-second order kinetic rate model best fitted the experimental data and therefore was the adsorption controlling mechanism for both adsorbents. Thermodynamic studies revealed that the adsorption process was spontaneous and exothermic for ACP with increased randomness at the solid solution interface, then exothermic but non-spontaneous for ACK. The results show that these activated carbons could be an alternative for more costly adsorbents for the purpose of tartrate ions elimination.

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## Keywords

Cola Nuts Shells, Activated Carbon, Adsorption, Tartrazine

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## 1. Introduction

Though industrial activities have contributed to the development of many countries, they have also generated undesirable by-products, which constitute the main part of the discharged effluents. These industrial effluents are organic (dyes, pesticides) and inorganic (heavy metals) pollutants. Owing to their appearance, coloured organic compounds are easily recognizable pollutants. These chemical pollutants in industrial effluents are mostly non-biodegradable and highly toxic as they affect aquatic ecosystems, destroy wildlife and affect human health, provoking conditions such as rashes, allergic reactions, dysfunction of the kidney, the reproductive system and the central nervous system in humans [1] [2].

Dye under investigation, tartrazine (otherwise known as E102 or FD & C Yellow 5), is a lemon yellow azo dye manufactured from coal-tar derivative and used as a food colouring. It is found in certain brands of fruit squash, fruit cordial, coloured fizzy drinks, instant puddings, cake mixes, custard powder, soups, sauces, ice cream, ice lollies, sweets, chewing gum, marzipan, jam, jelly, marmalade, mustard, yoghurt and many convenience foods [3]. It is cheaper than beta-carotene and therefore used as an alternative to beta-carotene to achieve similar colour [4]. Water-soluble tartrazine is used in drugs, especially shells of medicinal capsules, syrups and cosmetics. The wide use of tartrazine in industry and its water-soluble nature maximize its chances to be found as contaminant in industrial effluents [5]. Tartrazine is also reputed to catalyse hyperactivity [6], and other behavioural problems [7], asthma [8] [9], migraines, thyroid cancer [10]. According to WHO, the acceptable daily intake (ADI) of tartrazine is 7.5 mg/kg of body mass, which classifies it as a very toxic substance. It is therefore important to treat wastewaters containing tartrazine before their injection into the environment.

Many methods including chemical precipitation, filtration, ion exchange, reverse osmosis, ultra-filtration, biological degradation, membrane separation, solvent extraction and adsorption have been employed to remove pollutants. Adsorption remains the most utilised process because of its simplicity, high efficiency and easy recovery [11]. In the scientific literature, typical adsorbents include zeolite, clay, silica gel, resins, activated alumina and activated carbon [12] [13]. Activated carbon (AC) is the most widely used owing to its well-developed pore structure, large active surface area, good mechanical properties and multiple functional groups at their surface [14] [15]. There are many precursors from which AC can be prepared some of these include corn cobs [2], apricot stone [16], sugarcane bagasse, coconut shells [17], peanut hull [18], rattan bam-

boo, sawdust [19], hazelnut bagasse [20], cotton stalk fibre [1], rice husk [21], cola nut shell [11], and olive stone [22].

The goal of the present study, is to evaluate the adsorption capacities of activated carbon prepared from cola nut shells activated separately with KOH and  $H_3PO_4$  to remove tartrazine from aqueous solution using batch system and to get an insight into the adsorption controlling mechanism by testing the experimental data with well-known linear and nonlinear kinetic models applied to liquid phase adsorption.

## 2. Experimental Methods

### 2.1. Preparation of Absorbents

The procedure for the preparation of the activated carbon (AC) used in this work has-been reported by [23]. The raw material constituted by kola nut shell was collected in the region of the Northwest Cameroon, more exactly in the department of Donga-Mantung; these cola nut shells are classified in the group of lignocellulosic compounds. These shells contain essentially organic, mineral substances and water, thus constitute a real source of agricultural waste, possessing interesting physico-chemical characteristics for the production of activated charcoals.

The kola nut shells collected are abundantly washed in the current water to eliminate the impurities, rinsed in the distilled water and then dried in air during two weeks. Once dried, they are crushed until the obtaining of fragments having a size between 1.25 and 2.5 mm. These fragments are impregnated with the potassium hydroxide (KOH) and the phosphoric acid ( $H_3PO_4$ ) with a ratio of 1:1 (mass activating agent/mass of raw material).

After impregnation, these fragments of cola nut shells were dried in the oven room at  $110^\circ\text{C}$  during 24 hours. The carbonization of material was made at  $500^\circ\text{C}$  during 1 hour and cool down until the room temperature.

After cooling, the activated carbon was washed with distilled water until neutral pH was obtained, then crushed in a mortar by means of a pestle, until the obtaining of the powder.

#### 2.1.1. Characterization of Activated Carbons

Samples of activated carbon were characterised using various techniques: Infra-red spectroscopy (IR) to probe the surface functional group, Scanning Electron Microscopy (SEM) to investigate the surface morphology, X-ray diffraction (XRD) analysis was to evaluate the crystalline or amorphous structure and the BET method to determine the specific surface area. The iodine number was determined to evaluate the microporosity.

#### 2.1.2. Preparation of Adsorbate

The tartrazine stock solution (60 ppm) was prepared by dissolving 0.015 g of tartrazine powder with distilled water in a 250 mL volumetric flask. The solution was stirred for 24 hours to obtain the homogeneity. From this solution, dilute

solutions of 1, 3, 5, 7, 9, 11, 13 and 15 mg/L were prepared. 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were also prepared for pH adjustments, by dilution of initial hydrochloric acid of 37% and 2 g of sodium hydroxide in conical flasks.

## 2.2. Batch Adsorption Experiments

Batch adsorption isotherm study was carried out through several experimental runs. For each run, 20 ml of tartrazine dye of known initial concentration was added to a known mass of adsorbent and agitated for a predetermined time. After agitation, the solution was filtered using whatman N°4 filtered paper and the concentration of the supernatant fluid measured using a TECHMEL-TECHMEL S-23A UV-visible spectrophotometer at the wave length of 420 nm. Similar measurements were carried out with varying adsorbent doses, solution pH and initial concentrations of tartrazine.

The quantity adsorbed ( $Q_e$ ) adsorbed per unit mass of adsorbent, and the percentage removal (% R) were calculated using the following equations:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_e)100}{C_0} \quad (2)$$

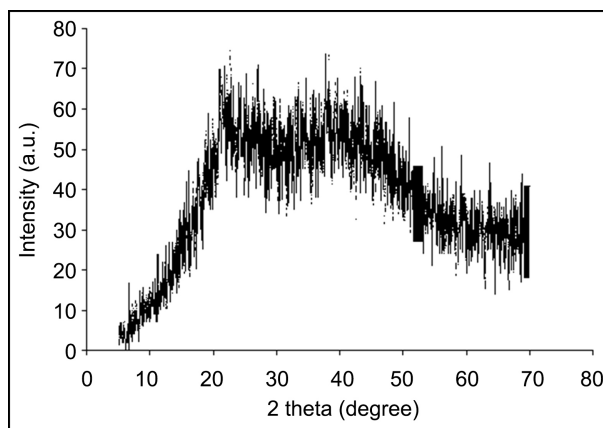
where  $C_0$  is the initial concentration,  $C_e$  the equilibrium concentration,  $V$  the volume and  $m$  is the mass of the adsorbent.

## 3. Results and Discussion

### 3.1. On the Characterization of Adsorbent

#### 3.1.1. Powder X-Ray Diffraction Analysis

The XRD spectrum of AC recorded between 5 to 70 degrees is presented in **Figure 1**. The region between 7 and 70 degrees indicates the absence of any crystalline structure with the absence of any well-defined peak, which is an indication of an amorphous structure

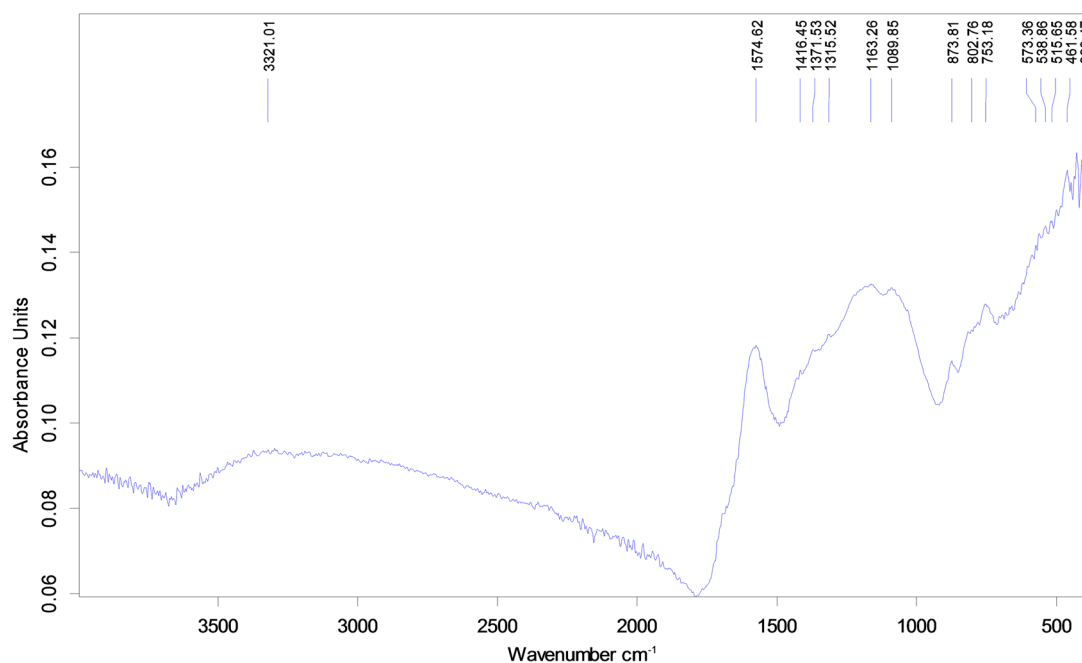


**Figure 1.** X-ray diffractogram of AC.

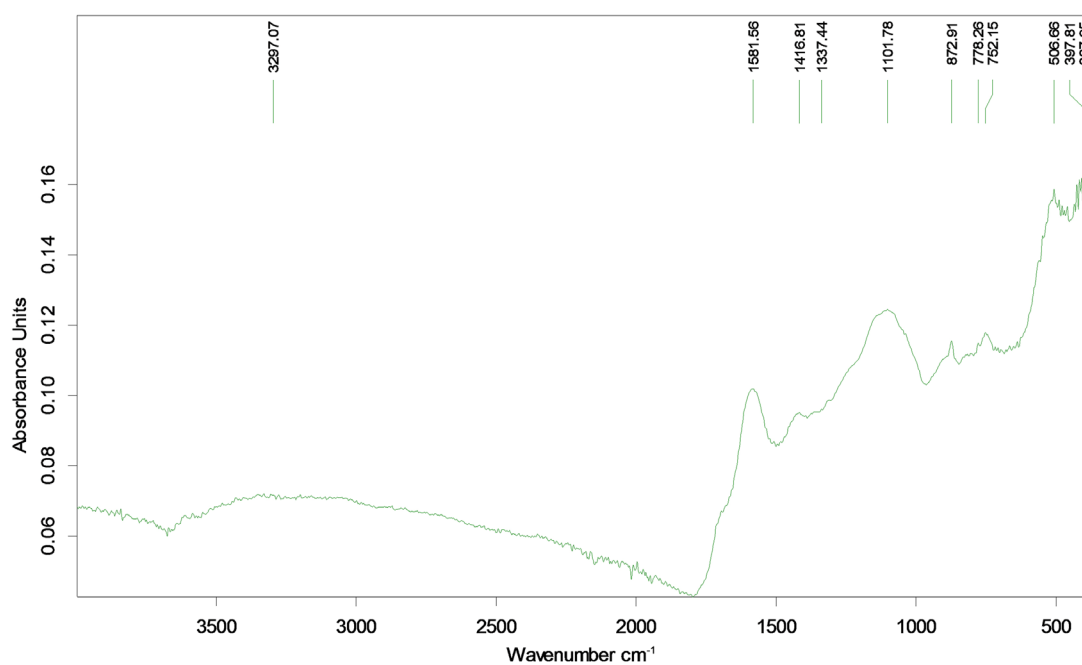
This result is in good agreement with the nature of activated carbon prepared by others researchers reported in literature.

### 3.1.2. Infrared Spectroscopy Analysis of ACK and ACP

The FT-IR spectroscopy analysis allows identifying functional groups present on the adsorbents surface. **Figure 2** and **Figure 3** below shows the FT-IR spectra of both AC before adsorption:



**Figure 2.** Infrared spectrum of ACK before adsorption.



**Figure 3.** Infrared spectrum of ACP before adsorption.

On the recorded spectra, there are bands at  $3321\text{ cm}^{-1}$  and  $1574\text{ cm}^{-1}$  corresponding to O-H and C=C stretching vibration of phenolic and aromatic rings, respectively. The bands at  $1416$  and  $1371\text{ cm}^{-1}$  are attributed to the N-H of amines and C-H of benzene bending vibration of respectively; the band at  $1163\text{ cm}^{-1}$  is attributed to C-O stretching vibration, whereas the bands at  $873$ ,  $802$  and  $753\text{ cm}^{-1}$  correspond to the C-H stretching vibration of benzene para, meta and ortho-substituted, respectively. The frequencies at  $573$ ,  $538$  and  $515\text{ cm}^{-1}$  are attributed to the O-K stretching vibration coming from the AC activation by KOH.

On the ACP spectra the bands which appear at  $3297$  and  $1581\text{ cm}^{-1}$  are attributed to O-H and C=C stretching vibration of phenolic and aromatic rings, respectively. The bands at  $1416$  and  $1337\text{ cm}^{-1}$  correspond to N-H of amines and C-H of benzene bending vibration respectively. The band at  $1101\text{ cm}^{-1}$  is attributed to C-O stretching vibration, whereas the bands at  $872$ ,  $778$  and  $753\text{ cm}^{-1}$  correspond to the C-H stretching vibration of benzene para, meta and ortho-substituted, respectively. The frequencies at  $506$ ,  $397$  and  $387\text{ cm}^{-1}$  are due to the O-P stretching vibration coming from the AC activation by  $\text{H}_3\text{PO}_4$  [24].

### 3.1.3. SEM Microstructural Analysis of ACP and ACK

To view the effect of activation on the pore structure of the precursor, SEM micrographs of the precursor before activation and after activation (ACP and ACK) were carried out. **Figure 4** illustrates the micrograph of the precursor before activation.

It is observed that the pores on the surface of the precursor are less developed. This poor pore distribution on its surface makes the precursor an unlikely candidate as an adsorbent. Nevertheless, activation could result to the presence surface functional groups which favoured ion exchange and increased porosity. **Figure 5** in turn displays the surfaces of the activated carbons ACP and ACK.

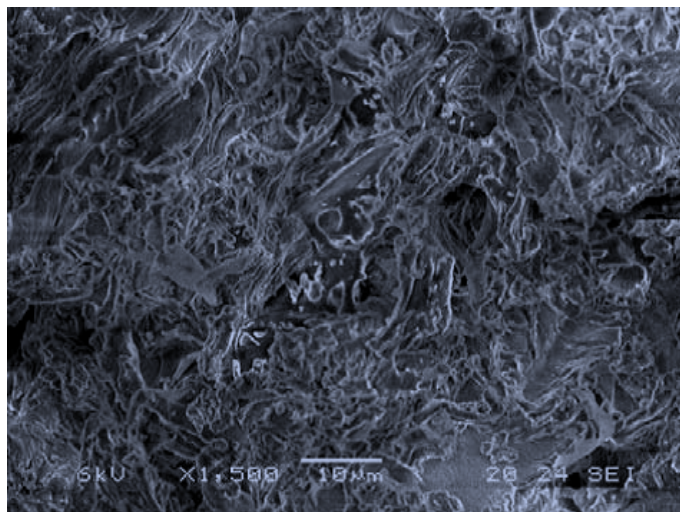
Compared to the micrograph of the precursor (**Figure 4**), the micrographs of ACP and ACK show a highly developed porosity over the entire sample surface resulting from the effect of chemical activation by phosphoric acid and potassium hydroxide. The pores are heterogeneous and not evenly distributed. It can also be seen that the pores of ACK are larger than those of ACP, but ACP has a more developed distribution of pores. This could explain the higher surface area for ACP than ACK (as seen in the BET results below).

### 3.1.4. Textural Properties of ACP and ACK

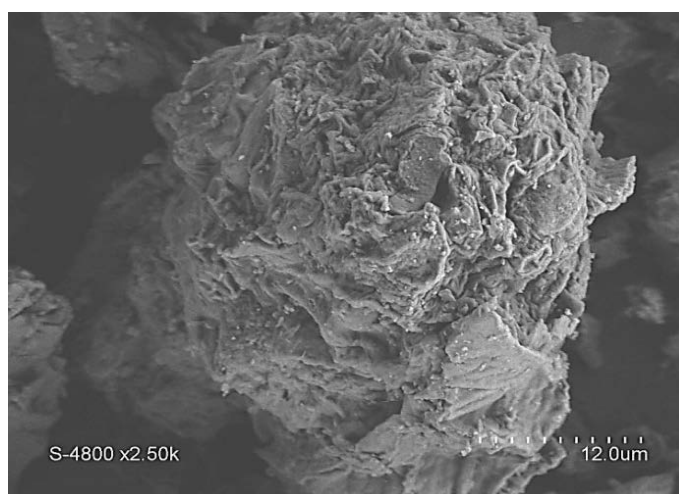
The textural properties of ACP and ACK were determined by the BET nitrogen adsorption-desorption, BJH analysis and the iodine number. These parameters are shown in **Table 1**.

The pore diameter of ACP and ACK is between  $2$  and  $50\text{ nm}$ , indicating that both materials are mesoporous. Interestingly, the mean pore size of ACK is bigger than that of ACP in good agreement with SEM analysis. The value of the iodine number ( $513.945\text{ mg/g}$ ) for ACK is within the  $500$  and  $1200\text{ mg/g}$  range and indicates the presence of micropores.

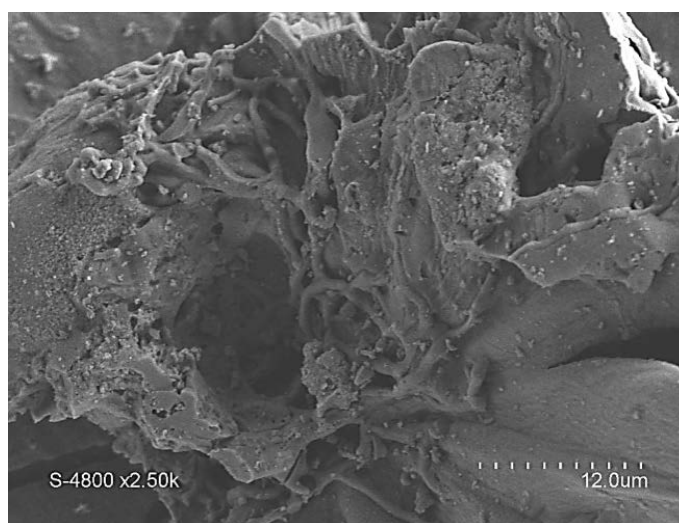




**Figure 4.** Scanning electron micrograph of cola nutshells [23].



(a)



(b)

**Figure 5.** SEM Micrographs of ACP (a) and the ACK (b) [23].

**Table 1.** Textural properties of the ACP and ACK [23].

Analysis	ACP	ACK
BET specific surface area (m <sup>2</sup> /g)	6.276	2.045
Pore adsorption cumulative surface area (m <sup>2</sup> /g)	3.255	0.992
Pore desorption cumulative surface area (m <sup>2</sup> /g)	0.992	2.672
Total pore volume (cm <sup>3</sup> /g)	0.009	0.005
Average pore diameter (Å)	61.000	94.000
Iodine Number (mg/g)	441.612	513.945

### 3.2. Adsorption

All adsorption experiments were carried out at pH 2 because at pH greater than or less than 2, the adsorbed quantities were near to zero. The same results was obtained by Sushmita Banerjee [25] during the Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. They found that tartrazine was better adsorbed under acid medium.

#### 3.2.1. Influence of Contact Time

**Figure 6** exhibits the effect of contact time on the adsorption of tartrazine and the experiments were tested by carrying out experimental runs from 5 to 70 min for ACP and ACK, at an initial tartrazine concentration of 20 mg/L, and with a mass of 0.01 g of ACP and ACK.

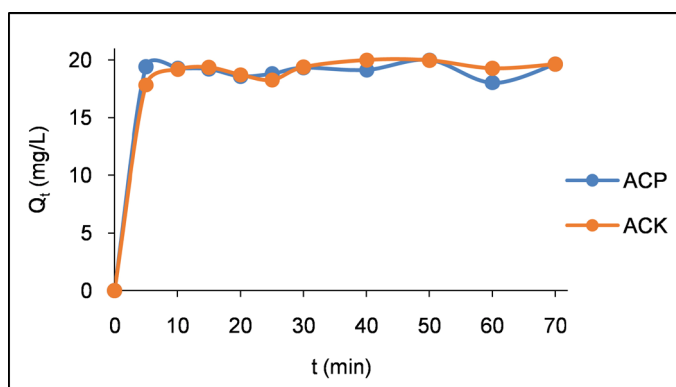
The adsorption of tartrazine is seen to rise steadily from 0 to 5 minutes with adsorbed quantities of 19.42 mg/L for ACP and 17.84 mg/L for ACK. This initial spurt may be due to the availability of adsorption sites on the surface of adsorbent materials [16]. After this time, the system is seen to attain equilibrium with the saturation of the active sites of both absorbents. This equilibrium is attained after 5 mins for ACP and 10 mins for ACK.

#### 3.2.2. Influence of the Mass of Adsorbent

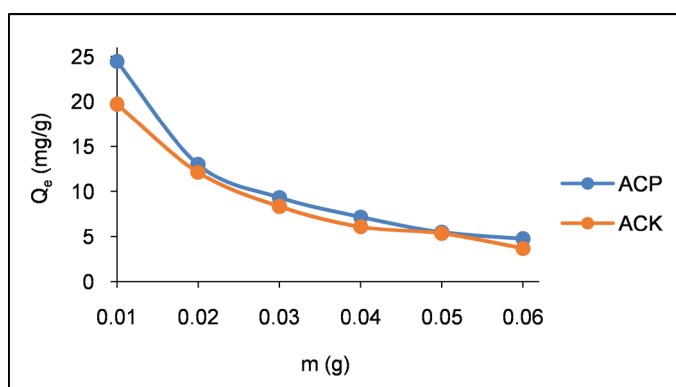
**Figure 7** below displays the influence of the adsorbent mass varying from 0.01 g to 0.06 g, at a contact time of 5 min for ACP and 10 mins for ACK and adsorbate dose of 20 mg/L.

From **Figure 7**, the amount adsorbed at equilibrium decreases as the mass of both adsorbents (ACK and ACP) is increased. At higher adsorbent mass, agglomeration of the adsorbent particles occurs due to electrostatic attractive forces between the AC particles. This impedes access to adsorption sites, hence the decrease in adsorbed quantity. This may be also due to the fact that as the amount of the adsorbent increases, the total surface area available for the adsorption of tartrazine molecules reduces as a result of the overlapping or aggregation of adsorption sites [26]. Similar results were obtained by [27] in the study of the adsorption of zinc ions on rice balls [17]. Maximum adsorption was thus recorded at a mass of 0.01 g.





**Figure 6.** Influence of contact time on the adsorption of tartrazine by ACP and ACK.



**Figure 7.** Influence of the mass of adsorbent on the quantity adsorbed.

### 3.2.3. Influence of Initial Concentration

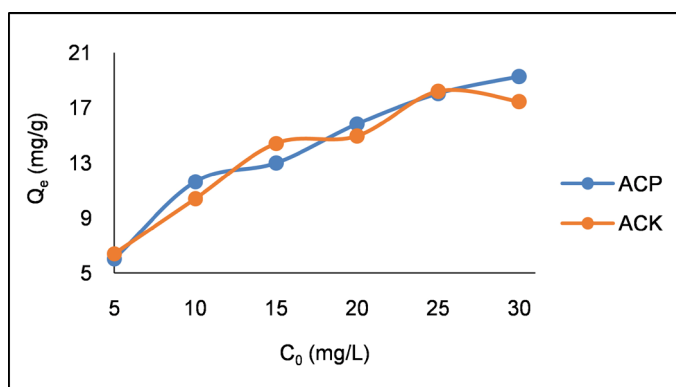
The initial concentration of the adsorbate was varied between 5 and 30 mg/L. As seen from **Figure 8**, the quantity of tartrazine adsorbed increases from 6.01 to 18.04 mg/g and from 6.4 to 18.19 mg/g respectively for ACP and ACK as the initial concentration rises from 5 to 25 mg/L. This observed increase results from a higher collision rate between tartrazine molecules and the adsorbent surface as the concentration of tartrazine increases [18]. This trend is observed for both adsorbents until an adsorbate concentration of 25 mg/L, beyond which it starts decreasing for ACK. This indicates that at higher concentrations, tartrazine molecules accumulate on the surface of ACK and block the pore openings [19], observed a similar trend for the adsorption of methylene blue on bamboo-based activated carbon.

From the batch adsorption studies, we note that the quantities adsorbed by the ACP and ACK are almost the same although ACP has a surface area almost three times higher than that of ACK. ACK however, has a higher mean pore diameter and a more pronounced surface heterogeneity than ACP due to the presence of both meso and micropores on its surface, which promote good adsorption. This parameter could therefore justify the near identical adsorbed quantities.

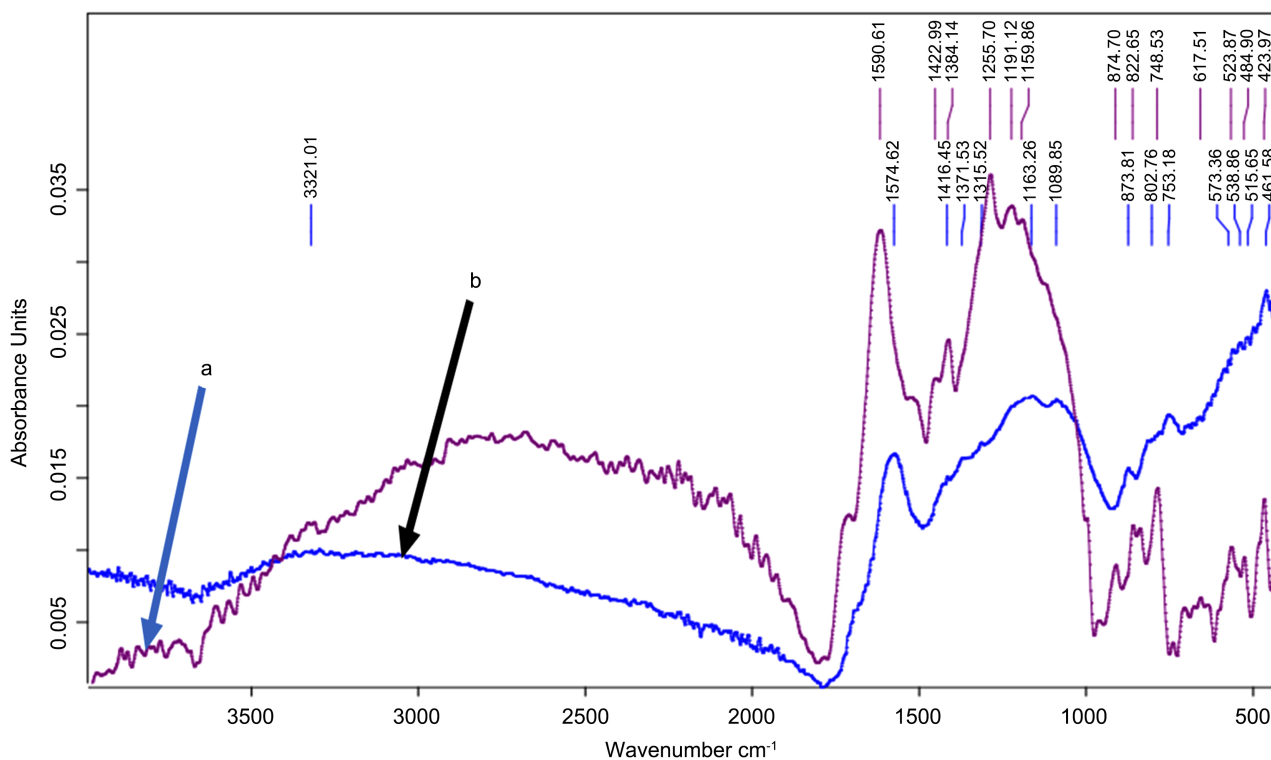
We also carried out FTIR analysis on the adsorbents after adsorption. The results are represented in **Figure 9** and **Figure 10**. Here we note the disappearance of the -OH stretching vibration at  $3321.01\text{ cm}^{-1}$  after adsorption on the spectrum of ACK (**Figure 9**); this disappearance could be as a result of the reaction between the acid group on adsorbents surface and sulphonates functional group of the tartrazine with the release of a water molecule.

### 3.3. Adsorption Isotherms

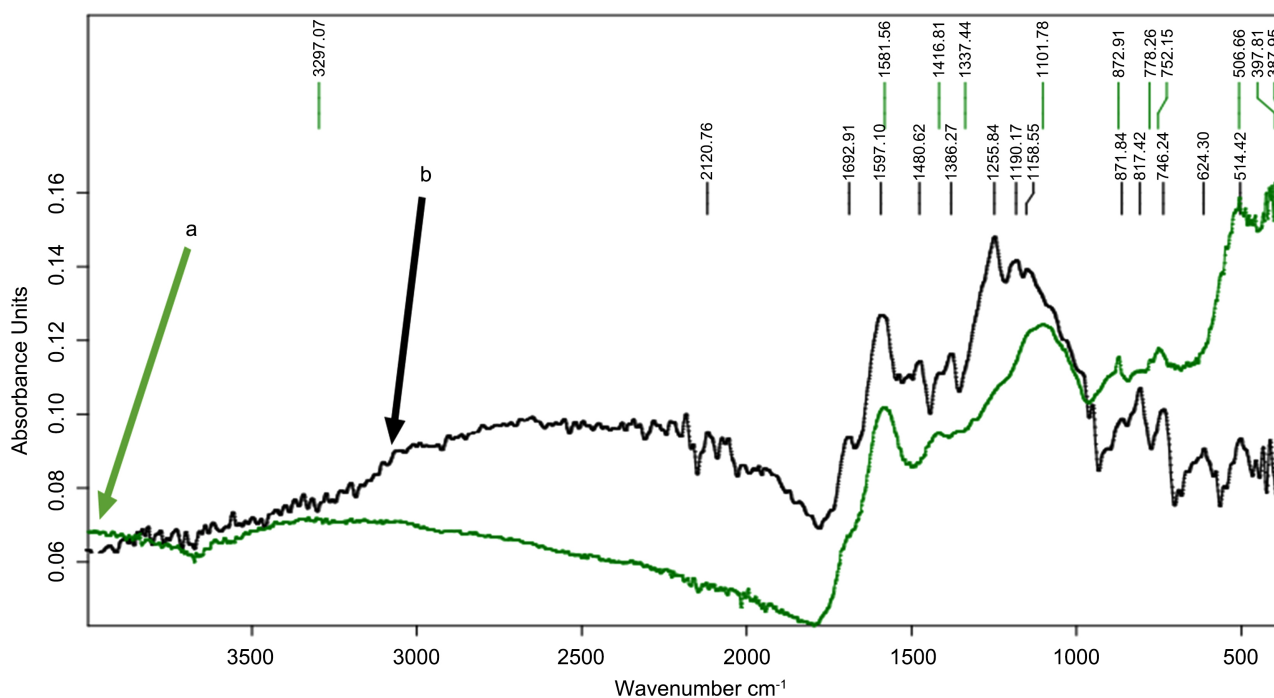
The equilibrium data was analysed using the using the following linearized isotherm models as given in Equations (3)-(5).



**Figure 8.** Influence of the initial concentration on the amount of tartrazine adsorbed by ACK and ACP.



**Figure 9.** Infrared spectrum of ACK before adsorption (a) and after adsorption (b).



**Figure 10.** Infrared spectrum of ACP before adsorption (a) and after adsorption (b).

#### Langmuir isotherm

$$\frac{1}{Q_e} = \frac{1}{Q_m K C_e} + \frac{1}{Q_m} \quad (3)$$

#### Freundlich isotherm

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

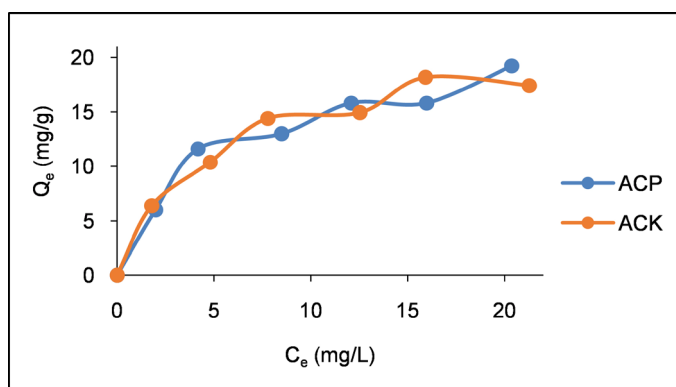
#### Dubinin-Kaganer-Radushkevich isotherm model

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2 \quad (5)$$

where:  $Q_e$  is the amount adsorbed at equilibrium (mg/g),  $K_F$  is the Freundlich constant,  $1/n$  is the heterogeneity factor which is related to the capacity and intensity of the adsorption,  $C_e$  is the equilibrium concentration (mg/L).  $\varepsilon = RT \ln(1 + 1/C_e)$  is the Dubinin-Kaganer-Radushkevich constant.  $Q_m$  = theoretical isotherm saturation capacity (mg/g),  $\beta$  is the Dubinin-Kaganer-Radushkevich isotherm constant (mol/k)<sup>2</sup>.

The adsorption isotherms for ACK and ACP obtained under optimal conditions are shown in **Figure 11**.

The adsorption isotherm of Tartrazine on ACP is type IV, characteristic of a mesoporous adsorbent. The presence of two layers result from the formation of a monolayer followed by a multilayer between the adsorbate and the adsorbent surface [28]. Here, the interaction between the molecules and the surface of the adsorbent are higher than those of the molecules themselves; the adsorption sites of the second layer will begin to be occupied when the first layer is fully saturated. The adsorption isotherm of tartrazine on ACK is also similar but the layers is less pronounced. The constants obtained from the isotherms models are given in **Table 2**.



**Figure 11.** Quantities adsorbed based on the equilibrium concentrations.

**Table 2.** Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich and Tempkin constants.

Isotherm	Constants	ACP	ACK
Langmuir	$R^2$	0.9805	0.9824
	$Q_m$ (mg·g <sup>-1</sup> )	24.57	21.598
	$K_L$ (L·mg <sup>-1</sup> )	0.165	0.222
	$R_L$	0.183	0.143
Freundlich	$R^2$	0.9408	0.9531
	$K_F$ (mg·g <sup>-1</sup> ) (L/mg) <sup>-1/n</sup>	4.912	5.289
	1/n	0.468	0.425
DKR	$R^2$	0.9221	0.8709
	$\beta$ (mol <sup>2</sup> ·J <sup>-2</sup> )	0.549	3.973
	$Q_m$ (mg·g <sup>-1</sup> )	16.815	15.863
	$E$ (kJ·mol <sup>-1</sup> )	0.954	0.355
Tempkin	$R^2$	0.970	0.954
	$K_T$ (L·mg <sup>-1</sup> )	1.623	2.079
	$b_T$ (kJ·mol <sup>-1</sup> )	0.456	0.513

The Langmuir model showed good correlation of experimental data indicating adsorption is specific (chemisorption) for both adsorbents [1]. This suggests that adsorption takes place at uniform energy sites on the adsorbents surface. This is in good agreement with the results from infrared after adsorption, which shows the formation of a chemical bond between tartrazine molecules and the surface active sites of both adsorbents. The  $R_L$  values of the Langmuir model are between 0 and 1 for both adsorbents, hence adsorption is favourable [21]. The Freundlich correlation coefficients values near unity indicate that the equilibrium data is also consistent with this model, to an extent. Thus, a 1/n value be-

tween zero and one shows that the surface of both adsorbents are heterogeneous [22]. This heterogeneity could be attributed to the different functional groups present on the adsorbent surface and to the existence of different pore sizes.

The Dubinin-Kaganer-Radushkevich isotherm adsorption energies are less than 8 kJ/mol for both materials and indicate a physisorption mechanism attributed to the multilayer formation [16], which is in good agreement with type IV isotherm. If this value were greater than 8 kJ/mol chemical adsorption or ion exchange could occur. However, given that the difference between the theoretical and experimental value of quantity adsorbed is large, this model does not accurately describe the adsorption of tartrazine ions on both materials. The value of the  $b_T$  constant of the Tempkin model is also less than 8 kJ/mol indicating that the adsorbent-adsorbate interactions are weak and are characteristic of physisorption in agreement with type IV isotherm [29]. However, the positive value of this constant suggests a gravitational adsorption on the both materials [26].

### 3.4. Study of Kinetic Models

Adsorption is a time-dependent process, and determining the rate of adsorption is highly significant in the design and evaluation of an adsorbent in removing pollutants from wastewater [29]. The linear equations of the following kinetic models were used to study the adsorption reaction mechanism:

**Pseudo-First order kinetic Model:**

$$\ln C_t = C_0 - K_1 t \quad (6)$$

**Pseudo-second order kinetic model:**

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

**Intra-particle diffusion model:**

$$Q_t = K_{id} t^{0.5} + C \quad (8)$$

**Elovich model:**

$$\frac{dQ}{dt} = \alpha e^{-\beta q_t} \quad (9)$$

Linearizing equation (9) using the  $\alpha\beta \gg t$ ,  $Q_t = 0$  to  $t = 0$ ,  $Q_t = Q_t$  at  $t = t$ , gives:

$$Q_t = \ln(\alpha\beta) + \ln t \quad (10)$$

where  $Q_e$  and  $Q_t$  are the sorption capacity (mg/g) at equilibrium and at time  $t$  respectively.  $K_1$  is the rate constant of pseudo-first order equation ( $\text{min}^{-1}$ ),  $K_2$  is the pseudo-second order rate constant ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ),  $K_{id}$  is the intra-particle diffusion constant ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ),  $C$  is a constant, which relates an idea about the boundary layer thickness of the boundary. **Table 3** below provides a comparison of the different kinetic models.

**Table 3.** Constants and speed correlation coefficients of kinetic models.

Kinetic Model	Constants	ACP	ACK
Pseudo-first order	$R^2$	0.182	0.165
	$K_1$ (min <sup>-1</sup> )	-0.015	-0.014
	$C_0$ (mg·L <sup>-1</sup> )	7.326	7.472
Pseudo-second order	$R^2$	0.995	0.999
	$K_2$ (g·min <sup>-1</sup> ·mg <sup>-1</sup> )	0.605	0.076
	$Q_e$ (mg·g <sup>-1</sup> )	19.157	19.802
	$h$ (mg·g <sup>-1</sup> ·min <sup>-1</sup> )	222.222	30.03
Intra-particle diffusion	$R^2$	0.007	0.491
	$K_{id}$ (mg·g <sup>-1</sup> ·min <sup>-1</sup> )	46.500	41.760
	$C$	0.003	0.031

From the above table, only the pseudo-second-order model has a correlation coefficient ( $R^2$  value) close to unity for both adsorbents. This indicates that the chemisorption is the rate-limiting step, the same results have been obtained by [27]. Furthermore, the theoretical and experimental adsorbed quantities are close enough and confirm the assertion that was has been made in interpreting the FT-IR spectra after adsorption. The adsorption rate constant for ACK is smaller than for ACP. This could be partly due to faster fixation ( $t = 5$  min) of tartrate ion on ACP than on ACK ( $t = 10$  min) [30]. This could attribute to the fact that ACP possesses higher surface area than ACK which lead to the more available surface active sites at the start of the process. This is also confirmed by the value of initial adsorption rate ( $h$ ) which shows that the flow of the tartrazine molecules is initially greater for ACP than ACK. Indeed the value of this parameter is seven times higher for ACP than that of ACK.

### 3.5. Thermodynamic Study and Effect of Temperature

To study the thermodynamic of the adsorption of tartrazine onto ACP and ACK, we carried experimental adsorption runs in which we varied the temperature of the adsorption milieu between the range of 30°C to 55°C. The thermodynamic parameters studied are enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ). The thermodynamic parameters were calculated from the following expressions [31]:

$$K_d = \frac{C_a}{C_e} \quad (11)$$

$$\Delta G = -RT \ln K_d \quad (12)$$

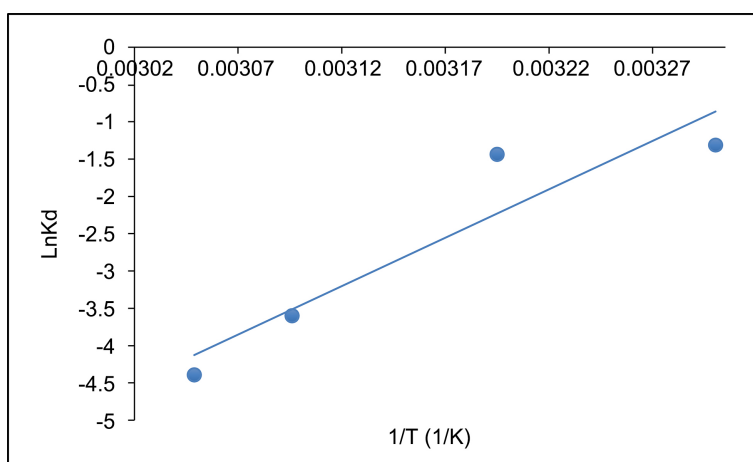
$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$



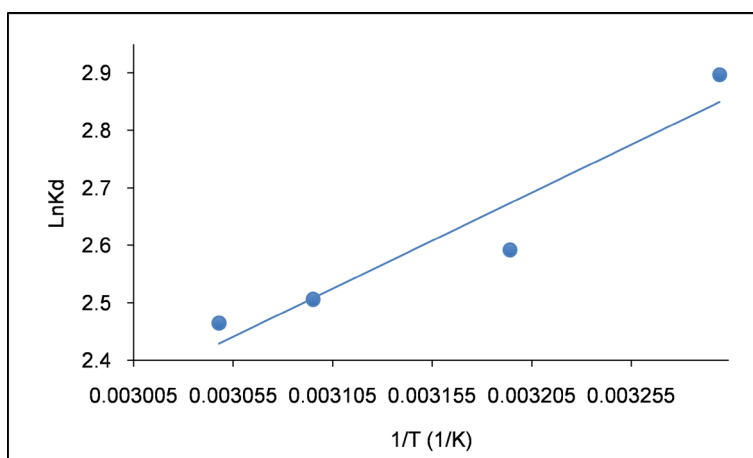
where,  $K_d$  is equilibrium constant,  $C_a$  the concentration of adsorbate in equilibrium on the adsorbent (mg/L),  $C_e$  the concentration of adsorbate in equilibrium in the solution (mg/L),  $R$  the ideal gas constant (8.314 J/K/mol),  $\Delta G^\circ$  (kJ/mol),  $\Delta H^\circ$  (kJ/mol),  $\Delta S^\circ$  (kJ/mol) are the change in free energy, enthalpy and entropy respectively.

By plotting a graph of  $\ln K_d$  versus  $1/T$  (**Figure 12** and **Figure 13**), the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be estimated from correlation coefficient value of ACK and ACP are respectively ( $R^2 = 0.8736$ ) and ( $R^2 = 0.9111$ ) indicating good linearity.

**Table 4** shows that the Gibbs energy ( $\Delta G^\circ$ ) and the enthalpy ( $\Delta H^\circ$ ) are positive. This indicates that the adsorption is exothermic and spontaneous for ACP, requiring no energy input. By contrast, the reaction is exothermic but non-spontaneous for ACK, hence it requires energy input to start the process. In addition, the negative value of  $\Delta S^\circ$  in both cases shows that the adsorption progresses with increasing disorder in the solid solution interface. We also note that the value of  $\Delta S^\circ$  for ACP is near to zero and shows that there is more disorder during adsorption of the latter, which is in agreement with the constant



**Figure 12.** Plot of  $\ln K_d$  versus  $1/T$  for adsorption of tartrazine on ACK.



**Figure 13.** Plot of  $\ln K_d$  versus  $1/T$  for adsorption of tartrazine on ACP.

**Table 4.** Thermodynamic parameters for adsorption of tartrazine by ACP and ACK.

Adsorbent	T (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol·K)
ACP	303	-7.297	-13.871	-22.090
	313	-6.745		
	323	-6.729		
	328	-6.723		
ACK	303	3.298	-107.832	-363.064
	313	3.733		
	323	9.658		
	328	11.974		

initial velocity model of pseudo-second order (seven times greater than that of ACK), showing a strong affinity between the ACP and tartrazine molecules. Moreover, examination of values of standard enthalpy of adsorption ( $< 40$  kJ/mol) [32] indicated the presence of physical attractive process made by Van Der Waals interaction during the multilayers formation. Therefore, it is reasonable to conclude that both physical adsorption and chemical adsorption equally participate in the overall process of tartrazine adsorption on ACK and ACP materials.

#### 4. Conclusion

Two adsorbents ACP and ACK were prepared and characterized. They were successfully applied to elimination of tartrazine in aqueous solution. Several factors affecting adsorption such as contact time, adsorbent dose, initial concentration of adsorbate and temperature were also studied. The variation of pH and initial concentration gave an optimum pH of 2; the quantity adsorbed increased with increasing initial concentration. We also found that the degree of heterogeneity affected the quantity adsorbed. Kinetic studies showed that chemisorption was the rate-limiting step; however, equilibrium studies revealed the presence of physical adsorption process. Additionally, thermodynamic study revealed that the adsorption was exothermic for both adsorbents, but it was spontaneous for ACP and not for ACK. The results obtained in this work confirm that AC obtained from Cola nutshells could be used for the removal of tartrazine from wastewater.

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#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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