The Effect of Activation Method on the Adsorption Performance of Saw-Dust Activated Carbon

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ABSTRACT

Aims: The present study was conducted to evaluate the ability of modified saw dust to remove para-nitrophenol (PNP) from aqueous solution.

Methodology: Batch adsorption studies were carried out under varying conditions of initial pH, contact time and temperature. The performance of saw dust activated carbon was characterized by BET surface area FTIR and SEM. Three simplified kinetic models including pseudo-first order, pseudo-second order and intra particle diffusion were selected to follow the adsorption process.

Place and Duration of Study: Experiments were carried out in the National Research Center, Department of Physical Chemistry at laboratory of Surface Chemistry and Catalysis.

Study Design: The adsorption abilities of saw dust after thermal and chemical treatment were investigated for its efficiency in removing para-nitrophenol (PNP) from aqueous solution.

Results: The Langmuir, Freundlich and Temkin models were used to describe the adsorption equilibrium studies of saw dust activated carbon. Results showed that the Langmuir isotherm showed better fit than Freundlich and Temkin isotherm. The kinetic data were found to follow the pseudo-second order model. Intraparticle diffusion is not the sole rate controlling factor. The negative values of ΔH˚ and ΔG˚ revealed the feasibility of adsorption, spontaneous and exothermic.
1. INTRODUCTION

Excessive presence of phenol and its derivatives in natural water sources is considered as a serious threat to human health and overall water quality [1]. The fate of phenols in the environment and their removal from the hyposphere is complicated by their low solubility, ability to ionize, low vapour pressure and tendency to undergo oxidation and oxidative polymerization with humic and fulvic acid-type products [2]. Phenols are frequently derived from petrochemicals, plastics, paints, pharmaceutical and steel industries [3]. The US Environmental Protection Agency (EPA) has identified 1777 National Priorities List (NPL) sites, with nitrophenols having been found at 14 of these sites. As EPA evaluates more sites, the numbers at which nitrophenols are found may change. These are manmade chemicals with no evidence of their formation from any natural source. The World Health Organization (WHO) is stricter on phenolic compounds regulation. It sets a 0.001 mg/l as the limit of phenol concentration in potable water [4]. Nitrophenols are known to be toxic to human and vegetal matter [5]. Indeed, nitrophenols are some of the most difficult pollutants to remove from industrial waste water. Nitrophenols and its derivatives result from the production of pesticides, herbicides [6,7]. Various methods were proposed for removal of phenolic compounds from water. Some are destructive such as biological degradation and chemical oxidation. Others are non-destructive such as solvent extraction and adsorption. The adsorption technique using activated carbon is one of the alternative treatment processes currently under consideration for achieving the required level of phenol removal. Accordingly, the adsorption of phenol and its derivatives has been the subject of numerous investigations [8-11]. p-Nitrophenol has been one (or the principle) adsorbate in all of these studies. An optimal adsorbent for the removal of organic compounds in waste water should have the following properties: low cost, ease of handling, environmental neutrality and high affinity for the sorbate at high capacity. Biomass mainly derived from agricultural solid waste is a preferable option for activated carbon precursors.

Numerous successful attempts have been done to develop activated carbons from various range of agricultural solid waste such as apricot stones, palm tree branches; rice husk, saw dust and coir pith [12-16]. Saw dust is considered as an agricultural waste and a by-product of manufacturing industries which can be easily identified to be a hazard especially, because of its flammability. Despite saw dust utilization in the form of saw dust pellets, biomass boiler feed power generation at demonstration stage [17], there is still an estimated 6 million tons/year of sawdust going to actual wastage. It is available in the country side at zero or negligible price i.e: simply open air saw dust going to actual energy capture or otherwise to reduce pile volumes at saw mills. The wasted saw dust provides a practical and sustainable source for development of better quality low-cost activated carbon for efficient abatement of toxic metal ions and organic chemicals from industrial and municipal waste waters at reduced cost.

The paper objective is to evaluate the feasibility of developing low-cost activated carbon obtained from saw dust of textural quality and aqueous phase p-nitophenol removal capacity. The equilibrium and kinetic data of the adsorption were then studied to understand the adsorption.

2. MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

The raw saw dust was collected from a local furniture manufacturing industry and sieved in the size ranges (0.85-1.15) mm. saw dust was washed with distilled water to remove muddy materials and impurities, then dried in an oven at 100-110°C and thus used as a starting raw material for preparation of activated carbons denoted as SDR. A common horizontal furnace was used for the different activation process, defined as follows:

Series A: Direct carbonization 300 gm of saw dust was subjected to carbonization at 700°C under the influence of nitrogen flow (150 ml/min) for 2 hrs, the carbonized product was repeatedly washed with distilled water. The sample was

**Conclusion:** It is thus concluded, high quality carbon can easily be produced from saw dust through chemical and thermal activation.

**Keywords:** Saw dust; active carbon; adsorption; thermodynamic parameters; intra-particle diffusion.
then oven-dried at 110°C for 24 hrs and designed as SDC.

Series B: An accurate weight of produced char (50 gram) was impregnated with the equivalent weight of potassium hydroxide (KOH) at impregnation ratio of 1:1. The mixture then was dehydrated in a drying oven at 100°C for overnight. The dried solid mixture then was employed to carbonized at 600°C for 2 hrs under its own atmosphere. The material was thoroughly washed with distilled water and soaked in dilute HNO₃ overnight to eliminate the residual alkali content from the pores of the carbon and designates as SDK.

Series C: 50 gm of produced char was impregnated with 50% (v/v) phosphoric acid and left overnight at room temperature. The impregnated sample was carbonized at 600°C for 2 hrs. The carbons thus produced were then repetitively washed with distilled water to recover the acid and further washed with 1% NaHCO₃ solution to remove the traces of residual acid and designates as SDP.

2.2 Characterization of Activated Carbon

Surface morphology of the produced saw dust activated carbon was investigated using scanning electron microscope (SEM) with a Joel instrument, Japan Probe Micro-Analyzer, JXA 840 A electron. Textural characterization of the produced saw dust activated carbon was carried out by N₂ adsorption at 77 K using (NOVA version 2.1 Quantachrome Corporation, USA). The samples were degassed under vacuum at 523 K for 2 hrs before measurements were made. Specific surface area (S_INFO m²/g) was calculated by applying the BET equation, total pore volume (V_INFO cm³/g) is obtained from the volume of nitrogen adsorbed at P/PO = 0.95, and average pore radius estimated by r = 2 V_INFO / S_INFO. Fourier transfer infera-red (FTIR) analyzer was used to investigate the presence of active carbon surface functional group (6100-JASCO). The spectrum was recorded from 4000 to 400 cm⁻¹ adopting the KBr pellet method of sample handling.

2.3 Adsorbate

Para nitrophenol was high grade chemical produced by Merck Co. Germany. The concentration of p-nitrophenol in the aqueous solution was determined using a double beam UV spectrophotometer (Shimadzu PC 2401) at wavelength 317 nm.

Table 1 listed the chemical structure, molecular weight, pKa solubility in water of PNP.

Table 1. Properties and chemical structure of p-nitrophenol

| Symbol | PNP |
|--------|-----|
| Molecular formula | C₆H₅O₃N |
| Chemical structure | ![Chemical Structure](image) |
| PKₐ at 25°C | 7.15 |
| Solubility at 25°C | 17 |

2.4 Adsorption Studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 ml) were 100 ml of (PNP) solutions with initial concentrations of (20-120 mg/L) were placed in these flasks. Equal mass of (0.1g) of the prepared saw dust activated carbon samples were added to each flask and kept in an isothermal shaker of 120 rpm at [298, 313 and 323K] for 24 hr to reach equilibrium. The pH of the solution was 6. Aqueous samples were taken from the solution and the concentrations were analyzed. The amount of PNP taken by the tested carbon at equilibrium qₑ (mg/g) was calculated by

\[ q_e = \frac{(C_0 - C_e)}{W} \times V \]  \hspace{1cm} (1)

where C₀ and Cₑ (mg/L) are, the liquid-phase concentrations of PNP at initial and equilibrium respectively. V (L) is the volume of the solution and W (g) is the mass of activated adsorbent used. For kinetic studies, 1(g) of saw dust activated carbon was introduce into 100ml of PNP solution of 500 mg/L at room temperature and pH= 6 and kept in a laboratory shaker for various mixing time. At predetermined intervals of time solutions were analyzed for the final concentrations of PNP. The amount of adsorption qₜ (mg/g) at time t (min) was calculated by

\[ q_t = \frac{(C_0 - C_t)}{W} \times V \]  \hspace{1cm} (2)

where C₀ (mg/L) is the concentrations of PNP at time t. The effect of pH on PNP removal on the saw dust activated carbon was examined by varying the pH of the solutions from 2 to 12 with initial PNP concentration of 100 mg/L, activated carbon dosage of 0.1g/100 ml and at room...
temperature. 0.1N HCl and 0.1N NaOH solutions are used for pH adjustments.

3. RESULTS AND DISCUSSION

3.1 Identification of Surface Functional Groups by FTIR

Oxygen-containing surface functional groups play an important role in influencing the surface properties and adsorption behavior of activated carbons. These groups can be formed during activation process or can be introduced by oxidation after preparation of activated carbon [18]. Saw dust mainly consists of lignin, cellulose, hemicellulose and some proteins which make them effective adsorbents. Although saw dust activated carbon was prepared via various activation methods, there is a slight similarity in the adsorption patterns (Fig. 1).

The spectra show that the surface functional groups of the tested samples do not exhibit significant difference independently of the activating agent used. Only slight difference on the intensity of the bands and some functional groups shifted to different frequency level. The major peaks recorded for tested samples are listed in Table (2).

The strong band around 3430-3420 cm\(^{-1}\) refers to the –OH stretching vibration due to inter and intra-molecular hydrogen bonding of polymeric compounds such as phenols, alcohols and carboxylic acids. Only SDC and SDK showed intense bands between 3900-3762 cm\(^{-1}\) corresponding to free–OH group [19].

In these spectra we can observe band around 1700-1600cm\(^{-1}\) refers to the stretching vibration of C=O of lactone or C=C (i.e: phenyl), [20]. Similarly, the strong peak seen at 1450-1480 cm\(^{-1}\) has been assigned to stretching vibrations of C—C bonds. A peak at 1592 cm\(^{-1}\) refers to C=O stretch of carbonyl group in quinone as well as representing γ-pyrene structure with strong vibrations from a combination of C=O and C=C, minor peak at 2920-2930 cm\(^{-1}\) which characterize symmetric and asymmetric vibrations of —CH\(_2\)— groups. The intensity of absorption band around 1300-1000cm\(^{-1}\) indicates the existence of C—O in carboxylic acids, alcohols and esters, or a P=O bond in phosphate esters and P=OOH [21]. Finally, the peaks in the region 870-500 cm\(^{-1}\) in FTIR spectra indicate aromatic C—H bending. From the spectra of the saw dust activated carbons, it can be noted that all the samples contain oxygenated surface functional groups of phenolic character causes acidic surface properties where as carbonyl, quinone and pyranose-like groups bring about surface basicity [22].

The morphological studies by SEM micrographs of tested samples are shown in (Fig. 2).

It is clear from Fig. (2A) that the surface morphology was characterized by a highly oriented structure in the form of filaments filled with material, conferring an anisotropic character. The micrograph of pyrolyzed char SDC (Fig. 2A) shows that the surface barely consists of pores. Among all the morphology surface of the activated carbon prepared by KOH and H\(_3\)PO\(_4\) processes Figs. (2B, 2C) shows the presence of pores. However, saw dust activated carbon impregnated with KOH Figs. (2B) shows highly defined pores and cavities. The mechanism by which potassium hydroxide activates an existing carbon are more complex and involves the disintegration (almost explosively) of structure following intercalation as well as some gasification by oxygen molecules of hydroxide.

Based on the data in Table (3), activation by H\(_3\)PO\(_4\) produced activated carbon with a higher surface area, total pore volume and possessed a texture with higher microprosity and mesoprosity characteristics. This character could be reflected in the removal capacity of this adsorbent towards large organic molecules from aqueous media [23].

3.2 Effect of Solution pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants. Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics, equilibrium characteristics and adsorption process. The corresponding results illustrated in (Fig. 3).
Fig. 1. FTIR-spectra of saw dust activated carbon A) SDC b) SDK c) SDP

Table 2. The appearances of functional groups on surface of saw dust activated carbon a) SDC b) SDK C) SDP

| Wave number cm⁻¹ | Vibrational mode | Functional group                                                                 |
|------------------|------------------|-----------------------------------------------------------------------------------|
| 3900-3800        | OH- Stretching   | In phenol, alcohol → free                                                         |
| 3400             | OH- Stretching   | H₂O, phenol, alcohol (intra and intermolecular hydrogen bonded)                   |
| 2900             | C-H Stretching   | CH₂-CH₃ [in vinyl and methyl group]                                               |
| 1700             | C=O Stretching   | Carboxyl in carboxylic acid                                                       |
| 1600             | C=O Stretching   | Carbonyl in ketone                                                                |
| 1500             | C=C Stretching   | Aromatic compound                                                                 |
| 1400             | O-H bending      | Alcohol, carboxylic acid                                                          |
| 1300             | C-H bending      | -CH₃ group                                                                        |
| 1200             | C-O Stretching   | Carboxylic acid                                                                   |
| 1100             | C-O Stretching   | Alcohol                                                                          |
| 800-700          | C- H deformation | C-H out of plane deformation                                                       |
| 600-500          | C-H out of plane | C-H out of plane of benzene derivatives                                            |

Table 3. Physico-chemical characteristics of prepared activated carbon

| Phsico-chemical characteristics | SDC  | SDK  | SDP  |
|----------------------------------|------|------|------|
| S_BET (m²/g)                     | 392  | 494  | 831  |
| V_p (cm³/g)                      | 0.106| 0.212| 0.39 |
| Average pore diameter (Å)        | 10.88| 17.25| 19.2 |
| pH_{ZPC}                         | 6    | 7    | 6    |
It can be observed that the removal of PNP increases with increasing pH from their minimum at lower pH of 2 (85% for SDC, 44% for SDK and 68% for SDP) to their maximum at pH of 6, where the removal of 95% of SDC, 84% of SDK, while for SDP maximum pH obtained at 4. An increase in pH above 6 shows a decreasing trend in adsorption. This can be explained by solubility dissociation equilibrium and Benzene ring. Introduction of NO$_2^-$ group to phenols resulted in increasing adsorption due to decrease water solubility [24]. The pH$_zpc$ of SDC, SDK, and SDP was found to be 7, 7 and 6 respectively. Above this pH carbon surface is negative. The protonation of the adsorbed surface and phenol molecules at lower pH leads to extensive repulsion. The pKa of PNP was found to be 7.1 and thus, at optimum conditions of pH the protonated species appear to be more readily adsorbed on the negative surface of the carbon. A donor-acceptor complex mechanism was reported earlier [24,25] for the adsorption of PNP on activated carbon. In this mechanism carbonyl oxygen group on the carbon surface acts as an electron donor whereas the aromatic ring of the phenol acted as the acceptor. As the presence of NO$_2$ group leads to the formation of bond between the surface carboxylic groups and the electron-poor aromatic ring of PNP. Reduction in the adsorption at higher pH is possibly due to the increased solubility of phenols and the abundance of OH$^-$ ions thereby increasing hindrance to diffusion of phenolate ions [26].

3.3 Adsorption Dynamics

Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive for a between the solute molecules on the solid and bulk phases.

The effect of the contact time on the adsorption capacity of the saw dust activated carbons is given in Fig. (4).

PNP solution was kept in contact with prepared samples for 24h, although, no significant variation in residual PNP concentration was detected after 2h of contact time. Thus, after 2h of contact, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted .The contact time varied in the range 0-135 min. (Fig. 4), illustrates, the time required to achieve the equilibrium was about 75 min for SDK and SDP while for SDC attains equilibrium earlier within 30 min. We can observe that the adsorption is rapid in the first minutes of contact time [27]. The nature of the samples had a market effect in PNP removal, leading to the SDP having higher adsorption capacity than the SDK and SDC. The selectivity of the saw dust activated carbons based on $q_t$ values followed the order SDC < SDK < SDP.

It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an adsorption treatment plant. In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transfer and chemical reaction. The kinetics of PNP adsorption onto the saw dust activated carbons was investigated using three different models: the pseudo-first-order (Lagergen model), the pseudo-second-order and intra particle diffusion. A relatively high $R^2$ value indicates that the
The pseudo-first order equation (3) is one of the most widely [29] being the first rate equation developed for sorption in solid/liquid systems.

The integral form of this model is:

\[ \log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \]  

where \( q_e \) and \( q_t \) are the amounts of PNP adsorbed at equilibrium and time \( t \) respectively (mg/g) and \( k_1 \) is the pseudo first-order rate (min\(^{-1}\)). The slopes and intercepts of plots \( \log(q_e - q_t) \) vs \( t \) figure not shown, were used to determine the rate constant \( k_1 \). The values obtained being presented in Table (4).

The adsorption data were also be described by a pseudo-second order kinetic reaction [30] using the equation:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \]  

where \( k_2 \) (g mg\(^{-1}\)min\(^{-1}\)) is the second-order rate constant of adsorption. This model assumes that the adsorption rate is proportional to the number of unoccupied sites on the adsorbent surface. The values of \( q_e \) and \( k_2 \) can be estimated experimentally from the slope and intercept of the plot \( t/q_t \) versus \( t \), as shown in Table (4).

It could be noted that adsorption of PNP on the saw dust activated carbons satisfactorily followed the pseudo-second order rate equation. This was reflected by the high \( R^2 \) values (>0.99). This reflect on the hypothesis that the rate limiting step may be chemisorption relating valency forces through sharing or exchange of electrons between adsorbent and adsorbate. The similar phenomenon have also been observed in the adsorption of 4-chlorophenol onto activated carbon from rattan saw dust.

Since neither the pseudo-first order nor the second order model can identify the diffusion mechanism, the kinetic results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism, which is expressed as [31],

\[ q_t = k_{id} t^{0.5} + C \]  

where \( k_{id} \) is the intra-particle diffusion rate constant and intercept \( C \) represents the value of the thickness of the boundary layer. Fig. 5 illustrates the plots of \( q_t \) versus \( t^{0.5} \) for different saw dust activated carbons at room temperature. The plots are not linear over the whole time range, indicating that more than one step affecting the PNP adsorption. For example, the first step is might due to the boundary layer diffusion at the initial stage of the adsorption and the intra-particle diffusion which gives the other
two linear parts. The intra-particle diffusion starts with a rapid transport of adsorbate molecules. The second portion of linear curve attributes to the gradual adsorption, where intra-particle diffusion is a rate limiting. The third portion refers to the final equilibrium stage signified by a formation of plateau, indicating a weak activity of the intra-particle diffusion due to low adsorbate concentration left in the solution [32]. On the other hand, most of the adsorption sites have been occupied after lapse of time thus limited free sites for the adsorbate molecules to attach on. If the intra-particle diffusion is the only rate controlling step then the plot passes through the origin, else the boundary layer diffusion affects the adsorption to some degree. The linear curve is deviated from the origin or near saturation because of the differences in the mass transfer rate in the initial and final stages of adsorption [33,34]. Plots of \( q_t \) versus \( t^{0.5} \) are shown in (Fig. 5) and the values of \( k_{id} \) and \( C \) were presented in Table (4).

### 3.4 Adsorption Isotherm

An important feature of modern engineering is the ability to adequately model the behavior of the system before committing to large-scale investment. Basic theoretical understanding, experimental observations and measurements of a system are required to develop a good model. Proper analysis and design of adsorption need relevant adsorption equilibrium as one of the vital information. Equilibrium concentrations of adsorbate and adsorbent are functions of temperature. Thus, the adsorption equilibrium relationship at a given temperature is referred as an adsorption isotherm. Several adsorption isotherms are available and readily adopted to correlate adsorption equilibrium. In the present study, Langmuir, Freundlich and Temkin were used to explain the phenomenon.

![Fig. 4. Effect of contact time on the removal of PNP](image)

#### Table 4. Kinetic model parameters of PNP onto saw dust activated carbons

| Sample | First order model | Second order model | Intraparticle diffusion |
|--------|-------------------|--------------------|-------------------------|
|        | \( k_1 (\text{min}^{-1}) = 5.77 \times 10^{-3} \) | \( K_2 (\text{g/mg min}^{-1}) = 0.073 \) | \( K_f (\text{mg/g min}^{-3/2}) = 0.09 \) |
|        | \( q_1 (\text{mg/g}) = 0.85 \) | \( q_2 (\text{mg/g}) = 1.11 \) | \( C_1 (\text{mg/g}) = 0.16 \) |
|        | \( R^2 = 0.75 \) | \( R^2 = 0.989 \) | \( R^2 = 0.98 \) |
| SDC    |                   |                    |                         |
|        | \( k_1 (\text{min}^{-1}) = 0.0063 \) | \( K_2 (\text{g/mg min}^{-1}) = 3 \times 10^{-3} \) | \( K_f (\text{mg/g min}^{-3/2}) = 4.8 \) |
|        | \( q_1 (\text{mg/g}) = 58 \) | \( q_2 (\text{mg/g}) = 116 \) | \( C_1 (\text{mg/g}) = 26 \) |
|        | \( R^2 = 0.76 \) | \( R^2 = 0.99 \) | \( R^2 = 0.98 \) |
| SDK    |                   |                    |                         |
|        | \( k_1 (\text{min}^{-1}) = 0.009 \) | \( K_2 (\text{g/mg min}^{-1}) = 5.5 \times 10^{-3} \) | \( K_f (\text{mg/g min}^{-3/2}) = 12.8 \) |
|        | \( q_1 (\text{mg/g}) = 30 \) | \( q_2 (\text{mg/g}) = 114 \) | \( C_1 (\text{mg/g}) = 71 \) |
|        | \( R^2 = 0.80 \) | \( R^2 = 0.99 \) | \( R^2 = 0.99 \) |
| SDP    |                   |                    |                         |
The Langmuir model presumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [35]. This model can be represented by the following equation:

$$\frac{C_e}{q_e} = 1/K_L q_{\text{max}} + \frac{C_e}{q_{\text{max}}}$$

where $q_{\text{max}}$ and $K_L$ are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When $C_e/q_e$ was plotted against $C_e$, a straight line was obtained. $q_{\text{max}}$ was calculated from the slope whereas $K_L$ was found from the intercept (figure not shown).

Freundlich [36] isotherm in the other hand assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, the well-known linear form of Freundlich model is given by the following equation:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

where $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). $K_F$ [(mg/g) (L/mg)$^{1/n}$] is the adsorption capacity of the adsorbent and $n$ is a measure of adsorption intensity or surface heterogeneity. The plot of $\ln q_e$ versus $\ln C_e$ (Figure not shown) gave a straight line with slope of $1/n$ whereas $k_F$ was calculated from the intercept value.

Another popular equation for the analysis of isotherms is Temkin and Pyzhev [37] which is based on the supposition that the decline of the heat of adsorption as a function of temperature is linear rather than logarithmic

$$q_e = (RT/b) \ln(K_T C_e)$$

Eq.(8) can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

where $B_1 = RT/b$ and $K_T$ are constants. $K_T$ is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant $B_1$ is related to the heat of adsorption. A plot of $q_e$ versus $\ln C_e$ (not shown) enables the determination of the isotherm constant $K_T$ and $B_1$. Their values are shown in Table (5) along with the value of the correlation coefficient.

As given in Table (5), the value of $q_{\text{max}}$ is significantly higher for SDK and SDP system than SDC. In adsorption mechanism of aromatic compounds in liquid phase on activated carbon, there are mainly two types of interactions electrostatic and dispersive [38]. Different authors have reported that the order of adsorption affinity may be interpreted on the basis of the chemical and physical characteristics of molecules, the nature of the different groups located on the aromatic ring and also on the type
of functional groups presented on the surface of the activated carbon.

The presences of carboxylic or lactonic groups, these groups are acidic which suppresses the adsorption of PNP. In addition, the water molecules cluster around the polar acidic surface groups again reducing the adsorption capacity. The adsorption of PNP is the highest when the carbonyl groups (quinonic) are the dominating surface groups. This increase in adsorption of PNP can be attributed to the theory of the formation of \( \pi-\pi \) bonds where activated carbon act as an electron donar and the solute benzene ring has an electron withdrawing character [39, 40]. The nitro-group of nitrophenol is electron withdrawing, thereby causing a decrease in electron density of the \( \pi \) electrons of the benzene ring. Therefore, dispersion forces between the carbon surface and PNP are expected to be the strongest according to the following order SDP > SDK > SDC.

### 3.5 Thermodynamic Study

As temperature is one of the parameters that can exercise greater influence on the adsorption process, the thermodynamic characterization of the solid liquid interface is important to the understanding of the adsorption mechanism [41]. Therefore, the effect of temperature on adsorption of PNP on SDC, SDK and SDP was studied at temperatures of (298, 313 and 333 K).

The Gibb’s free energy \( \Delta G^\circ \) can be calculated from equation (10) and (11).

\[
\Delta G^\circ = RT \ln K_L
\]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

It can be seen in Table (6) that the amount of PNP adsorbed onto the three saw dust activated carbons \( (q_e) \) and \( K_L \) decreases with the increase of adsorption temperature.

As depicted from Fig. (6) the decrease in the uptake of PNP with the increase in temperature may be explained as a result of the increase in the average kinetic energy of the PNP phenolate anions and negatively charged activated saw dust surface. This could lead to desorption or cause the PNP to bounce of the surface of the activated saw dust instead of colliding and combining with it. Therefore, the increase in temperature may be associated with the decrease in the stability of PNP phenolate anion-adsorbent complex [42].

Based on the data in Table (7), that the values obtained for \( \Delta G^\circ \) are negative indicating the spontaneity of the process especially at lower temperature. The values of \( \Delta H \) for different saw dust activated carbons are negative, involved libration of energy, characterizing an exothermic process. The negative value of \( \Delta S \) (entropy) represents that the motion of molecules restricted towards the surface of saw dust activated carbons and their disordered decreased resulting in the decrease in entropy.

**Table 5. Isotherms constants for adsorption of PNP onto saw dust activated carbons at room temperature 298K**

| Isotherm | SDC  | SDK  | SDP  |
|----------|------|------|------|
| Langmuir |      |      |      |
| \( q_e \) (mg/g) | 29.5 | 60.2 | 62   |
| \( K_L \) (L/mg) | 0.084 | 0.16 | 0.40 |
| \( R^2 \) | 0.99 | 0.989 | 0.99 |
| Freundlich |      |      |      |
| \( K_F \) (mg/g(L/mg)) \( ^{1/n} \) | 15.13 | 17.37 | 15.84 |
| \( N \) | 3.1 | 3.6 | 7.5 |
| \( R^2 \) | 0.80 | 0.78 | 0.81 |
| Temkin  |      |      |      |
| \( B_1 \) (kJ/mol) | 658 | 366.8 | 728 |
| \( K_T \) (L/mg) | 5.9 | 54.5 | 109 |
| \( R^2 \) | 0.68 | 0.80 | 0.86 |
Fig. 6. Thermodynamic parameters of saw dust activated carbons 1) SDC (2) SDP (3) SDK

Table 6. Influence of adsorption temperature on the parameters of the Langmuir isotherm for different saw dust activated carbons

| Temperature | SDC |  | SDK |  | SDP |  |
|-------------|-----|---|-----|---|-----|---|
|             | K   | q_o (mg/g) | K_L (L/mg) | q_o (mg/g) | K_L (L/mg) | q_o (mg/g) | K_L (L/mg) |
| 298         | 29.5 | 0.084 | 60.2 | 0.16 | 62 | 0.4 |
| 313         | 17 | 0.05 | 43 | 0.14 | 43 | 0.2 |
| 333         | 14 | 0.04 | 6 | 0.02 | 31 | 0.19 |

Table 7. The thermodynamic parameter for saw dust activated carbons

| Adsorbent | Temperature K | ΔG° | ΔH° | ΔS° |
|-----------|---------------|-----|-----|-----|
| SDC       | 298           | -23.18 |      |     |
|           | 313           | -22.97 | -2.5 | -27.42 |
|           | 333           | -23.83 |      |     |
| SDK       | 298           | -27.04 | -5  | -31.5 |
|           | 313           | -25.67 |      |     |
|           | 333           | -21.9  |     |     |
| SDP       | 298           | -27.04 | -2  | -14.12 |
|           | 313           | -26.59 |      |     |
|           | 333           | -28.15 |     |     |

In general, the enthalpy change due to chemical adsorption is considerably larger than that due to physical adsorption (< 40 kJ/mol). Hence, the adsorption of PNP on the prepared carbons is due to physical adsorption for the described temperature ranges [43,44].

4. CONCLUSION

The ability of modified saw dust to remove PNP from aqueous solution was investigated in equilibrium, kinetics and thermodynamics. Equilibrium data agreed well with Langmuir
isotherm models. The kinetic data were found to follow the pseudo-second order model. Intraparticle diffusion is not the sole rate controlling factor. The negative values of ΔH° and ΔG° revealed the feasibility of adsorption. Solution pH has great effect on the uptake of PNP.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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