Sorption Studies of Dyestuffs on Low-cost Adsorbent

T. Nwabanne Joseph[1], Okpe Emmanuel Chinonye[1*],
Asadu Christian Oluchukwu[2] and Onu Chijioke Elijah[3]

[1]*Department of Chemical Engineering, Nnamdi Azikiwe University, P.M.B. 5025, Awka, Anambra State, Nigeria.*
[2]*Department of Chemical Engineering, Enugu State University of Science and Technology, P.M.B 01660, Enugu State, Nigeria.*
[3]*Department of Chemical Engineering, Odumegwu Ojukwu University, P.M.B 01, Uli, Anambra State, Nigeria.*

Authors' contributions

This work was carried out in collaboration between all authors. Authors OEC and ACO designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors TNJ and OCE managed the analyses of the study. Author OEC managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

This work presents the results of sorption studies of orange G and phenol Red dyes onto palm kernel shell activated carbon (PKS-AC). The adsorbent was prepared by chemical activation using zinc chloride. The effect of various parameters such pH, initial ion concentration, contact time, temperature and adsorbent dosage has been investigated in the present study. The result showed that the percentage removal of dye was concentration dependent, decreasing with an increase in dye concentration. Isotherm modelling was investigated and Freundlich isotherm model fits the equilibrium data very well. The kinetic modelling showed that Pseudo-first orders kinetic model best described the kinetics of the adsorption. The thermodynamic parameters were evaluated. The negative values of ΔG and ΔH indicate that adsorption process was spontaneous and exothermic.

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*Corresponding author: E-mail: chanel731@gmail.com;

The negative value of ∆S shows decreased randomness with the adsorption. The study has shown that palm kernel shell activated carbon is a good adsorbent for the removal of phenol red and orange G dyes respectively.

1. INTRODUCTION

The removal of dyes from coloured effluents, particularly from textile industries, is one of the major environmental concerns these days [1]. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye- containing effluents [2]. Many problems that have been associated with most of the above methods include high cost, low efficiency, generation of toxic products and inability to regenerate the starting materials [3]. Owing to these problems, the emphasis has now been shifted to the use of adsorption for the removal of wastewater pollutants, which is now one of the efficient techniques [4].

Adsorption is a process in which a solid is used for removing a soluble substance from water. It involves the transfer of a mass of a fluid to the surface of an adsorbing solid. The molecules that diffuse from the bulk of the fluid to the surface of the solid adsorbents form a distinct adsorbed phase [5]. The fluid (either a gas or a liquid) that is transferred is called the Adsorbate while the solid that adsorbs them is called the Adsorbent. Adsorption is also a process by which fluid molecules become attached to a surface by physical or chemical forces or a combination of both. The adsorption process has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions. Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area, microporous structure, high adsorption capacity and a high degree of surface reactivity [6]. Some materials that have been used as activated carbon include rice husk, chitin [7], sawdust [8], Barley straw and its ash [9], fluted pumpkin [10], Sveta Sariva plant root [11] etc.

But considering the high cost of importing activated carbon and also that a substantial fraction of the activated carbon is lost during each regeneration cycle [12], there is no increase in researches that have been directed towards investigating the adsorption potentials and characteristics of cheaper, effective and efficient adsorbents from natural solid waste materials.

Recently, special attention has been focused on the use of low-cost adsorbents mainly from agricultural waste products as an alternative to replace the conventional adsorbents [6].

The present investigation reports on the use of PKS-AC to adsorb the dyestuffs (phenol red and orange G) from aqueous solution in a batch study. The main advantages being that palm kernel shells are available freely, locally and abundantly, easy to prepare in large scales. These dyestuffs were selected to carry out the sorption studies because the release of a large quantity of dyes into water bodies by textile industries poses serious environmental problems due to persistent and recalcitrant nature of these dyes. According to one estimate over 7×10^5 tonnes and approximately 10,000 different types of dyes and pigments are produced worldwide annually [13]. Untreated or partially treated effluents from other industries namely, paper, plastics, leather, cosmetics, food, woollen, etc also contribute to the pollution load. The colouration of the water by the presence of dyes, even in small concentrations, is easily detectable [14] and many have an inhibitory effect on the process of photosynthesis and thus affecting the land flora and the aquatic ecosystem.

Following the level of environmental pollution and recent moves by the Federal Government of Nigeria towards industrialization and use of indigenous materials, the present investigation was undertaken to explore the feasibility of finding a low-cost effective adsorbent, PKS-AC, for the treatment of wastewater, containing phenol red and orange G dyes respectively from aqueous solution. The effect of various parameters such as pH, the initial concentration of dye solution, contact time temperature and adsorbent dosage were investigated in the batch experiments. Also investigated was isotherm, kinetic and thermodynamic studies, for the chosen dyes.

2. MATERIALS AND METHODS

2.1 Adsorbent

The palm kernel shells (obtained from Aku in Igbo-Etiti Local Government in Enugu State, Nigeria) were further dried in the sunlight to

reduce the moisture content. The dried material was mixed with $ZnCl_2$ (ratio 1:1), to achieve high specific surface area because $ZnCl_2$ also known as Lewis acid is a strong dehydrating agent which could alter the structure of carbon to form the porous structure [15], and kept in an oven at 383K for 24 hours. Then it was washed severally with distilled water and was leached with warm water to remove any trace of metal. The material was placed in a muffle furnace and the temperature was gradually raised up to 773K and the material was kept at the same temperature for an hour. After cooling, the material was taken out and ground well by using mortar and pistil and then sieved to a particle size of 75µm, preserved in air tight container for further studies on adsorption.

2.2 Adsorbates

The phenol red and orange G used in the present study were procured from, Onitsha main market, Nigeria. 0.1 gram of the dye was accurately weighed and made up to 1000ml of distilled water.

2.3 Characterization of Adsorbent

The physical properties of the carbon before and after activation were determined using standard methods. The ash content and moisture content were determined using ASTM D 28866-70 and ASTMD 2867-70 respectively. The pH was determined using standard test of ASTM D 3838-80. The surface area was determined using the Sears method [16,17]. The carbon was also characterized using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) to examine the surface morphology of the carbon and to determine the functional groups present in the carbon respectively.

2.4 The Batch Adsorption Studies

The activated carbon was characterized by its adsorption capacity on Phenol Red and Orange G dyes. The synthetic wastewater was prepared by dissolving 0.1 g of the dyes in 1000 ml of distilled water each to get a solution of 100 mg/L. After the adsorption, the solution was allowed to settle and the absorbance measured at their wavelengths. The amount of equilibrium adsorption, q_e (mg/g) was calculated as given in equation 1. At equilibrium, the solution was filtered and the absorbance of the filtrate measured using a UV spectrophotometer at 478

nm and 435 nm wavelengths for Orange G and Phenol Red respectively.

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

Where, C_o and C_e (mgL^{-1}) are the liquid – phase concentrations of dye at initial and equilibrium respectively.

V is the volume of the solution (L) and m is the mass of activated carbon used (g)

The percentage adsorbed (%) is as calculated in equation 2

$$\text{Percent adsorbed \%} = \left(\frac{C_o - C_e}{C_o}\right) X \ 100 \qquad (2)$$

2.5 Fourier Transform Infra-red (FTIR)

An FTIR-8400S Fourier Transform Infrared Spectrophotometer, made by SHIMADZU, was used to identify the types of chemical bonds (functional groups) in the molecule by producing an infra-red absorption spectrum.

The solid samples were dissolved in a methylene chloride solvent, and the solution placed onto the plate as a cast film. The Solution was then analyzed in a liquid cell. A small container made from NaCl (or other IR-transparent material) which was filled with liquid that created a longer path for the sample, which led to increased sensitivity.

2.6 Scanning Electron Microscope (SEM)

SEM is a type of microscope that uses electrons rather than light to form an image. SEM was used to determine the surface morphology of the solid samples. Crystal shape size of the crystalline solid phase could be identified from the micrograph. The observation was done using a JOEL scanning electron microscope model JSM 6400. The solid samples were placed on a brace stub sample holder using double stick carbon tape. Then, the samples were coated with layers of gold approximately 20-25Å thick using Blazer sputtering coater. The micrograph was recorded with 12 KV, 5000 x magnification.

2.7 Isotherm Study

Isotherm models such as Langmuir and Freundlich models were investigated by using 0.5 g of activated carbon at a different initial concentration of the dye solution (50-500mg/L) for 60 minutes. Then the final concentration of the dye solution was determined.

2.8 Kinetic Study

0.5g of the activated carbon was used in 100mg/L of the dye solution at different temperatures (303-333K). The final concentration was determined at a time of 60 minutes. Different kinetic models were applied.

2.9 Thermodynamic Study

The thermodynamic parameters such as a change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using the following equations:

$$\Delta G = -RTlnK \qquad (3)$$

$$InK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (4)$$

Where R (8.314J/mol K) is the general gas constant, T (K) is the absolute temperature and K (L/g) is the standard thermodynamic equilibrium constant defined as q_e/C_e. By plotting a graph of InK versus /T, the values ΔH and ΔS can be estimated from the slopes and intercepts respectively.

3. RESULTS AND DISCUSSION

3.1 Physical Properties of the Carbon

The result of the physical properties of the carbon before and after activation with zinc chloride is shown in Table 1. The result showed that the surface area of the PKS-AC was more than the surface area of unactivated palm kernel shell. The unactivated palm kernel shell has a surface area of 192.6 m^2/g while the activated Palm kernel shell has a surface area of 567m^2/g. This was in corroboration with the range recommended by [18] in their book, that widely used activated carbon adsorbents have a specific surface area on the order 500 to 1500 m^2/g. The change in the surface area between activated carbon and unactivated carbon was due to the chemical effect of the activation of the carbon at a given temperature. The activation causes a reaction that takes place on all the internal surfaces of the carbons, removing carbon from the pore walls and thereby enlarging them [19].

3.2 Characterization of Adsorbent Using FTIR

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool for identifying the characteristic functional groups, which are instrumental in adsorption of organic compounds [20]. The FTIR spectra of carbons before and after activation were used to determine the vibrational frequency changes in the functional groups in the adsorbent.

Table 1. Physical properties of the carbon

Property	Unactivated palm Kernel Shell	PKS-AC
Surface area (m^2/g)	192.6	567
pH	8.4	6.8
Moisture content (%)	8.2	0.51
Ash content (%)	-	6.0
Bulk density	-	0.8

3.3 FTIR Result of Unactivated Palm Kernel Shell

The peaks between 3044.6 – 3793.9 /cm indicate the existence of free hydroxyl groups, the C-H stretching vibration around (2061.4 – 2905.5 /cm) indicates the presence of alkenes. The peaks (1620.9 – 1716.65/ cm) correspond to the C=O stretching that may be attributed to the hemicellulose and lignin aromatic groups [21]. The C=C stretching vibrations ranging between 1541.12 /cm and 1697.3/ cm are indicative of alkenes and aromatic groups [20]. The peaks around 1131.2 to 1399.6 cm^{-1} and 723.17 to 942.55/ cm, corresponding to Si -O- Si and Si-H groups respectively. The presence of silicon in the Unactivated Palm Kernel Shell could be attributed to sand impurities in the material.

3.4 FTIR Result of PKS – AC

The FTIR of $ZnCl_2$ activated carbon shows the bands between 3081.5 - 3757.4/ cm to indicate the existence of carboxylic groups [22]. The bands at (2192.1 – 2930.5/ cm), ascribed to C≡C vibration in alkyne groups, which are more intense than the unactivated Palm Kernel Shell at this range is due to release of light volatile matter such as H, resulting from the heat treatment process [23], reported that the peak between 1283.5 to 1171.8 /cm may be attributed to the phosphorus-containing group P=O, C-O stretching vibrations in P-O-C linkage. The decrease in the band between 3757.5 and 3375.2 /cm indicates the removal of ash in the carbon.

3.5 Characterization of Adsorbent Using SEM

Plate 1 and Plate 2 show the morphological characteristics of unactivated palm kernel shell and PKS-AC. The large pores of different shapes could be observed for the activated carbon. This may be attributed to the fact that the activating agents promote the contact area between the carbon and the activating agent, and therefore, increases the surface area and porosity of carbon. The mechanism for zinc chloride activation tends to produce a well-developed porosity besides high carbon yield since zinc chloride degrades the cellulose, hemicelluloses and lignin. According to the micrograph, it seems that the cavities on the surfaces resulted from the evaporation of the activating agent during carbonization, leaving the space previously occupied by the activating agent [24].
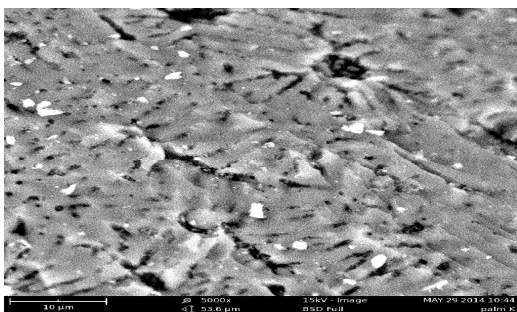

Plate 1. SEM of unactivated palm kernel shell at 75µm particle size

3.6 Adsorption of Dyes

The mechanism of dye adsorption was investigated in the study using different parameters such as pH, initial ion concentration, contact time, temperature and adsorbent dosage.
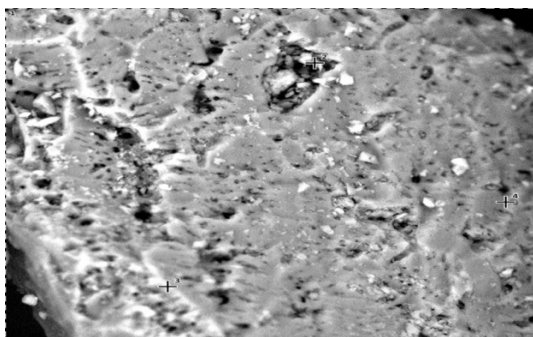

Plate 2. SEM of PKS -AC at 75µm particle size (Mag.= 5000x)

3.7 Effect of pH

The percentage of removal of the dyes was studied over the pH range of 2 to 10 as shown in Fig. 1. The result showed that for Orange G, the maximum removal occurred at pH of 2 and decreased as the pH increased up to pH 10. This is because at low pH, the degree of protonation of the surface of the activated carbon will be more which will result in an increase in diffusion and subsequently increase in adsorption due to electrostatic attraction [25].

For Phenol Red, the percentage removal was found to increase as the pH increased from pH 2 to 8. The lower adsorption of Phenol Red at low pH value was due to the presence of excess H^+ ions competing with dye cations for the adsorption sites of the adsorbent. This agrees with [26,27].

3.8 Effect of Initial Concentration at a Different Temperature

The effect of initial ion concentration was studied for the initial ion concentration ranging from 50 to 500 mg/L. The results showed that while the amount of Phenol Red and Orange G adsorbed per unit mass increased with increase in initial ion concentration, the adsorption percentage decreased as shown in Figs. 2 and 3. This is because, at a lower concentration, the ratio of the initial number of the dye molecules to the available surface area was low [28]. This is because for a fixed number of active sites remaining the same, the number of substrates ions accommodated in the interlayer space increased so that the removed ions were decreased. This was in corroboration with [29, 30].

3.9 Effect of Contact Time

The result of the effect of time on adsorption showed that the removal of dyes increases with increase in agitation time to some extent until equilibrium was reached at about 60mins for both Phenol Red and Orange G as shown in Figures 4 and 5. The initial rapid adsorption was due to the availability of the positively charged surface of the adsorbents for the adsorption of Phenol Red and Orange G [31]. The increase in the extent of removal of the dyes with increasing time was because adsorbate generally formed a monolayer on the surface of the adsorbent. Hence, the removal of dyes from aqueous solution was controlled by the rate of the transport of the adsorbate species from the outer

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sites to the interior sites of adsorbent. This is in agreement with the result obtained by other researchers [32-34].

3.10 Effect of Temperature

Temperature values ranging from 303K to 333K were used to study the effect of temperature on the adsorption process. It was found out that with an increase in temperature, the percentage removal was much less as shown in Fig. 6. This is because as the temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent particles increases [35]. Temperature affects the rate of removal of dyes by altering the molecular interactions and the solubility of the dyes. Some other researchers that reported the same trend include [36].

3.11 Effect Adsorbent Dosage

The effect of dosage was studied for adsorbent dosages in the range of 0.1 g to 0.5 g. The results showed that, for Phenol Red and Orange G, as the adsorbent dosage increased, the percentage of adsorption also increased as can be seen in Fig. 7. The increase in the percentage removal of dyes with the increase in adsorbent dosage was due to the increased surface area with more active functional groups which also gave rise to more availability of more adsorption sites [25,28]. The decrease in unit adsorption with increasing adsorbent amount was mainly due to adsorption sites remaining saturated during the adsorption reaction [37]. Similar results were obtained by many other researchers [32].
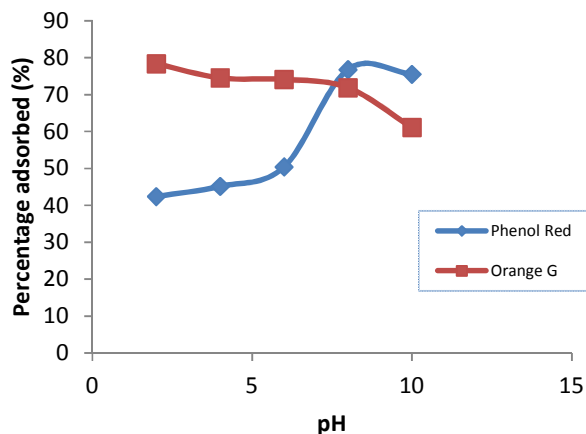

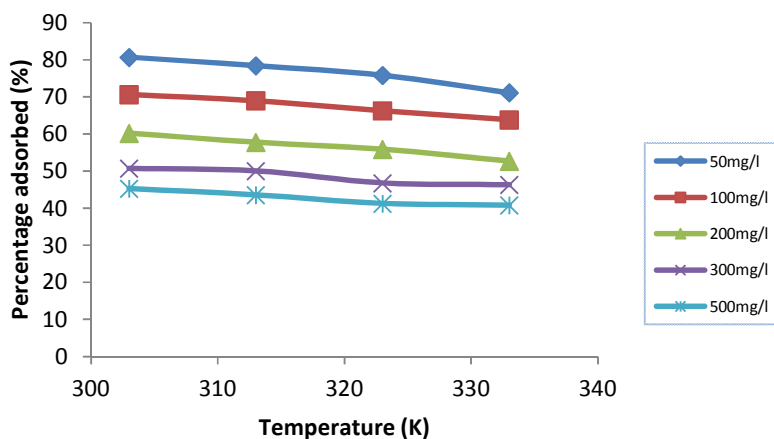**Fig. 1. Effect of pH on adsorption of phenol red and orange on PKS-AC**

Fig. 2. Effect of concentration in the removal of Phenol red by PKS-AC
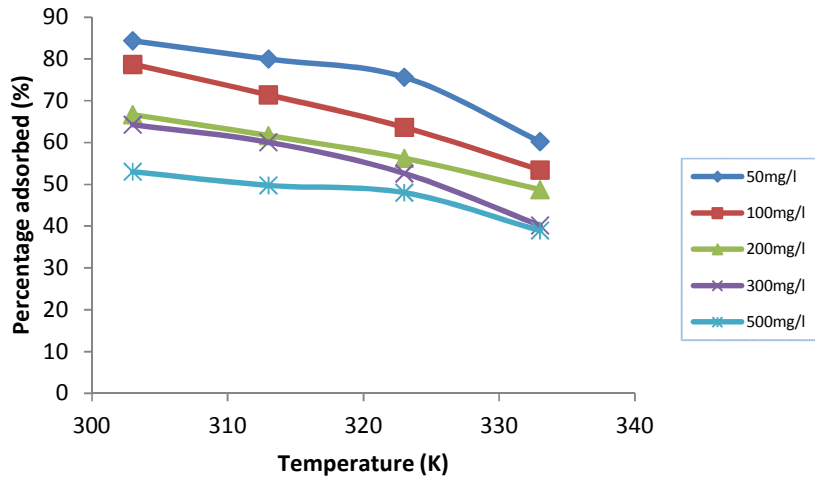
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Fig. 3. Effect of concentration in the removal of Orange G by PKS-AC
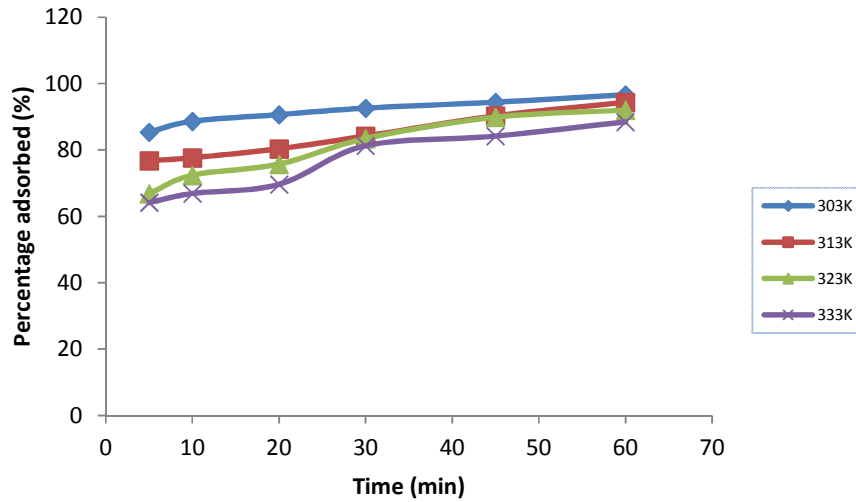

Fig. 4. Effect of time on adsorption of phenol red on PKS-AC
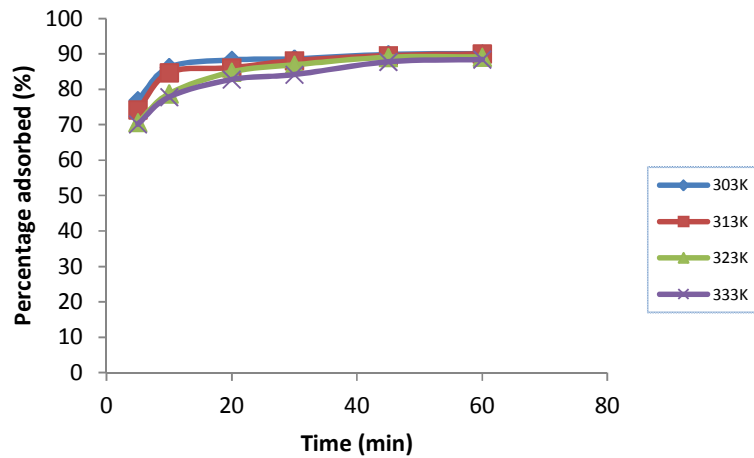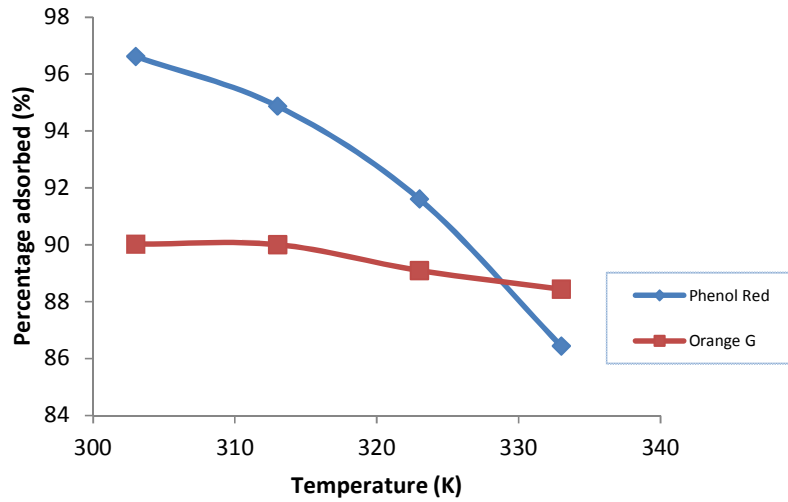

Fig. 5. Effect of time on adsorption of orange G on PKS-AC

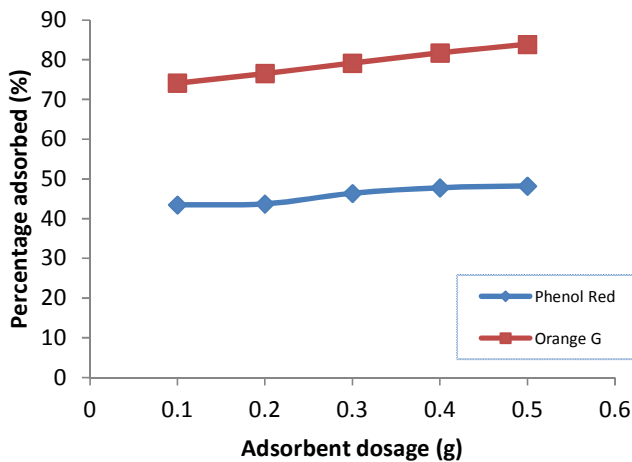**Fig. 6. Effect of temperature on the removal of dyes by PKS-AC**

Fig. 7. Effect of dosage on adsorption of phenol red and orange G on PKS-AC

4. ADSORPTION ISOTHERM MODELLING

4.1 Langmuir Isotherm Model

The Langmuir model assumes that the uptake of adsorbate molecules occurs on a homogeneous surface by monolayer adsorption. The linear form of Langmuir isotherm is:

$$\frac{c_e}{q_e} = \frac{1}{b q_m} + \left(\frac{1}{q_m}\right) c_e \tag{5}$$

Where qe is equilibrium amount of solute adsorbed per unit weight of adsorbent in (mg/g); Ce is equilibrium concentration in aqueous phase (mg/L); q_m is the maximum amount adsorbed per unit mass of adsorbent for a complete monolayer (mg/g); **b** is a constant related to the affinity of the binding sites and energy of adsorption in (l/mg). Hence, plotting the values of 1/qe against 1/Ce (as shown in Figs. 8 and 9), the constants q_m and b were calculated from the intercept and the slope respectively of the linear plot and presented in Tables 2 and 3.

The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is 'favorable' or 'unfavorable'. A dimensionless separation factor, R_L, as an essential feature of the Langmuir isotherm is defined as:

$$R_L = \frac{1}{1 + b\,C_{ref}} \tag{6}$$

Where, C_{ref} is the reference fluid-phase concentration of adsorbate (mg/L) and **b** is the Langmuir constant. For a single adsorption system, C_{ref} is usually the highest fluid-phase concentration encountered. The value of R_L indicates whether the adsorption isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Therefore, the values of R_L were calculated and presented in Tables 4 and 5 respectively. For the adsorption of both Phenol Red and Orange G on the adsorbent, the R_L values were less than 1 and greater than zero showing that the adsorption was favorable.

4.2 Freundlich Isotherm Model

The Freundlich isotherm is commonly used to describe adsorption characteristics for the heterogeneous surface. Freundlich isotherm can be expressed as Equation 7:

$$q_e = K_F C_e^{1/n} \tag{7}$$

Where, K_F is the constant related to overall adsorption capacity (mg/g); $1/n$ is the constant related to surface heterogeneity (dimensionless). The plotting of q_e versus C_e as shown in Figures 10 and 11 helps to determine $1/n$ and K_F values presented in Tables 2 and 3. The values of the freundlich constants K_F and n were calculated

from the intercept and the slope respectively. For beneficial adsorption, the value of n will be between 1 and 10 [25]. In this work, the values of n range from 1 to 3, showing beneficial adsorption of Phenol Red and Orange G on the carbon. The correlation coefficient R^2 ranges from 0.93 to 0.99 for both Phenol Red and Orange G adsorption indicating that the adsorption followed Freundlich isotherm model very well.

4.3 Temkin Isotherm Model

The Temkin isotherm model assumes that the fall in the heat of adsorption is linear rather logarithmic as stated by freundlich [38]. It involves a study of the heat of adsorption and the adsorbent-adsorbate interaction. Temkin isotherm can be expressed as Equation 8:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \tag{8}$$

Where $\dfrac{RT}{b} = B$, T is the absolute temperature in K, R is Universal gas constant, 8.314 J/mol K, and B is related to the heat of adsorption [39]. The constants for Temkin isotherm were determined from the plot of q_e against $\ln C_e$ as depicted on Figs. 12 and 13 and presented in Tables 2 and 3. The Temkin constant B shows that the heat of adsorption decreases indicating exothermic adsorption [37].
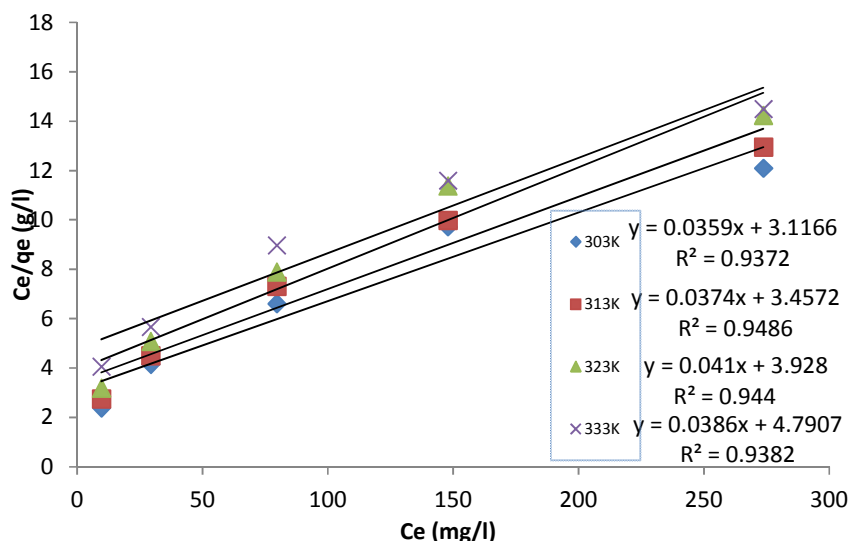

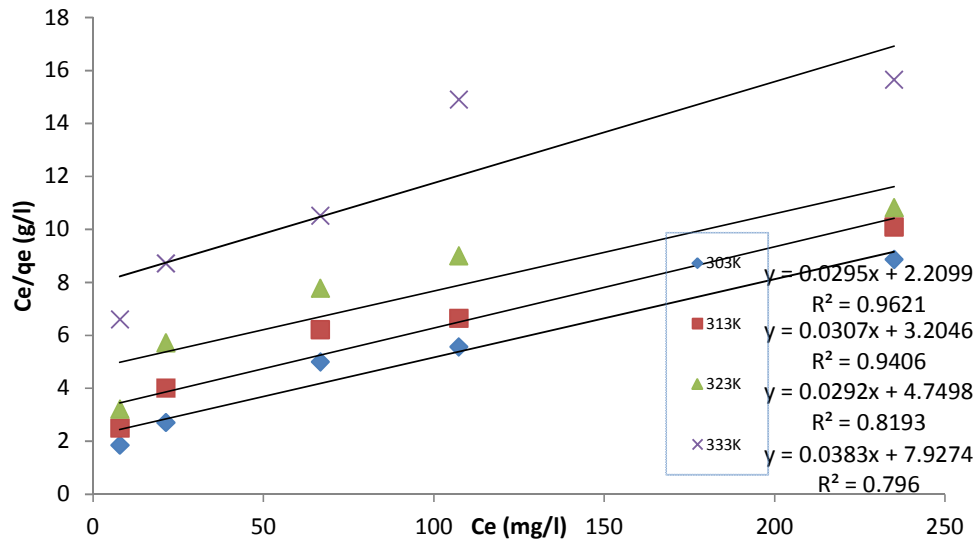Fig. 8. Langmuir isotherm for the adsorption of phenol red on PKS-AC

Fig. 9. Langmuir isotherm for the adsorption of orange G on PKS-AC
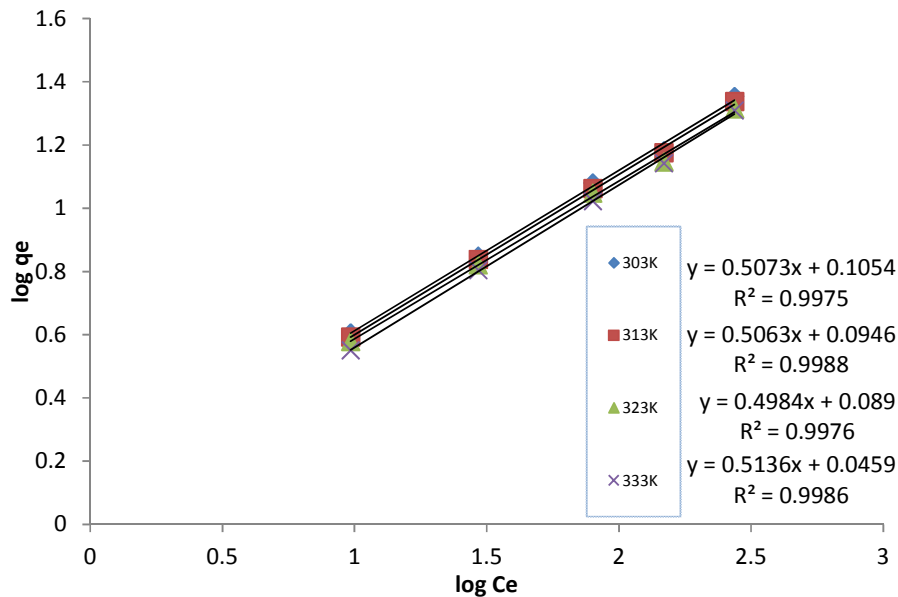
Fig. 10. Freundlich isotherm for the adsorption of phenol red on PKS-AC

4.4 Dubinin – Radushkevich Isotherm Model

This model involves temperature effects and quite fairly predicts the experimental data over a wide concentration range [40].

The linear form of Dubinin-Radushkevich Isotherm model [38] is:

$$\ln q_e = \ln q_m - \beta \mathcal{E}^2 \qquad (9)$$

Where q_m is the Dubinin-Radushkevich model monolayer capacity (mmol/g), β a constant related to sorption energy, and Ɛ is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\mathcal{E} = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (10)$$

Where, R is the gas constant (8.314 J/mol K) and T is the absolute temperature .The constant β gives the mean free energy, E, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship [41].

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$$E= \frac{1}{\sqrt{2\beta}}$$ (11)

The constants were calculated from the plot of ln q_e versus $\mathcal{E}^2$ as shown on the figures 14 and 15 and presented in Table 2 and Table 3. From the values R^2 obtained, the result

showed that both Phenol Red and Orange G adsorption did not follow Dubinin-Radushkevich Isotherm model well. The results of E obtained greater than 8KJ/mol obtained indicate that the adsorption is predominantly chemisorptions [42].

Fig. 11. Freundlich isotherm for the adsorption of orange G on PKS-AC

Fig. 12. Temkin isotherm for the adsorption of phenol red on PKS-AC

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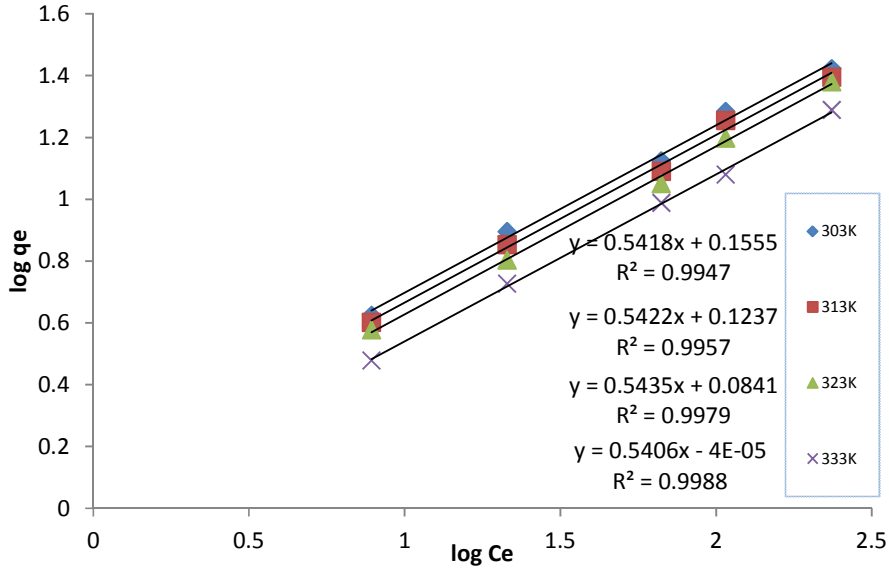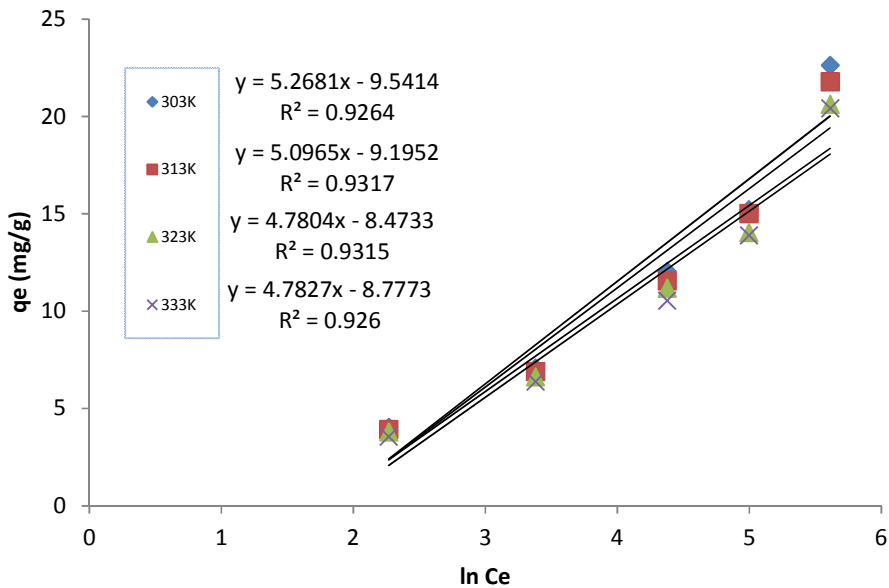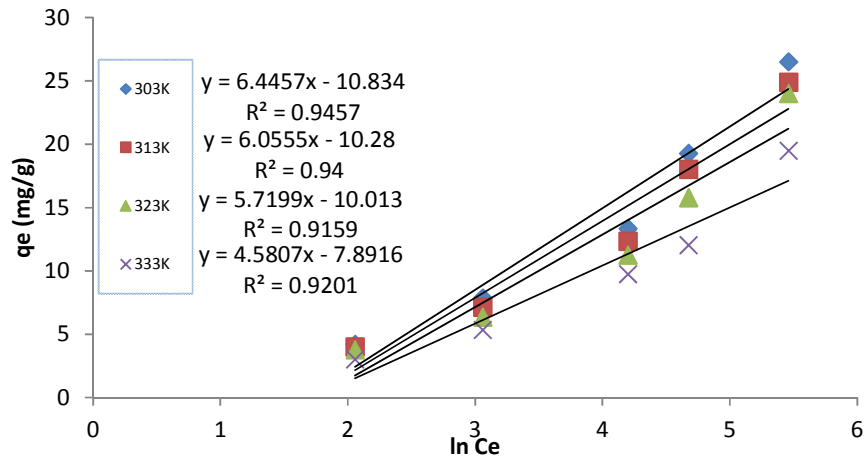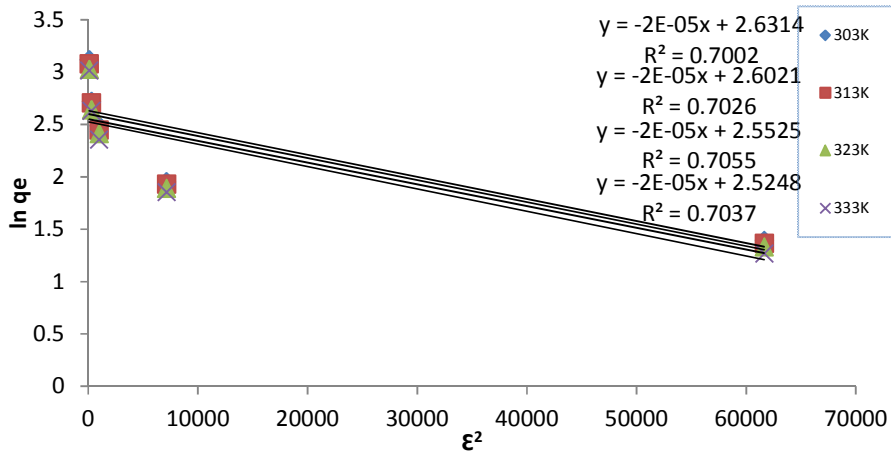**Fig. 13. Temkin isotherm for the adsorption of orange G on PKS-AC**

Fig. 14. Dubini-Radushkevich isotherm for the adsorption of phenol red on PKS –AC
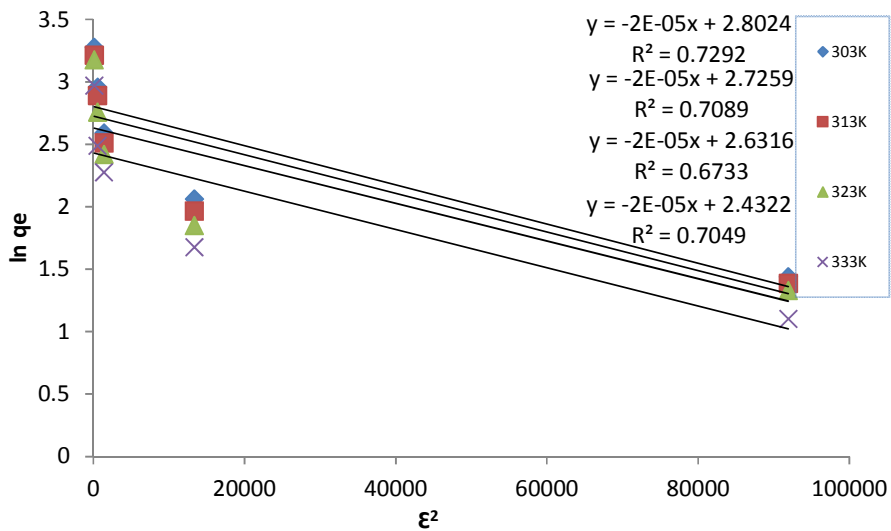

Fig. 15. Dubini-Radushkevich isotherm for the adsorption of orange G on PKS –AC

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Table 2. Calculated isotherm parameters for the adsorption of phenol red on PKS-AC

Isotherm model	Temperature K			
	303	313	323	333
Langmuir				
Q (mg/g)	27.855	26.738	24.390	25.907
b (L/mg)	0.0115	0.0108	0.0104	0.0081
R_L	0.1736	0.1849	0.1916	0.2482
R^2	0.9372	0.9486	0.9442	0.9382
Freundlich				
n	1.971	1.975	2.006	1.947
K_f (L/g)	1.275	1.243	1.227	1.112
R^2	0.9975	0.9988	0.9976	0.9986
Temkin				
b (J/mg)	478.19	510.60	561.76	578.87
A (L/g)	0.1635	0.1646	0.1699	0.1596
R^2	0.9264	0.9317	0.9315	0.9260
Dubinin-Radushkevich				
q_D (mg/g)	13.893	13.492	12.839	12.488
β (mol^2/J^2)	2.0×10^{-5}	2.0×10^{-5}	2.0×10^{-5}	2.0×10^{-5}
E (KJ/mol)	158.11	158.11	158.11	158.11
R^2	0.7002	0.7026	0.7055	0.7037

Table 3. Calculated isotherm Parameters for the Adsorption of Orange G on PKS-AC

Isotherm model	Temperature K			
	303	313	323	333
Langmuir				
Q (mg/g)	33.898	32.573	34.247	26.110
b (L/mg)	0.0133	0.0096	0.0062	0.0048
R_L	0.1303	0.1727	0.2455	0.2928
R^2	0.9621	0.9406	0.8193	0.7960
Freundlich				
n	1.8457	1.8443	1.8399	1.8498
K_f (L/g)	1.4305	1.3295	1.2137	0.9999
R^2	0.9947	0.9957	0.9979	0.9988
Temkin				
b (J/mg)	390.83	429.74	469.49	604.40
A (L/g)	0.1862	0.1831	0.1737	0.1786
R^2	0.9457	0.940	0.9159	0.9201
Dubinin-Radushkevich				
q_D (mg/g)	16.484	15.270	13.896	11.384
β (mol^2/J^2)	2.0×10^{-5}	2.0×10^{-5}	2.0×10^{-5}	2.0×10^{-5}
E (KJ/mol)	158.11	158.11	158.11	158.11
R^2	0.7292	0.7089	0.6733	0.7049

4.5 Isotherm Statistical Analysis for the Batch Adsorption

The statistical analyses on the isotherm studies are used to determine the best isotherm model for the adsorption. The Root Mean Square Deviation (RMSD), Coefficient of Variance (C.V), Variance and Mean were estimated. The smaller the values of variables and the RMSD, the better the model. Also, by comparing the correlation coefficient, R^2 values it can be seen that the Freundlich isotherm model best fitted the data than the other isotherm models. Equally, the isotherm equations obtained from the experimental data are presented in Tables 4 and 5 respectively.

Table 4. Isotherm statistical analysis for phenol red using PKS –AC

Isotherm model	R^2	Adj R^2	Mean	RMSD	Variance	C.V	Normalised RMSD (%)
Langmuir $\frac{C_e}{q_e} = \frac{1}{0.32} + (\frac{1}{27.86})C_e$	0.9370	0.9160	6.994	3.963	15.71	0.5667	40.87
Freundlich $\log q_e = \log 1.28 + \left(\frac{1}{1.97}\right) log C_e$	0.9980	0.9601	1.014	0.2927	0.0857	0.2885	39.06
Temkin $q_e = \left(\frac{RT}{478.2}\right) ln 0.16 + \left(\frac{RT}{478.2}\right) ln C_e$	0.9260	0.9013	12.20	7.262	52.73	0.5954	39.04
Dubinin-Radushkevich $ln q_e = ln 13.89 - 2\ x\ 10^{-5}\varepsilon^2$	0.7002	0.6000	2.336	0.6739	0.4541	0.2885	39.09

Table 5. Isotherm statistical analysis for Orange G using PKS –AC

Isotherm Model	R^2	Adj R^2	Mean	RMSD	Variance	C.V	Normalised RMSD (%)
Langmuir $\frac{C_e}{q_e} = \frac{1}{0.451} + (\frac{1}{33.90})C_e$	0.962	0.9493	4.798	2.749	7.557	0.5729	39.19
Freundlich $\log q_e = \log 1.43 + \left(\frac{1}{1.846}\right) log C_e$	0.995	0.9933	1.071	0.3171	0.1006	0.2961	39.74
Temkin $q_e = \left(\frac{RT}{390.8}\right) ln 0.1 + \left(\frac{RT}{390.8}\right) ln C_e$	0.946	0.9280	14.24	8.909	79.38	0.6257	39.99
Dubinin-Radushkevich $ln q_e = ln 16.48 - 2\ x\ 10^{-5}\varepsilon^2$	0.729	0.6387	2.466	0.7302	0.5332	0.2961	39.73

5. KINETIC ADSORPTION MODELLING

The kinetic models are used to investigate the mechanism of adsorption and the potential rate controlling steps such as mass transport and chemical reaction processes [26]. The First-order, Pseudo-first order and Bhattacharya-Venkobachor kinetic models were used to test the experimental data.

5.1 First-order Kinetic Model

The first-order rate expression of Lagergren [43] can be given as:

$$-\ln \left(\frac{C_t}{C_o}\right) = k_1 t \qquad (12)$$

Where C_o and C_t are the initial concentration of dye and concentration at a given time t, respectively (mg/l), and k_1 is the rate constant of first-order adsorption (/min). The first-order kinetic model was investigated by plotting $-\ln (C_t/C_o)$ against t. The rate constants were calculated from the slope and presented in Tables 6 and 7 together with the values of the correlation coefficient, R^2. Save for adsorption of orange G on PKS -AC, which gave R^2 values of less than 0.9, all the others gave R^2 values greater than 0.9 showing that the adsorption followed first-order to an extent.

5.2 Pseudo- first Order Kinetic Model

The Pseudo- first order rate expression of Lagergren [44] can be expressed as:

$$\log (q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (13)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), K_1 is the rate constant of pseudo first-order adsorption ($Lmin^{-1}$).

Plots of log (q_e – q_t) against t was used to express the pseudo-first order at different temperatures. The values of the correlation coefficient R^2 were shown in Tables 6 and 7 as well as the constants K_1 and q_e that were evaluated. It can be seen that for the adsorption of both dyes on the adsorbents, correlation coefficient R^2 values were all > 0.9 indicating that the adsorption may have followed the pseudo-first order. But it must be stated that the q_e values calculated were different from the experimental q_e. It has been reported that if the values of q_e calculated were not close to the experimental value of q_e, the adsorption is assumed not to have followed the kinetic model even if it has a high correlation coefficient, R^2 value [45]. Hence, this adsorption did not follow the Pseudo- first order. Some works that followed this trend include [46,47]

5.3 Bhattacharya-Venkobachor Model

Bhatta-Venkobachor model [31] is expressed as:

$$\ln(1-U_t)=K_B.t \qquad (14)$$

$$U_t = (C_o - C_t)/(C_o - C_e) \qquad (15)$$

The effective diffusion coefficient D_2, is obtained from the equation:

$$D_2 = \frac{k_B}{\lambda^2} \cdot r^2 \qquad (16)$$

Where, **r** is particle radius.

The plot of ln[1 – U_t] against **t** was used to investigate the Bhattacharya-Venkobachor model. The values of the rate constant K_B which was obtained from the slope of the linear plot was used to calculate the effective diffusion coefficient D_2 and presented in Tables 6 and 7.

The Effective diffusion coefficients D_2 determined were of the order 2.0×10^{-13} to 6.0×10^{-13} m^2/s. The correlation coefficient, R^2 was (> 0.90) which shows that the adsorption process conformed to the Bhattacharya-Venkobachor model. Similar result was obtained by [32].

5.4 Thermodynamic Studies

The mechanism of adsorption was determined through thermodynamic quantities such as a change in free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS). The thermodynamic equilibrium constant, K for the sorption was determined from the intercept of the plots of ln (qe/Ce) versus qe of langmuir isotherm. Then, the ΔG, ΔH and ΔS are calculated from the Van't Hoff equations shown in equations 4 and 5. The thermodynamic parameters were calculated from the values of the thermodynamic equilibrium constant, K by plotting of ln K versus 1/T. Then the slope and intercept were used to determine ΔH and ΔS, and the Van't Hoff Equation (Equation 4) was applied to calculate ΔG. The values of ΔH, ΔS and ΔG are given in Tables 8 and 9 respectively.

The negative values of ΔG indicate the feasibility of the adsorption process at room temperature and also the spontaneity of adsorption reaction [31]. The negative values of ΔH indicate the exothermic nature of the adsorption in accord with the decreasing adsorption capacity associated with increasing adsorption temperature. This also confirms the possibility of physical adsorption as with the increase in temperature of the system [48]. The negative value of ΔS means the decreased randomness with adsorption of the dyes on PKS -AC [49]. This is because the number of water molecules surrounding the dyes increased during the adsorption process and thus, the degree of freedom of the water molecules decreased indicating that the degree of randomness at the solid-solution interface of the adsorption decreased [50].

5.5 Activation Energy

The activation energy of adsorption was calculated from the linearized Arrhenius equation:

$$\ln K = \ln A - \frac{E_a}{RT}$$

$$(17)$$

Where A is the frequency factor (g/mg.min), K = rate constant value for Second-order kinetics (g/mg.min). E_a = activation energy in kJ/mol. T is temperature (K) and R is the gas constant = 8.314KJ/molK. The value of E_a can be calculated by the slope of graph 'lnK versus 1/T'. The activation energies from the present system are **-** 32.712 KJ/mol and -24.787 KJ/mol, for phenol red and orange G respectively. The values were in corroboration to the values obtained by [50].

Table 6. Calculated kinetic parameters for the adsorption of phenol red on PKS-AC

Kinetic model	Temperature K			
	303	313	323	333
First order				
K_1(/min)	0.0247	0.0258	0.0268	0.0213
R^2	0.9863	0.9616	0.9840	0.9647
Pseudo first order				
K_1 (/min)	0.0389	0.0357	0.0596	0.0463
q_e (mg/g)	1.285	2.444	4.008	3.451
R^2	0.9926	0.918	0.9373	0.9369
Bhattacharya-Venkobachor				
K_B	-0.0018	-0.0032	-0.0045	-0.0046
D_2 (m^2/s)	-2.56 x 10^{-13}	-4.56 x 10^{-13}	-6.41 x 10^{-13}	-6.6x10^{-13}
R^2	0.9458	0.9919	0.9589	0.9436

Table 7. Calculated kinetic Parameters for the Adsorption of Orange G on PKS-AC

Kinetic model	Temperature K			
	303	313	323	333
First order				
K_1(/min)	0.0118	0.0141	0.0173	0.0161
R^2	0.634	0.740	0.8356	0.8912
Pseudo first order				
K_1 (/min)	0.0924	0.0795	0.0887	0.0161
q_e (mg/g)	1.457	1.786	2.857	2.687
R^2	0.9363	0.9579	0.9888	0.9536
Bhattacharya-Venkobachor				
K_B	-0.0018	-0.0023	-0.0031	-0.003
D_2 (m^2/s)	-2.56 x 10^{-13}	-3.28 x 10^{-13}	-4.42 x 10^{-13}	-4.3x10^{-13}
R^2	0.5533	0.6381	0.7542	0.8176

Table 8. Thermodynamics parameters for the adsorption of phenol red on the adsorbents

Adsorbent	T (K)	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)
PKS -AC				
	303	-6.153		
	318	-6.192	-9.206	-9.033
	323	-6.289		
	333	-5.791		

Table 9. Thermodynamics parameters for the adsorption of orange G on the adsorbents

Adsorbent	T (K)	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)
PKS -AC				
	303	-6.556		
	318	-5.886	-29.72	-29.72
	323	-4.900		
	333	-4.343		

4. CONCLUSIONS

The PKS-AC as an adsorbent has shown to be effective for the removal of phenol red and orange G dyes from aqueous solutions. The effect of adsorption parameters such pH, initial ion concentration, contacts time, temperature and adsorbent dosage on the performance of the PKS-AC as an adsorbent were studied. The result showed decreased adsorption percentage with an increase in dye concentration. The isotherm models have been investigated and Freundlich isotherm fits the equilibrium data. Similarly, the Pseudo-first order kinetic model fits very with the dynamical adsorption behavior of the dyes. The thermodynamic studies showed that ΔG (-5.556 KJmol^{-1}) and ΔH (-29.72 KJmol^{-1}) were negative at different temperatures, indicating that the adsorption process is spontaneous and exothermic. The negative value of ΔS shows decreased randomness with adsorption of dye. It may be concluded that PKS-AC can be very effectively employed for the removal of the dyestuffs in aqueous solutions. The main advantages being that palm kernel shells are available freely, locally and abundantly, easy to prepare in large scales.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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