Adsorptive Removal of p-Nitrophenol from Aqueous Solution by Bone Char: Equilibrium and Kinetic Studies

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Abstract: Para-nitrophenol adsorbed on bone char synthesized from cow bones has been studied. The Langmuir Freundlich and Sips models were applied to the equilibrium data to describe the adsorption process. The Langmuir model best described the adsorption process with $R^2 = 0.919$; and maximum adsorption capacity, q_{max} of 365.76 mg/g. Batch kinetic studies conformed to pseudo-second-order indicating that several mechanisms may be involved in the process and gave a value of 2.5×10^4 g/mg/min for the rate constant for the sorption of p-nitrophenol on bone char. The values of thermodynamic parameters, free energy \approx -22.0 kJ/mol, enthalpy -20.2 kJ/mol and entropy 5.34 J/K mol for the adsorption of p-nitrophenol on bone char showed that the adsorption was spontaneous and exothermic.

Key words: Adsorption, bone char, kinetics, p-nitrophenol, thermodynamics.

1. Introduction

The treatment of wastewater and remediation is one of increasing importance as issues with contaminated water and wastewater from industry become more and more prevalent. Huge amounts of water are used in petroleum refineries and, consequently, large flow of industrial wastewater is generated. These waters are extremely heterogeneous, their quantity and quality vary depending on the operated process used. They often present a wide spectrum of chemical pollutants consisting solid dissolved of or state, organic-inorganic materials. dyes, metals. hydrocarbons, solvents, etc., at various levels of toxicity which are mostly discharged into the environment. Organic pollutants originate from oil refinery wastewater, domestic sewage and agricultural wastewater and these include phenols, hydrocarbons, esters, surfactants, phthalates, biphenyls oils, greases, detergents and pharmaceuticals [1]. Phenolic compounds are common contaminants in wastewater,

being generated from petroleum and petrochemical, coal conversion, pulp and paper and phenol producing industries. They are considered priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health [2]. Due to the enormously increasing importance of petroleum for industrial development during the last century, petrochemical effluents have had a significant impact on the pollution of surface water systems. Conventional treatment technologies, for example, precipitation and coagulation, flocculation, sedimentation, filtration, etc., of water treatment seem impractical, become less effective and more expensive when situations involving high volumes and low level concentrations of organic compounds are encountered. It is expedient to find alternative methods of removing organic pollutants from wastewater by using readily available cheap raw materials because to be widely used, any treatment system must be inexpensive, nontoxic, fast, convenient, and effective having a high potential to be regenerated. One of the major methods that have

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proved effective for the removal of pollutants from wastewater and aqueous solutions is by adsorption onto porous solid adsorbents. The solid-liquid adsorption is a treatment process that has been accepted in environmental treatment applications around the world and is based on the ability of certain solids to concentrate substances from a solution on their surfaces which includes physical adsorption (driven by van der Waals forces) and chemisorption (involving the formation of chemical bonds) [3-5]. Adsorption is an important procedure used for the removal of pollutants from the environment. The use of different adsorbents in the removal of organic pollutants present in aqueous media has been extensively studied over the last few years [6-12]. The use of activated carbons as adsorbents for the removal of organic pollutants is a very common practice but the major disadvantages of using these carbons are their high price and regeneration cost [6]. More recently, low-cost adsorbents including agricultural waste and by-products have been tested and applied to wastewater treatment. Agricultural by-products and wastes present highly recommendable sources because their use provides a two-fold environment and economic advantage: a recycling path is devised and new adsorbents are produced from a low-cost material for used in wastewater treatment plans. Amongst agricultural wastes, bone char produced from the carbonization of animal bones has been shown to adsorb considerable quantities of organic compounds and metal ions from aqueous medium [11-15].

Bone char consists mainly of calcium phosphate and a small amount of carbon. It is a mixed compound adsorbent in which carbon is distributed throughout the porous structure of hydroxyapatite, (Ca₁₀(PO₄)₆(OH)₂), which is a good adsorbent and successfully used as a permeable reactive barrier for immobilizing various heavy metals and treating acid mine drainage [13]. Bone char is a naturally occurring hydroxyapatite biological derived from the carbonization of crushed animal bones under high temperatures in the range of 400-500 °C in an oxygen-depleted atmosphere. Although the use of bone char in the removal of heavy metals from aqueous medium is fairly well studied, the adsorption capacity of bone char for organic contaminants has received relatively less attention. The overall purpose of this study is the production of low-cost adsorbent that would be effective in the treatment of refinery wastewaters.

2. Materials and Methods

2.1 Materials

The adsorbate used in this study was p-nitrophenol (Aldrich) with 99% purity and used without further purification.

2.2 Preparation of Bone Char

Cow bones were collected from an abattoir in Agbarho, Delta State, Nigeria. The bones were pre-heated to remove fat and residual protein pieces, air-dried and charred. The bones were then pyrolysed in a furnace at 450 °C for 2 hours. After cooling at room temperature, the BC was pulverised and sieved using a standard sieve to obtain particle size fractions of 212 μ m.

2.3 Characterization of Bone Char

The elemental analysis of BC was performed using EDX (energy dispersive X-ray) apparatus, Quanta FEG, attached to a scanning electron microscope (Quanta FEG 250) to analyze the solid structure. The chemical composition of the bone char sample was determined using XRF (X-ray fluorescence) (Spectro Xepos II). The surface area was determined by the iodine adsorption method [16].

2.4 Analytical Techniques

The concentrations of p-nitrophenol solutions were measured using Campsec M501 UV-visible spectrophotometer at a wavelength of 400 nm [17]. Seven calibration standards (10, 20, 30, 40, 50, 60 and 70 mg/L) were prepared and the samples measured in duplicates.

2.5 Agitation Time for Sorption Equilibrium Studies

The equilibrium time for sorption is initially unknown and the required agitation time to reach equilibrium was determined by weighing 0.5 g bone char into a test bottle, adding 10 mg/L of p-nitrophenol solution and shaken at various times (2, 5, 10, 40, 60, 90, 120 and 180 mins). The removal percentages were calculated and plotted against time. The p-nitrophenol solution was observed to reach equilibrium with the bone char after 90 mins. To ensure equilibrium was attained, 120 minutes of agitation time was used for all equilibrium experiments.

2.6 Batch Equilibrium Adsorption Experiments

Adsorption experiments were carried out using a fixed mass of bone char (0.5 g) at ambient temperature. Different initial concentrations (10, 20, 30, 40, 50, 60 and 70 mg/L) of p-nitrophenol were prepared by proper dilution from stock solution (70 mg/L). The amount of bone char was weighed into test bottles and 50 mL of p-nitrophenol pipette into the test bottles. The contents were shaken for 120 mins at 200 rpm using a mechanical shaker. The contents were filtered and the filtrate analysed for the organic contaminant using uv-visible spectrophotometer. The adsorbed amount of p-nitrophenol at equilibrium, q_e (mg/g), was calculated using the mass balance Eq. (1) [18]:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where, q_e is the amount of p-nitrophenol adsorbed (mg/g), C_o is the initial concentration of p-nitrophenol (mg/L); C_e is the equilibrium concentration of p-nitrophenol (mg/L); V is the volume of adsorbate solution (L) and m is the mass of adsorbent (g).

2.7 Theoretical Background

Adsorption processes are usually described using

isotherm models that provide information on the distribution of adsorbate species within the liquid and adsorbent based on a set of assumptions related to the heterogeneity or homogeneity of the adsorbents, the type of coverage and the possibility of the interaction between the adsorbates [19]. One of the most commonly used isotherm models for equilibrium studies is the Langmuir isotherm which is a theoretical model derived based on a monolayer homogeneous surface adsorption process with a finite number of identical sites. The Langmuir isotherm model is represented by the following relationship Eq. (2):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where, C_e is the equilibrium concentration of p-nitrophenol adsorbate (mg/L) and q_e is the amount of p-nitrophenol adsorbed (mg) at equilibrium per unit of the adsorbent (g). q_{max} and K_L are the Langmuir constants relating to adsorption capacity (mg/g) and the energy of adsorption (L/g) respectively. On further analysis of the Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by Eq. (2)

$$R_L = \frac{1}{1 + K_L C_o} \tag{3}$$

where, C_o (mg/g) is the initial amount of adsorbate.

The R_L parameter is considered as a more reliable indicator of the adsorption process [20-22] and there are four indications for the R_L value: (i) for favourable adsorption, $0 < R_L < 1$, (ii) for unfavourable adsorption, $R_L = 1$, (iii) for linear adsorption, $R_L = 1$ and (iv) for irreversible adsorption, $R_L = 0$.

The Freundlich isotherm model is also applied to establish the relationship between the amount adsorbed onto the adsorbent and its equilibrium concentration in aqueous solution. It assumes that adsorption sites have different affinities for the adsorbate, which means that the adsorption occurs on a heterogeneous surface and so sites with stronger attractive forces are occupied [23]. Freundlich isotherm is defined mathematically by Eq. (4):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where, K_F (mg/g) and *n* are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. These constants can be obtained from the intercept and slope of the linear plot of $logq_e$ versus $logC_e$ respectively.

To account for the limiting behaviour of Langmuir and Freundlich isotherm models, the Sips isotherm equation (also known as Langmuir—Freundlich equation) was used to describe the equilibrium of the organic contaminant—bone char system as it is characterized by the homogeneity factor, n, which is used to describe heterogeneous systems [24]. The model is valid for localized adsorption without adsorbate—adsorbate interactions [19]. When C_e approaches a low value, the Sips isotherm effectively reduces to Freundlich, while at high C_e , it predicts the Langmuir monolayer sorption characteristic. The Sips non-linear Eq. (5) is expressed as [19, 24, 25]

$$q_{e} = \frac{q_{\max} bC_{e}^{\frac{1}{n}}}{1 + bC_{e}^{\frac{1}{n}}}$$
(5)

where, *b* and q_{max} are the Sips equilibrium constant and maximum adsorption capacity values obtained from the slope and intercept of the plot of $In \frac{q_{max}}{q_e}$ against $In C_e$; *n* is the Sips isotherm exponential constant which is the dimensionless heterogeneity factor, *n*, used in describing the system's heterogeneity when *n* is between 0 and 1. When *n* = 1, the Sips equation reduces to the Langmuir equation and it implies a homogeneous adsorption process [26].

3. Results and Discussion

3.1 Characterization of Bone Char

The elemental and chemical composition of bone char carried out using EDX and XRF measurements are given in Table 1.

The chemical analysis of BC showed the presence of several elements with calcium 51.54 wt% and phosphorus 28.99 wt% being the most abundant. The Ca:P ratio in the bone char (1.78) is close to the ratio (1.65) reported for hydroxyapatite in cow bones [1, 27]. This result corroborates reports from previous studies which suggest that carbonization of bones between 200 °C and 600 °C has little influence on the Ca/P ratio of hydroxyapatite [28]. Other physic-chemical characteristics of the bone char are pH 7.90; surface area 58.03 m²/g; bulk density 2.47 g/cm³; pore volume 2.37 g/cm³; ash content 1.69% and moisture content 0.05%.

The surface structure of the bone char sample analysed using scanning electron microscopy is shown in Fig. 1.

The scanning electron micrograph of bone char reveals high porosity of the bone char particles for effective adsorption confirming the value obtained for the pore volume $(2.37 \text{ cm}^3/\text{g})$.

3.2 Adsorption Equilibrium Studies

The sorption equilibrium data of p-nitrophenol onto bone char are shown in Fig. 2.

 Table 1
 Elemental and chemical composition of bone char sample.

Elemental composition				Chemical composition		
Element	Wt%	Atomic %	Symbol	Element	Concentration Wt%	
Calcium (Ca)	51.54	41.00	Na ₂ O	Sodium (Na)	2.58	
Phosphorus (P)	28.99	29.78	MgO	Magnesium (Mg)	3.08	
Oxygen (O)	17.40	26.86	Al_2O_3	Aluminium (Al)	0.36	
Sodium (Na)	0.11	0.11	SiO ₂	Silicon (Si)	1.20	
Magnesium (Mg)	1.86	2.18	P_2O_5	Phosphorus (P)	44.93	
Potassium (K)	0.10	0.07	CaO	Calcium (Ca)	50.38	

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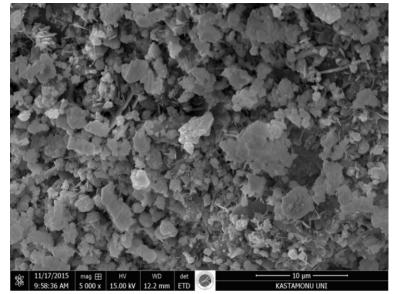


Fig. 1 Scanning electron micrograph of bone char (10 µm).

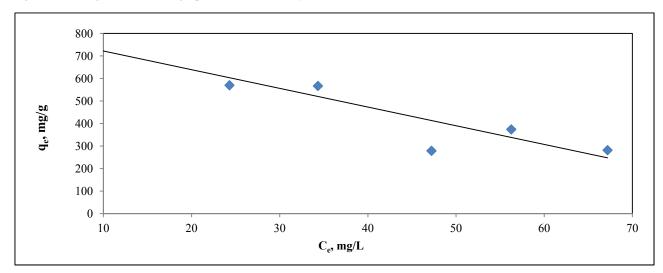


Fig. 2 Adsorption equilibrium graph of p-nitrophenol onto bone char.

As seen in Fig. 2 above, for a given quantity of adsorbent (0.5 g), there is a steady decrease in the adsorption of p-nitrophenol onto bone char with increase in the initial adsorbate concentration in the range of 10-70 mg/L. Increasing the concentration of p-nitrophenol in solution increases the amount present with limited number of active sites on the surface of the bone char. In other words, as the initial concentration of p-nitrophenol increases, the active sites present on the surface of the bone char are saturated (less adsorbent surface) resulting in decrease in the adsorption efficiency of the adsorbent [29].

Adsorption equilibrium data using isotherms describe the capacity of the adsorbate onto the surface of an adsorbent. These adsorption isotherms describe how pollutants interact with the adsorbent materials, thus, the information obtained from these isotherms is critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents and effective design of the adsorption system. In this study, the equilibrium between the adsorbed p-nitrophenol onto bone char was described using the Langmuir, Freundlich and Sip isotherm models.

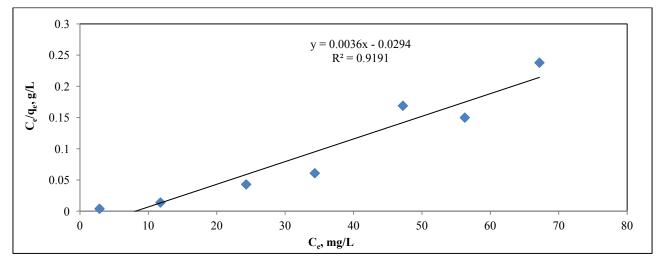


Fig. 3 Langmuir isotherm plot for the adsorption of p-nitrophenol onto bone char.

The Langmuir isotherm defines the equilibrium parameters of homogeneous surfaces, monolayer adsorption and distribution of adsorption sites. The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) defined by Fig. 3. In this study, the R_L values were less than 1 and found to approach zero with increase in C_o ($0 < R_L < 1$) indicating the suitability of bone char as adsorbent for the adsorption of p-nitrophenol from aqueous solution. Fig. 3 shows the application of the Langmuir isotherm for p-nitrophenol adsorption onto bone char.

It has been shown and reported that [30, 31] in the adsorption mechanism of aromatic compounds in liquid phase on activated carbons, there are two main types of interactions: electrostatic and dispersive. The former are produced by interactions between delocalised electrons in the carbon basal planes and the aromatic rings in the adsorptive molecules. The latter are produced by charged groups on the carbon surface and ions from dissociation of the adsorptive molecules in solution. The functional group linked to the adsorptive aromatic ring can activate or deactivate it thereby delocalizing its electronic charge. Activating groups are electron-withdrawing groups on an aromatic ring creating a partial negative charge in the ring while deactivating groups produce opposite effect, creating a partial positive charge. Because the aromatic ring has a much larger size than the functional group, the interaction of the former with the basal planes of the carbon is more effective. In this study, the Langmuir equation seemed to describe the experimental data fairly well. A good correlation between experimental data and Langmuir model was observed ($R^2 = 0.919$). The equation parameters, sorption constant, K_L and sorption capacity, q_{max} , are given in Table 2.

Here, p-nitrophenol is in the molecular form and so dispersive interactions will be the most important in the adsorption process [31]. The presence of the deactivating group, -NO₂, on the aromatic ring creates a partial positive charge and whose interactions with the bone char surface creates effective adsorption as seen from the value of q_{max} (365.76 mg/g) obtained by applying the Langmuir equation.

3.3 Adsorption Kinetic Studies

The removal of p-nitrophenol by adsorption onto bone char increased with time attaining a maximum value at about 90 minutes (Fig. 4) and thereafter it remained constant. The results obtained were used to study the rate-limiting step in the adsorption process. Two kinetic models: pseudo-first order and pseudo-second order rate equations were used to test the experimental data and examine the adsorption kinetics.

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lsotherm	Non-linear form	Linear form	Graphical plot	Isotherm constants
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	$\frac{C_{e}}{q_{e}} = \frac{C_{e}}{q_{max}} + \frac{1}{q_{max} K_{L}}$	C_e/q_e versus C_e	$R^{2} = 0.919$ $q_{max} = 365.76 \text{ mg/g}$ $K_{L} = -0.0943 \text{ L/g}$ $R^{2} = 0.282$
		$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L C_e}$	$1/q_e$ versus $1/C_e$	R = 0.232 $q_{max} = 250 \text{ mg/g}$ $K_L = 2.00 \text{ L/g}$
		$q_e = q_{max} - \frac{q_e}{K_L C_e}$	$q_e \ versus \ \frac{q_e}{K_L C_e}$	$R^2 = 0.376$ $q_{max} = 533.3 \text{ mg/g}$ $K_L = 4.29 \times 10^{-6} \text{ L/g}$
		$\frac{q_e}{C_e} = K_L q_{max} - K_L q_e$	$\frac{q_e}{C_e}$ versus q_e	$R^2 = 0.376$ $q_{max} = 3.88$ mg/g $K_L = -0.033$ L/g
reundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	log q _e versus logC _e	$ \frac{K_L = -0.033 \text{ L/g}}{R^2 = 0.615} n = -3.247 K_F = 1.3 \times 10^3 R^2 = 0.103 $
ips	$q_e = \frac{q_{\max} bC_e^{\frac{1}{n}}}{1 + bC_e^{\frac{1}{n}}}$	$\frac{1}{n}InC_e = -In\left(\frac{q_{max}}{q_e}\right) + Inb$	$In \frac{q_{max}}{q_e} versus InC_e$	$R^2 = 0.103$ n = 6.6 b = 1.7
98	36.5			
	986 -			•
9	985 -			
9 % m g/g	84.5 -			
<i>de</i> ¹	94.5 - 984 - 33.5 -			
98	984 - 33.5 - 983 -			
98	984 - 33.5 -	40 60 80	100 120 140	160 180 200

Table 2	Adsorption isotherm constants obt	tained from Langmuir.	Freundlich and Sips isotherm models.

Fig. 4 Agitation time graph for the adsorption of p-nitrophenol onto bone char.

3.3.1. Pseudo-first Order Model

The pseudo-first order equation of Lagergren as reported and frequently used in adsorption kinetic studies [2, 14, 20] is generally expressed as Eq. (6):

$$\frac{d_q}{d_t} = k_1 \left(q_e - q_t \right) \tag{6}$$

where, q_e and q_t are the amounts of adsorbate sorbed per unit weight of adsorbent at equilibrium and time t, respectively (mg/g) and k_1 is the rate constant (min⁻¹). Integrating with boundary conditions for t = 0, q = 0, Eq. (6) becomes Eq. (7):

$$log(q_e - q_t) = logq_e - \left(\frac{k_1}{2.303}\right)t$$
 (7)

The pseudo-first order adsorption rate constant, k_l , 2.50 × 10⁻² min⁻¹, was determined from the plot of log $(q_e - q_t)$ versus *t*.

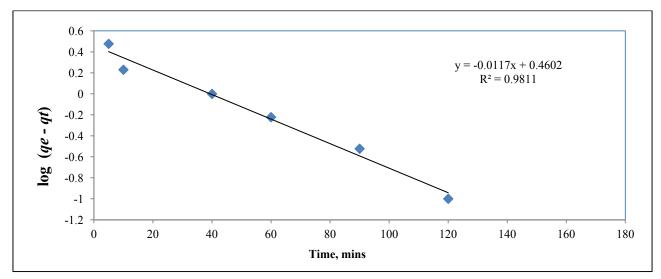


Fig. 5 Pseudo-first order kinetic plot for the adsorption of p-nitrophenol onto bone char.

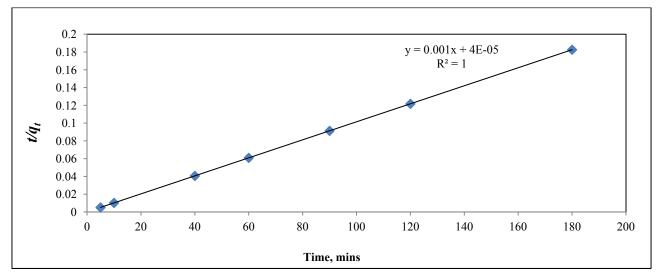


Fig. 6 Pseudo-second order kinetic plot for the adsorption of p-nitrophenol onto bone char.

3.3.2. Pseudo-Second Order Model

The pseudo-second order equation assumes that the sorption process involves chemisorption and the rate of site occupation is proportional to the square of the number of unoccupied sites. Therefore, if the rate of sorption follows a second order rate mechanism, the kinetic rate equation Eq. (8) is expressed thus [14, 32]:

$$\frac{d_q}{d_t} = k_2 (q_e - q_t)^2$$
(8)

where k_2 is the pseudo-second order rate constant $(g \cdot mg^{-1} \cdot min^{-1})$. Integrating and applying boundary conditions for t = 0 and q = 0, Eq. (8) becomes Eq. (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(9)

The rate constant, k_2 , 2.5×10^4 g·mg⁻¹·min⁻¹, was obtained from the intercept of the linear plot of $\frac{t}{q_t}$ versus *t* with the slope equal to $\frac{1}{q_e}$ and intercept equal to $\frac{1}{k_2}$. Fig. 6 shows good compliance of the adsorption

data using the pseudo-second order rate equation.

The experimental data fitted the pseudo-second order model ($R^2 = 1$) better than the pseudo-first order model ($R^2 = 0.981$) though the plot had good linearity

the interactions do not appear to have followed first-order kinetics.

3.4 Thermodynamic Studies

The original concept of thermodynamics assumes that in an isolated system, change is the driving force when energy cannot be created or destroyed. The Gibbs free energy change (ΔG^o) is the fundamental criterion of spontaneity and reactions that occur spontaneously at a given temperature has ΔG^o as a negative quantity. The thermodynamic parameters for the adsorption of p-nitrophenol onto BC, ΔH^o (kJ/mol), ΔS^o (J/K mol) and ΔG^o (kJ/mol) were evaluated using Eqs. (10) and (11) [20, 33].

$$\Delta G^o = -RT \ln K_a \tag{10}$$

$$In K_a = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
(11)

 K_a is the adsorption equilibrium constant otherwise known as the distribution coefficient of the adsorbate (= $\frac{q_e}{c_e}$); *R* is the universal gas constant (8.314 J/mol·K) and *T* is the absolute temperature (K). A plot of *ln* K_a versus $\frac{1}{T}$ gives a linear graph where ΔH^o and ΔS^o can be calculated from the slope and intercept respectively.

The amounts adsorbed in the temperature range 301-318 K from which the thermodynamic parameters were calculated are given in Table 3.

In this study, the experiments were carried out only over a small temperature interval due to relatively high ambient temperatures. The overall free energy change during the adsorption process was negative for the experimental range of temperature corresponding to a spontaneous physical process of p-nitrophenol adsorption and that the system does not gain energy from an external source. The spontaneity of the adsorption process is an indication that the adsorptive forces were strong enough to break the potential and shift the reaction to the right leading to the binding of p-nitrophenol onto the surface of bone char. However, the decrease in ΔG° as the temperature increased indicates that the reaction becomes unfavourable with increasing temperature of p-nitrophenol solution.

Table 3 Adsorbed amounts and thermodynamic parameters for the adsorption of p-nitrophenol on bone char.

	• •	•		
Temperature, K	q_{e} , mg/g	$C_{e,}$ mg/L	ΔG^{o} , kJ/mol	
301	985.0	0.150	-22.0	
303	982.0	0.180	-21.7	
308	977.8	0.222	-21.5	
313	977.7	0.223	-21.8	
318	977.6	0.234	-22.0	

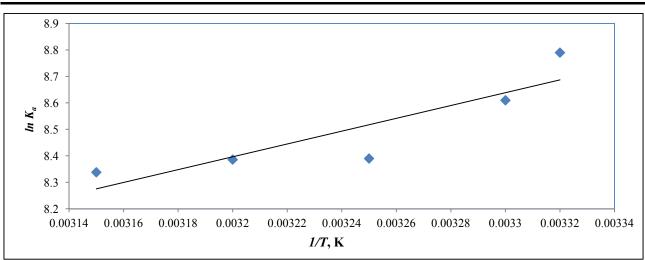


Fig. 7 Thermodynamic plot of $\ln K_a$ versus 1/T for the adsorption of p-nitrophenol onto bone char.

The other thermodynamic parameters, ΔH^o and ΔS^o , were found to be -20.2 kJ/mol and 5.34 J/Kmol respectively. The negative value of the enthalpy change shows that the adsorption of p-nitrophenol onto bone char was an exothermic process. The positive value of ΔS^o reflects the affinity of bone char for p-nitrophenol suggesting the occurrence of some structural changes in bone char and p-nitrophenol during the adsorption process. In addition, the positive entropy is an indication of the increasing randomness at the solid-liquid interface during adsorption [34, 35]. These results compare favourably with that obtained for the removal of 4-nitrophenol using zeolite and bentonite as low cost adsorbents [35].

4. Conclusion

The bone char obtained by the pyrolysis of cow bones at 450 °C was found to have high surface area and fairly well developed pore structure. Equilibrium sorption data obtained for p-nitrophenol on the bone char were represented by the Langmuir isotherm suggesting homogeneous adsorption sites on the bone char. Bone char characteristically has the calcium hydroxyapatite and carbon distributed on its surface. These results suggest that the removal of p-nitrophenol from aqueous medium may be due largely to the carbon sites on the bone char; and indicate that bone char may represent low-cost substitutes for activated carbon in the removal of contaminants from wastewaters.

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