Original Research Article

Biosorption ofNitrophenol from Aqueous Mixture of Phenolic Compounds using Sawdust of *Parkiabiglobosa*.

ABSTRACT

The present study investigated the potential of sawdust of *Parkiabiglobosa*, an agroforestry by-product, for the removal of 4-Nitrophenol (4NP), from its aqueous solutions (singly) and in combination with phenol (binary) and chlorophenol (ternary) . The effects of sawdust dose, initial concentration of phenolics and pH of the solution on the adsorption were investigated through batch adsorption experiments. Five isotherm models were employed to describe the equilibrium experimental data. The adsorption kinetics and thermodynamics were also studied. The equilibrium time for the sorption was observed to be 720 min, while the optimum dose was 0.500 g. The kinetics of the adsorption could be best described by the pseudo-second order model, while Freundlich isotherm gave the best fit in all the systems studied. The thermodynamics of the adsorption revealed that the process was not spontaneous at low temperatures as ΔG was positive; but it was endothermic in the single, binary and ternary systems.

KEYWORDS: Pollution;Nitrophenol;*Parkiabiglobosa*; isotherm; kinetics; binary; ternary

1. INTRODUCTION

Pollutants such as phenols present in trace amounts in wastewater may have several short and long term effects on the flora and fauna as well as on the human health. Increased awareness of their effects on the environment and the increasingly stringent environmental laws have created an urgent demand for the development of equipment and processes for the abatement of trace pollutants from processed wastewater [1].Phenol and its compound (Phenolics) is a class of organic substance which are similar in structure with the more common herbicides and insecticides in that they are resistant to biodegradation [2]. Phenol, as the basis of the phenolics, is a protoplasmic poison having the potential to

damage all kinds of cells. Phenolics are present in wastewater from oil refineries, coke plants, pharmaceutical, pesticide manufacturing, synthetic resins, wood pulp production [3, 4].Phenol and its compounds have both short and long term effects on human health as they are readily absorbed into the body systems through inhalation, oral and dermal routes [5]. The short term effects can be observed by symptoms such as headache, vomiting, fainting, liver and kidney damage, mental disorder, eye irritation, skin irritation, diarrhoea, anaemia, anorexia and difficulty in swallowing [6]. Long term effects often expressed itself by convulsions, coma, cardiac disorder, respiratory failure and death if there is internal ingestion of phenol in large areas of skin (25% of total). The minimum reported lethal dose on humans was 4.8g or approximately 70mg/kg [1, 5,6, 7, 8, 9]. The Environmental Protection Agency has classified phenol as a group D, not classifiable to human carcinogenicity [10].

Dephenolation (i.e. removal or reduction of phenolics) has been classified into two basic categories : (1) Destructive process comprising of destructive oxidation with ozone, hydrogen peroxide, biological or microbial degradation, MnO_2 and ClO_2 and (2) Recuperative processes namely membrane separation, solvent extraction, ion exchange and adsorption.Recently, adsorption technique has been found to be more effective and less expensive than previous methods of dephenolation[1, 2,5, 6, 11].Activated carbon is very effective in removal of many impurities present in wastewater, however they are often found to be costly. Hence, to further reduce the cost of treatment many researchers studied non-conventional materials as adsorbent. These includemontmorillonite[12], chitosan [13], fly ash [14, 15], phosphate rock [16], water hyacinth ash [17], banana peel [18], pecan, cocoyam [19] and castle nutshell [20] etc. Hence, this study examined the sorptive properties of *Parkiabiglobosa*sawdust as a low cost adsorbent for the removal of 4 – nitrophenol (4NP) from aqueous solution in the presence of phenol and 4 – chlorophenol. Though several studies have been carried out on the adsorption of phenolics in single adsorbate system using agricultural waste materials, there has been hardly any report on their adsorption in ternary mixture especially onto the sawdust of *Parkiabiglobosa.Parkiabiglobosa* also known as Africa locust bean tree is a perennial deciduous tree with height ranging from 7 to 20 m. It produces fruit which comprise of pod and seed. Its seed when fermented is used to produce ‘dawadawa’; a strong smelling

tasty food, high in protein and lipid. It is also called "iru" by some people and can be used as seasoning in some traditional soup [21].

2. MATERIALS AND METHODS

2.1. Preparation of adsorbent

Sawdust of *Parkiabiglobosa* used in this work was collected from a local sawmill in Ogbomoso, Southwest, Nigeria. Debris and other unwanted foreign materials were manually removed from the collection, after which it was thoroughly washed with distilled water, drained and oven dried. The washed and dried sawdust material was sieved and washed again several times with large quantities of distilled water until the wash water was clear so as to ensure the removal of any soluble component that may interfere with adsorption processes. It was then oven-dried at 105 ^{o}C and stored as*Parkiabiglobosa* sawdust (PSD) adsorbent.

2.2. Characterization of adsorbent

The PSD adsorbent was characterized by examining its surface morphology using Hitachi 2300 scanning electron microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectrum of the PSD was recorded before and after the adsorption process on Nicolet Avatar FT-IR in the range of 4000 to 450 cm^{-1} using KBr disk as reference. The samples were coated with gold before being subjected to SEM analysis

2.3. Preparation of adsorbate

4-nitrophenol (Product No, 29379, $\lambda_{max.}$, 319 nm, molecular weight, 139.11) used in this study was obtained in commercial purity (BDH Chemicals Ltd) and was used without further purification.Stock solutions of 4-nitrophenol, phenol and chlorophenol were prepared by dissolving 1000 mg of each of them separately in distilled water to make a 1000 mg/L solution. Appropriate working solutions were prepared from the stock solution by accurate dilution with distilled water. Experimental solutions of both binary and ternary phenol mixture of desired concentrations were prepared by mixing appropriate volumes of the stock solutions and accurately diluting it with distilled water.

77 **2.4. Batch Adsorption Studies**

78 A 100 mL aqueous solution of varying concentrations (10 to 100 mg/L) of 4NP was prepared in a
79 250 mL reaction bottles and a varying amount of PSD ranging from 0.1 to 0.5 g, was added to the bottles
80 respectively to evaluate the effects of dosage. The bottles were agitated continuously in a temperature-
81 controlled horizontal water bath shaker (SM 101 by Surgafriend Medicals) for 12 h to establish
82 equilibrium; then the adsobate-adsorbent mixture was left for 10 mins before being filtered. The effects
83 of the initial pH of the solution on the equilibrium uptake of 4NP by PSD were investigated over pH
84 range of 1 – 12 at the initial 4NP concentration of 50 mg/L and adsorbent dosage of 0.5 g. Changes in pH
85 of 4NP solution were adjusted with 0.1 M HCl or 0.1 M NaOH. The mixtures were agitated for 14 h. It
86 was then filtered, and the concentration of 4NP in the filtrate quantified. To study the thermodynamics,
87 50mL aqueous solution of 50 mg/L 4NP was prepared in the reaction bottle and 0.5 g PSD was
88 introduced at varying temperatures of 303, 313, 323 and 333 K. The data obtained were processed to
89 obtain the parameters needed.

90 **2.5 Analytical methods**

91 Concentration of 4-nitrophenol in the filtrate was determined by measuring the absorbance with UV–
92 Visible Spectrophotometer (Genesys 10 UV-VIS Scanning Spectrophotometer) adjusted to the
93 wavelength of the maximum absorbance (λmax) of the chemical specie (319 nm). The absorbance so
94 measured was converted to the corresponding concentration on the calibration curve of 4-ntro phenol
95 earlier constructed. The adsorption capacity (mg/g) at any given initial concentration was thus evaluated
96 using the following relationship:

97 $$q = \frac{(C_o - C)V}{m} \quad \text{.....} \quad (1)$$

98 where:

99 q is the amount of 4NP adsorbed (mg/g); C_o and C are the initial concentration (at t = 0) and equilibrium
100 concentration (mg/L) respectively; m is the mass of PSD (g) and V is the volume of 4NP (L).

For further verification of the applicability of the models, in addition to the Linear regression analysis (R^2), the data were tested with the sum of error squares (SSE, %) given by:

$$\sqrt{\frac{\sum (q_{e,\exp} - q_{e,calc})^2}{N}} \text{ ----------(2)}$$

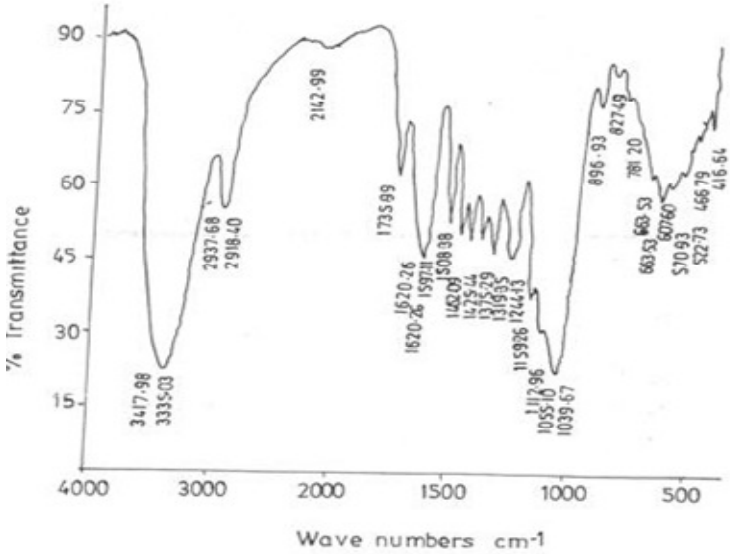
where$q_{e,exp}$is the experimentally determined sorption capacity; $q_{e,calc}$ is the theoretical sorption capacity from the model and *N* is the number of data points.The higher the value of R^2 and the lower the values of the other SSE, the better is the goodness-of-fit and therefore the applicability of the given model.

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

The FTIR spectrum of PSD (Fig. 1a) displays a number of absorption peaks, indicating the complex nature of the material under study. There are two broad bands at 3417 and 3335 cm^{-1}representing bonded – OH in the oxygen-containing functional groups. The positions of the C–H (2918 and 2937 cm^{-1}), aliphatic C – C (1244 cm^{-1}), aromatic C = C (1620 cm^{-1}) and carboxyl/carbonyl (1735 cm^{-1}) vibrations, also triple bond C≡C / C≡N (2142 cm^{-1}) contributed by those in the structure of cellulose, hemicellulose and lignin, are indicated by the spectrum of SD [22]. Thus, the FTIR analysis indicates that PSD comprises functional groups such as COOH, C = O, C=C, C≡C and C≡N that could be potential adsorption sites for interaction with the adsorbates.

The spectrum after the adsorption of the phenolics (Fig. 1b) presents slight shifts in the absorption peaks. For example, the bands at 3417 and 1620 cm^{-1} shifted to 3396 and 1626 cm^{-1}, respectively. This is an indication that adsorption might have taken place.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1735.99
1620.26
1597.11
1508.38
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1319.35
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1055.10
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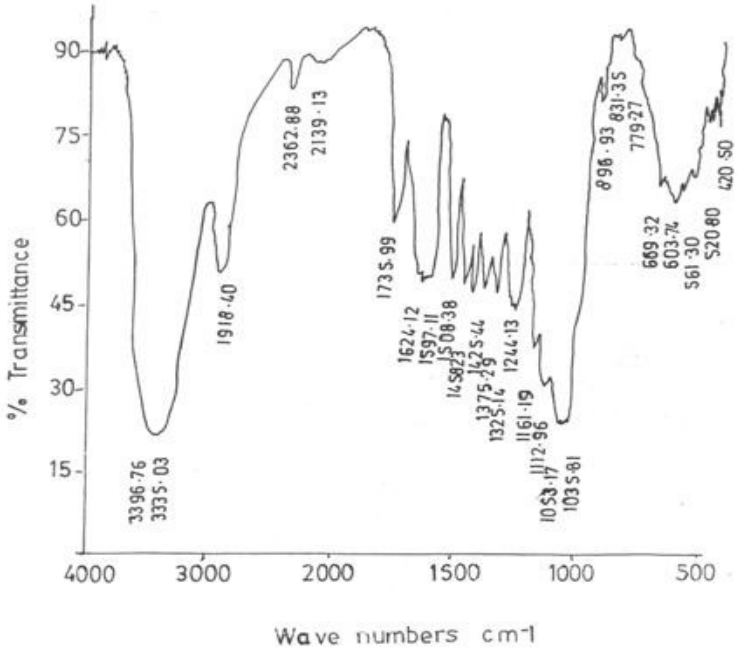
(a)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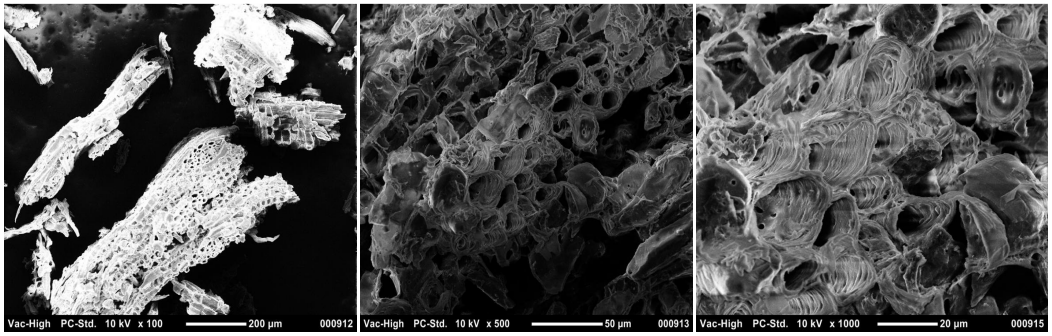
1375.29
1325.14
1244.13
1161.19
1112.96
1053.17
1035.81
896.93
831.35
779.27
669.32
603.74
561.30
520.80
420.50

(b)

Figure 1: FTIR spectrum of sawdust (PSD):(a) before and (b) after adsorption

The Scanning Electron Microscope (SEM) was used to study the surface morphology of the adsorbent. The textural structure of sawdust (PSD) presented as scanning electron micrographs of three different magnifications (x 100, x 500 and x 1000) (Figure 2).The surface topography provides important information on the degree of interaction between the adsorbent and phenol[23]. The SEM images showed the irregular texture and porous nature of PSD (Fig. 2). This seemingly rough surface is an indication of high surface area [24].



(a) SEM image of PSD(x100) (b) SEM image of PSD (x500) (c) SEM image of PSD (x1000)

Figure 2: SEM images of PSD at different magnifications (a) x 100 (b) x 500 and (c) x 1000

3.2. Effects of Initial Concentration

The effects of the initial concentration of 4NP on its adsorption by PSD are shown in Figure 3. Adsorption capacity (q_e) increases with increasing initial concentration of 4NP. The increase in the initial concentration of 4NP enhances the interaction between the adsorbate molecules and the surface of the adsorbent. For instance, an increase in the initial concentration of 4NP from 10 mg/L to 100 mg/L led to an increase in adsorption capacity (q_e) from 3.72 to 78.46 mg/g. Similar observation had also been reported by other researchers [16, 17,25, 26], where increasing initial concentration of sorbate resulted in increased adsorption capacity of the adsorbent for the adsorbate.

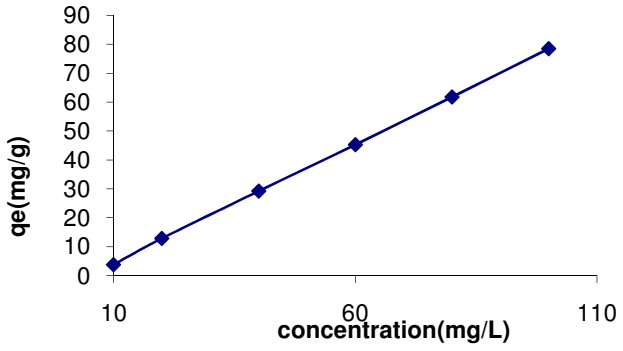


Figure 3: Effect of initial 4NP concentration on PSD adsorption

3.3. Effect of PSD Dose

The effect of PSD dosage on 4NP-sorption was studied by varying the adsorbent dosage from 0.10 to 0.50g in 100 mL of 50 mg 4NP/L solution while keeping other parameters (contact time, agitation speed, particle size, temperature) constant.Figure 4 indicates that the adsorption capacity (q_e) decreases with increasing adsorbent dosage. An increase in the sorption with lower sorbent dosage can be attributed to effective utilization of active adsorption sites. At higher dosage, however, the incremental sorption becomes low, as there is overlapping of these sites causing a decrease in quantity of 4NP adsorbed per unit mass of the adsorbent[27].

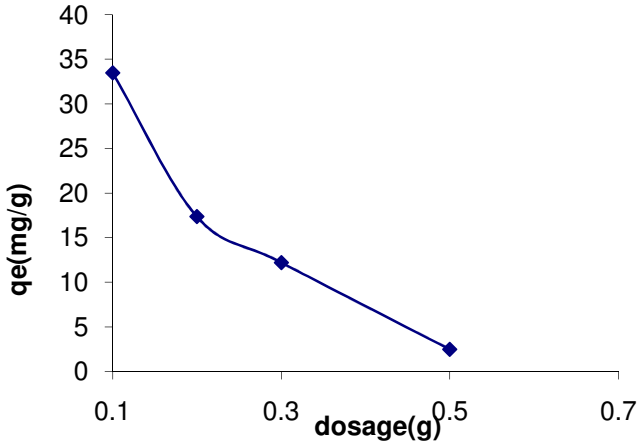


Figure 4: Effect of PSD dose on 4NP adsorption

3.4. Effect of pH

The adsorption of 4NP by PSD were studied at various pH values, obtained by addition of adequate amounts of 0.1 MHCl or 0.1 M NaOH, of 4NP solution. The effect of pH on 4NP adsorption can be explained from the view that there is change in the properties of both 4NP and PSD. It is recognized that oxygen-containing functional groups were present on the surface of PSD. These functional groups are subject to protonation and deprotonation, depending on pH. An increase in pH usually results in surface functional groups partially (or fully) deprotonated and thus a loss of positive charge and/or buildup of negative charge. Figure 5 reveals that an increase in pH from 1 to 6 increases the adsorption efficiency asthe q_e increased from 1.75 mg/g to 35.67 mg/g and then becomes constant from 7 to 11 after which it decreases. Similar results have been reported in the literature [15].The adsorptive increment with increasing pH at the acidic region resulted clearly from the protonation of the functional groups on the surface of SD. The protonation resulted in an increased blockage of SD surface by water molecules associated with negative charge. It is thus inferred that 4NP was primarily adsorbed on the negative surface of PSD[28]. It may be attributed to the presence of large amount of H^+ ions which compete for active adsorption sites on PSD with the positive ions of 4NP [17]. The presence of H^+ ions in the system makes the surface of the adsorbent to acquire positive charge, which then repel 4NP electrostatically [29]. The number of positively charged active sites on the adsorbent in alkaline medium decreases as a result of a decrease in the concentration of H^+ ions and increasing amount of hydroxyl ions, thereby making its surface to be effectively negatively charged. Thus, there exists an electrostatic attraction between 4NP cations and the negatively charged PSD surface, leading to an enhanced dye uptake. There was also report in literature where there was reduced repulsion between the adsorbent surface and 4NP at higher pH (pH 9) [15].This was also obtained by [30].

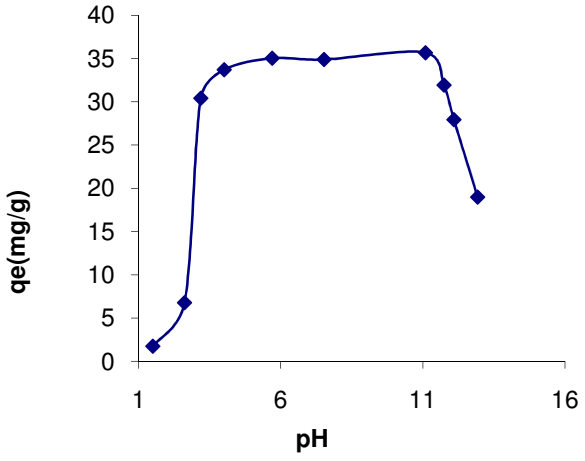


Figure 5:Effect of pH on the adsorption of 4NP

3.5. Effect of contact time

The rate of adsorption of a molecule onto a surface is an important factor in the design of a sorption system [31]. For 4NP, it was observed that as contact time increased, the amount adsorbed at time t (q_t) increased until it becomes constant and the equilibrium time was found to be 360 min (Fig. 6). The rate of 4NP uptake was faster in the first 6 has over 90% removal was accomplished.This is similar to the observations of [32]

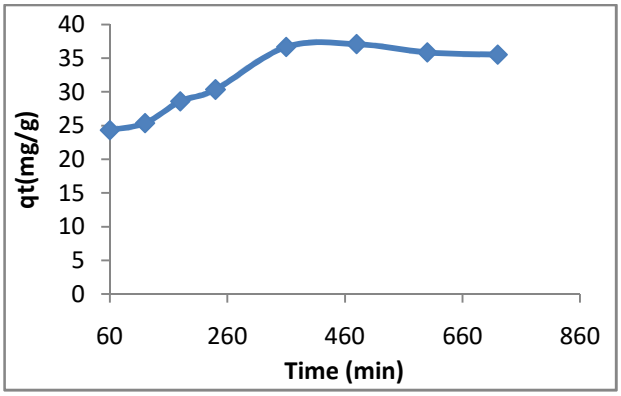


Figure 6: Effect of contact time on the adsorption of 4NP on PSD

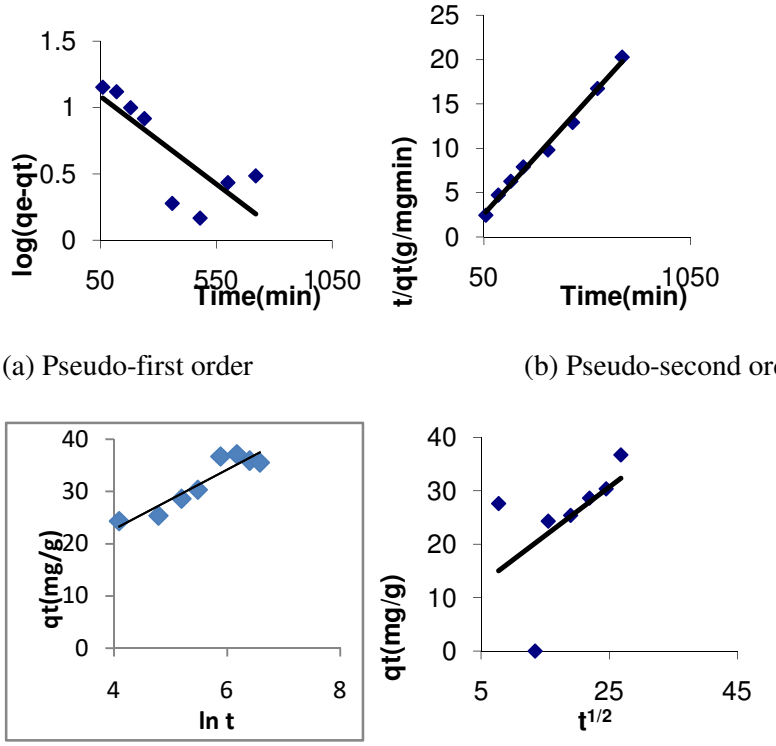
3.6. Kinetic Modelling

Three different models of kinetics were used to study the adsorption of 4NP on PSD in single, binary and ternary system. The examined models were pseudo-first order [33], pseudo-second order

[34]and Elovich [35]. Intraparticle diffusion model [36] was also used to know if diffusion was involved and if it is the rate determining step in the process. The kinetic data was fitted into four models and they are presented in Figures 7(a-d) while the kinetic parameters are presented in Table 1.In the single system, with only 4NP present in the medium, pseudo-second order model gave the best fit. This is evident from the high R^2 value of the model (0.993) while the R^2 for pseudo-first order and Elovich model were lower (0.631 and 0.873 respectively). In addition, the sum of square error analysis carried out also corroborate the findings, as the SSE (sum of error square) value for the pseudo-second order model was lower than for pseudo-first order and Elovich model (Table 1).

In the binary system, in which 4NP was being adsorbed in the presence of phenol, the high R^2 value of the pseudo-second order model (0.999) showed that the model can be used to explain the adsorption process of 4NP in this binary system other than the two other models with lower R^2; pseudo first order (0.817) and Elovich (0.975). The SSE value of pseudo-second order model support this finding (Table 1). Also, in the binary system, in which 4NP was being adsorbed in the presence of 4-chlorophenol, the R^2 for the models were 0.575, 0.999 and 0.996 for pseudo-first order, pseudo-second order and Elovich model respectively (Table 1). The R^2 value showed that the pseudo-second order model gave the best fit while the lower value of SSE (0.29) corroborates this.This is in contrast with [37] where the process fitted pseudo – first order model.In the ternary system, in which 4NP was being adsorbed in the presence of phenol and 4-chlorophenol, the kinetics followed the same model as that of single and binary system where the pseudo-second order gave the best fit based on the high R^2 value and low SSE value (Table 1).

In all the systems, the pseudo-second order model can be used to explain the adsorption of 4NP and from Table 1, it is evident that the intraparticle diffusion is not the rate determining step for all the systems. The assumption of the pseudo-second order model is that the rate limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between the hydrophilic edge sites of the PSD and 4NP in all the systems [38]. This was also observed by others [17, 26].



(a) Pseudo-first order (b) Pseudo-second order

(c) Elovich (d) Weber-Morris

Figure 7: (a)Pseudo-first order (b)Pseudo-second order (c) Elovich and (d) Weber-Morris plot for the adsorption of 4NP onto PSD

Table 1: Comparison of rate constants and other parametersfor various kinetic models for 4NP in single, binary and ternary systems

Parameters	**Adsorbate System**			
	4NP	4NP+5Ph	4NP + 5C-Ph	4NP+5Ph+5C-Ph
$q_{e(expt)}$	38.59	30.81	25.36	26.65
Pseudo-first order				
R^2	0.631	0.817	0.575	0.892
K_1(L/min)	0.0023	0.00023	0.0046	0.0035
q_e (cal)	14.19	19.19	10.76	14.65
SSE (%)	8.63	3.35	4.40	3.62

Pseudo-second order				
R^2	0.993	0.999	0.999	0.9995
K_2(L/mg.min)	$4.87x10^{-4}$	$7.87x10^{-4}$	1.08×10^{-3}	3.29×10^{-4}
q_e (cal)	40.00	18.18	26.32	29.24
H (mg/g.mim)	0.78	0.26	0.75	0.26
SSE (%)	0.50	3.65	0.29	0.78
Elovich model				
R^2	0.873	0.975	0.996	0.959
A(mg/g.min)	6.65	2.08	0.064	3.04
B (g/mg)	0.17	0.40	0.37	0.18
SSE(%)	0.89	3.76	2.05	3.67
Weber-Morris				
R^2	0.271	0.897	0.931	0.856
K_{id} ($mgg^{-1}min^{0.5}$)	0.906	0.257	0.336	0.569
X_i	8.026	9.047	16.05	9.933
SSE (%)	0.078	3.98	0.333	0.604

*4NP-4-nitrophenol,5Ph–5ppmPhenol,5C-Ph–5ppm Chlorophenol.

K_1 – sorption rate constant, K_2 – sorption rate constant, H – initial adsorption rate, K_{id} – sorption rate constant, X_i – boundary layer thickness, A – initial adsorption rate, B – desorption rate constant

3.7. Adsorption Isotherm

Five different models of isotherm were used to explain the adsorption of 4NP onto PSD in single, binary and ternary systems. They are Langmuir [39], Freundlich[40], Temkin[41], Dubinin-Radushkevich[42] and Harkin-Jura [43]. The equilibrium data were fitted into the models and their isotherms parameters are presented in Table 2.

In the single system, the Freundlich model gave the best fit having the highest regression co-efficient of 0.992. The order of fitness is Freundlich>Temkin>Dubinin-RadushKevich> Langmuir > Harkin - Jura.This is contrary to [44] where the process follows Langmuir model.

In the binary system, in which 4NP was being adsorbed on the presence of 5ppm phenol, Freundlich still gave the best fit as evident from the high R^2 (0.976) compared to that of Dubinin-RadushKevich (0.946), Temkin (0.945), Langmuir (0.692) and Harkin-Jura (0.648). But in the binary system, in which 4NP is being adsorbed in the presence of 5ppm chlorophenol, Dubinin-RadushKevich model seems to explain the adsorption better having high R^2 of 0.989 while the order of fitness of the other four models is Temkin>Freundlich> Harkin-Jura > Langmuir. Furthermore, in ternary system, in which 4NP was adsorbed in the presence of 5ppm phenol and 5ppm chlorophenol, the trend in the fitness of the isotherm model changed to Temkin having the best fit as shown by the high R^2 (0.971) compared to the R^2 of Dubinin-RadushKevich (0.927), Freundlich (0.911), Langmuir (0.404) and Harkin-Jura (0.179). On the overall, Freundlich seems to describe well the isotherm of the adsorption of 4NP onto SPD indicating that the adsorption may be chemisorption and multilayer. This is similar to the reports by [15, 17].The maximum adsorption capacity (Q_m) for PSD in single system was 56.82 mg/g which was higher than that obtained by [45]

255 **Table 2:** Isotherm model parameters for adsorption of 4NP onto PSD

Model/Parameters	**4NP**	**4NP+5ppm Phenol**	**4NP+ 5ppm C-Phenol**	**4NP+5ppmPhenol+5ppm C-Phenol**
Langmuir				
R^2	0.808	0.692	0.657	0.404
Q_m (mg/g)	56.82	17.04	40.49	14.10
K_a(L/mg)	0.0285	0.0431	0.0321	0.0431
Freundlich				
R^2	0.992	0.976	0.960	0.911
1/n (L/g)	0.619	0.449	0.548	3.193
K_f(mg/g)	0.575	0.100	0.301	0.209
Temkin				
R^2	0.965	0.945	0.981	0.971
β (J/mol)	57.81	56.81	64.56	13.57
K_T (L/mg)	0.163	0.161	0.143	0.010
Dubinin-Radushkevich				
R^2	0.962	0.946	0.989	0.927
β (mol^2/j^2)	2×10^{-5}	2×10^{-5}	3×10^{-5}	2×10^{-5}
X_m (mg/g)	83.07	77.68	97.29	94.50

Harkin – Jura				
R^2	0.789	0.648	0.691	0.179
A	86.21	12.18	69.44	140.8
B	1.267	1.217	1.278	9.099

Q_m–adsotption capacity, K_a–equilibrium sorption constant,

n – sorption intensity, K_f – adsorption capacity, β–heat of sorption, K_T – equilibrium binding constant, β – mean sorption energy, X_m– maximum sorption capacity

3.8. Thermodynamics

A plot of ln K_C($Kc = q_e/C_e$) versus 1/T for the adsorption of 4NP onto PSD for all the systems are graphically presented in figures 8&9 and the thermodynamic parameters (ΔG, ΔH and ΔS) are shown in Table 3.In the single system, ΔG was positive but reduced in magnitude, tending towards negative, as the temperature increased. Thisimplies that the process was not spontaneous at lower temperatures, but at elevated temperatures, it may be spontaneous.The ΔH was positive indicating that the process was endothermic, and ΔS was positive showing good affinity between the adsorbate and the adsorbent. In the binary and ternary systems, ΔG, ΔH and ΔS remain positive; this shows that the presence of other phenols in the system has little or no effect on the thermodynamics of the adsorption of 4NP onto PSD.

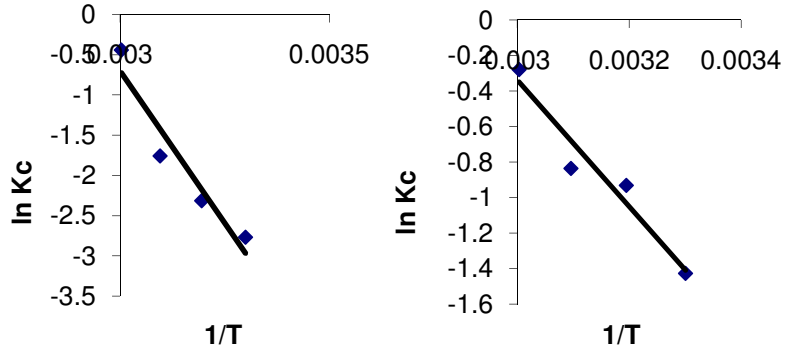


Figure 8: Thermodynamic plot for the adsorption of 4NP onto PSD in (a) single system and (b) binary (4NP+5Ph) system.

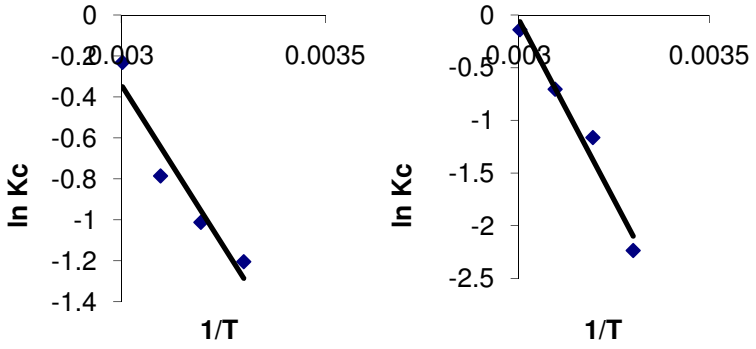


Figure 9: Thermodynamic plot for the adsorption of 4NP onto PSD in (a) binary(4NP+5C-Ph) and (b) ternary (4NP + 5-Ph + 5-C-Ph) system.

276 **Table 3:**Thermodynamics parameters for the adsorption of 4-Nitrophenol in Single, Binary and Ternary Systems on PSD.

Temp	**Single system(4NP only)**			**Binary system(4NP+5Ph)**			**Binary System (4NP+5C-Ph)**			**Ternary system**		
(K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
303	+6.97			+3.59			+3.03			+5.63		
313	+6.03	+62.75	+0.18	+2.42	+29.63	+0.086	+2.63	+26.16	+0.076	+3.03	+56.87	+0.17
323	+4.72			+2.25			+2.11			+1.89		
333	+1.22			+0.77			+0.64			+0.39		

4. CONCLUSION

The study investigated the potential of raw sawdust, a well-known agroforestry by-product, for removing 4-Nitrophenol, from aqueous solutions of phenolic compounds in single, binary and ternary systems.The optimum time for the sorption process was 720 mins, while the optimum dose was 0.500 g. The kinetics of the adsorption in all the systems could best be described by the pseudo-second order model. Freundlich isotherm seems the best to explain the adsorption isotherm as evidently seen from the high regression coefficient (R^2). The maximum monolayer coverage, $Q_{m,}$ of the adsorbent for the single nitrophenol system was 56.82 mg/g. The value was lower in the binary and ternary adsorbate systems.The sorption of 4NP was not spontaneous at low temperature as ΔG values obtained are positive (0.77 – 5.63 kJ/mol) single, binary and ternary systems; the spontaneityof the process increased with increased temperature.The enthalpy and entropy changes associated with the biosorption were also positive in the four systems investigated.

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