

Characterization of Adsorption Capacity of Phenol Using Groundnut Husk-based Activated Carbon

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Authors' contributions

This work was carried out in collaboration among all authors. Author WOM designed the study, performed the statistical analysis; wrote the protocol and first draft of the manuscript. Authors CAW and APY managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Equilibrium adsorption studies of phenol onto activated carbon prepared from groundnut husk was investigated for effectiveness. Groundnut husks were washed, dried at temperatures between 110°C and 160°C, pulverized and finally activated at 200°C for 3 hours. Optimum conditions of carbon dosage, pH, contact time and influence of concentration of phenol on carbon were investigated. Several analyses of isotherm data were tested by fitting them into different isotherm (Temkin, Langmuir, Dubinin-Kaganer-Rushkevich and Freundlich) models. The results of the optimization studies indicated an optimum adsorption of phenol with carbon dosage of 2.2 g; pH = 5 and contact time = 5 hours. Temkin, Dubinin-Kaganer-Rushkevich and Freundlich had high correlation coefficients in the range of 0.853 – 0.9501. The experimental data fitted adequately into these models but not into the Langmuir isotherm model with extremely low regression coefficient of 0.0038. The high correlation coefficients connoted strong interactions between the adsorbate and the adsorbent and a good interpretation of the adsorption behaviour of phenol. However, the Temkin and Dubinin-Kaganer-Rushkevich models showed indications of chemisorptions with high heat of adsorption of 1531.39 J mol⁻¹ and mean energy of 5227.1 Jmol⁻¹ respectively and the value of the

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separator factor R_L (0.1805) that was less than unity obtained from the Langmuir model indicated favourable adsorption. The value of $1/n = 0.9277$ that was less than unity from the Freundlich model depicted strong adsorption intensity. The adsorption of phenol by the activated carbon was best described by Freundlich model with the highest regression coefficient of 0.9501. It was evident from the Freundlich adsorption isotherm that adsorption capacity increased as the initial concentration of phenol was increased until a possible removal efficiency of 100% could be achieved. The adsorbent was found to be suitable and effective in the treatment of wastewater laden with phenol.

Keywords: Optimum; adsorption capacity; adsorption intensity; chemisorptions.

1. INTRODUCTION

The adsorption phenomenon is probably the most widely employed procedure as separation method, waste effluents treatment, refrigeration, environmental control and life support system in space crafts and obviously heterogeneous catalysis [1]. To describe the adsorption on solid surfaces, several models and empirical equations have been proposed. Some of them have solid thermodynamic bases and other are no more than empirical equations having at least two adjustable parameters [2]. This kind of equation has been proposed to describe the adsorption on heterogeneous surfaces and some effort has been devoted to assign a physical meaning to the equation parameters [3]. Phenol has been chosen as model adsorbate by many researchers to study the adsorption process from solution on a large variety of adsorbent, the interest is mainly due to the presence of this species and its derivatives in wastewater effluents originated from many industries [4]. According to [5] several characteristics of the process have been disclosed but there are still more questions that need answers for example, there is general agreement on the influence of the surface chemical composition on the adsorption mechanism for several compounds like phenol, aniline, nitrobenzene, etc. [5]. According to [6] at the other hand, there is one crucial aspect on which there is no agreement concerning the reversibility or not, of the adsorption of phenol and phenolic compounds. Activated carbon filters primarily remove taste and odours in water treatment systems. Activated carbons are processed from carbon materials (such as groundnut husk, corn husk coconut shell, etc.) that are capable of adsorbing various substances from gas and liquid streams because of their highly developed pore structure and large internal specific surface areas.

The growing problem of the degradation of water caused by chemical substances activities which result to odor in water and the ability or the

possibility of activated carbon to adsorb phenol in liquid has made it important for continuous monitoring of some characteristic chemical from substances adsorbed on activated carbon. Information obtained from such a study will help in selecting suitable and effective adsorbent for chemical substances such as phenol. It is in the light of the above that the present study considered the characterization and equilibrium adsorption studies of phenol onto groundnut husk-based activated carbon.

2. MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

200 g of groundnut husks were taken and washed with water to remove the earthy materials and then kept in an oven at a temperature of 120°C. It was subsequently treated with concentrated tetraoxosulphate (VI) acid, H_2SO_4 and kept back into the oven at a temperature of 160°C for 24 hours. It was afterward washed repeatedly with distilled water. During the last washing two drops of $BaCl_2$ was added to test for the presence of H_2SO_4 , dried in a hot air oven at 110°C, sieved in a 20 - 40 mesh size to obtain carbon particles of uniform mesh size and activated for three hours at 200°C.

2.2 Standardization of Phenol by Bromination

The phenol was standardized following standard procedure adopted by [7]. 20 mL of phenol solution was taken in a 250 mL Erlenmeyer flask to which 40 mL of distilled water, 20 mL of Winkler's reagent and 5 mL of concentrated HCl were added and shaken manually for about two minutes then allowed to stand for 10 minutes. After the 10 minutes, 10 mL of $K_3[Fe(CN)_6]$ solution was added. The mixture was titrated against sodium thiosulphate until the colour changed to pale-yellow, followed by the addition of 2-3 drops of starch indicator and the titration continued until the colour first disappeared. The

burette reading was recorded. The titration was repeated with fresh samples until three concordance readings were obtained.

Phenol concentration was calculated using the formula: mg/L phenol = 7.842(AB - C)

Where;

A = volume of sodium thiosulphate used for the blank

B= volume of Winkler's reagent used for the sample divide by 10

C = volume of sodium thiosulphate used for the sample

2.3 Optimization Studies

Optimization studies were carried out to determine the optimum conditions for carbon dosage, pH and contact time required for efficient removal of phenol from wastewater.

The established conditions were subsequently applied to adsorption isotherm studies so as to investigate the influence of phenol concentration on the adsorbent.

2.4 Optimization of Carbon Dosage

26 mg/L of phenol was prepared from a stock, 150 mL each of the solution was taken in eight conical flasks and the prepared groundnut husk-based activated carbon dosage of 0.2, 0.4, 1.2, 1.6, 1.8, 2.0, 2.2 and 2.4 g were added to the flasks. The flasks were shaken on a mechanical shaker for 3 hours at 200 r.p.m. and then filtered using number 42 Whatman filter paper. Extraction and analysis were carried out following procedures described by [7]. To 50 mL of the filtrate, 2 mL buffer solution of pH 10, 2 mL of 4-aminoantipyrene, 3 mL of potassium ferricyanide solution were added, shaken thoroughly and allowed to stand for 10 minutes to develop colour. The solutions were then extracted with 20 mL trichloromethane (chloroform) in a 500 mL separating funnel in each case; the extracts obtained were filtered with Whatman No. 42 filter paper containing 5 g layer of anhydrous Na₂SO₄ and dry extracts were collected into clean conical flasks. The concentration values of phenol were read off on spectrophotometer at a wavelength of 510 nm. Amount of phenol adsorbed was plotted versus carbon dosages.

2.5 Optimization of pH

150 mL of 26 mg/L of phenol were taken in several 250 mL conical flasks and treated with the optimum carbon dosage in each of the flasks. The pH of each solution was adjusted to the desired values of (1, 3,4,6,9, and 13) and the flasks were shaken on a mechanical shaker for 3 hours at 200 r.p.m. To 50 mL of the filtrate in each case was added 2 mL buffer solution of pH 10, 2 mL 4-aminoantipyrene and 3 mL K₃[Fe(CN)₆], then extracted with 20 mL chloroform in 500 mL separating funnel and filtered with 5 g anhydrous Na₂SO₄. The dry extracts obtained were analysed on UV-spectrophotometer at wavelength of 510 nm. The procedure was repeated for the various pH values.

2.6 Optimization of Time

150 mL of 26 mg/L of phenol were taken in several 250 mL conical flasks. The solutions were subjected to the optimum conditions of carbon dosage and pH. The samples were shaken on a mechanical shaker for 7 hours at 200 r.p.m. After each hour, replicate samples were taken out filtered, extracted, dried and analysed on UV-spectrophotometer at a wavelength of 510 nm. A plot of % adsorption versus time was drawn.

2.7 Adsorption Isotherm Studies

Adsorption was studied for various concentrations (25, 55 and 80 mg/L) to investigate the influence of phenol concentration on carbon. The adsorption was studied by applying the optimum conditions of time, pH and carbon dosage. The samples were shaken at an optimum time (5 hrs). After filtration, the filtrate were treated, extracted, and dried as per the standard procedure then analysed on UV-spectrophotometer at a wavelength of 510 nm.

3. RESULTS AND DISCUSSION

3.1 Standardization of Phenol

The result obtained from standardization of phenol is given in Table 1 below:

Average volume of Na₂S₂O₃ used

$$= \frac{18.70 + 18.7 + 18.70 + 18.5}{4}$$

$$= 18.70 \text{ mL}$$

Using the formula: mg/L of phenol

$$= 7.842 (AB - C)$$

$$\text{mg/L of phenol} = 7.8427[(20.90 \times 6) - 18.70] \\ = 836.74 \text{ mg/L}$$

This result was crucial and enabled the preparation of stock and working standards used for the construction of calibration curve for phenol with high degree of accuracy. It was also indicative that the quality of the phenol used in the research was of high grade with 83.67% purity.

3.2 Calibration Curve

The result of the 5-point calibration curve for phenol is displayed in Fig. 1.

The regression coefficient (R^2) was 0.9998 close to unity and connoted good linearity.

3.3 Effect of Carbon Dosage

The result of optimization of carbon dosage is displayed in Fig. 2. It was evident that adsorption was chiefly a surface phenomenon; the amount of surface vacant for adsorption thus the mass of the adsorbent can extensively influence the removal efficiency of phenol from water.

It was observed that as the concentration of the adsorbent increased from 0.2 g to 2.2 g, the removal efficiency of phenol from water was considerably improved from 25.7% to 38.06% (Fig. 2). The plausible explanation to the observed improvement could be that there was an increment in the number of active sites in unit volume of solution as the adsorbent dosage increases thus increases the percent removal of phenol.

3.4 Effect of pH

pH seems to play a major role in the removal of phenol from aqueous solutions by adsorption. It is known to alter the surface charges of the adsorbent and several mechanisms such as electrostatic interaction, complexation, ion exchange and surface charge on carbon have been proposed to have contributed [8]. At pH < 5, percent removal of phenol increased with the increase in solution pH. The highest phenol removal of 35.88% was attained at pH 5 and suddenly decreased remarkably with increase in solution pH up to 13 (Fig. 3). This confirmed the earlier assertion that the surface charges on the activated carbon and the behaviour of phenol in water had a strong influence on the efficiency of phenol removal. It was found that the phenol adsorption was more effective at pH 5 (Fig. 3).

Table 1. Standardization of phenol

Burette readings	1 st reading	2 nd reading	3 rd reading	4 th reading
A = mL of Na ₂ S ₂ O ₃ used for blank	20.90	20.90	20.90	20.90
B = mL of bromate-bromite solution used divided by 10	6	6	6	6
C = mL of Na ₂ S ₂ O ₃ used for sample	18.70	18.70	18.50	18.70

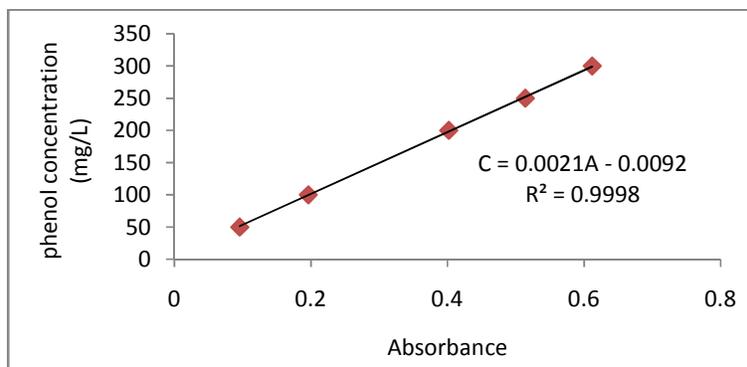


Fig. 1. Calibration curve for phenol

3.5 Effects of Contact Time

The amount of phenol adsorbed by the adsorbent was found to vary with time. The result is depicted in Fig. 4. From the result it was observed that optimum removal of phenol

required a period of 5 hours shaking time. At the 3rd hour 41% of the phenol had been removed from water while at the fifth hour considerable removal efficiency of 72.67% was attained (Fig. 4).

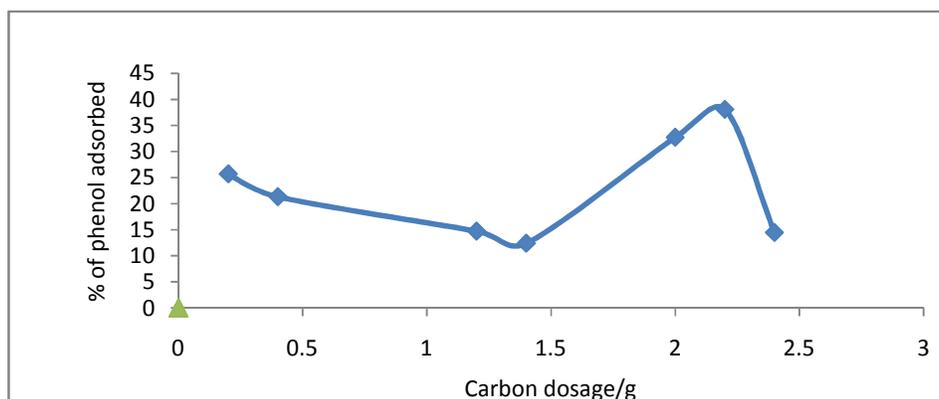


Fig. 2. Plot of carbon dosages against phenol adsorbed

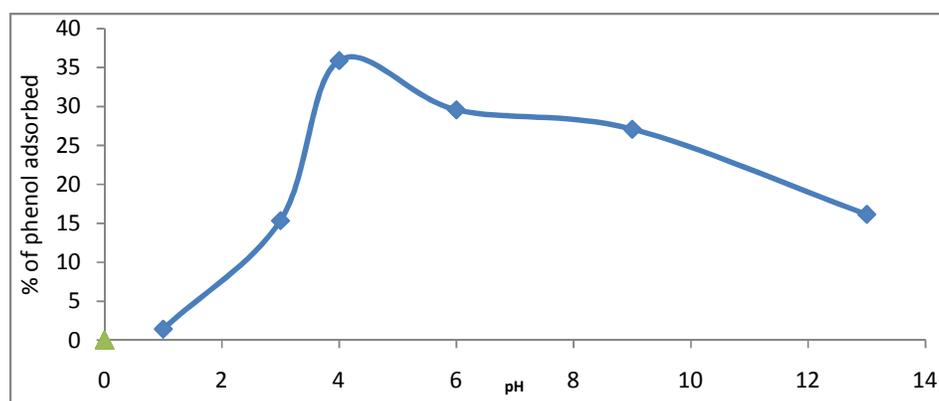


Fig. 3. Adsorption of Phenol at different pH

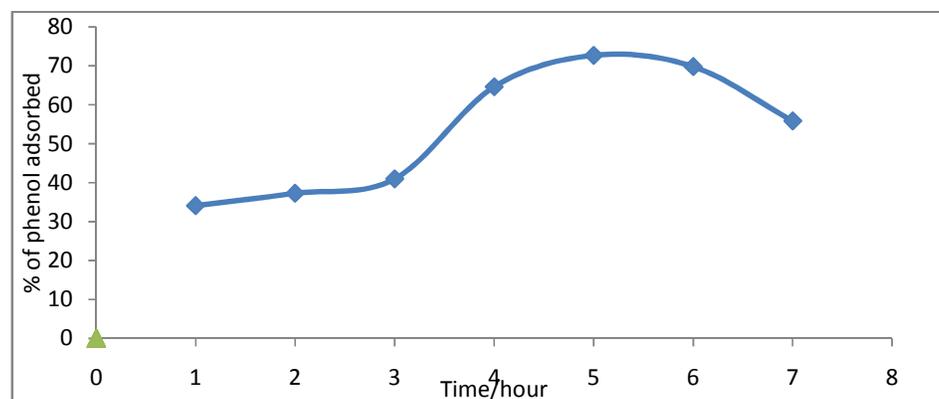


Fig. 4. Plot of % of phenol adsorbed versus time

3.6 Equilibrium Adsorption Studies

Adsorption isotherm test is one of the important tests employed in selecting a particular type of carbon for water, wastewater and industrial treatment systems. The equilibrium adsorption also presented as adsorption isotherm is a useful parameter for predicting the performances of activated carbon. According to [9], adsorption capacity is a prime factor to be taken into consideration in the optimization of activated carbon. The equilibrium relationships between adsorbate and adsorbent are described by adsorption isotherm as the ratio between the quantity adsorbed and the amount remaining in solution at a fixed temperature at equilibrium [10]. Several analyses of isotherm data were tested by fitting them into different isotherm models with the view of finding suitable model(s) that can be used to reproduce the experimental result obtained thereby giving a leeway to industrial design purposes.

3.6.1 Langmuir isotherm

The Langmuir isotherm is given as:

$$q_e = bC_eQ^0 / (1 + bC_e) \dots \dots \dots (1)$$

where:

- q_e = amount of adsorbate per unit weight of carbon
- Q^0 = a constant relating to monolayer adsorption capacity
- b = a constant that measures the surface energy of the adsorption process
- C_e = equilibrium concentration of the adsorbate solution.

Other linear forms of the Langmuir equations are presented as:

$$C_e/q_e = 1/bQ^0 + C_e/Q^0 \dots \dots \dots (2)$$

$$1/q_e = 1/Q^0 + [1/bQ^0] [1/C_e] \dots \dots \dots (3)$$

It is interesting to consider an important and reliable dimensionless parameter of the Langmuir model known as the separation factor, R_L and expressed as [11]:

$$R_L = 1 / (1 + bC_o) \dots \dots \dots (4)$$

Where C_o is the highest initial concentration and b is the Langmuir constant expressing the adsorption rate. The separator factor potentially predicts the shape of the isotherm and the nature of the adsorption and the nature of the adsorption processes as reported by [12], given as: $R_L > 1$ (unfavourable); $R_L = 1$ (linear); $0 < R_L < 1$ (favourable) and $R_L = 0$ (irreversible). A plot of C_e/q_e versus C_e was an inverse straight graph as displayed in Fig. 5.

The slope of the plot $1/Q^0$ was 0.0258 with an intercept of $1/b = 16.544$ and very low correlation coefficient of 0.0357. The values of the adsorption capacity Q^0 and the constant, b that measures the surface energy of the adsorption process were evaluated from the slope and intercept of the plot as 38.7597 L/mg and 0.060445 mg/g respectively. The separator factor (R_L) was 0.17136 and suggested that adsorption of phenol onto the groundnut husk-based activated carbon was favourable since the R_L value was between 0 and 1 [12].

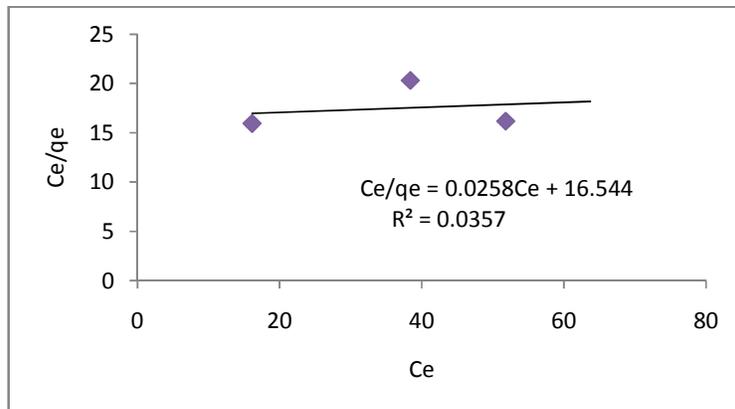


Fig. 5. Langmuir isotherm plot for adsorption of phenol by activated carbon at 30°C

3.6.2 Dubinin-Kaganer-Rushkevich (D-K-R)

The Dubinin-Kaganer-Rushkevich (D-K-R) adsorption is given by [13]:

$$\ln q_e = \ln q_m - \beta \xi^2 \dots\dots\dots (5)$$

Where:

q_m = adsorption capacity (mg/g); β = constant related to energy of adsorption ($\text{mol}^2\text{kJ}^{-2}$)

ξ = Polanyi potential = $RT \ln [1 + (1/C_e)]$; R = universal gas constant = $0.008314 \text{ kJ deg.}^{-1} \text{ mol.}^{-1}$

E = mean energy and is usually calculated from the β value as:

$$E = (-2\beta)^{-0.5} \dots\dots\dots (6)$$

A plot of $\ln q_e$ versus ξ^2 gave a slope (β) = $-0.0183 \text{ mol}^2\text{kJ}^{-2}$ and an intercept ($\ln q_m$) = 0.0209 as displayed by Fig. 6.

The adsorption capacity (q_m) was calculated as 1.02112 mg/g and the mean energy was 5227.1 Jmol^{-1} . This high energy value suggested chemisorptions.

3.6.3 Temkin adsorption isotherm

Temkin adsorption isotherm is characterized by a uniform distribution of the binding energy since it assumes that the heat of adsorption of all molecules in the layer decreases linearly with the coverage owing to adsorbent-adsorbate interactions [11]. The Temkin adsorption isotherm equation is given as:

$$q_e = (R_T/b_T) \ln K_T \ln C_e + (R_T/b_T) \dots\dots\dots (7)$$

Where:

$1/b_T$ = adsorption potential of the adsorbent (KJ mol^{-1})

K_T = Temkin isotherm constant (dm^3g^{-1}).

A plot of q_e versus $\ln C_e$ gave a straight line graph of slope $R_T/b_T = 1.645$ and intercept of $R_T/b_T \ln K_T = -3.789$ with a correlation coefficient of 0.8567 as shown in Fig. 7.

The high correlation coefficient of 0.8567 (Fig. 7) characterized by this plot indicated the experimental data adequately fitted into the model. The Temkin isotherm constant was $0.6411 \text{ dm}^3\text{g}^{-1}$ and the value of b_T , which is related to the heat of adsorption was $1531.39 \text{ Jmol}^{-1}$. This high value also suggested chemisorptions and was earlier predicted by the D-K-R model in this work. The Temkin adsorption potential, $1/b_T$ of the activated carbon was calculated as 0.6530 Jmol^{-1} .

3.6.4 Freundlich adsorption isotherm

The Freundlich equation has the general form that is expressed as [14]:

$$q_e = K_f C_e^{1/n} \dots\dots\dots (8)$$

where, n is a constant related to adsorption efficiency and energy of adsorption, K_f is a constant measuring adsorption capacity, q_e is the amount of adsorbate per unit weight of carbon. It describes adsorption processes on surface sites that are energetically heterogeneous. The Freundlich equation can be written in the logarithm form as:

$$\log q_e = \log K_f + 1/n \log C_e \dots\dots\dots (9)$$

A plot of $\log q_e$ versus $\log C_e$ gave a straight line graph (Fig. 8) with the slope $1/n$ and the intercept $\log K_f$.

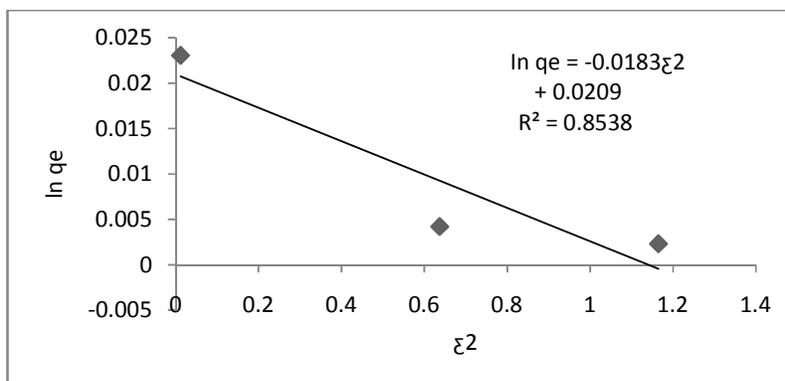


Fig. 6. Dubinin-Kaganer-Rushkevich isotherm plot for adsorption of phenol by activated carbon at 30°C

The K_f value increases with the total adsorption capacity of the adsorbent to bind to the adsorbate. The numerical value of n is a useful index of adsorption efficiency and is known to be related to the energy of adsorption. This implies that the intercept is roughly an indicator of sorption capacity and the slope indicates adsorption intensity [15]. The experimental data fitted into the Freundlich adsorption isotherm model as shown in Fig. 8. The adsorption capacity (K_f) value was 0.0740 while intensity of adsorption ($1/n$) was 0.9277. Generally, $1 < 1/n < 10$ is characteristic of cooperative adsorption and indicative of favourable adsorption process as reported in literature [11,16,17]. Although the Temkin and D-K-R isotherm models had high regression coefficients

of 0.8567 and 0.8538 respectively (Figs. 6 and 7), the Freundlich isotherm model with a higher regression coefficient (R^2) of 0.9501 (Fig. 8) best described the adsorption behaviour of phenol on groundnut husk based - activated carbon. Apparently, the experimental data did not adequately fit into the Langmuir adsorption isotherm with extremely low regression coefficient of 0.0357 (Fig. 5). However, the separator factor, R_L with a value of (0.17136) that was less than unity suggested a favourable adsorption. The other models accounted for some phenomenon such as chemisorptions, nature of the process, adsorption potential etc. that the Freundlich isotherm model failed to address.

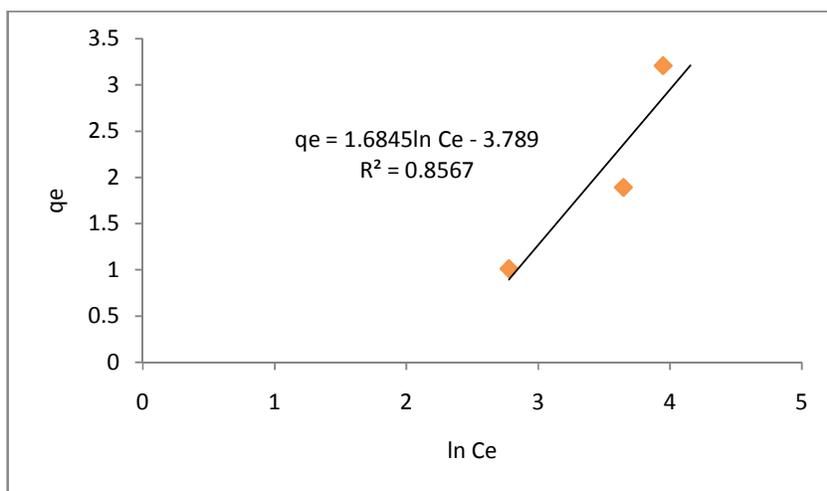


Fig. 7. Temkin isotherm plot for adsorption of phenol by activated carbon at 30°C

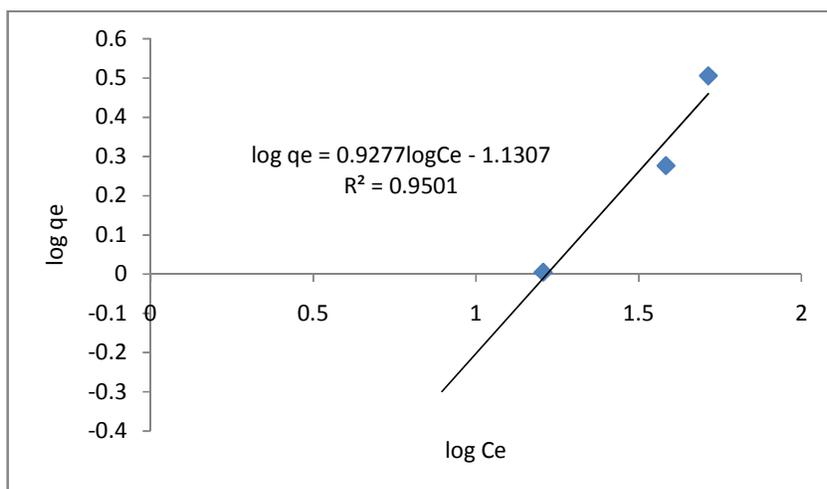


Fig. 8. Freundlich isotherm plot for adsorption of phenol by activated carbon at 30°C

4. CONCLUSION

In conclusion, it was evident from the Freundlich adsorption isotherm that adsorption capacity increased as the initial concentration of phenol was increased until a possible 100% removal efficiency could be achieved. The research therefore concluded that activated carbon prepared made from locally and cheaply available groundnut husk was found to be suitable and effective in the treatment of wastewater laden with phenol.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Derbyshire F, Jagtoyen M, Andrew R, Rao A, Martin Guillon I and Grulke EA. Chem. Phys. Carbon; 2001.
- Jaroniec M, Madey R. "Physical Adsorption Heterogeneous solids". Studies in Physical and Theoretical Chemistry. Elsevier.1988; 59.
- Ruszynski W, Evereth DH. Adsorption of Gases on Heterogeneous surface. Academic Press; 1992.
- Eltkova NA, Berek D, Novak I, Belliardo F. Adsorption of Organic Compounds on Porous Carbon sorbents. Carbon. 2000; 38:373 –377.
- Okolo B, Park C, Keane MA. Some Characterization of Phenol Adsorption on Activated Carbon. J. Colloid Inter. Sci. 2000;226:308.
- Bertoncini C, Odetti H, Bottani EJ. Computer Simulation of Phenol Physisorption of Graphite. Langmuir. 2000; 16:7457-7463.
- Ademoroti CMA. *Standard Methods of Treatment of Water and Wastewaters*. Fodulex Press Ltd., Ibadan; 1996.
- Guo R, Chakrabarti CL, Subramanian KS, Ma X, Lu Y, Cheng J and Pickering WF. Sorption of low levels of cyanide by granular activated carbon. Water Environ. Res. 1993;65:640-644.
- Wang K and Do DD. Sorption equilibria and kinetics of hydrocarbons onto activated carbon samples having different micropore size distributions. Adsorption. 1999;5:25 –37.
- Muhammad NP, Smith DM and Wheatley AD. Adsorption of heavy metals in slow sand filters. 24th WEDC Conference, Islambad, Pakistan; 1998.
- Hameed BH, Din ATM and Ahmad AL. Adsorption of Methylene Blue onto Bamboo-based activated carbon: Kinetics and Equilibrium studies. J. Hazard Matter; 2006.
- Kannan N and Meenakshisundaram M. Adsorption of Congo red on Activated Carbons: A comparative study. Water, Air and Soil Pollution. 2002;138:289–305.
- Kannan N and Rengasamy G. Comparison of cadmium ion adsorption on various activated carbons. Water, Air and Soil Pollution. 2005;163:185–201.
- Thomas JW and Crittenden B. Adsorption technology and design. Butterworth Heinemann. 1998;1-55.
- Ribeiro MHL, Lourenco PAS, Monteiro JP, Ferroira-Dias S. Kinetics of selective adsorption of impurities from a crude vegetable in hexane to activated earths and carbon Euro Food Res Technol. 2001; 213:132–138.
- Shabudeen SSP, Venkatesh R, Pattabhi S. Preparation and utilization of Kapok Hall Carbon for the removal of Rhodamine-B from aqueous solution. E- Journal of Chemistry. 2006;3(11):83–96.
- Anusiem ACI, Onwu FK, Ogha SPI. Adsorption isotherm studies of Ni(II), Cd(II) and Pb(II) ions from aqueous solution by African White Star apple (*chrysophyllum albidum*) shell. Intern. Journ. Chem. 2010; 20(4):265-274.

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