

KINETICS OF CHLOROPHENOL ADSORPTION ONTO COMMERCIAL AND FLUTED PUMPKIN ACTIVATED CARBON IN AQUEOUS SYSTEMS

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ABSTRACT

Experiments were carried out in a batch process for the removal of chlorophenol from fluted pumpkin stem waste and a commercial activated carbon. The results of equilibrium studies showed that equilibrium was reached within one hour of exposure time. Five kinetic models were applied to fit the experimental data namely pseudo first order, pseudo second – order, Elovich, intra-particle and liquid –film diffusion models. The interpretation of the released results have shown that, pseudo second order model is the most suitable dynamic theory describing the adsorption of chlorophenol onto both activated carbons predicting therefore a chemisorptions process. Chlorophenol thermodynamic data on FPAC and CAC indicates the feasibility and spontaneous nature of the process with ΔG° , ΔH° , ΔS° being negative. Fluted pumpkin stem an abundant waste in Nigeria, if used for the wastewater treatment process would serve as an economically viable option to the increasing toxic threat to the environment.

Keyword: Chlorophenol, adsorption, fluted pumpkin, temperature, kinetic modelling

INTRODUCTION

2-chlorophenol is a derivative of phenol. It is used as a disinfectant and pesticide. 2-chlorophenol is a liquid at room temperature, but all other chlorophenols are solids. 2-chlorophenol is used as bactericides, fungicides and preservatives. The water solubility of chlorophenols is low, in the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste that is quite pronounced, and objectionable (Mahvi et al., 2004; Duarte-Davidson et al., 2004; Denzeli et al., 2005). Chlorine substitution on phenols does not only increase water taste and odour, but also its toxicity effects (Mostafa et al., 1989; Rengaraj et al., 2002 and Srivastava et al., 2006).

Residues of chlorophenol have been found worldwide in soil, water, air sample, food products, human, animal tissues and body fluids. Due to their slow degradation, chlorophenol represent a major threat to ecosystems (Denzeli et al., 2004; Sofia et al., 2005 and Zumriye and Yener 2001).

Chronic toxic effects due to phenolic compounds reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbance. Among the different organic pollutions of aquatic ecosystems, phenols, especially the chlorinated ones, are toxic to animals and human even at low concentration (Asheh et al.,

2003). The aim of this present work is to investigate the sorption potential of a powdered commercial activated and a carbon derived from fluted pumpkin stem waste for the removal of chlorophenol from aqueous medium. The objective of this study is to carry out an investigation on the kinetics of chlorophenol sorption onto fluted pumpkin activated carbon (FPAC) and a powdered commercial activated carbon (CAC).

MATERIALS AND METHODS

The fluted pumpkin stem waste (*Telfairia occidentalis HOOK.F*) used for this study was obtained from Iwofe market Rumuolumeni, Port-Harcourt. The stems collected were washed thoroughly with water, cut into smaller bits rinsed with distilled water, air dried and later oven dried at 105°C for 10h. The oven dried fluted pumpkin was carbonized to obtain the carbonized biomass. The carbonization and activation method is as stated in Ekpete et al., 2010. The commercial activated carbon (Sifico England) was bought from a scientific store in Port-Harcourt Nigeria.

Preparation of solutions

The test solutions were prepared by diluting a stock solution of chlorophenol to the desired concentrations. A stock solution of chlorophenol was obtained by dissolving 1.0g of chlorophenol (obtained from Merck, India), in distilled water and diluted to 1000ml. Before mixing the adsorbents, the pH of each solution was adjusted to the required value with dilute

0.1M H₂SO₄ and NaOH solutions. Several dilutions of stock solution were made to obtain specific concentrations required for the adsorption study.

Determination of contact time at 30°C

0.2g each of FPAC and CAC of 106µm mesh particle size were weighed and put in twenty two (250ml) conical flasks. 50ml of 100mgL⁻¹ concentration of chlorophenol solutions prepared in de-ionized water from the stock solution was added to the biomass. The pH values of these suspensions were adjusted to 6.0. The flasks were labelled for time interval of 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 minutes. The flasks were tightly covered with cellophane and shaken at 150 rpm for the appropriate time intervals on an electric shaker. The suspensions was filtered through Whatman No 40 filter paper and centrifuged for 5 minutes. The supernatants were analyzed using UV-Visible spectrophotometer. Determinations were run in duplicate.

Effect of temperature.

50ml of chlorophenol solutions with an initial concentration of 100mgL⁻¹ was placed in fourteen (250ml) conical flasks. 0.2g each of activated carbon was added to these solutions. The conical flasks were labelled at temperatures of 30, 40, 50, 60, 70, 80 and 90 °C respectively. The flasks were agitated at 150rpm and heated on a thermostat water bath to the appropriate temperatures for 1h. The suspensions were filtered using Whatman No 40 filter paper and centrifuged for 5 minutes. The supernatants were analysed using UV-Visible spectrophotometer. Determinations were run in duplicate.

DATA ANALYSIS

The amount of adsorption at equilibrium, q_e (mg/g) and the percent adsorption (%) was computed as follows:

$$q_e = \frac{(c_o - c_e)V}{M} \dots \dots \dots (1)$$

$$\text{percent adsorption} = \frac{(c_o - c_e) \times 100}{c_o} \dots \dots \dots (2)$$

Where C_o and C_e are the initial and equilibrium concentrations of chlorophenol (mg/l), respectively. V is the volume of the aqueous solution (L) and M is the mass of the activated carbon used in the adsorption (g).

Sorption kinetic studies

The rate at which sorption takes place is of utmost importance when designing batch sorption systems. Consequently, it was important to establish the time dependence of such systems under various process conditions in an attempt to understand the sorption process, various kinetic rate expression models have been applied to the experimental data in this study.

The time dependent experimental data in this study was analysed using five kinetic models, namely pseudo first order, pseudo second – order, Elovich, intra-particle and liquid –film diffusion models.

Pseudo –first order

The linearized form of the pseudo –first order equation is generally expressed as follows:

$$\text{Log} (q_e - q_t) = \text{log} q_e - \frac{k_1}{2.303}t \dots \dots \dots (5)$$

Where q_e is the amount of chlorophenol adsorbed at equilibrium (mg/g), q_t is the amount of chlorophenol adsorbed at time t (mg/g), k_1 is the first order rate constant (min^{-1}) and t is time in (min). The straight line plot of $\text{log} (q_e - q_t)$ against time t , should give a linear relationship from which the pseudo –first order rate constant (k_1) and equilibrium sorption capacity (q_e), can be calculated from the slope and intercept respectively.

Pseudo second order

The linearized form of the kinetic rate expression for a pseudo second-order model as expressed by Ho et al., (1995) was applied to the experimental data using (equation 6).

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} t \dots \dots \dots (6)$$

Where q_t is the amount of chlorophenol molecules on the activated carbon surface (mg/g) at time t , q_e is the amount (mg/g) of chlorophenol sorbed at equilibrium, the initial sorption capacity (mg/min), h_o , is obtained as shown in equation (6).

$$h_o = k_2 q_e^2 \dots \dots \dots (7)$$

Where k_2 is the Pseudo-second order rate constant (g/mg/min).The parameters h_o and k_2 are determined experimentally from the slope and intercept of a plot of $\frac{t}{q_t}$ against t .

In this case, t/q_t versus time was taken to obtain straight lines. From the slopes and intercepts of these plots, the pseudo-second order rate constants K_2 (g/mg/min), the equilibrium sorption capacity q_e (mg/g) and the initial sorption capacity, h_o (mg/min) were computed.

Elovich model

The linearized form of the Elovich equation is mainly applicable for chemisorptions kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous Ho and McKay (1999).

The Elovich model is generally expressed as

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$$

Integrating the equation for the boundary conditions gives

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots \dots \dots (8)$$

A plot of q_t versus $\ln t$ should give a linear trace with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$. Where α is the initial adsorption rate (mg/gmin) and β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg) and are calculated from the slope and intercept respectively.

Intraparticle diffusion

To investigate if intra-particle diffusion was the sorption rate limiting step, intra-particle diffusion model of Srivastava et al., (2006) was employed.

According to this expression of equation (9) given as:

$$q_t = k_{id} t^{0.5} + C \dots \dots \dots (9)$$

Where, k_{id} is the intraparticle diffusion rate constant (mg/g/min^{1/2}) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e. the larger the value of C the greater the boundary layer effect (Kannam and Sundaram, 2001). If Srivastava plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant K_{id} . However, if the data exhibit multi-linear plots then two or more steps influenced the sorption process.

Liquid film diffusion

The liquid film diffusion model was also employed to investigate, if the transport of the sorbate molecules from the liquid phase up to the solid phase boundary plays a major role in the adsorption as shown in equation 10

$$\ln(1-F) = -k_{id}t \dots \dots \dots (10)$$

Where F is the fractional attainment of equilibrium $F = \frac{q_e}{q_t}$, K_{id} is the adsorption rate constant.

A linear plot of $-\ln(1-F)$ versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid surrounding the solid sorbent.

Thermodynamic analysis of experimental data

Experimental data derived from the effect of temperature on the sorption process was analysed using different equations which made it possible to determine some thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). The adsorption equilibrium constant K_o was estimated from the expression

$$K_o = \frac{c_e}{c_o} \dots \dots \dots (11)$$

The thermodynamic parameters were determined according to equations (12 and 13) as given below

$$\Delta G^o = RT \ln K_o \dots \dots \dots (12)$$

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \dots \dots \dots (13)$$

The values of ΔH^o and ΔS^o are calculated from the slope and intercept of the linear plot of $\ln K_o$ against reciprocal of temperature ($1/T$).

RESULTS AND DISCUSSION

The effect of contact time on sorption of chlorophenol on to FPAC and CAC was studied over a shaking time of 20 to 120 min, using 0.2g of adsorbents at pH 6.0

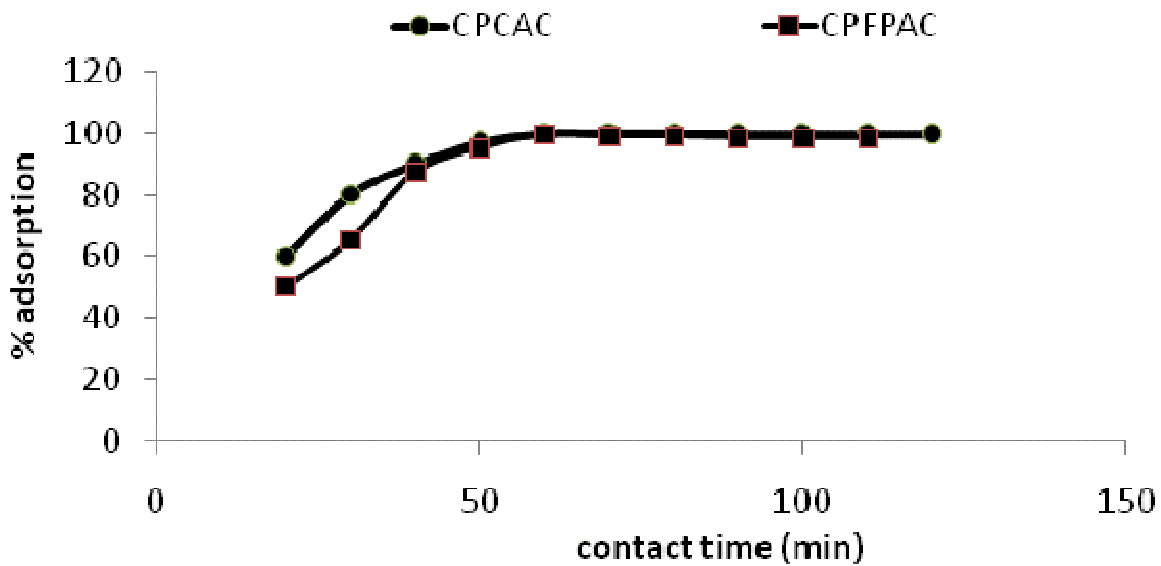


Fig 1: Effect of carbon contact time on the percentage removal of chlorophenol from FPAC and CAC

Figure 1 shows that the contact time needed for chlorophenol solutions of 100mg/l to reach equilibrium is 60 minutes. Almost, no remarkable improvement was observed after longer contact time. After this equilibrium period, the amount of solute adsorbed did not change significantly with time, indicating that 60min is sufficient to attain equilibrium for the maximum removal of chlorophenol from aqueous solutions by FPAC and CAC, respectively. So the optimum contact time was selected as 60 minutes for further experiments.

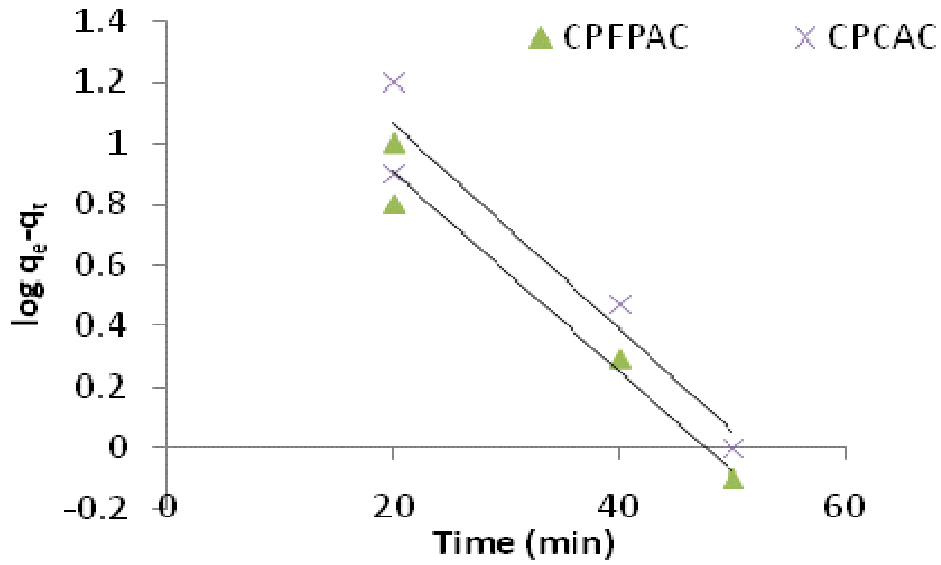


Fig 3: Pseudo-first order sorption kinetics of chlorophenol on FPAC and CAC.

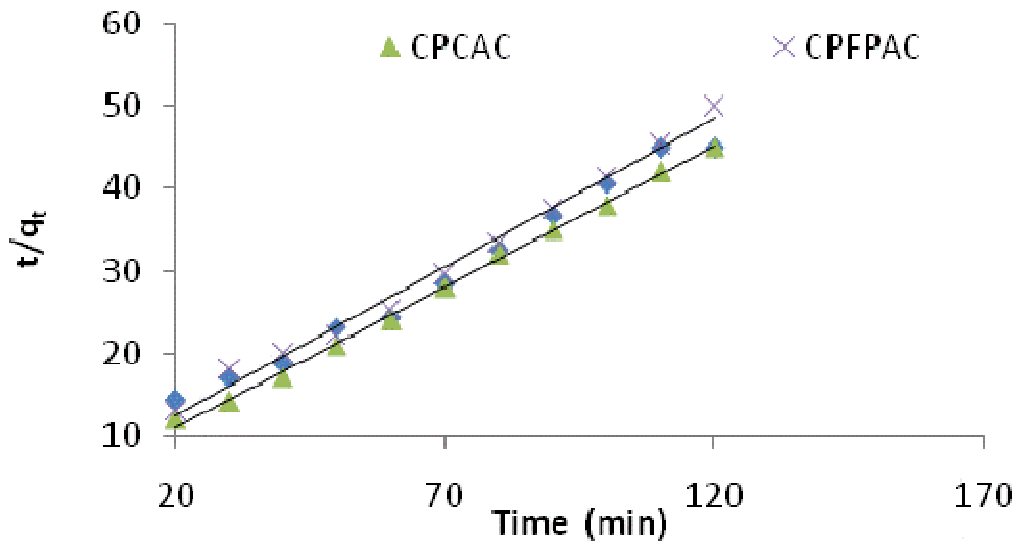


Fig 4: Pseudo-second order kinetics of chlorophenol on FPAC and CAC

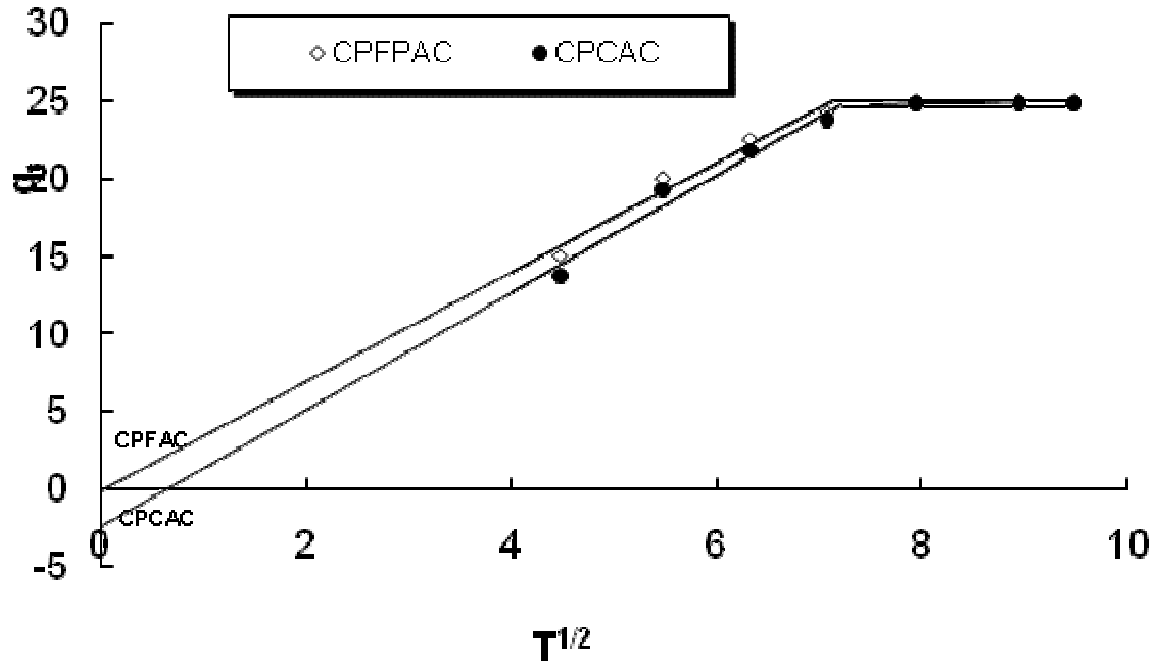


Fig 5: Intraparticle diffusion kinetics of chlorophenol on FPAC and CAC.

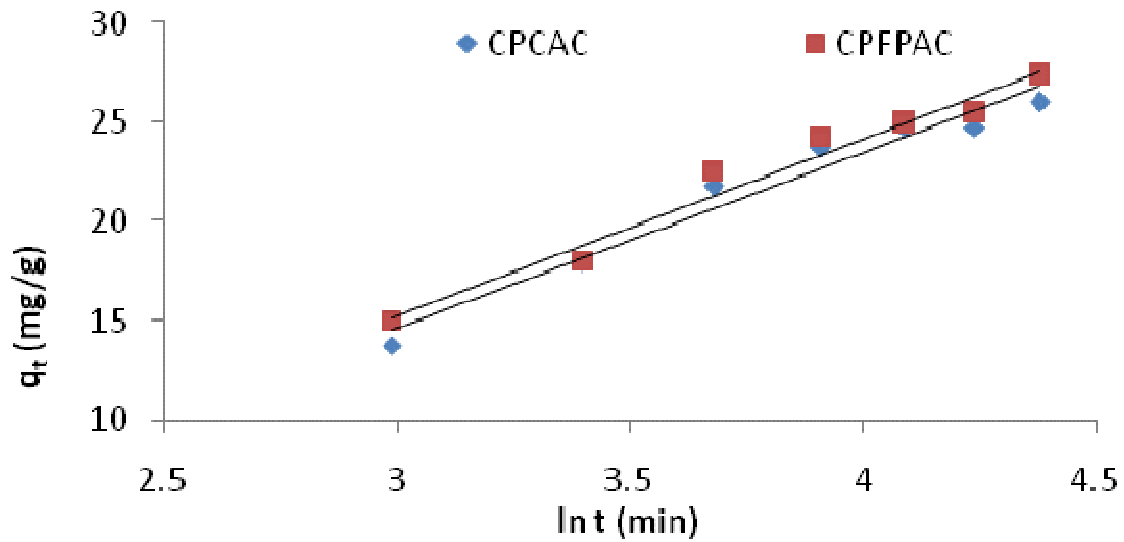


Fig 6: Elovich diffusion kinetics of chlorophenol on FPAC and CAC

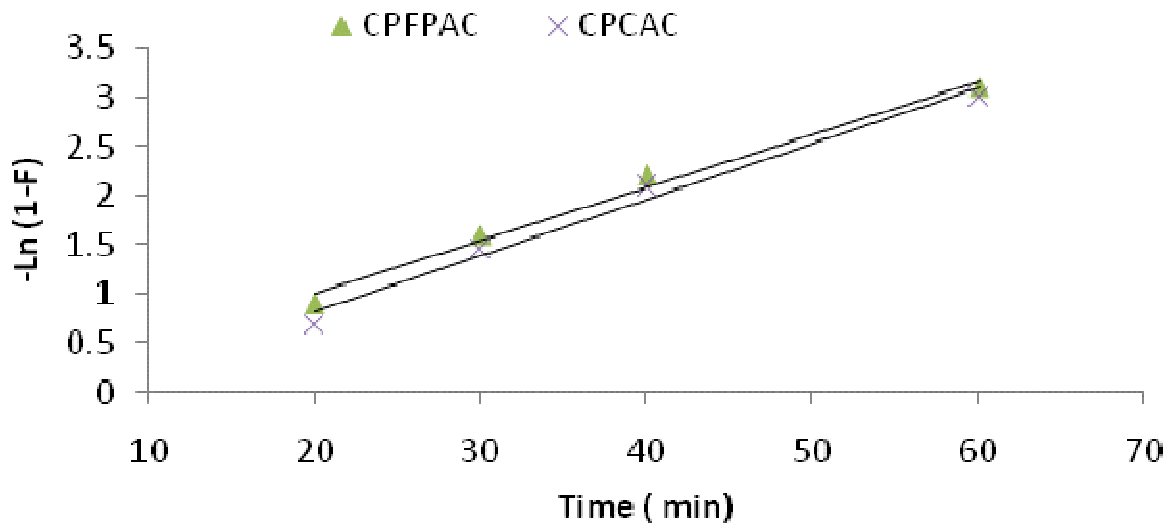


Fig 7: Liquid film diffusion kinetics of chlorophenol on FPAC and CAC

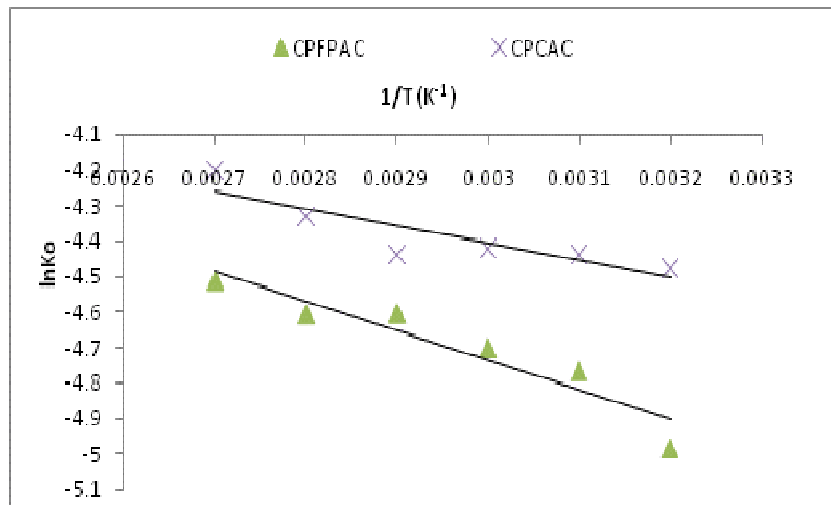


Fig 8: Linear plots of $\ln K_0$ versus $1/T$ for the sorption of chlorophenol onto FPAC and CAC

Table 1. Pseudo first order, Pseudo second order, Intra –particle rate diffusion, Elovich diffusion model, Liquid film diffusion and thermodynamic parameters for the sorption of phenol on to FPAC and CAC carbon samples.

Adsorbent	Sorption capacity at equilibrium q_e (mg/g)	Pseudo first order rate constant. K_1 (g/(mg/min))		Regression coefficient (R^2)		
CPFPAC	36.30	7.3×10^{-2}		0.970		
CPCAC	54.45	7.5×10^{-2}		0.933		
Pseudo second order rate parameters						
Adsorbent	Sorption capacity at equilibrium q_e (mg/g)	Initial sorption rate, h_0 (mg/gmin)	Pseudo second order rate constant. K_2 (mg/g/min ^{1/2})	Regression coefficient (R^2)		
CPCAC	34.48	1.94×10^{-2}	9.75×10^{-4}	0.999		
CPFPAC	32.25	2.45×10^{-2}	2.40×10^{-3}	0.997		
Intra –particle rate diffusion parameters						
Adsorbent	K_{id1}	intercept	R_1^2	K_{id2}	intercept	R_2^2
CPFPAC	3.536	0.000	0.968	0.000	24.970	1.000
CPCAC	3.801	-2.546	0.966	0.000	24.750	1.000
Elovich model diffusion parameters						
Adsorbent	α (mg/g/min)	β (g/mg)	R^2			
CPFPAC	2.79	0.112	0.970			
CPCAC	2.32	0.113	0.960			
Liquid film diffusion parameters						
Adsorbent	K_{id}	Intercept	R^2			
CPFPAC	0.054	-0.085	0.988			
CPCAC	0.056	-0.318	0.982			
Thermodynamic parameters						
Adsorbent	ΔH (KJmol ⁻¹)	ΔS (KJmol ⁻¹)	ΔG^0 KJ/mol			
CPFPAC	-7.035	-0.018	-2.131			
CPCAC	-3.995	-0.027	-1.209			

The time dependent experimental data in this study were analysed using the pseudo first order rate equation of Lagergren. In order to determine the rate constants, the straight line plot of log ($q_e - q_t$) against time was taken as presented in Figure 3 and Table 1.

Table 1 shows that the equilibrium sorption capacity trend followed the order CPCAC (54.45) > CPFPAC (36.30). Further observation showed that the pseudo-first order rate constant, K_1 was higher for CPCAC (0.075) than for CPFPAC (0.072). The regression coefficient (R^2) values

ranges from 0.933 to 0.970, which indicated that the pseudo first order model was slightly suitable for the adsorption of chlorophenol on FPAC and CAC respectively.

The initial sorption rate (h_0) was higher for the sorption process of CPFAC (0.0245) than CPCAC (0.0194) which should follow that FPAC adsorbs better than CAC based on the initial sorption rate but the equilibrium sorption capacity for the pseudo second order kinetics for CAC (34.48) is greater than for FPAC (32.25) as shown in Table 1. The pseudo second order rate constant increases in the order CPFAC (2.40×10^{-3}) > CPCAC (9.75×10^{-4}). The table further indicates that the correlation coefficients for chlorophenol are high ranging from 0.997 to 0.999 showing that the kinetic sorption experimental data followed the pseudo order isotherm model.

The plot of q_t against $t^{1/2}$ shows that the data points can be related by two straight lines. The first, sharper portion depicts macropore diffusion and the second portion describes the gradual adsorption stage, where, micropore diffusion is rate limiting (Bhattacharyya and Sharma 2004; Ozacar, 2006). Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts, which provide a measure of the boundary layer thickness. The lines for CPFAC which passed through the origin (Fig 4) indicates no degree of boundary layer and these further shows that the intraparticle diffusion is not the only rate controlling step (Crini et al., 2007).

The slope of the (Srivastava et al., 2006) plots are defined as a rate parameter, characteristic of the rate of adsorption in the region where intraparticle diffusion is rate controlling. The values of rate parameters (K_{id1} and K_{id2}) are given in Table 1. A comparison of the K_{id} values for both the macropore and micropore diffusion (Table 1) shows that the rate limiting step is the micropore diffusion stage. This is because the K_{id2} values are lower than the K_{id1} values which are a pointer to the fact that the rate of micropore diffusion is the slower step and the rate determining step. The boundary layer effect, as obtained from the intercept of the plot as shown in Table 1 was also of greater effect at the micropore diffusion stage than at the macropore diffusion stage.

The Elovich equation which has been shown to be useful in describing chemisorptions on highly heterogeneous adsorbents, gives a good account of the adsorption of chlorophenol with R^2 values ranging from 0.960 to 0.970. Table 1 shows that the initial sorption rate, (α) followed the order CPFAC > CPCAC, indicating that adsorption was better on CPFAC than CPCAC. β which is related to the extent of surface coverage and the activation energy for chemisorption followed the order CPFAC (0.112mg/g) < CPCAC (0.113mg/g).

The significance of liquid film diffusion in rate determination of the sorption process indicated that the intercept values were less than zero and close to the origin as shown in Table 1 The liquid film diffusion constant K_{id} was highest for chlorophenol on CAC (0.056) and lower for chlorophenol on FPAC (0.054). The high regression values > 0.980 on both carbons shows the relevance of film diffusion as a rate determining factor in the sorption process.

The negative values of ΔH° , indicates the exothermic nature of the sorption process while the negative values of ΔS° indicate strong bond formation between the adsorbent and adsorbate molecules. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption (McKay and Poots 1980; Ho et al., 2005), thus, confirming a chemical sorption, as was earlier suggested in pseudo-second order studies of this work.

Table 2: Comparison of regression values of pseudo first order- pseudo second order, intraparticle, and Elovich and Liquid diffusion kinetic models.

Adsorbent	Pseudo first order (R_1^2)	Pseudo second order (R_2^2)	Intraparticle diffusion R_3^2	Elovich R_4^2	Liquid Diffusion model R_5^2
CPFPAC	0.970	0.999	0.968	0.970	0.988
CPCAC	0.933	0.997	0.966	0.960	0.982

From Table 2, it was observed that the values of the correlation coefficients R_1^2 , R_2^2 , R_3^2 , R_4^2 and R_5^2 were extremely high (>0.930). This shows that the results fit these five models very well. However, the pseudo –second order correlation coefficient values were found to be slightly higher than those of Elovich, Liquid-film, pseudo-first order and intraparticle values, indicating that the sorption follows better the pseudo-second order model.

CONCLUSIONS

1. Fluted pumpkin activated carbon compared favourably to commercial activated carbon for chlorophenol removal in aqueous solution.
2. The thermodynamic adsorption of chlorophenol ΔG^o , ΔH^o , ΔS^o were all negative.
3. Pseudo second order favoured the kinetic adsorption process.

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