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**Keywords:** *activated carbons; isotherms; nitrates; oil-palm shells; physicochemical activation.*

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# Adsorption Equilibrium of Nitrates Ions onto Oil Palm Shells-based Activated Carbons

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**Abstract-** In this study, two oil palm shells-based activated carbon adsorbents were prepared by physicochemical activation and were evaluated for their ability to remove nitrate ions from an aqueous solution in a batch process. Steam was used as physical activation agent in combination with H<sub>3</sub>PO<sub>4</sub> and KOH as chemical activating agents, respectively. The H<sub>3</sub>PO<sub>4</sub>-carbon (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and the KOH-carbon (ACOPS-KOH) oil palm shell activated carbons had a BET surface area of 564 and 838 m<sup>2</sup>/g, respectively, and were essentially microporous. The effects of various parameters such as contact time, initial solution pH and adsorbent dosage on nitrate ions uptake were investigated. The experimental results obtained showed that the adsorption equilibrium was reached within 70 mn. The amount of nitrate intake was observed to gradually increase when the amount of adsorbent used was varied from 0.2 to 1.2 g reaching a maximum value as from 1 g of adsorbent. The initial pH of sample solutions, varied from 3.5 to 6.5, significantly influenced the adsorption of nitrate by both adsorbents; increase in pH decreased the adsorption, with the maximum adsorption occurring at pH 3.5. The equilibrium adsorption data for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH were well correlated by Langmuir isotherm model ( $r^2 = 0.969$  and  $0.995$ , respectively) and by Freundlich isotherm model ( $r^2 = 0.967$  and  $0.961$ , respectively), indicating that both models were suitable for the description of the adsorption process. The maximum adsorption capacities were found to be 65 mg/g, and 68.166 mg/g for (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and for (ACOPS-KOH) oil palm shell activated carbons, respectively. The kinetic studies performed showed that the pseudo-second-order kinetic model best described the adsorption process of nitrate ions onto both prepared activated carbons. The results proved that the prepared oil palm shells-based activated carbons were effective adsorbents for removal of nitrate ions from aqueous solution.

**Keywords:** activated carbons; isotherms; nitrates; oil-palm shells; physicochemical activation.

## 1. INTRODUCTION

Nitrate ions in the water are of various origins and are toxic even at very low concentrations. Nitrate salts such as potassium nitrate, sodium nitrate, calcium nitrates or ammonium nitrate are used in the manufacture of nitrogen-based fertilizers. Nitrates are also used in the formulation of special cement, as food

additives and dyes, for the coagulation of latex, in nuclear industries and for the control of odors and corrosion in hydraulic systems. Thus, due to their high solubility in water nitrate ions are found in groundwater and are disastrous for aquatic ecosystems through eutrophication process. The main risk for human health associated with intake of nitrate is related to the capacity of the human organism to transform nitrates to nitrites. No studies seem to exist that report chronically toxic effects of nitrates without relating them to nitrites effects. These nitrites attach to hemoglobin and cause the disease known as methemoglobinemia which is more frequently encountered with infants. Nitrates can also be converted in the gastrointestinal tract to nitrosamines whose presence seems to favor the development of prostate, pharynx, esophagus or colon cancers.

Elimination of these substances is achieved through processes resorting to several techniques: biological treatment for biodegradable ones, coagulation, oxidation, precipitation, filtration, ions exchange, ultra filtration, reversible osmosis, electrochemical deposition and adsorption [1-3]. Many of these methods are not economically feasible in small- and medium-size and even in large industries since they are very costly. Besides, their use may sometimes expose to different forms of pollution, hence the necessity to choose simple, economical, and efficient and above all nonpolluting techniques such as adsorption onto a microporous solid like an activated carbon [3].

In short, activated carbon is a solid heat-resistant material with an adsorption capacity defined by its pore volume and functional groups, typically oxygenated functional groups present at the surface. Activated carbon main applications are, among others, in discoloring, deodorization, detoxifying of potable waters as well as purification of air, chemicals, food products, etc. It is also used as a catalyst or catalyst support.

The main objective of the present study is to prepare oil palm shells-based activated carbons and evaluate their ability to remove nitrates from an aqueous solution. To this effect, activated carbons are prepared from oil palm shells by carbonization and physicochemical activation using steam for physical activation in combination with H<sub>3</sub>PO<sub>4</sub> and KOH as chemical activating agents, respectively.

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Textural characterization of the adsorbents as well as investigation of some effects such as contact time, initial solution pH and adsorbent dosage on nitrates uptake are conducted. The equilibrium adsorption data are analyzed with Langmuir and Freundlich isotherm models to establish the most appropriate correlation for the adsorption system. Kinetics studies are performed to investigate the compliance of nitrate ions adsorption onto the prepared adsorbents with three commonly used kinetic models: pseudo-first-order, pseudo-second-order, and intra particle diffusion models.

## II. MATERIALS AND METHODS

### a) Preparation of activated carbons

#### i. Carbonization

The method adopted in this study was physicochemical activation. It consisted in carbonizing the oil palm shells first, followed by impregnation using a series of chemical agents and finally by steam activation.

A mass of 60 g of the oil palm shells sample with particles mesh size within 1–2 mm, was fed in the furnace reactor. The furnace was brought to the carbonization temperature (800°C) and maintained at this temperature for a residence time of 60 min under nitrogen atmosphere supplied at a flow rate of 100 mL/min during the temperature rise as well as the furnace cooling stages. The char produced was then recovered and weighed. The carbonization apparatus was a large electrical automatic regulator-fitted furnace (CARBOLITE 1200C Tube Furnaces, KEISON Products).

#### ii. Impregnation

##### a. Impregnation of the oil palm shell char with KOH

A quantity of the char obtained was weighed and introduced in an Erlenmeyer containing saturated potassium hydroxide (KOH) solution to achieve the desired impregnation ratio. The mixture was agitated for

two hours at 60°C. The product was then dried at 120°C for 24 h to allow for complete water evaporation.

##### b. Impregnation of the oil palm shell char with $H_3PO_4$

A quantity of the char obtained was weighed and introduced in an Erlenmeyer containing phosphoric acid ( $H_3PO_4$ ) solution to achieve the desired impregnation ratio. The mixture was agitated for two hours at 60°C. The product was then dried at 120°C for 24 h to allow for complete water evaporation.

##### iii. Activation

*Preparation of adsorbent:* The reactor was filled with a mass of 10g of impregnated char and then placed in the furnace. The furnace was brought to the activation temperature between 600 and 799°C and maintained at this temperature for three hours under steam activation with a supply flow rate of 0.1 mL/min. The sample was withdrawn following the cooling down of the furnace to ambient temperature. Two samples,  $H_3PO_4$ -impregnated (ACOPS- $H_3PO_4$ ) and KOH-impregnated (ACOPS-KOH), were prepared in this work. After the activation process, both samples were thoroughly washed with distilled water several times until pH 6–7 was achieved, the KOH-impregnated sample being washed with a 0.1 N hydrochloric acid solution before the use of distilled water. The washing process is continued until complete elimination of chloride and phosphate ions from the residual water [4]. The samples washed were dried in an oven at 110°C for 24 h. The extent of activation was obtained by calculating the ratio of the masses obtained after activation to the masses before activation. The samples were ground in a porcelain mortar, sifted with a sieve of mesh size less than 0.1mm and kept for subsequent tests. The activation process was carried out in an electrical THERMOLYNE Type 21100 furnace. The temperature was controlled by a thermocouple type K, and the activation reactor was made of stainless steel and equipped with a degassing system at the inlet. Figure 1 describes the time and energy aspects of the carbonization-activation procedure used in this study.

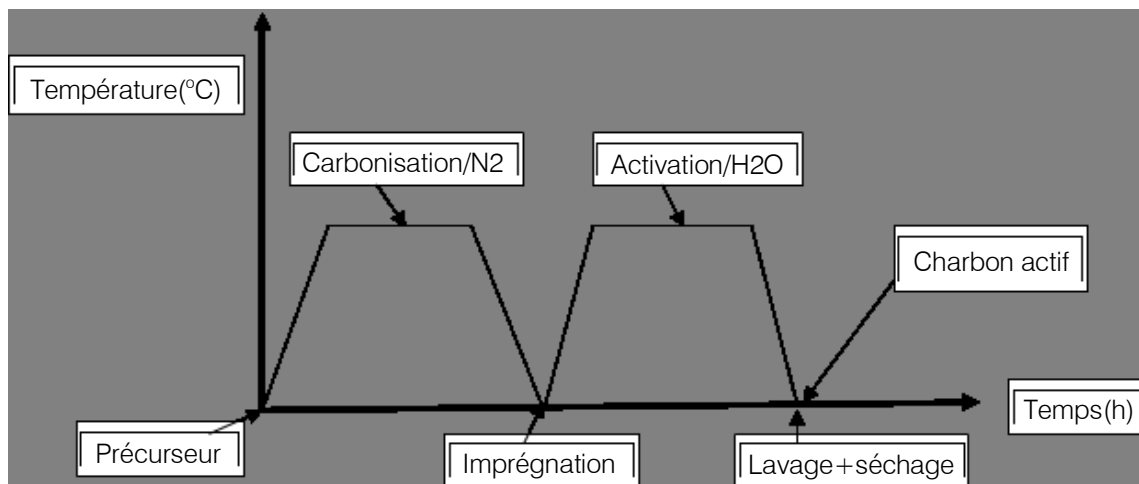


Figure 1: Main scheme of the activated carbons preparation from oil-palm shells

b) *Characterization of the activated carbons*

Adsorption of N<sub>2</sub> is a standard procedure used for the determination of the specific surface area of the activated carbons prepared. Before adsorption process, all the molecules susceptible to be present in the porous structure of the sample are eliminated by degassing under vacuum at an appropriate temperature during a definite period. In this work, the degassing was carried out for six hours at 200°C. The adsorption-desorption isotherms are obtained from liquid nitrogen at 77 K and under atmospheric pressure using Micro meritics TriStar 3000 V6.08 instrument.

c) *Batch adsorption equilibrium studies*

Batch adsorption was carried out at room temperature. For each experiment, 20 mL of nitrate ions solution of known concentration was mixed with a known mass of adsorbent. The pH of the solution was adjusted either with 0.1 N HCl or 0.1 N NaOH. The concentration of nitrate in the solution was determined by using the colorimetric method as described by Namasivayam et al.[5,6]. The concentration was determined at the wavelength of 410 nm using a UV-Visible spectrophotometer TECHMEL S23A with the maximum absorption wavelength of 1000 nm.

Batch adsorption tests were carried out by adding a fixed amount of adsorbent (0.1 g) into some 250 mL conical flasks containing a definite volume (20 mL in each case) of different initial concentrations (20-100mg/L) of nitrate solution without changing pH (2) at room temperature. The flasks were placed on a shaker and suspension was agitated for 45 minutes with S-BEL and 50 minutes with S-TIK by using a magnetic stirrer.

The amount of nitrate adsorbed onto the adsorbent at equilibrium, q<sub>e</sub> (mg/g), was calculated by the following expression:

$$q_e = (C_0 - C_e) \cdot V/W \quad (1)$$

where C<sub>0</sub> and C<sub>e</sub>(mg/L) are the initial and equilibrium nitrate concentration, respectively, V (L) is the volume of solution, and W (g) is the mass of the ACOPS adsorbent.

d) *Kinetics adsorption experiments*

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of nitrate were similarly measured.

The amount of adsorption at time t, q<sub>t</sub> (mg/g) was calculated by:

$$q_t = (C_0 - C_t) \cdot V/W \quad (2)$$

where C<sub>0</sub> and C<sub>t</sub> (mg/L) are the liquid phase concentrations of the nitrate at initial and any time t, respectively. V (L) is the volume of solution and W (g) is the mass of the ACOPS adsorbent.

### III. RESULTS AND DISCUSSION

a) *Textural and surface characteristics of prepared activated carbons*

Two activated carbons prepared from oil palm shells by physicochemical activation under inert atmosphere were obtained. ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH were the activated carbons obtained after impregnation of the char by phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and potassium hydroxide (KOH), respectively.

Nitrogen adsorption-desorption curve provides qualitative information on the adsorption mechanism and porous structure of the carbonaceous materials [7-10]. The adsorption-desorption isotherms of N<sub>2</sub> for the activated carbons are presented in Figure 2. It could be seen that both samples exhibited type I isotherms corresponding to micro pores by the International Union of Pure and Applied Chemistry (IUPAC) classification since neither displayed a hysteresis loop. The pore texture parameters obtained from the N<sub>2</sub> adsorption isotherms were summarized in Table 1. The BET surface areas of the prepared activated carbons were found to be 564.03 m<sup>2</sup>/g and 838.03 m<sup>2</sup>/g, with the total pore volume of 0.23 cm<sup>3</sup>/g and 0.39 cm<sup>3</sup>/g for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively. From the data, it was inferred that the BET surface area and total pore volume of ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH were greatly improved, implying pore development during the H<sub>3</sub>PO<sub>4</sub>- and KOH-activation stage[10]. The impregnation of the two samples by KOH and H<sub>3</sub>PO<sub>4</sub> during the preparation contributed strongly to the development of a micro porous structure. Additionally, the sample ACOPS-KOH presented greater adsorption volume of N<sub>2</sub> compared with ACOPS-H<sub>3</sub>PO<sub>4</sub>. The extent of porosity governs the sorption kinetics of adsorbates depending upon the nature of both adsorbate and adsorbent. [11]. This showed that H<sub>3</sub>PO<sub>4</sub> and KOH were effective in creating well-developed pores on the surface of the char, leading to activated carbons with the large surface area and porous structure. The structural heterogeneity is characterized regarding pore size distribution. According to the classification of IUPAC-pore dimensions, the pores of adsorbents are grouped into micropore (d < 2 nm), mesopore (d = 2-50 nm) and macropore (d > 50 nm). The pore size distributions of the prepared activated carbons are shown in Figure 3 with a sharp peak detected at pore diameter between 1 and 2 nm. Moreover, as can be seen from Figure 3, the majority of pores were of size within the interval of the diameter corresponding to micropores since 72% of pores had a diameter less than 2 nm with however the presence of super-micropores which are pores whose diameters are in the range 2-4 nm. This revealed that the activated carbons derived from oil palm shells were predominantly microporous.

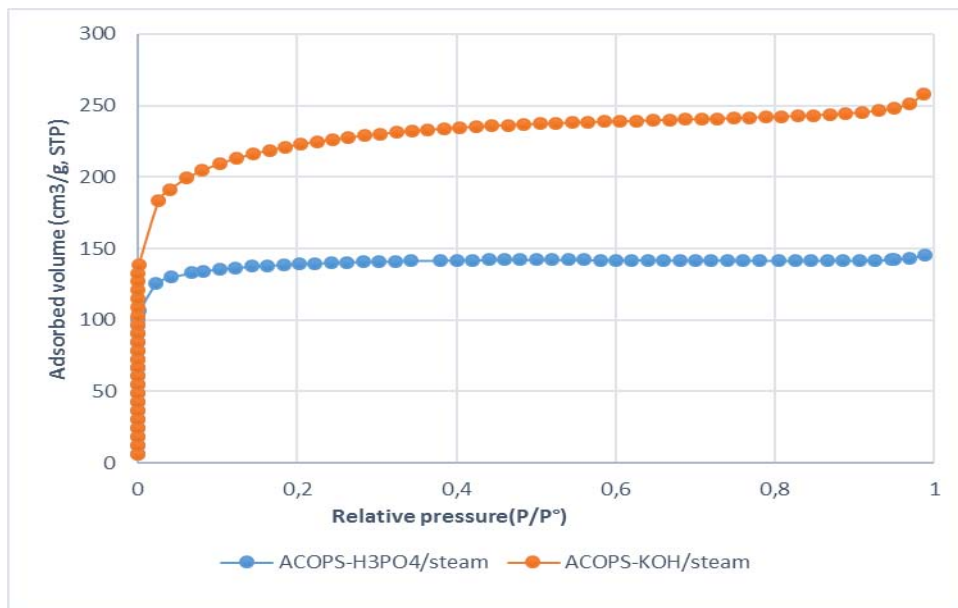


Figure 2: Isotherms for the adsorption-desorption of N<sub>2</sub> onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

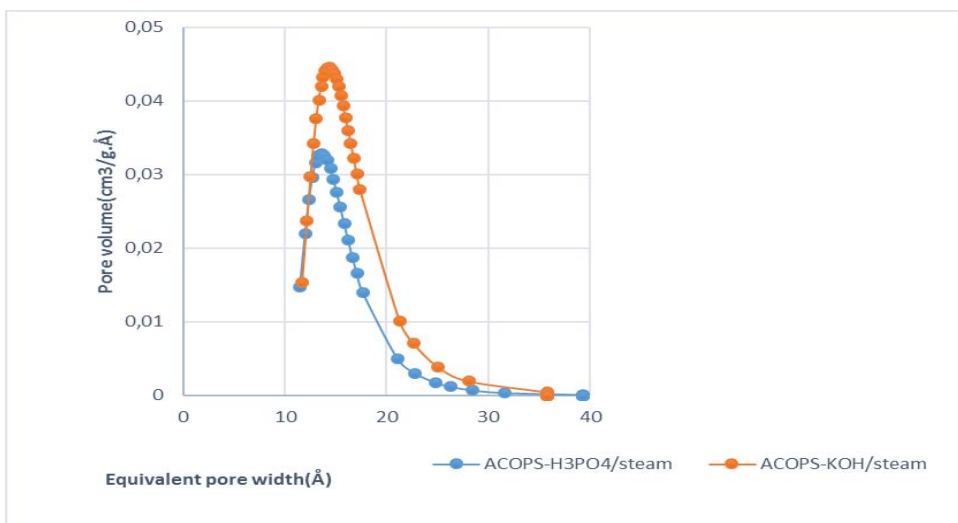


Figure 3: Pore size distribution of the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

Table 1: Pore structure parameters of the oil palm shells-derived activated carbon adsorbents

Type	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>mic</sub> (m <sup>2</sup> /g)	V <sub>tot</sub> (cm <sup>3</sup> /g)	V <sub>mic</sub> (cm <sup>3</sup> /g)	V <sub>mes</sub> (cm <sup>3</sup> /g)	Pore structure
ACOPS-H <sub>3</sub> PO <sub>4</sub>	564.03	538.89	0.23	0.21	0.02	Microporous
ACOPS-KOH	838.03	813.46	0.39	0.33	0.06	Microporous

S<sub>BET</sub>: BET surface area; S<sub>mic</sub>: micropore surface area; V<sub>tot</sub>: total pore volume; V<sub>mic</sub>: micropore volume; V<sub>mes</sub>: mesopore volume.

b) Fourier Transform Infrared (FTIR) spectra

Oxygen-containing surface functional groups which can be formed during activation process or introduced by oxidation after preparation of activated carbon play important role in influencing the surface

properties and adsorption behavior of activated carbons [12]. The FTIR spectroscopy has been performed on the prepared activated carbons to reveal such surface functional groups.



Textural characteristics and surface functional groups of raw palm shell as well as of  $H_3PO_4$ -pre-impregnated activated carbons were previously investigated. The main surface functional groups present in the palm shell were reportedly found to be carbonyl groups (such as ketone and quinone), ethers and phenols [13].

The spectra of analysis by Fourier Transform Infrared spectroscopy (FTIR) of the various activated carbon samples prepared in this study are presented in Figure 4. The spectra show that the surface functional groups of the activated carbons do not exhibit significant differences, independently of the activating agent used. Only slight differences on the intensity and broadness of the bands could be observed. Both activated carbon samples absorb nearly at the same bands, the peaks relating to the KOH-activated sample being broader than those about  $H_3PO_4$ -activated sample. For the  $H_3PO_4$ -activated sample the main surface functional groups present were presumed to be phenols, carboxylic acids (or carboxylic anhydrides if they are close together) and carbonyl groups (either isolated or arranged in quinone-like fashion), all of which are typical acidic functional groups [14-15].

The various spectra display the following bands:

- Two broad overlapping bands at 3010-2800 characteristic of H—C—H asymmetric and symmetric

- stretch of alkanes and 3010-3600  $cm^{-1}$  characteristic of O—H bond refer to the O—H stretching in hydroxyl functional groups and adsorbed water.
- A band at around 1750  $cm^{-1}$  which is assigned to the stretching vibration of the C=O bond in carboxylic acids, anhydrides, aldehydes, ketones, and lactones or isolated carbonyl groups.
- A broad band in the range 1480 to 1650  $cm^{-1}$  which can be due to C=C stretching in aromatic rings.
- A broad band of 1250-650  $cm^{-1}$  which is ascribed to C—O bending in carboxylic acids and derivatives and also possibly to C—OH stretching in phenols and C—O—C stretching in ethers.
- A peak between 450-510  $cm^{-1}$  attributed to C—H out-of-plane bending in benzene derivatives.

The spectra reveal that for the KOH-activated carbon, the greater extent of oxidation by KOH enhances absorption bands at 500  $cm^{-1}$ , 1000  $cm^{-1}$ , and 3000  $cm^{-1}$  and broaden the one around 3400  $cm^{-1}$ . Moreover, it is to be noted that the various samples absorb with different intensities which indicates that the treatment of the activated carbon by the various activating agents has led to important modifications of surface functional groups.

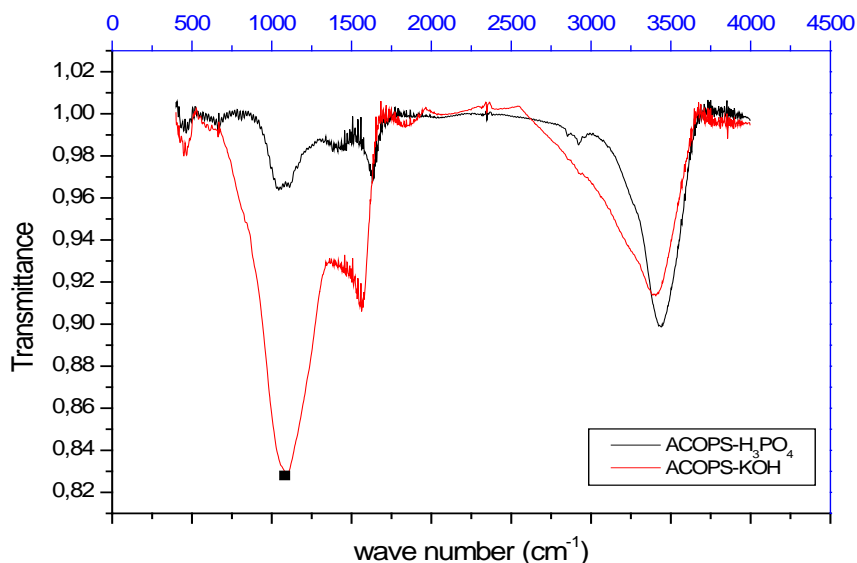


Figure 4: FTIR spectra of the oil-palm-shell activated carbon prepared by  $H_3PO_4$  and KOH activation

c) Surface characterization by SEM

Scanning electron microscopy (SEM) was used to observe the surface physical morphology of the activated carbons prepared. The surface physical morphology of the activated carbon samples ACOPS- $H_3PO_4$  and ACOPS-KOH prepared was examined using the scanning electron micrographs as depicted in Figure

5 (a and b). The surface texture of the precursor oil palm shell carbon was previously described as being dense, compact, constricted and covered by deposited tarry substances. Conversely, it can be seen (Figure 5 (a) and (b)) that SEM images of the  $H_3PO_4$ - and KOH-activated carbons display a series of pores and irregular cavities of different sizes and different shapes on the external

surface of carbons as compared to the precursor. These pores and cavities were the results from the release of volatile components and the evaporation of the  $H_3PO_4$  and KOH impregnating agents from the  $H_3PO_4$ - and KOH-impregnated derived compounds leaving the

space previously occupied by the reagent. [16]. This shows that  $H_3PO_4$  and KOH were effective in creating well-developed pores on the surface of the precursor, hence leading to the activated carbon with the large surface area and porous structure.[17].

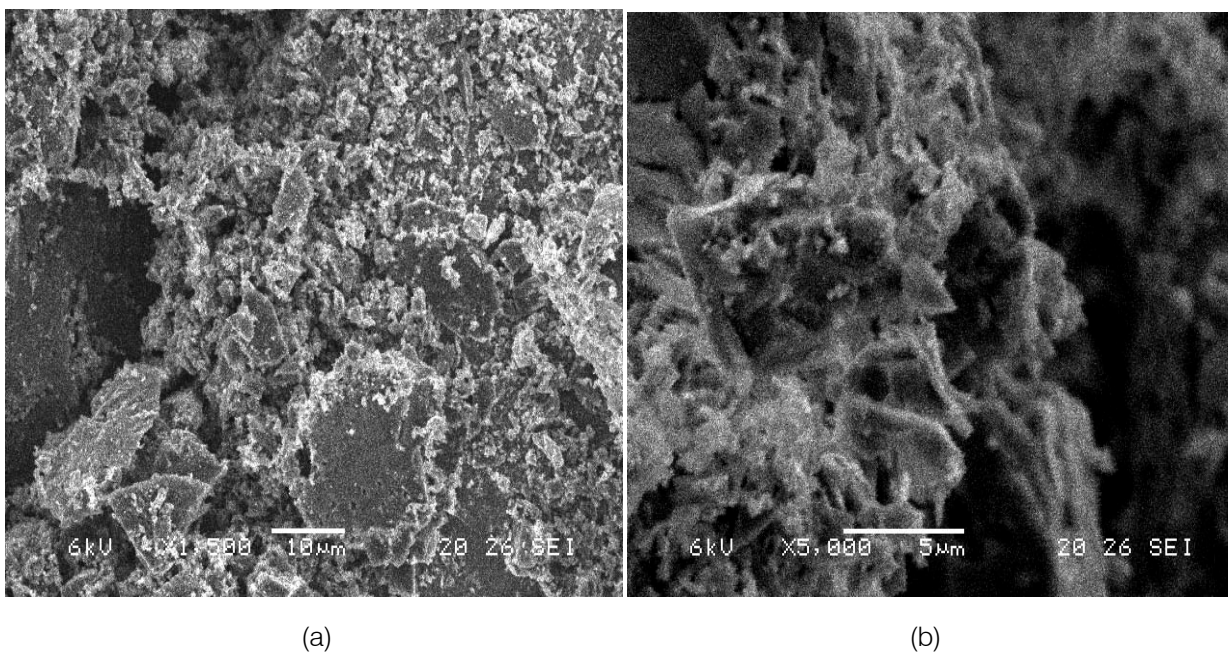


Figure 5: Scanning electron microscope (SEM) images of the activated carbon (a) ACOPS- $H_3PO_4$  and (b) ACOPS-KOH

d) *Effect of contact time on the adsorption of nitrate ions*

Adsorption kinetic is an important characteristic for evaluating the efficiency of adsorption. The amount of nitrate adsorbed,  $q_t$  versus times is depicted in Figure 6. As can be seen from Figure 6, the amount of nitrate adsorbed on the activated carbons increases as the contact time increases; at some point in time, it reaches a constant value beyond which no more nitrate is further removed from the solution. At this point, the amount of nitrate desorbing from the activated carbons is in a state of dynamic equilibrium with the amount of nitrate being adsorbed on the activated carbons. The amount of nitrate adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. It is apparent from Figure 6 that the kinetic of nitrate adsorption consists of two phases, an initial stage when the adsorption process increased sharply and a second gradually slower phase when it approached equilibrium. During the rapid adsorption period, whose duration time was approximately 50 minutes in the present study, the tendency of adsorbent to adsorption was high and therefore, the slope of adsorption curve was steep. The initial high rate of nitrate adsorption was attributed to the greater availability of binding sites on the surface of the adsorbents at the early stages of the adsorption

process. Slow adsorption period was between 50 and 80 minutes in the present study. During this period, the slope of adsorption curve was gradually flattened, and the nitrate adsorption was gradually decreased until reaching zero. This phenomenon is attributed to the reduction of immediate solute adsorption due to the lack of available open sites for nitrate adsorption. This usually occurs as the external surface of adsorbent is rapidly saturated by nitrate anion, and therefore the adsorption rate reduces [18].

Moreover, the time profiles of nitrate adsorption as can be seen in Figure 6 are single, smooth and continuous curves leading to saturation, suggesting possible monolayer coverage of nitrate onto the surface of the activated carbons. The equilibrium time was around 70 min for both ACOPS- $H_3PO_4$  and ACOPS-KOH and the adsorption capacities at equilibrium ( $q_e$ ) were found to be 48 and 55 mg/L for ACOPS- $H_3PO_4$  and ACOPS-KOH, respectively. The present findings are consistent with the results obtained by other researchers who investigated the adsorption of nitrate onto various adsorbents [19].

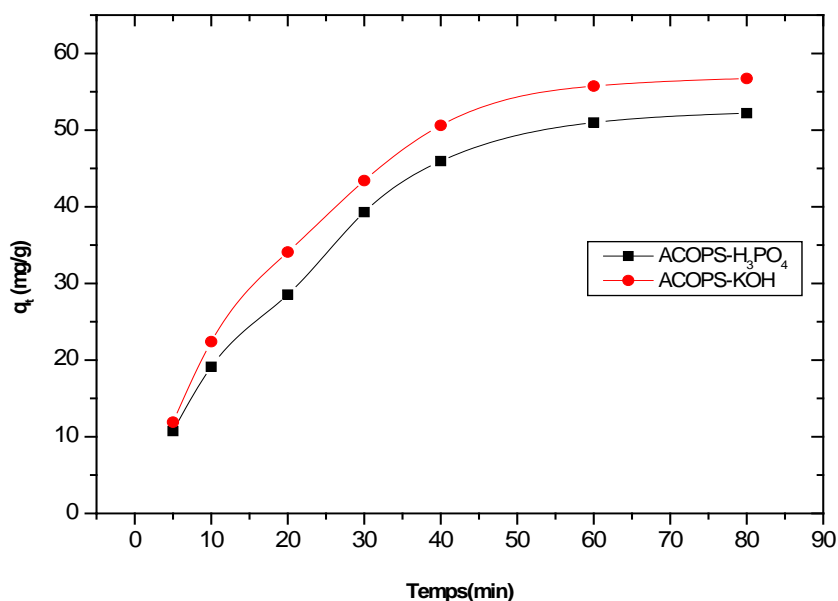


Figure 6: Effect of contact time on the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

e) *Effect of adsorbent dosage on nitrate adsorption*

To assess the optimum amount of the activated carbon prepared to be used for the adsorption of nitrate ions from aqueous solution, adsorption experiments were performed in which different amounts of the activated carbons samples were used with 10 mg/L nitrate solutions. The amount of adsorbent was varied from 0.2 g to 1.2 g. Figure 7 shows the removal of nitrate as a function of adsorbent dosage. It is apparent from the figure that by increasing the adsorbent dose the amount of adsorbed nitrate increases from 20 mg/g to 48 and 55 mg/g for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively which is due to the increase in the adsorbent surface area of the adsorbents. In general, increasing the amount of solid adsorbent in the system causes an increase in adsorption area, and thus more sites are available. It is readily understood that the number of sites available for adsorption increases by increasing the adsorbent dose and it, therefore, results in an increase of the amount of nitrate adsorbed. This study showed that the adsorption capacity of the activated carbons increased with increase in adsorbent dose up to a particular region and then reaches an equilibrium level at higher doses. It is observed that after a dosage of about 1g, the amount of nitrate adsorbed remained essentially constant at 48 and 55 mg/g for the activated carbon samples of ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively; there was no significant change in the amount of nitrate removed by either adsorbent. Therefore the results indicate that the removal efficiency increases up to optimum dosage beyond which the removal efficiency is negligible. This may be due to the difficulty for the nitrate particles to come closer to the adsorption sites either because of

the accumulation of these particles around active sites or because of the agglomeration of adsorbent particles which reduces the total adsorption surface[20].



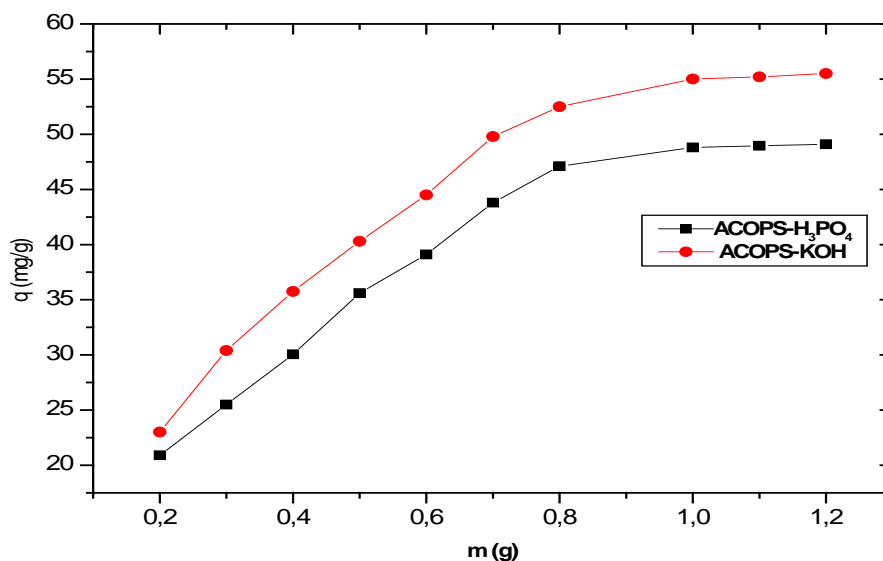


Figure 7: Effect of adsorbent dose on the adsorption of nitrate ions on to the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

f) *Effect of initial solution pH on nitrate adsorption*

The pH of an aqueous solution exerts a profound influence on the extent of adsorption of adsorbate molecule by regulating the charge of the surface functional groups of the adsorbent as well as the ionization of the adsorbate molecules. The effect of pH on nitrate removal from aqueous solution by ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH samples was investigated in the pH range 3.5 – 6.5. The initial pH of the nitrate solution was adjusted by addition of 0.10 M HCl or NaOH. The experimental result of the adsorption of nitrate on ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH as a function of pH is shown in Figure 8. Figure 8 shows a clear decrease of the number of nitrate ions adsorbed by the adsorbent as the solution pH increased. Nitrate uptake was higher at lower pH, and as the pH of the solution increased, the extent of nitrate adsorption decreased significantly. This decrease in the adsorption capacity observed for both adsorbents as the pH increased could be attributed to the depletion of the positive hydrogen ions thereby promoting activities of electrostatic repulsion between the negative charge of nitrate anions and the adsorbents surface. Competition between OH<sup>-</sup> (at high pH) and nitrate anions for positively charged adsorption sites could also be suspected of being responsible for the decrease in nitrate uptake [21]. The reason for good removal of nitrate at the lower acidic pH is that due to the excess of protons in solutions, the functional groups of activated carbon become protonated and thereby reducing the negative charges on the surface. This enhances nitrate adsorption through electrostatic attraction. [22]. In the present study, nitrate adsorption is highest at pH 3.5. It could be suggested that the surface of ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH adsorbents becomes more positively

charged. Positively charged surface sites on the adsorbents favor the adsorption of the nitrate anions due to electrostatic attraction. Similar trends in connection with the influence of the pH of the medium on the extent of adsorption of various solutes onto different adsorbents were reported in the literature [23, 24].

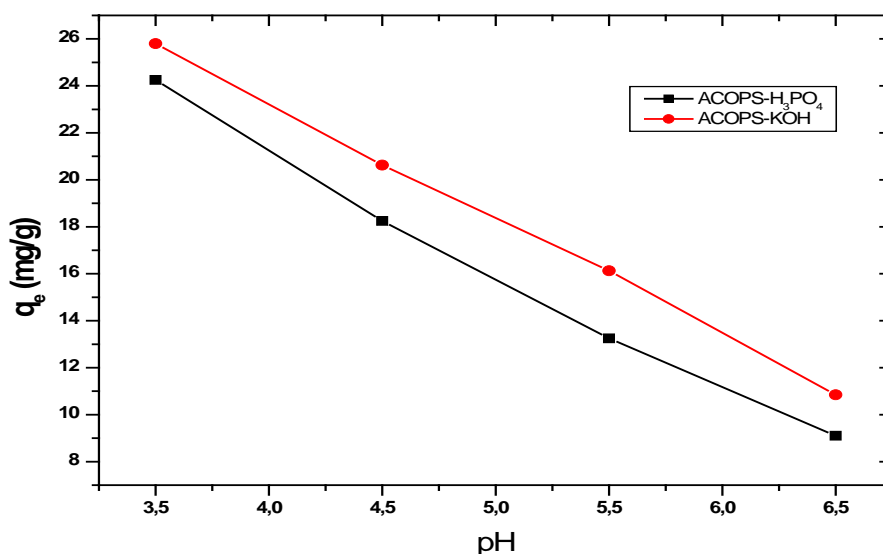


Figure 8: Influence of pH on the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

g) Equilibrium adsorption isotherms

The equilibrium adsorption isotherm model is fundamental in describing the interactive behavior between adsorbate and adsorbent and is very important to understand the adsorption behavior of solid-liquid adsorption system. It indicates the distribution of adsorbate between solution and adsorbent at equilibrium state of the adsorption process. It is expressed by relating the amount of adsorbate taken up per gram of adsorbent, q<sub>e</sub> (mg/g), to the equilibrium solution concentration, C<sub>e</sub> (mg/L), and at different concentrations of adsorbate solutions [25, 26]. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required to ascertain the adsorption effectiveness of an adsorbent. Several isotherm models are used for this purpose. In the present study, two commonly used isotherm models, the Langmuir and the Freundlich models [27] are selected to analyze the experimental equilibrium data to establish the most appropriate correlation for the adsorption of nitrate onto the prepared activated carbons.

h) The Langmuir isotherm

The Langmuir isotherm is based on the assumptions that adsorption takes place on the surface of the adsorbent at a finite number of localized active sites that are identical and equivalent with a homogeneous distribution of adsorption energies, without significant lateral interaction and steric hindrance among adsorbed species, even on the adjacent sites. The model does not consider the surface heterogeneity of the adsorbent and assumes monolayer coverage of adsorbate, that is, the adsorbent is saturated after the formation of one layer of adsorbate on the surface of adsorbent [28].

The mathematical expression of Langmuir isotherm is given as:

$$q_e = q_{max} K_L C_e / (1 + K_L C_e) \tag{3}$$

The linearized form of the Langmuir model is given as:

$$C_e/q_e = 1/K_L q_{max} + C_e/q_{max} \tag{4}$$

Where C<sub>e</sub> (mg/L) is the equilibrium concentration of the remaining solute in the solution, q<sub>e</sub> (mg/g) is the amount of the solute adsorbed per unit mass of adsorbent at equilibrium, q<sub>max</sub> (mg/g) is the amount of adsorbate per unit mass of adsorbent at complete monolayer coverage, related to adsorption capacity, and K<sub>L</sub> (L/mg) is the Langmuir constant related to adsorption energy and rate of adsorption. In this work, the experimental data are plotted in (Figure 9) as C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> in the nitrate concentration range of 10 to 30 mg/L for both samples of the activated carbons prepared by the linear form of Langmuir isotherm equation (4). Two straight lines were obtained. The Langmuir isotherms parameters q<sub>max</sub> and K<sub>L</sub> values were calculated from the slopes (1/q<sub>max</sub>), and intercepts (1/K<sub>L</sub>q<sub>max</sub>) of linear plots of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> (Figure 9) are given in Table 2. It can be seen from Table 2 that for the Langmuir model, the values of the monolayer adsorption capacity (q<sub>max</sub>) of the adsorbents are 65.488 mg/g and 68.166 mg/g for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively indicating that ACOPS-KOH had a greater total adsorption capacity than ACOPS-H<sub>3</sub>PO<sub>4</sub>. The values of maximum adsorption capacity (q<sub>max</sub>) of the adsorbents were 65.488 mg/g and 68.166 mg/g for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively indicating that ACOPS-KOH had a greater total adsorption capacity than ACOPS-H<sub>3</sub>PO<sub>4</sub>. It appears (Table 2) that the correlation coefficients (R<sup>2</sup>) of Langmuir model are 0.969

and 0.995 for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH samples, respectively. The linearity of the plots (Figure 9), as confirmed by the correlation coefficients being close to 1 for both adsorbents, together with a good agreement observed between the theoretical monolayer adsorption capacity  $q_{max,cal}$  and the experimental value  $q_{max,exp}$  (Table 2) indicate the compliance of the adsorption data with Langmuir model and illustrate the homogeneous character of the surface of the adsorbents.

The value of Langmuir constant  $K_L$  indicates the favorability of the process as well as the affinity between solute and adsorbent. Thus, the higher the value of  $K_L$ , the greater the driving force for adsorption.  $K_L$  values obtained, 0.3201 L/mg and 0.3056 L/mg for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively were large enough to lead to the conclusion that the adsorption of nitrates onto these activated carbons was favored in the concentration range considered [29].

In general, the  $K_L$  value for the adsorption of nitrate is less than 1 L/mg [30]. The values of  $K_L$  as obtained by several authors and reported in the literature for the adsorption of NO<sub>3</sub><sup>-</sup> on different types of adsorbents together with the ones determined in work are presented in (Table 3). In comparison with the values

shown herein, the  $K_L$  values obtained in the present study (0.3201 and 0.3056 L/mg for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively) were within the suggested interval and indicated good affinity and a high-energy adsorption process.

One of the essential characteristics of the Langmuir model can be expressed by a dimensionless constant called separation factor,  $R_L$ , which is determined as follows [31]:

$$R_L = 1/(1 + K_L C_0) \tag{5}$$

Where  $C_0$  is the initial adsorbate concentration (mg/L). The value of  $R_L$  indicates the type of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavorable ( $R_L > 1$ ). In the present study,  $R_L$  values calculated by equation (5) for nitrate adsorption onto the activated carbons prepared ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH for the initial nitrate concentration interval considered ( $10 \leq C_0 \leq 30$  mg/L) are shown in Table 2. The  $R_L$  values obtained for ACOPS-H<sub>3</sub>PO<sub>4</sub> ( $0.0943 \leq R_L \leq 0.238$ ) and ACOPS-KOH ( $0.0983 \leq R_L \leq 0.246$ ) lie well within the range  $0 < R_L < 1$  indicating that the adsorption process onto both ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH sample is favorable [32,33].

Table 2: Constants for equilibrium isotherm models with error analysis values

Adsorbent	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R_L$	Error analysis $R^2$
<i>Langmuir isotherm model</i>				
ACOPS-H <sub>3</sub> PO <sub>4</sub>	65.488	0.3201	$0.0943 \leq R_L \leq 0.238$	0.969
ACOPS-KOH	68.166	0.3056	$0.0983 \leq R_L \leq 0.246$	0.995
Adsorbent		$K_F$	1/n	Error analysis $R^2$
<i>Freundlich isotherm model</i>				
ACOPS-H <sub>3</sub> PO <sub>4</sub>		19.935	0.543	0.967
ACOPS-KOH		10.007	0.800	0.961

Table 3:  $q_{max}$  and  $K_L$  values for the adsorption of nitrate on different types of coals

Adsorbent	$q_{max}$ mg/g	$K_L$ L/mg	Ref.
Sugar beet bagasse charcoal	9.14	0.070	Reference 34
Cationic polymer-modified GAC	27.56	0.048	Reference 35
Activated carbon	14.5	0.027	Reference 4
ZnCl <sub>2</sub> activated coir pith carbon	10.30	0.096	Reference 29
Activated carbon modified with CaCl <sub>2</sub>	1.83	0.140	Reference 30
ZnCl <sub>2</sub> modified lignite granular activated carbon (LGAC5)	12.06	0.156	Reference 36
Mineral Clay (New Clay)	250	0.307	Reference 37
NaOH activated rice husk carbon	86.2	0.017	Reference 38
H <sub>3</sub> PO <sub>4</sub> activated oil-palm shell carbon	65.49	0.320	This study
KOH activated oil-palm shell carbon	68.17	0.306	This study

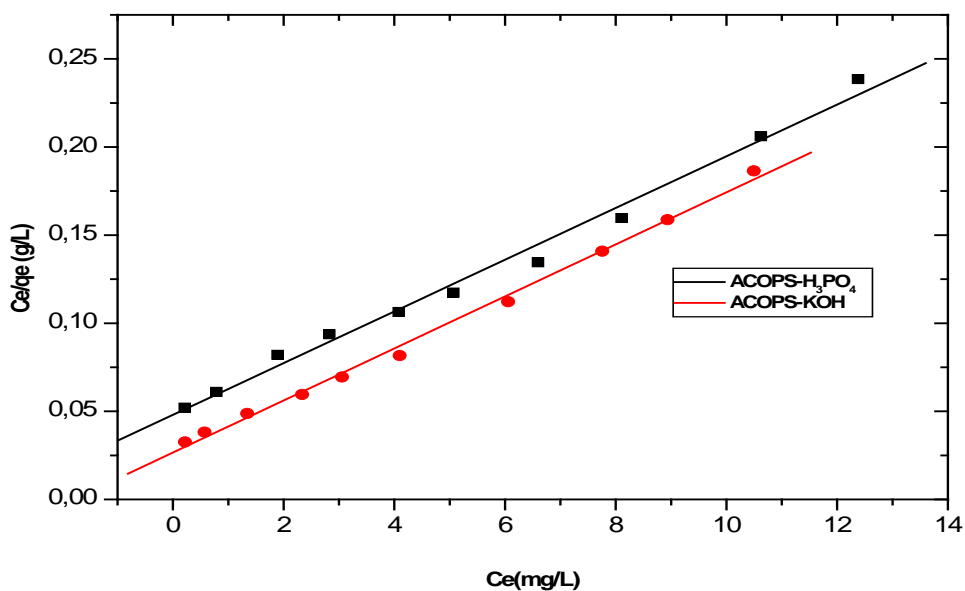


Figure 9: Langmuir isotherm linear plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

i) The Freundlich adsorption isotherm

Freundlich isotherm [39] model is an empirical equation proposed for the description of surface heterogeneity of the adsorbent and multilayer adsorption. This model states that interactions take place in several active adsorption sites accompanied by interactions between adsorbed molecules with a non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. It assumes that as the amount of solute adsorbed rises, the binding surface energy decreases exponentially which is characteristic of multilayer adsorption[40].

The Freundlich isotherm model mathematically expresses the surface heterogeneity and exponential distribution of the active sites and their energies; it is defined as:

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

The linearized logarithmic form of Freundlich isotherm model is given as follows:

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

Where C<sub>e</sub> (mg/L) is the equilibrium concentration of the adsorbate, Q<sub>e</sub> (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, K<sub>F</sub> [(mg/g)(L/mg)<sup>1/n</sup>] and n are the Freundlich adsorption constants. K<sub>F</sub> relating to the extent of adsorption indicates the adsorption capacity of the adsorbent, and 1/n is a dimensionless quantity related to the adsorption intensity and the surface heterogeneity of the adsorbent material (the surface becoming more heterogeneous as 1/n value approaches zero)[42]. The

value of 1/n indicates how favorable the adsorption process is. A value 1/n between 0 and 1 indicates high adsorption capacity and favorable adsorption. When 1/n > 1, the adsorption is not favorable, the adsorption interactions become weak, and the adsorption capacity decreases. [43-46]. This model was shown to give good results for low adsorbate concentrations. The adsorption data obtained from the samples studied were plotted according to the linearized Freundlich adsorption isotherm and are shown as a plot of ln Q<sub>e</sub> versus ln C<sub>e</sub> in Figure 10. The values of the parameters of Freundlich equation, K<sub>F</sub>, and 1/n, were determined from the intercept and slope of the plot of ln Q<sub>e</sub> versus ln C<sub>e</sub> and are listed in Table 2. The values of the adsorption constants K<sub>F</sub> and the exponent 1/n in the Freundlich equation (Table 2) inferred from the curves of Figure 10 allow assessing whether the adsorption of nitrate ion on the samples of the activated carbons studied is favorable or not. The smaller the value of 1/n (that is 0 < 1/n < 1) and the greater the value of K<sub>F</sub>, the stronger are the interactions between the nitrate ions and the adsorbent signifying greater affinity between the nitrate ions and the activated carbon. [47]. The constant K<sub>F</sub> may be used to compare the adsorption process of the same solute for different adsorbents. These comparisons help establish the system with the most efficient adsorption. The Freundlich adsorption constants K<sub>F</sub> obtained from Figure 10 were (19.935 and 10.007) for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively. As can be seen from Table 2, the values of 1/n in the present study were in the range 0-1 (0.543 and 0.800 for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively) revealing favorable adsorption conditions of nitrate by both activated carbons[48]. Moreover, the



correlation coefficients of the linearized Freundlich isotherm model for nitrate adsorption onto the samples ACOPS-H<sub>3</sub>PO<sub>4</sub> ( $r^2 = 0.967$ ) and ACOPS-KOH ( $r^2 = 0.961$ ) were both close to 0.96, which implied that in the range of concentrations considered in this study, Freundlich

adsorption model was appropriate for explaining the adsorption of nitrate ions on the samples investigated.

In summary, both of Langmuir and Freundlich isotherms were greatly suitable to explain experimental data due to  $r^2$  greater than 0.96.

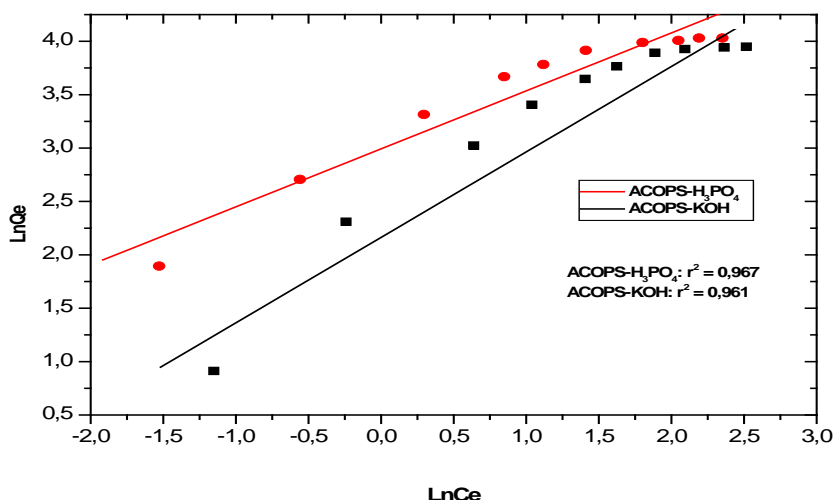


Figure 10: Freundlich isotherm linear plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

j) Adsorption kinetics

The application of the pseudo-second-order kinetic model to the data by plotting  $t/q_t$  concerning to time  $t$  is shown in Figure 11. The values of the equilibrium adsorption capacity, ( $q_e$ ), the pseudo-second order rate constant, ( $k_2$ ), the initial adsorption rate, ( $h$ ), calculated from the slope and the intercepts of the straight lines of the  $t/q_t$  versus  $t$  plots shown in Figure 11 together with the correlation coefficients, ( $r^2$ ), are listed in Table 4. The correlation coefficient ( $r^2$ ) values for pseudo-second-order equation are 0.995 and 0.994 for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively indicating a good fit of pseudo-second-order rate model to experimental kinetic data. It suggests that this model is capable of describing the kinetic behavior for the adsorption of nitrates onto the activated carbons prepared. Furthermore, the equilibrium adsorption capacities calculated from the pseudo-second-order model ( $q_{ecal}$ ) are similar to the experimental values ( $q_{eexp}$ ) for both activated carbons. The pseudo-second-order rate constants ( $k_2$ ) are 5.433 g/mg min for ACOPS-H<sub>3</sub>PO<sub>4</sub> and 5.014 g/mg min for ACOPS-KOH. The  $h$  value calculated from pseudo-second-order equation is higher for ACOPS-H<sub>3</sub>PO<sub>4</sub> than for ACOPS-KOH, indicating a higher mass transfer rate for ACOPS-H<sub>3</sub>PO<sub>4</sub>, indicating a higher mass transfer rate for ACOPS-H<sub>3</sub>PO<sub>4</sub>[49].

The intra particle diffusion plots for the adsorption of nitrate onto ACOPS are presented in Figure 12.  $k_p$  ( $mg/g \text{ min}^{0.5}$ ), the intra particle diffusion rate constant can be obtained from the slope of the  $q_t$  versus

$t^{0.5}$  plot and is listed in Table 4. The plot of  $q_t$  versus  $t^{0.5}$  using kinetic data up to 80 min gives correlation coefficients ( $r^2$ ) values of 0.961 for ACOPS-H<sub>3</sub>PO<sub>4</sub> and 0.966 for ACOPS-KOH adsorbents. The linearity of the plots indicates that intra particle diffusion might play a significant role in the initial stage of adsorption of nitrate onto ACOPS adsorbents because the intra particle diffusion equation is valid only for initial kinetic data [50].

The adsorption kinetics of nitrate onto ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH using both pseudo-second-order and intra particle diffusion models show a good fit to experimental kinetic data, but the pseudo-second-order rate model is a better fit than the intraparticle model. This second-order kinetic behavior suggests that the adsorption mechanism is the rate-controlling step [51].

Table 4: Constants of different kinetic and intra particle diffusion models

Adsorbent	C <sub>0</sub> (m <sup>2</sup> /g)	q <sub>e</sub> (exp) (mg/g)	Pseudo-second-order equation				Intraparticle diffusion	
			q <sub>e</sub> (cal) (mg/g)	k <sub>2</sub> (g/mg min)	h (mg/g min)	r <sup>2</sup>	k <sub>p</sub> (mg/g min <sup>0.5</sup> )	r <sup>2</sup>
ACOPS-H <sub>3</sub> PO <sub>4</sub>		52.200	76.336	5.433	31659.1	0.995	7.519	0.961
ACOPS-KOH		56.738	72.516	5.014	26366.5	0.994	6.918	0.966

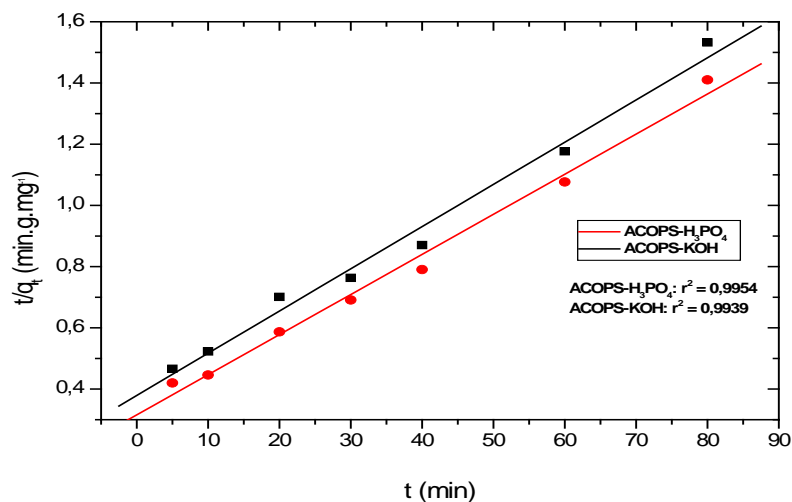


Figure 11: Pseudo-second-order kinetic plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

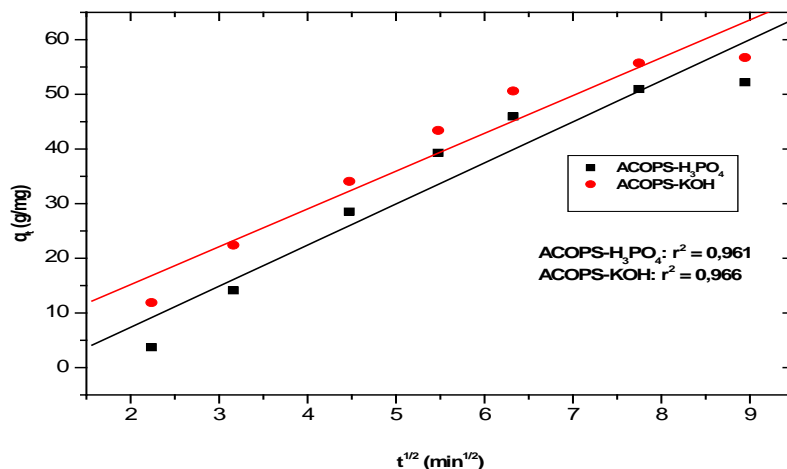


Figure 12: The intra particle diffusion model for the adsorption of nitrate ions onto the activated carbons (ACOPS-H<sub>3</sub>PO<sub>4</sub>) and (ACOPS-KOH) prepared from oil-palm shells

#### IV. CONCLUSION

Activated carbons were prepared from oil palm shells by physicochemical activation using H<sub>3</sub>PO<sub>4</sub> and KOH as the chemical activating agents on the one hand and steam as the physical activating agent on the other. The ability of the H<sub>3</sub>PO<sub>4</sub> and KOH activated carbons, labeled ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH respectively, to remove nitrate ions from aqueous solutions was

investigated. The N<sub>2</sub> adsorption showed that the adsorbents were essentially of micro porous nature and mesopores if present were situated at the surface and served as gateways to micropores. Experimental data indicated that the adsorption process was influenced by the solution pH as well as by the adsorbent dosage. The more acidic the solution pH the greater the number of nitrate ions adsorbed by both adsorbents. The adsorption capacities of both adsorbents were higher at

higher adsorbent dosage values. Kinetics studies of the adsorption of nitrate ions onto the sample adsorbents showed that the adsorption process was rapid with 90% of the nitrate ions uptake being achieved within the first forty minutes of the process and that the adsorption mechanism could be described by pseudo-second-order kinetics. The adsorption isotherms of nitrate ions onto the activated carbons prepared were adequately described by Langmuir and Freundlich models. The maximum adsorption capacities as determined from Langmuir isotherms were 65 and 68.166 mg/g for ACOPS-H<sub>3</sub>PO<sub>4</sub> and ACOPS-KOH, respectively. These results revealed that high adsorption capacity of nitrate could be achieved from oil-palm-shell H<sub>3</sub>PO<sub>4</sub> or KOH activated carbons. Furthermore, the higher adsorption capacity of nitrate onto ACOPS-KOH, 68.166 mg/g, compared with that of ACOPS-H<sub>3</sub>PO<sub>4</sub>, 65 mg/g, suggested ACOPS-KOH was a better adsorbent for removal of nitrate from aqueous solution.

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