

Assessment of ZnCl₂ Activated Unripe Musa Paradisiaca Peels for Adsorption of Phenol from Aqueous Solution

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Abstract

The study assessed the adsorption of phenol from aqueous solution using unripe plantain peel activated carbon (UPPAC) produced by chemical activation with ZnCl₂. Equilibrium adsorption data were calibrated using Langmuir, Freundlich and Temkin isotherms. Results of the equilibrium data fitted very well into all models with high correlation coefficients (R^2) of 0.998, 0.909 and 0.939 respectively for Langmuir, Freundlich and Temkin isotherms with a maximum monolayer adsorption capacity of q_0 1.085mg/g and a heterogenous adsorption capacity of K_f 0.485mg/g. The Langmuir separating factor (R_L) 0.067 indicates a favourable adsorption and the heat of adsorption from the Temkin model (b_T) 5325.82 J/mol indicating the adsorbent-adsorbate interaction. The kinetic data followed Pseudo second order kinetic model indicating chemisorption as the limiting step in the adsorption process. Modelling the percentage of Phenol adsorbed onto UPPAC using XLSTAT 2014 gave a model equation as “% Phenol Adsorbed = 90.53704 + 3.25000 * Co + 17.57222 * CT - 11.32778 * pH - 4.46111 * Co² - 14.39444 * CT² - 4.09444 * pH² - 2.25000 * Co * CT + 2.83333 * Co * pH + 5.92500 * CT * pH” with R^2 value of 0.902. These parameters indicated that adsorption of phenol onto UPPAC was feasible, monolayer, multilayer and chemisorption in nature. The model can be used when modelling the adsorption process of Phenol unto UPPAC.

Keywords: Phenol, Isotherms, Unripe plantain peel, Kinetic, Adsorption

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1. Introduction

Phenol compounds are common contaminants found in industrial effluents including plastics, leather, paint, insecticides, pharmaceuticals, textile, petrochemical and many others (Kennedy et al., 2007). It's presence in wastewater or drinking water is of great concern due to its toxicity and carcinogenicity. Even in low concentration, phenol is toxic and causes foul odour to water. It is also very reactive as it reacts with chlorine (Cl) and nitrate (NO₃) in the soil to form chlorophenol and nitrophenol, respectively. The release of phenol and its derivative compounds to the environment can lead to serious impact on human and animal health like liver and kidney damage, central nervous system impairment, diarrhea, and excretion of dark urine (Sarkar and Acharya, 2006) and (Olujimi et al., 2010). According to world health organization, the permissible limit of phenol in drinking water is 1 µg/l while Environmental Protection Agency (EPA) has set a limit of 0.1mg/l of phenol in wastewater (Senturk et al., 2009).

Several methods are available for treating wastewater containing phenol before its disposal into the environment. The methods include reverse osmosis, anaerobic processes, electrochemical degradation method, combined applications of flotation and coagulation processes, stripping and oxidation, solvent extraction, adsorption and many others (Busca et al., 2008). Among the various methods, adsorption process is considered the best option due to its simplicity of design, ease of operation, highly efficient and cost effective. Adsorption is a separation process in which specific component of the adsorbate accumulate on the surface of the adsorbent. It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). Thus, phenol and other pollutants are efficiently removed from the wastewater with the production of minimum sludge as compared to the sludge formed from other treatment processes like coagulation and precipitation processes.

However, high cost of conventional activated carbon limits the use of adsorption process for treatment of wastewater. It has been reported that the production cost of activated carbon per ton of coal is around \$2500 (Girods et al., 2009). Thus, due to limited sources and increasing demand, activated carbon is very expensive and this has generated to various researchers on low-cost adsorbents for use in adsorption process. Furthermore, if the adsorbent is abundant, the regeneration is not required as in case of conventional activated carbon except the disposal. Also, since low-cost adsorbents are mostly agricultural organic materials which has good calorific value, the spent adsorbent (sludge) can be used as fuel in boilers instead of regeneration, if air pollutants are not emitted above the permissible limit due to burning of residue pollutant, otherwise the sludge can be managed in sanitary landfills. Many agricultural waste materials have been used directly or indirectly by producing activated carbon for the removal of phenol from wastewater. They include grain husk (Laszlo and Hodur, 2007), apricot stone shell, plum kernel (Juang et al., 2000), beet pulp (Dursun et al., 2005), corn grain (Park et al., 2010), sugarcane bagasse and wood charcoal (Mukherjee et al., 2007), babul sawdust (Ingole and Lataye, 2015) and many others. This study assessed the adsorption of phenol from wastewater using activated plantain peels carbon.

2. Materials and methods

2.1 Preparation of activated carbon

Unripe plantain peels were sourced from a food vendor making plantain chips in Port Harcourt, Rivers State, Nigeria. They were cut into smaller pieces and thoroughly washed with distilled water to remove dirt's, sand and oil and then sun-dried until it was very dry. The samples were chemically activated with zinc chloride (ZnCl₂) at impregnation ratio of 1:2 and then carbonized in a muffle furnace at 400°C for 2hrs and then ground into powder after cooling in a desiccator. The activated carbon produced was named UPPAC.

2.2 Batch adsorption studies

Batch adsorption studies were conducted to obtain the effect of adsorbent concentration, adsorbate pH and contact time for the adsorption of phenol from aqueous medium using the UPPAC. The initial adsorbate concentrations used were 2, 16 and 30mg/l; the pH used were 2, 6.5 and 11 while the contact time used were 30, 105 and 180mins. A fixed amount of adsorbent dose (5g)

was used for the study. This was in accordance with the experimental design (DoE) and a total of 27 experiments were ran with all possible combinations of parameters for the study. The phenol stock solution used was diluted with distilled water to obtain the desired initial concentration. All the chemicals used were of analytical grade. The adsorption efficiency was calculated from Equation (1).

$$\% R = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

where R is the adsorption efficiency (%), C_e is the equilibrium concentration of the adsorbate (mg/l), and C_i is the initial conc. of adsorbate (mg/l).

2.3 Batch equilibrium adsorption

The equilibrium adsorption studies were conducted by varying the initial concentrations of phenol from 5 to 30 mg/l at a fixed adsorbent dosage (5g) using the optimum adsorbate pH of 2. The batch adsorption was shaken at 200rpm for 155mins (optimum contact time) using the temperature-controlled incubator shaker. The solution was filtered and the residual phenol concentration was determined using HACH method. The equilibrium adsorption capacity (q_e) of the adsorbent was calculated using the mass equilibrium in Equation (2).

$$q_e = \frac{(C_o - C_e)V}{M} \quad (2)$$

where C_o is the initial concentrations of the adsorbate (mg/l), C_e is the equilibrium concentration of adsorbate (mg/l), V is the experimental volume of wastewater (L) and M is mass of adsorbent (g).

2.4 Adsorption isotherms

Adsorption isotherms are used to describe adsorbates interaction with adsorbents and how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Nwabanne, and Igbokwe, 2008). Results of the equilibrium adsorption data were used to calibrate three isotherm models (Langmuir, Freundlich and Temkin) to describe the relationship between the amount of Phenol adsorbed and its concentration in the equilibrium solution at constant temperature. These models were linearized to calculate the adsorption capacity (q_o) and the rate of adsorption (k). The linear form of the models is stated in

Equations (3) to (5). Linear form of Langmuir equation is given in Equation (3) as:

$$\frac{C_e}{q_e} = \frac{1}{q_o k} + \frac{C_e}{q_o} \quad (3)$$

where C_e is equilibrium concentration of the adsorbate (mg/l), q_e is mass of solute adsorbed per unit mass of adsorbent, q_o is a constant related to the adsorption capacity (mg/g) and k is experimental constant. Also, a dimensionless constant (R_L) known as Langmuir separation factor which indicates if adsorption is favourable or unfavourable is given as:

$$R_L = \frac{1}{(1+kC_e)} \quad (4)$$

where k is the Langmuir constant and C_e is the initial concentration of the adsorbate (mg/l). The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Thus, lower R_L value reflects that adsorption is more favourable. Linear form of Freundlich equation is given in Equation (5):

$$\log(q_e) = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

where C_e is equilibrium concentration of the adsorbate, q_e is mass of solute adsorbed per unit mass of adsorbent, k_f and n are Freundlich constants representing the adsorption capacity of adsorbents and the intensity of the adsorption, respectively. Linear form of Temkin equation is given in Equation (6):

$$q_e = \frac{RT}{b_T} \log A_T + \frac{RT}{b_T} \log C_e \quad (6)$$

where b_T and A_T are the Temkin constants, A_T is the equilibrium binding constant corresponding to the maximum binding energy, b_T is related to the heat of adsorption (J/mol), R is the universal gas constant (8.314) J/mol K) and T is the absolute temperature in kelvin (K).

2.5 Batch kinetics studies

Kinetic models are used to investigate the rate of adsorption process and potential rate controlling steps. This would help to select optimum operating conditions for the full-scale batch process. The adsorption kinetics was conducted at varying time intervals of 15 to 210 mins using initial phenol concentration of 22mg/l at pH 2. Fixed adsorbate dosage (5g) of UPPAC was added to 50ml of phenol in different 100ml containers and they were shaken at 200rpm using the temperature-controlled

incubator shaker. The samples were withdrawn at specific interval of time (t) and then filtered using Whatman paper and thereafter, the filtrates were analyzed for phenol residual concentration (C_t) using HACH method. The adsorption capacity (q_t) of the UPPAC at specific time intervals were calculated from Equation (7).

$$q_t = \frac{(c_o - c_t)}{w} \times V \quad (7)$$

where c_o is the initial adsorbate conc. (mg/l), c_t is the final adsorbate conc. (mg/l), V is the volume of solution used (L) and W is the weight of adsorbent used (g).

2.6 Kinetics of adsorption

The adsorption mechanism for the removal of Phenol with UPPAC was investigated using Pseudo first order and second order equations. The logarithmic form of Pseudo first order equation is shown in Equation (8):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{p1}}{2.303} t \quad (8)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), k_{p1} , is the rate constant of first order adsorption (mg/min). Linear correlation of the values of $\log(q_e - q_t)$ against t gave k_{p1} and q_e which were determined from the slope and intercept of the plots, respectively. Linear form of Pseudo Second order equation is given in Equation (9):

$$\frac{t}{q_t} = \frac{1}{k_{p2} q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_{p2} is the rate constant of pseudo second order adsorption (mg/min). Plots of $\frac{t}{q_t}$ against t of Equation (9) gave a linear relationship from which q_e and h values was determined from the slope and intercept respectively. Note that $h = k_{p2} q_e^2$.

3. Results and discussion

3.1 Equilibrium adsorption

The equilibrium data from the adsorption of phenol onto UPPAC were modelled using Langmuir, Freundlich and Temkin isotherm models in order to obtain the best fitting isotherm. The values of Langmuir constants, q_o and k obtained from Equation (3) were found to be 1.085mg/g and 0.6341/mg respectively, with correlation coefficient (R^2) of 0.998 and separation factor (R_L) of 0.067 indicating a favourable adsorption (ie that UPPAC is a suitable adsorbent for adsorption of phenol from aqueous solutions). The values of Freundlich

constants K_f and $1/n$ obtained from Equation (5) were found to be 0.485mg/g and 0.289 respectively, with correlation coefficient (R^2) of 0.909. The Freundlich constant $1/n$ was smaller than unity indicating that the adsorption process was favourable under studied conditions. Furthermore, the values of Temkin constant A_T and b_T obtained from Equation (6) were found to be 9.979 1/mg and 5325.82 J/mol, with correlation coefficient (R^2) of 0.939. Note that Temkin isotherm accounts for adsorbent-adsorbate

interaction and assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly with coverage than logarithmic (Tempkin and Pyzhev, 1940; Aharoni, and Ungarish, 1977). Thus, there will be a uniform distribution of binding energies up to some maximum binding energy. The b_T value is an indication of the heat of sorption indicating a physical adsorption process. The linear models and the corresponding isotherm parameters for all the isotherm models tested are presented in Table 1.

Table 1: Equilibrium model parameters for adsorption of phenol onto UPPAC

Linearized Models	Parameters	Value
Langmuir Isotherm $Y = 0.9221x + 1.4536$	R^2	0.998
	q_0 (mg/g)	1.085
	K (L/mg)	0.634
	R_L	0.067
Freundlich Isotherm $Y = 0.2896x - 0.3141$	R^2	0.909
	K_f (mg/g)	0.485
	$1/n$	0.289
Temkin Isotherm $Y = 0.4652x + 0.4648$	R^2	0.939
	A_T (L/mg)	9.979
	b_T (J/mol)	5325.82

Langmuir Isotherm: $Y = \frac{C_e}{q_e}$ and $x = \frac{1}{q_0}$

Freundlich Isotherm: $Y = \log(q_e)$ and $x = \log C_e$

Temkin Isotherm: $Y = q_e$ and $x = \log C_e$

3.1.1 Model validation

The authenticity of these isotherm models on phenol adsorption were verified with another set of data. The calculated isotherm parameters were fitted into the isotherm model equations to get the

calculated (q_e) values for model verification. It was observed that the experimental ($Exp\ q_e$) and calculated ($Cal\ q_e$) correlated Langmuir, Freundlich and Temkin models. The correlated models are shown in Fig. 1 to 3.

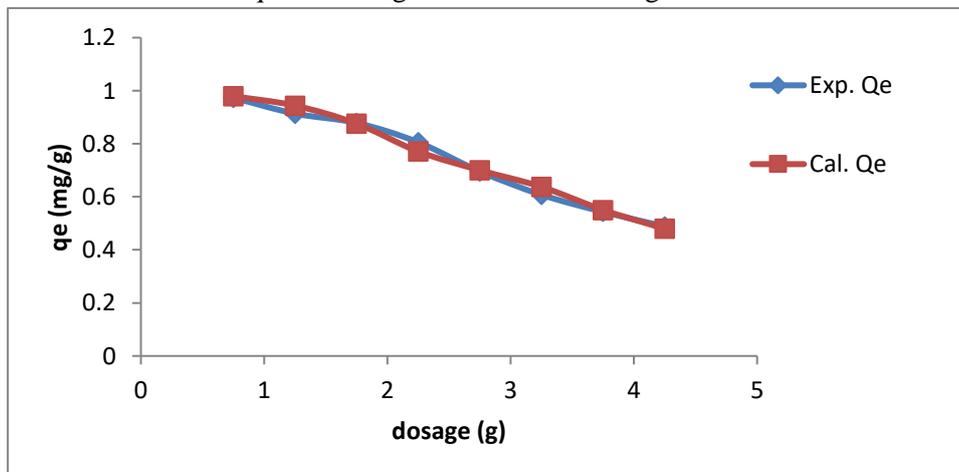


Fig. 1: Langmuir plot of $q_{e-Exp.}$ Vs q_{e-Cal} for phenol adsorption onto UPPAC

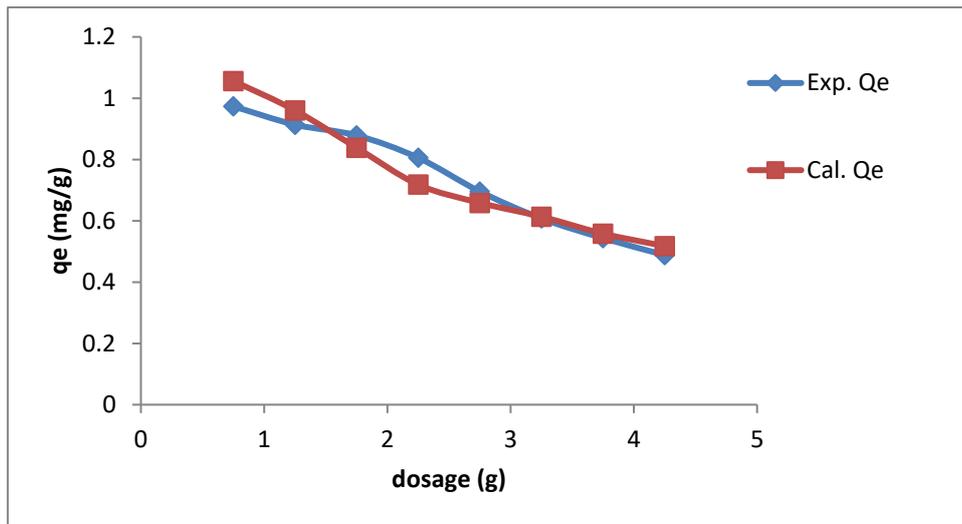


Fig. 2: Freundlich plot of q_{e-Exp} . Vs q_{e-Cal} for phenol adsorption onto UPPAC

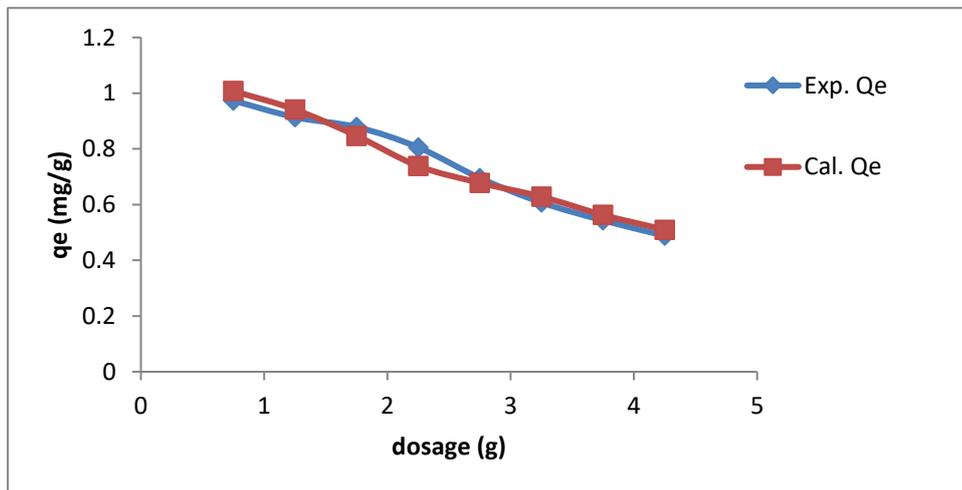


Fig. 3: Temkin plot of q_{e-Exp} Vs q_{e-Cal} for phenol adsorption onto UPPAC

3.1.2 Test for isotherm models

The applicability of these isotherm models for adsorption was further verified using the sum of error squares (SSE, %) calculated from Equation (10) using Excel software:

$$SSE, (\%) = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (10)$$

where N is the number of data points. From the results of the SSE % for each isotherm model presented in Table 1, it was observed that Langmuir isotherm model had the least error with SSE value of 0.0014% while Freundlich and Temkin had 0.0022%, 7% and 0.0027%, respectively. Note that the higher the value of R², the lower the value of SSE % and the better the

goodness of fit. From these results, the adsorption pattern of phenol onto UPPAC fitted well into Langmuir, Freundlich and Temkin models. This may be due to both homogeneous and heterogeneous distribution of active sites on the surface of the UPPAC forming either a monolayer or multilayer adsorption onto surfaces of the carbon. This process will be a reversible reaction (physical adsorption process) with energy of the adsorption (b_T) as 5325.82 J/mol. Similar observations were made by Senturk et al. (2009), Adeolu et al. (2016) and Badmus et al. (2007).

3.2 Adsorption kinetics

The experimental data were linearly correlated with Pseudo First order and Pseudo second order models. The correlation coefficient for pseudo second order kinetics was higher than that of

pseudo first order model with correlation coefficient (R²) of 1.0 and 0.0755, respectively. However, the Pseudo Second Order equation gave high correlation coefficient (R²) of 1.0. Thus, calculated values (Cal q_e) for Pseudo Second Order model were extremely close to the experimental data (Exp q_e) whereas the gap between calculated values and experimental data for pseudo-first-order model was very obvious. This showed that the adsorption perfectly complied with pseudo-second order reaction and the adsorption of phenol may be controlled by the chemisorption process. Therefore,

the adsorption of phenol occurred through surface exchange reactions until the surface functional sites were fully occupied; thereafter, phenol molecules diffused into the UPPAC network for further interactions which may include hydrogen bonding, hydrogen-phobic interactions and many others (Hao et al., 2018). Similar results were reported by Zhang et al. (2016), Lütke et al. (2019) and Xie et al. (2020). Fig. 4 shows linear correlation of experimental data with pseudo second order models.

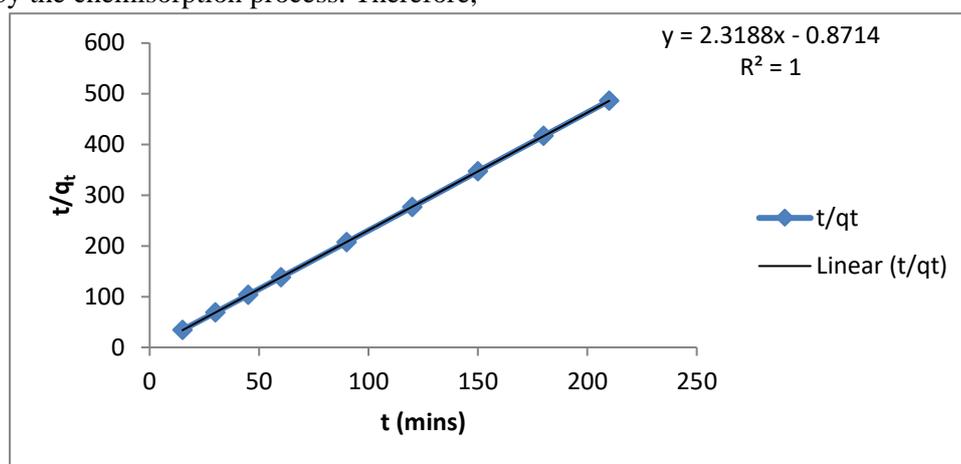


Fig. 4: Pseudo-second order kinetic plot for removal of phenol with UPPAC

3.2.1 Test for kinetic model

The test for kinetic models was determined with Equation (10) (SSE %) using Excel software. From the results as presented in Table 2, Pseudo second order kinetic model had the least error (0.000003%). Thus, the adsorption of phenol onto UPPAC fitted well into Pseudo Second Order

Kinetics. This suggests that Chemisorption may be the limiting step in the adsorption process. Similar observation was also reported by Kennedy et. al, (2007) and Senturk et. al, (2009). The linear models and the corresponding kinetic constants for all the kinetic models tested are presented in Table 2.

Table 2: Adsorption kinetic and corresponding constants for the adsorption of phenol onto CPTAC at initial conc. of 22mg/l

Adsorption Kinetic Model	Parameter/Model	Values
Pseudo-first order	q _{e.exp.} (mg/g)	0.4372
	q _{e cal.} (mg/g)	0.0008
	k _{p1}	-0.0033
	R ²	0.0755
	SSE%	0.004
	Linearized model	Y = -0.033x-1.8615
Pseudo-second order	q _{e.exp.} (mg/g)	0.4372
	q _{e cal.} (mg/g)	0.4313
	K _{p2}	6.169
	R ²	1
	SSE%	0.000003
	Linearized model	Y = 2.3188x-0.8714

3.3 Modelling phenol adsorption process onto UPPAC using response surface methodology

The adsorption of phenol onto UPPAC was modelled using XLSTAT 2014 software in which

the results of the DoE of the experiments were used to model the adsorption process. The results from the experiment performed using a response surface design of experiment is presented in Table 3.

Table 3: Experimental design (full factorial design with 3 Levels)

Observation	Sort order	Run order	Repetition	Initial Conc	Time	pH	% Absorbed
Obs1	1	1	1	2	30	2	70
Obs2	2	2	1	16	30	2	70.9
Obs3	3	3	1	30	30	2	69
Obs4	4	4	1	2	105	2	89
Obs5	5	5	1	16	105	2	88
Obs6	6	6	1	30	105	2	95
Obs7	7	7	1	2	180	2	91
Obs8	8	8	1	16	180	2	96.9
Obs9	9	9	1	30	180	2	97
Obs10	10	10	1	2	30	6.5	56
Obs11	11	11	1	16	30	6.5	58
Obs12	12	12	1	30	30	6.5	56
Obs13	13	13	1	2	105	6.5	89.5
Obs14	14	14	1	16	105	6.5	91
Obs15	15	15	1	30	105	6.5	86
Obs16	16	16	1	2	180	6.5	83
Obs17	17	17	1	16	180	6.5	93.2
Obs18	18	18	1	30	180	6.5	89
Obs19	19	19	1	2	30	11	4
Obs20	20	20	1	16	30	11	42.9
Obs21	21	21	1	30	30	11	49
Obs22	22	22	1	2	105	11	74
Obs23	23	23	1	16	105	11	82
Obs24	24	24	1	30	105	11	69
Obs25	25	25	1	2	180	11	78
Obs26	26	26	1	16	180	11	81
Obs27	27	27	1	30	180	11	83

3.3.1 Modelling the percentage (%) adsorbed

Phenol adsorption onto UPPAC was modelled using XLSTAT 2014 to predict the percentage (%) of phenol adsorbed. The model is presented in Equation (11). The coefficient of determination (R²) value for this model is 0.902 indicating a very

good relationship between predicted and measured values. The relationship between amount adsorbed and other variables such as adsorbate concentration, contract time and pH are shown as trace cures in Fig. 5 to 7.

$$\% \text{ Adsorbed} = 90.53704 + 3.25000 * Co + 17.57222 * CT - 11.32778 * pH - 4.46111 * Co^2 - 14.39444 * CT^2 - 4.09444 * pH^2 - 2.25000 * Co * CT + 2.83333 * Co * pH + 5.92500 * CT * pH \quad (11)$$

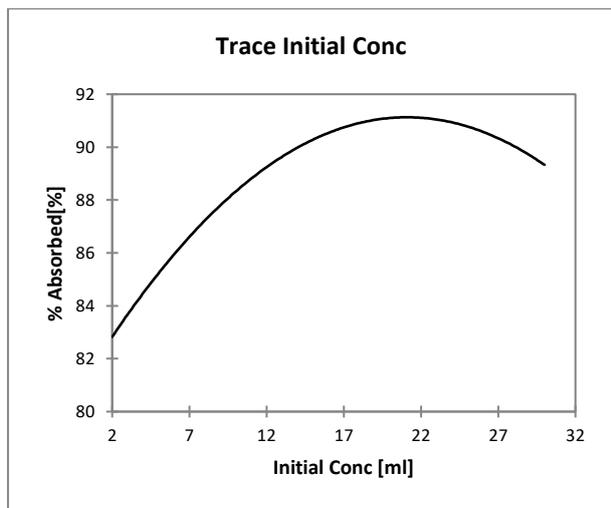


Fig 5: Percentage adsorbed vs adsorbate concentration

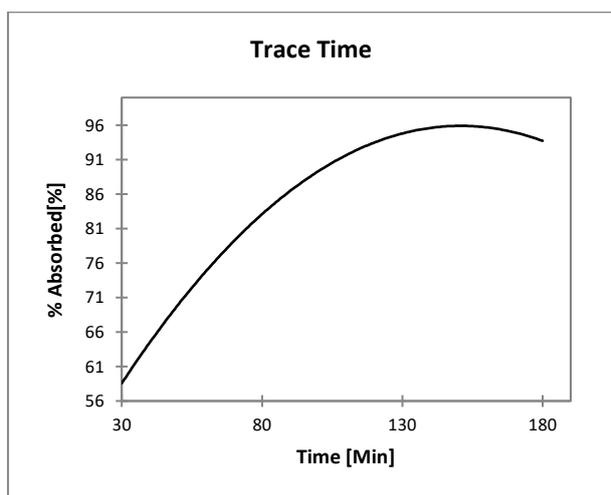


Fig 6: Percentage adsorbed vs contact time

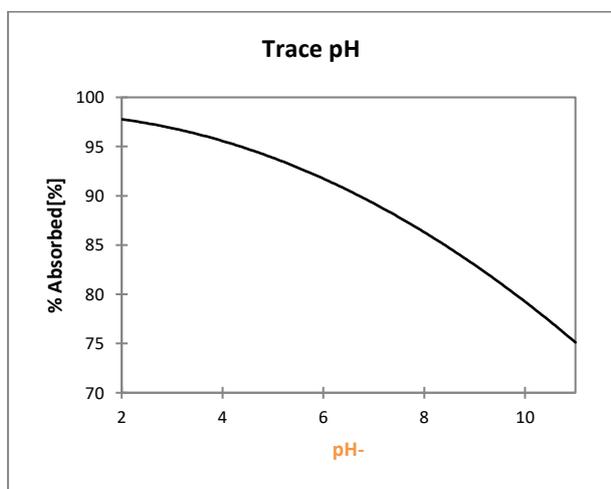


Fig 7: Percentage adsorbed vs adsorbate pH

The concentration trace curve shown in Fig. 5 revealed that the % of phenol adsorbed increased as the adsorbate concentration increases which may be as a result of more metal ions available for adsorption at higher concentration. This adsorbate concentration provided the necessary driving force to overcome the resistances to the mass transfer of phenol between aqueous and solid phases and this increase in adsorbate concentration also enhanced the interaction between phenol and the activated carbon. Thus, an increase in phenol concentration enhanced the adsorption uptake. However, adsorption decreased when concentration increased further and this may be due to saturation of adsorption sites of the activated carbon because at much higher concentrations, the number of phenol ions is relatively higher than available sites for adsorption. Equilibrium was reached at 20mg/l with 91% phenol adsorbed. Similar trend was reported by Xie et al. (2020) and Srivastava et al. (2006).

The trace curve for contact time as shown in Figure 6 revealed that the rate of phenol adsorption increased rapidly during the initial 130mins and thereafter, the percentage adsorbed reached equilibrium after 150mins. This behaviour can be explained because a large number of vacant surface sites are available for adsorption during the initial stage, and after sometime, the remaining vacant surface sites were difficult to occupy due to repulsive forces between the solute molecules and the adsorbent. At equilibrium, the % adsorbed was 95% at 150 mins, after which desorption started. Similar observation was reported by Srivastava et al. (2006).

Furthermore, the trace curve for pH as shown in Figure 7 revealed that the percentage of phenol adsorbed decreased at a steady rate as the adsorbate pH increased from 2 to 11. Maximum adsorption was observed at pH 2 with 97% removal efficiency indicating that phenol adsorption was pH dependent and was better at acidic conditions. This implies that pH affects the degree of ionization of phenol on the surface of unripe plantain peel activated carbon. Similar trend was reported by Kennedy et al. (2007) and Uddin et al. (2007) in which it was observed that at low pH, the surface of the adsorbent would be protonated, and this would result in a stronger attraction for the negatively charged phenolate ion. These negatively charged ions would be directly attracted to the protonated surface of the unripe plantain peel

activated carbon by electro-static force while the unionized phenol molecules would also be attracted by physical force. Thus, at high pH, the hydroxyl ions (OH⁻) would compete with the phenol molecules for adsorption sites thereby resulting in decrease of adsorption.

4. Conclusion

The study modelled the adsorption of phenol from aqueous solution using unripe plantain peel activated carbon (UPPAC) produced by chemical activation with ZnCl₂. The batch equilibrium adsorption studies were calibrated using Langmuir, Freundlich and Temkin isotherms. Results of the equilibrium data fitted very well into all models with a monolayer adsorption capacity (q₀) of 1.085mg/g and a heterogenous adsorption capacity (K_f) of 0.485mg/g. The Langmuir separating factor (R_L) 0.067 indicates a favourable adsorption and the heat of adsorption from the Temkin model (b_T) 5325.82 J/mol) indicates adsorbent-adsorbate interaction and the uniform distribution of binding energies during adsorption. The kinetic data followed Pseudo second order kinetic model indicating chemisorption as the limiting step in the adsorption process. Modelling the percentage of Phenol adsorbed resulted to Equation (11) with R² value of 0.902. These parameters indicated that adsorption of phenol onto UPPAC was feasible, monolayer, multilayer and chemisorption in nature. The model indicates that Equation (11) can best be used when modelling the adsorption process of Phenol onto UPPAC.

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