

Adsorption Kinetics and Thermodynamics Study of Butylparaben on Activated Carbon Coconut Based

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Abstract

In this work, low cost coconut biochar based activated carbon (CBAC) was used for adsorption of Butylparaben (BPB) from aqueous medium. The prepared CBAC was characterized using BET, Boehm analysis and the adsorption equilibrium, kinetics and thermodynamics studies of BPB adsorption were carried out. During batch adsorption runs, the effects of factors, such as contact time (0 - 300 min), CBAC dose (200 - 800 mg), pH (3 - 11) and solution temperatures (303 - 348 K) were investigated on BPB removal. Experimental results reveal that the BPB removal efficiency on CBAC is higher than 97% under acidic and neutral conditions. Equilibrium data were fitted by Langmuir, Freundlich and Temkin isotherm models with correlation coefficient more than 0.9. The pseudo-second order kinetic model was observed to fit well the adsorption data. Thermodynamic analysis shows positive values of standard Gibb's free energy, suggesting the non-spontaneity of the process. The changes in enthalpy ($0.2 \text{ J}\cdot\text{mol}^{-1}$) and entropy ($19 \text{ J}\cdot\text{mol}^{-1}$) were found to be endothermic with an increase of randomness. The high adsorption efficiency of the synthesized coconut biochar materials with low cost indicates that it may be a promising adsorbent for removing organic compounds.

Keywords

Coconut Shell, Activated Carbon, Adsorption, Butylparaben, Kinetics, Isotherm

1. Introduction

During these last 20 years, concerns about the consequences of human and wild-

life to long term exposure to substances in the environment that can interact with the endocrine system, are increasingly criticized. These substances, leading to biological perturbations, are commonly referred to “endocrine disruptors”. According to the WHO definition, endocrine disruptors are natural or artificial chemical substances foreign to the body that can interfere with the operating systems and induce endocrine resulting in deleterious effects on the body or on his descendants [1].

Several studies have shown the potential and actual harmful effects of these compounds on wildlife and humans [2] [3] [4] [5]. Among these compounds, parabens, which are antimicrobial, antifungal and antioxidant agents, are widely used in the food, cosmetic and pharmaceutical industries [6]. Their presence in the aquatic environments at different concentrations is ranging from $\text{ng}\cdot\text{L}^{-1}$ to $\mu\text{g}\cdot\text{L}^{-1}$ [7]. Recently, the estrogenic effects of parabens, in particular Propylparaben and Butylparaben (BPB), affecting adversely the secretion of testosterone and the male reproductive system function in rats and mice, were demonstrated [2] [3] [4] [5] [8]. Furthermore, studies have shown that some parabens exhibit toxicity on testicular mitochondria at low concentration [9]. Gomez *et al.* [10] indicated that the main source of parabens in the aquatic environment remains wastewater treatment plant. Therefore, the removal of endocrine disruptors from waste water is an urgent need to preserve the environment and aquatic life. Several research teams are focusing their research to remove or degradate these compounds through various physical and chemical techniques, such as photocatalysis [11], sonolysis [12], photosonolysis [13], adsorption [14], nanofiltration [15] or reverse osmosis [16], with satisfactory results. Very few reports are there about the removal of BPB using photodegradation, photosonolysis and adsorption. Among these methods, adsorption is more efficient than other methods in the removal of organic compound from waste water. One of the great advantages of activated carbon is their large surface area and large porous volumes to adsorb high quantity of pollutant. Many researchers have shown great interest in the development of low cost adsorbent prepared from agricultural waste [17] [18]. In addition to their low cost, activated carbon prepared from agricultural waste bioproducts, allows limiting waste stocks and transforming waste into more valuable products with an added value. Since activated carbons possess large surface area, porosity and surface chemistry, these properties give them great adsorption ability for the uptake of organics compounds.

The objective of the present work is to prepare biochar based activated carbon from coconut shells of Côte d’Ivoire (West Africa), which are rejected by the farmers as waste materials [19] and to evaluate its use as adsorbent material for adsorption of BPB from aqueous solution in batch process. Adsorption kinetics, isotherms models and thermodynamics parameters of BPB on the synthesized biochar were investigated.

2. Materials and Methods

2.1. Materials

Butyl parahydroxybenzoate (BPB) (purity > 99%) was obtained from an analytical grade reagent, Sigma Aldrich, US. The physico-chemical properties and molecular structure of BPB are summarized in **Table 1** and **Figure 1**, respectively. Fisher Scientific supplied NaOH and H₂SO₄. All the chemicals and reagents used in this study were of analytical grade and used as received. All the solutions and reagents were prepared with deionized water.

2.2. Synthesis of Coconut Biochar Based Activated Carbon and Characterization

The adsorbent used in this study was prepared from coconut shell biochar. The experimental conditions and activated carbon characteristics were described by Atheba [20]. Briefly, a barn containing the coconut shells and fire embers is kept in a closed enclosure protected from oxygen. The heat exchanges inside the barrel will transform the coconut shells into inactive carbon, this is the carbonization process. Since the carbonization of the coconut shell was done on an artisanal basis, parameters such as temperature and atmosphere were not determined. The obtained carbon is crushed and sieved until carbon grains with a diameter of between 1 and 2 mm are obtained followed by its physical activation in a thermo-programmable furnace. **Table 2** summarizes the furnace parameters.

The Brunauer-Emmett-Teller (BET) specific surface area and Barrett-Joyner-Halenda (BJH) pore size of the sample were measured by adsorption of nitrogen liquid at 77 K collected from a Micromeritics Tristar 3000 surface area and pore size analyzer. The surface functional groups were determined according to the method of Boehm [21]. This method consists in the neutralization of the various oxygenated groups. Therefore, the carboxylic, lactone

Table 1. Physico-chemical properties of BPB.

Parameter	Value
Molecular Formula	C ₁₁ H ₁₄ O ₃
Molecular Weight (g·mol ⁻¹)	194.23
Solubility in water (mg·L ⁻¹)	158
Absorption Maxima (nm)	255

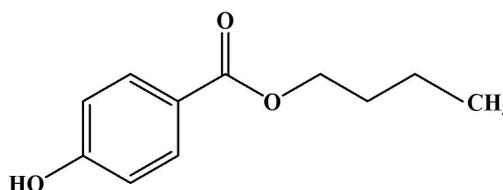


Figure 1. Butylparaben molecular structure.

Table 2. Parameters for carbon activation.

Time	Atmosphere	Activation parameters		
		Flow rate	Temperature	Heating rate
3 h	N ₂ + CO ₂	100 ml·min ⁻¹	From 20°C to 800°C	20°C min ⁻¹

and phenol functions were dosed with increasing force bases (NaHCO₃, Na₂CO₃, NaOH) while the total basicity was determined with hydrochloric acid.

2.3. Batch Mode Adsorption

The ability of activated carbon to uptake BPB from aqueous solution was evaluated in batch mode adsorption. BPB stock solution of 100 mg·L⁻¹ was prepared by dissolving the appropriate amount of BPB in 1000 ml of volumetric flask and completing the volume with deionized water up to mark. The experimental solutions of the desired concentration were obtained by successive dilutions.

The first set of tests consisted to determine equilibrium time of adsorption. For this purpose, 3 erlenmeyer flasks containing 200 ml of 10 mg·L⁻¹ BPB and activated carbon (4 g·L⁻¹) were shaken at 150 rpm, room temperature (25°C ± 2°C), during 300 min expected to reach equilibrium and the measured pH was 7.0 ± 0.5. At the regular interval time (0, 5, 15, 30, 60, 120, 180 and 300 min) samples were withdrawn and the amount of BPB adsorbed was determined by measuring the residual BPB concentration in the liquid phase using an OMEGA-UV-Vis (Thermoscientifique, France) spectrophotometer calibrated at the wavelength of 255 nm.

The effect of activated carbon dose on BPB adsorption process was conducted at fixed pH (pH 7 ± 0.5) and fixed initial BPB concentration (10 mg·L⁻¹) in 200 ml of solution. Different activated carbon masses were used (1, 2, 3 and 4 g·L⁻¹). The flasks were shaken at 150 rpm for 180 min (according the equilibrium time determined above) and samples were collected for analysis.

The next set of tests was performed to determine the effects of pH on adsorption process. Adsorption was studied at pH 3, 5, 7, 9 and 11 at 25°C ± 2°C, in 10 mg·L⁻¹ of initial BPB concentration, 200 ml of solution and 4 g·L⁻¹ of activated carbon. The solution initial pH value solution was adjusted using 0.1 M H₂SO₄ and 0.1 M NaOH, solutions. The flasks were shaken at 150 rpm for 180 min, and samples were collected for analysis.

The adsorption isotherms experiments were carried out using different initial concentrations of BPB (5, 10, 15, 20, 25, 30, 40, 50 mg·L⁻¹) and the same dose of activated carbon (4 g·L⁻¹). The mass of activated carbon was fixed according to the result obtained during the effect of activated carbon dose on BPB adsorption process. The flasks were shaken at 150 rpm for 180 min and samples were taken for analysis. Room temperature and optimum pH were used for test.

The adsorption kinetic experiments were carried out using 200 ml of 10 mg L⁻¹ of BPB solution and at a fixed concentration of activated carbon (4 g·L⁻¹). The flasks were shaken at 150 rpm, 25°C ± 2°C, and pH 7.0 ± 0.5. Samples were

withdrawn at regular interval times and analyzed.

The last set of analysis was consisted to evaluate the thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes, to understand the feasibility and nature of the adsorption process. For this, erlenmeyer flasks containing 200 ml of solution at $10 \text{ mg}\cdot\text{L}^{-1}$ of BPB and $4 \text{ g}\cdot\text{L}^{-1}$ of activated carbon were shaking at 150 rpm and different temperatures (10°C , 22°C , 30°C , 40°C) during 180 min.

The percentage of BPB removal is calculated using the following equation:

$$\text{Percentage Removal (PR\%)} = 100 \times (C_i - C_f) / C_i \quad (1)$$

The amount adsorbed in ($\text{mg}\cdot\text{g}^{-1}$) is calculated using Equation (2):

$$q_e = (C_i - C_f) \times V / m \quad (2)$$

where C_i and C_f are the initial and final concentrations ($\text{mg}\cdot\text{L}^{-1}$) of BPB in liquid phase, respectively; V (L) represents the volume of solution and m (g) the mass of activated carbon.

3. Results and discussion

3.1. Characterization of the Adsorbent

The most used materials in adsorption process are activated carbons. This is because of their high adsorption capacity, high surface area, micro porous structure, high degree of surface and high chemical and mechanical stability [22]. Therefore, N_2 adsorption isotherm was measured to determine the surface area and pore size of the adsorbent. The surface area was determined by a fitting analysis based on the BET equation. The quantitative assessment of the acido-basic functions of the surface was obtained by Boehm titration. According to the IUPAC classification of absorption isothermal curves, the N_2 -sorption (Figure 2) would be of type I, indicating the presence of micropores with an average pore size of $\approx 2.36 \text{ nm}$. The as prepared AC possesses a high surface area up to $443.13 \text{ m}^2\cdot\text{g}^{-1}$ with a pore volume of $\approx 0.22 \text{ cm}^3\cdot\text{g}^{-1}$. Table 3 gives the

Table 3. Structural and physico-chemical features of the adsorbent.

	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	443.134
Physical	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.220
	Pore size (\AA)	23.619
	-OH	0.172
Chemical	Acid ($\text{meq}\cdot\text{g}^{-1}$)	-COO-
	-COOH	2.780
	Base ($\text{meq}\cdot\text{g}^{-1}$)	1.075
	pH	10.2
Structure	Grain size (mm)	$1 < \phi < 2$
	Appearance	Spangle

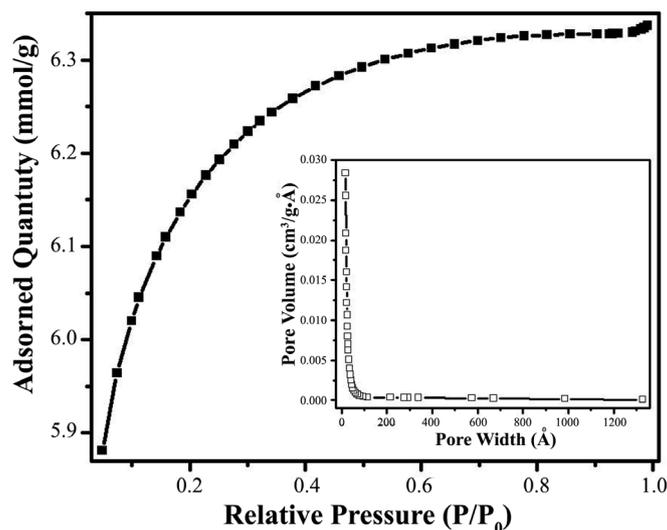


Figure 2. Adsorption isotherm of N_2 at 77K on AC and pore size distribution (inset) of AC.

structural and physico-chemical properties of the prepared adsorbent. It is interesting to note that the activated carbon is more acid, but has also some basic functions.

3.2. BPB Removal by Coconut Shell Biochar

3.2.1. Effect of Contact Time

The impact of contact time on the adsorption capacity of activated carbon (AC) for BPB removal was evaluated. In **Figure 3**, it clearly depicts that, the removal of BPB by AC increases as the contact time increases. The removal of BPB occurred in two main phases. The sorption of BPB is fast during the first 60 minutes, where about 85.2% of the initial concentration of BPB were removed; then slows down around 3 h, until the end of the run. The equilibrium is achieved almost in 3 h. At this time, the adsorption efficiency was 97.4%. A contact time of 3 h was thus established for the following runs. The fast adsorption could be due to the high availability of free active sites at the beginning of adsorption process, whereas after a specific period of time, active sites will be gradually occupied which will make the process of adsorption slower [23]. Similar results have been highlighted in the literature on the removal of dye [14] [24].

3.2.2. Effect of Adsorbent Dosage

The effect of activated carbon dose on BPB ($pH\ 7$ and $10\ mg\cdot L^{-1}$) removal was studied and the result obtained is depicted in **Figure 4**. It is observed that the adsorption efficiency of BPB by activated carbon increases with an increase in concentration of sorbent. The adsorption efficiency increases from 41% to 95% with increasing the adsorbent dose from 1 to $4\ g\cdot L^{-1}$. This may be due to an increase in the availability of surface active centers. The same observation is also reported in literature [25] [26]. A contact time of 3 h and the dosage of activated

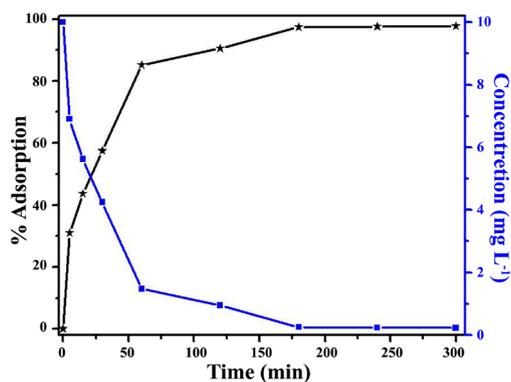


Figure 3. Effect of contact time on the uptake of BPB by AC.

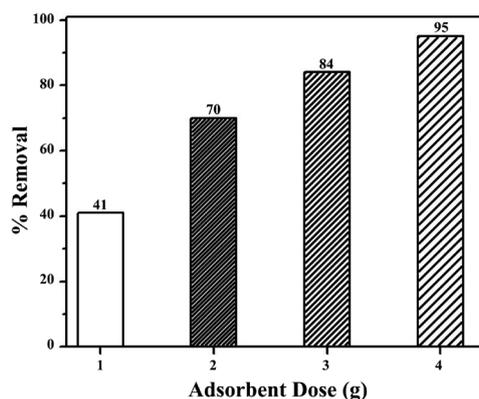


Figure 4. Effect of adsorbent dose on the BPB removal from aqueous solutions by AC.

carbon of 4 g·L⁻¹, were thus considered for the following runs.

3.2.3. Effect of pH on BPB Removal

The influence of the initial aqueous solution pH value is an important parameter that affects the adsorption process [11]. The study of BPB adsorption on activated carbon coconut shell-based is carried out during 3 h, at different pH values (3 - 11) of 10 mg·L⁻¹ BPB solution. This pH range (Figure 5) allows to investigate the evolution of BPB in two chemical forms due to its pKa 8.24 [3]. At pH < pKa, BPB existed as a neutral molecule, while it mainly existed as a negative species when pH value was higher than pKa.

Figure 6 shows the initial pH effect of BPB adsorption by AC. The maximum percentage of BPB uptake (97.87%), occurs at pH 3. However, increasing pH to 11, the adsorption capacity decreases to 82.51%. As the pH of the system increases, the number of negatively charged binding sites would increase. Therefore, at low pH range, the surfaces of activated carbon might become positively charged due to the excess of H⁺ ion in solution. The electrostatic attraction between BPB molecule and the adsorbent surface increase the amount of BPB adsorbed. At the high pH range, the surface of activated carbon might become negatively charged due to excess of OH⁻ ions concentration, which will compete with BPB for the available positively charged sites on the adsorbent

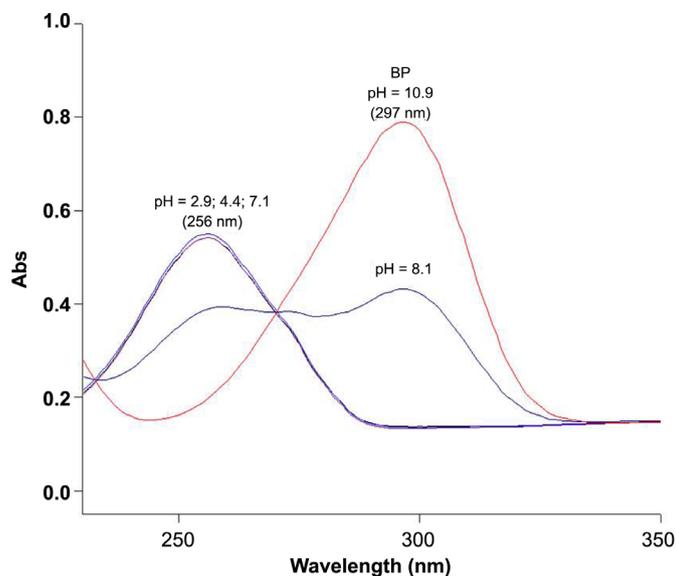


Figure 5. BPB species versus pH.

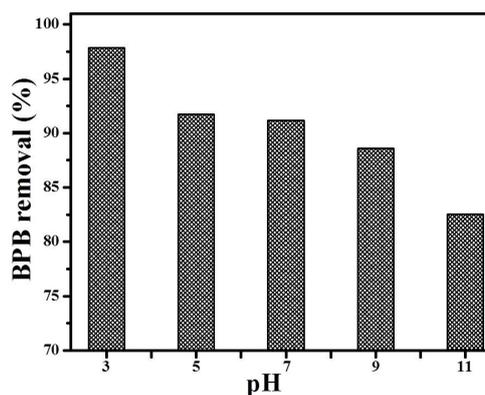


Figure 6. Effect of initial pH solution on the BPB adsorption from aqueous solutions by AC.

surface, thus decreasing the removal efficiency of BPB. **Figure 5** shows in addition that, at $\text{pH} > \text{pKa}$, BPB is in its deprotonated ionic (maximum wavelength is 297 nm) form due to the ionization of the hydroxyl group, increasing its hydrophobicity. In these conditions, the adsorption process was governed by physical phenomenon. The high removal value (85.51%) was mainly due to the BPB ionization, that gave an ionic form with different wavelength (297 nm).

Some authors [27] [28] assumed that the presence of functional groups on the adsorbent surface influences the adsorption ability. The activated carbon efficiency could be depend on several mechanisms in the removal of the BPB. In this study, the adsorption process versus pH shows that ion-exchange, electrostatic interactions, capillarity and BPB ionization form are involved in the removal mechanism. Similar phenomena were observed in the work reported by Hawari *et al.* [29].

3.2.4. Adsorption Isotherm Studies

The equilibrium adsorption isotherms are important in the development of adsorption process. Adsorption characteristics of an adsorbent are used to estimate the adsorbent/adsorbate interaction. In this study, four isotherm models were used to investigate and elucidate the adsorption behavior of BPB onto activated carbon. Data obtained from the experiments were fitted by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models.

1) Langmuir isotherm

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface [30]. The linearized form of the Langmuir isotherm is described by the following equation:

$$1/Q_e = 1/Q_m K_L C_R + 1/Q_m \quad (3)$$

where, Q_e is the amount of BPB adsorbed per mass of adsorbent ($\text{mg}\cdot\text{g}^{-1}$), C_r is the residual concentration of BPB, Q_m is the monolayer adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) and K_L is the Langmuir constant. The isotherm parameters, Q_m , K_L and the coefficient of correlation are presented in **Table 4**. The sorption capacity, Q_m , which is a measure of the maximum sorption capacity corresponding to the complete monolayer coverage showed that the activated carbon adsorption capacity for BPB was $7.519 \text{ mg}\cdot\text{g}^{-1}$. The adsorption coefficient, K_L , related to the apparent energy of sorption is $0.093 \text{ L}\cdot\text{mg}^{-1}$ and the correlation coefficient 0.979. This observation showed that the energy of adsorption is not very favorable to BPB, probably due to its weak interaction between BPB molecules and the activated carbon surface properties. The same capacity order was reported [28] for organic compounds sorption on coconut shell activated carbon. According to the Langmuir model this could suggest some homogeneity in the surface or pores of the activated carbon [31].

The essential factor K_L is used to evaluate the feasibility of the adsorption process as favorably and nature of the isotherm.

$$R_L = 1/(1 + K_L C_i) \quad (4)$$

where K_L is the Langmuir constant and C_i is the initial concentration of BPB.

The R_L value for BPB adsorption on activated carbon is 0.64 ($0 < R_L < 1$), indicating that the adsorption process is favorable [32].

2) Freundlich isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The linearized form of the Freundlich isotherm is given by:

$$\ln Q_e = \ln \ln K_F + \ln C_e \times 1/n \quad (5)$$

where K_F is the Freundlich isotherm constant related to the adsorption capacity, whereas n describes the adsorption intensity [33]. **Table 4** shows that the adsorption data for activated carbon were found to fit with Freundlich model having a correlation coefficient of 0.973. The Freundlich adsorption equation assumes that a multi-layer adsorption could occur on the surface of the

Table 4. Adsorption isotherm parameters for the removal of BPB by activated carbon.

Isotherm					
Langmuir			Freundlich		
Q (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	K_f (mg·g ⁻¹)	n	R^2
7.52	0.093	0.979	0.773	1.553	0.973
Temkin			Dubinin-Radushkevich		
b_T (kJ·mol ⁻¹)	K_T (L·mg ⁻¹)	R^2	Q_m (mg·g ⁻¹)	K_{D-R} (mol·kJ ⁻¹) ²	R^2
24.49	0.874	0.909	0.390	2.681	0.785

adsorbent [26]. The value of n obtained ($n > 1$) indicates that BPB is adsorbed on the activated carbon. This observation seems to explain the co-adsorption phenomenon due to the attraction generated by the BPB molecule after recovery the activated carbon surface, creating a multi-layer. Djilani *et al.* [34] reported similar results, when they studied the removal of methyl orange and methylene blue using activated carbon prepared from apricot stones and commercial activated carbon.

3) Temkin isotherm

The Temkin isotherm [35] reflects the fact that the heat of adsorption of all the molecules of the cover layer decreases linearly with the recovery due to the decrease of adsorbent/adsorbate interactions. The linearized form of Temkin isotherm is expressed by:

$$Q_e = RT \ln K_T \times 1/b_T + RT \ln C_e \times 1/b_T \quad (6)$$

where, b_T is the Temkin constant related to the heat of adsorption (J mol⁻¹), K_T is the equilibrium binding constant (L g⁻¹), R the gas constant (8.314 J mol⁻¹·K⁻¹), T is the absolute temperature (K), Q_e is the amount of BPB adsorbed per mass of adsorbent (mg·g⁻¹) and C_e is the residual concentration of BPB at the equilibrium. The values of the parameters are given in **Table 4**. The correlation coefficient ($R^2 = 0.909$) indicates that Temkin's model fits the BPB adsorption on the activated carbon. The constant of Temkin K_T (0.317 mg·g⁻¹) is less than unity, suggesting a low affinity between the adsorbate/adsorbent, and the positive value of b_T (24.49 kJ mol⁻¹) indicates that the heat of adsorption due to interactions with adsorbate decreases linearly with the recovery rate [35], and that adsorption reaction seems to be exothermic. Furthermore the surface of activated carbon can be considered homogeneous energy. This result is related to the Langmuir observation about the homogeneity of the activated carbon surface.

4) Dubinin-Raushkevich isotherm

Dubinin and Radushkevich (D-R) proposed another isotherm used for analysis [36]. D-R hypothesis involve heterogeneity of the activated carbon surface. This isotherm equation is applied to estimate the characteristics porosity and the apparent free energy adsorption [37]. The linear form of the D-R equation is represented below:

$$\ln Q_e = \ln \ln X_m - K_{D-R} \epsilon^2 \quad (7)$$

where, $\epsilon = RT \ln(1 + 1/C_e)$, Q_e is the amount adsorbed per unit mass of adsorbent ($\text{mg}\cdot\text{g}^{-1}$), X_m is the adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), C_e is the equilibrium concentration of BPB in solution ($\text{mg}\cdot\text{L}^{-1}$), R the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), K_{D-R} is the constant related to the adsorption energy ($\text{mol}^2\cdot\text{kJ}^{-2}$) and T is the absolute temperature (K).

The plot of $\ln Q_e$ versus ϵ^2 gives a straight line. The values of X_m ($0.309 \text{ mg}\cdot\text{g}^{-1}$) and K_{D-R} ($2.681 \text{ mol}^2\cdot\text{kJ}^{-2}$) are calculated from the intercept and slope (Table 4). The porosity factor (K_{D-R}) for activated carbon toward BPB was found to be more than unity, indicating that sorption of BPB on activated carbon may not be significant. That result confirms the weak adsorption capacity calculated by the Langmuir isotherm (Figure 7). From K_{D-R} value, the mean energy of adsorption E ($\text{kJ}\cdot\text{mol}^{-1}$) is calculated using the following equation:

$$E = -1/\sqrt{2K_{D-R}} \quad (8)$$

The adsorption mechanism estimated by the magnitude of E ($0.43 \text{ kJ}\cdot\text{mol}^{-1}$) is less than $16 \text{ kJ}\cdot\text{mol}^{-1}$ for activated carbon, which indicates that adsorption seems to be given by particle diffusion.

Since there are no other published results on BPB removal by adsorption at our knowledge, the comparison with other adsorbents is done based on the adsorption capacity of activated prepared from coconut shell (Table 5).

3.2.5. Kinetic of Adsorption

The kinetics of the adsorption phenomenon are determined by the mass transfer

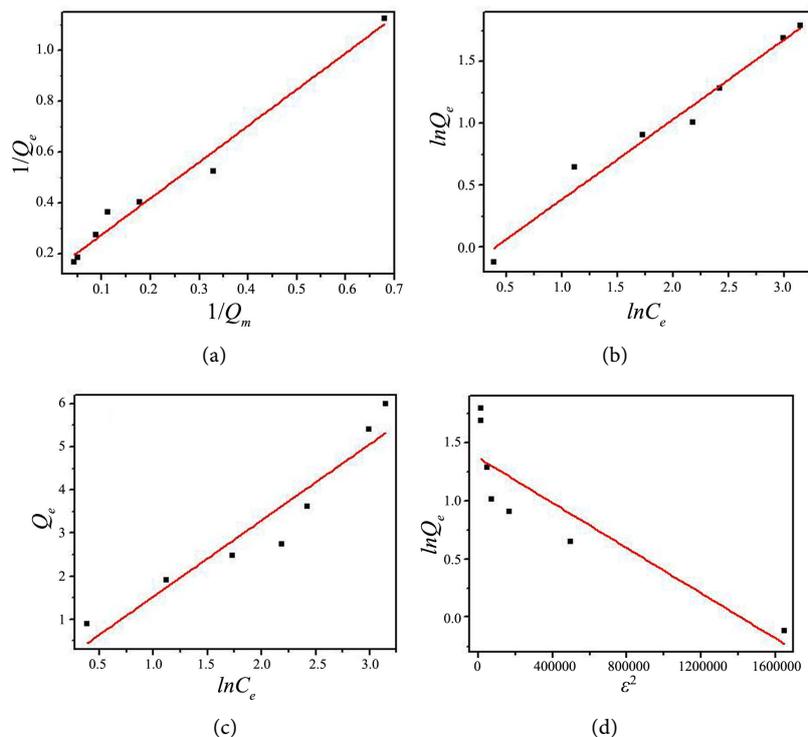


Figure 7. The Langmuir (a); Freundlich (b); Temkin (c) and Dubinin-Radushkevich (d) isotherm models for BPB adsorption using AC.

Table 5. Comparison of adsorption capacity of activated carbon based on coconut shell.

Pollutant	Adsorption Capacity (mg·g ⁻¹)	Reference
Reactive Blue 19	2.78	[28]
Ammonium ions	2.32	[38]
Zn (II)	4.28	[39]
BPB	7.52	This study

to the liquid-solid interface. Adsorption kinetics modelling provides best information about the reaction pathways. The results are fitted according to different kinetics models such as the pseudo-first order equation [40], pseudo-second order equation [41] and intra-particle diffusion [35].

There are three steps in an adsorption process [42]. The first one is the external mass transfer of the adsorbate from the bulk solution to adsorbent. The second one is the internal diffusion of the adsorbate to the sorption sites and the last step is the sorption itself. The pseudo-first order and the pseudo-second order are based on the fact that the sorption is the rate limiting step in the adsorption process.

1) Pseudo-first order model

The adsorption of pseudo-first order equation is established by Lagergren in 1898 [40] and the corresponding equation is given as below:

$$\ln \ln(Q_e - Q) = \ln Q_e - k_1 t \quad (9)$$

where k_1 (min⁻¹) is the rate constant of the adsorption, Q and Q_e are the amount adsorbed at any time and at equilibrium respectively. The plot of $\ln(Q_e - Q)$ versus t give a straight line with correlation coefficient of 0.988, indicating the applicability of this equation. The values of k_{ad} and Q_e are calculated from the slope and intercept. The calculated value Q_{theo} (0.31 mg·g⁻¹) found from pseudo-first order equation (Table 6) is lesser than the experimental Q_{exp} (0.39 mg·g⁻¹).

2) Pseudo-second order model

The experimental data are tested for pseudo-second order, according to Ho and McKay's [41] equation:

$$t/Q = 1/K_2 Q_e^2 + t/Q_e \quad (10)$$

where k_2 is the rate constant of sorption (g mg⁻¹·min⁻¹); Q_e is the amount of adsorbate at equilibrium (mg·g⁻¹); Q is the amount of adsorbate on the surface of the adsorbent at any time (mg·g⁻¹). The plot of t/Q versus t gives a straight line with correlation coefficient 0.995. The calculated adsorption capacity from the pseudo-second order equation (Table 6) is more than the experimental Q_{exp} (0.39 mg·g⁻¹).

3) Normalized standard deviation equation ($\Delta Q(\%)$)

According to the correlation coefficient, the two models are close to the unity which accurately shows that the adsorption of BPB on this activated carbon follows pseudo second order. A normalized standard deviation, $\Delta Q(\%)$ is

Table 6. Kinetic parameters for adsorption of BPB on AC by Lagergren equations.

Pseudo-first-order model					Pseudo-second-order model			
$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg·g ⁻¹)	k_1 (min ⁻¹)	ΔQ (%)	R^2	$q_{e,cal}$ (mg·g ⁻¹)	$\frac{K_2}{(g\ mg^{-1}\cdot\min^{-1})}$	ΔQ (%)	R^2
0.39	0.31	0.022	20.4	0.988	0.43	0.109	10.2	0.995

calculated to compare the efficiency of adsorption isotherms.

$$\Delta Q(\%) = 100 \times \left(\sum \left[\frac{(Q_t^{\text{exp}} - Q_t^{\text{cal}})}{Q_t^{\text{exp}}} \right]^2 \right)^{1/2} / (n-1) \quad (11)$$

where, Q_t^{exp} is the experimental amount adsorbed at different time t , Q_t^{cal} is the calculated amount adsorbed at different times and n is the number of observations. The $\Delta Q(\%)$ value of pseudo second order ($\Delta Q(\%) = 10.2$) is smaller than that of the pseudo first order ($\Delta Q(\%) = 20.4$), confirming that the adsorption of BPB on activated carbon follows the pseudo second order equation (Figure 8) which is in good agreement with experimental Q_e for the activated carbon (Table 6).

4) Intra-particle diffusion model

The intra-particle diffusion model (Figure 9) was used to verify the effect of mass transfer resistance on the binding of BPB to activated carbon. This model was described by [35]:

$$q_t = K_p t^{1/2} + C \quad (12)$$

where, q_t is the amount of BPB adsorbed at time t , C is the resistance to the mass transfer in the film and K_p is the intra-particle diffusion rate constant (mg g⁻¹·min^{1/2}).

The value of (K_p), C and the correlation coefficient are given in Table 7. The correlation coefficient ($R^2 = 0.943$) indicates that the intra-particle transport is not the only rate of BPB adsorption onto activated carbon. This could be due to the adsorption of the solvent on the activated carbon area. Which would prevent the molecules of BPB to penetrate into the pores of activated carbon.

3.2.6. Adsorption Thermodynamics

The effect of temperature on the adsorption of BPB by AC is shown in Figure 10(a). The amount of BPB adsorbed decreased slightly with increasing temperature. In order to understand more deeply the adsorption process of BPB on activated carbon from coconut carbon, thermodynamic parameters such as changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°), were evaluated.

Thermodynamic adsorption parameters are determined from the following relationships:

$$\Delta G^\circ = -RT \ln K_L \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

where, K_L is Langmuir constant determined from the Langmuir isotherm.

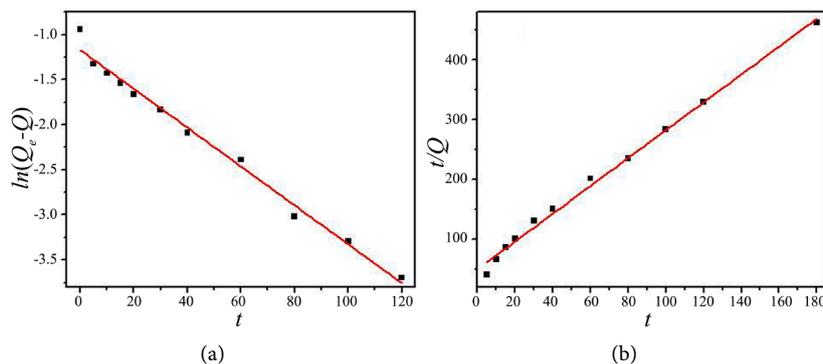


Figure 8. The pseudo-first-order (a) and pseudo-second-order (b) kinetics data of BPB adsorption on AC.

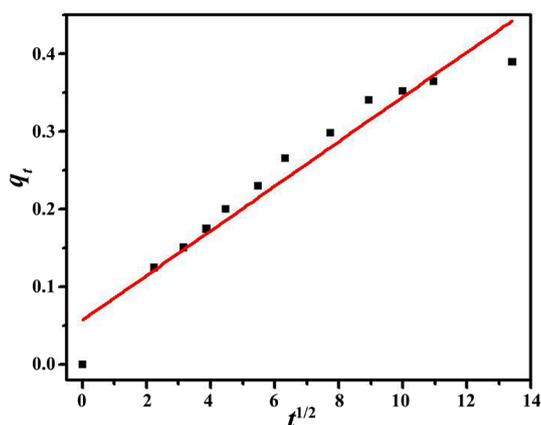


Figure 9. The intra-particle diffusion kinetics data of different BPB adsorption on AC.

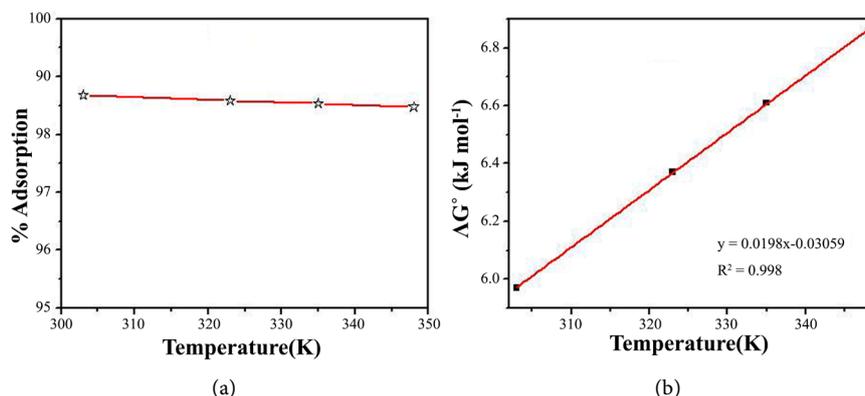
Table 7. Kinetic parameters for adsorption of BPB on AC by intra-particle diffusion equation.

Intra-particle diffusion		
k_p (mg g ⁻¹ min ^{-1/2})	C (mg g ⁻¹)	R^2
0.029	0.058	0.943

The results are summarized in **Table 8**. The values of ΔH° and ΔS° can be determined from the intercept and the slope values, respectively, of the straight line of the plot of ΔG° against T (K) (**Figure 10(b)**). The positive values of ΔG° indicate that the adsorption of BPB on the activated carbon is not spontaneous. This result is in accordance with the intra-particle diffusion observation. The endothermic nature of the process was verified by the positive value of ΔH° (0.0002 kJ·mol⁻¹). The positive value of ΔS° (0.019 kJ mol⁻¹·K⁻¹) explains that the degree of randomness at the solid-liquid interface increased during BPB adsorption onto the activated carbon. Similar behavior was also reported for adsorption of Reactive Blue-19 on coconut shell based activated carbon [28].

Table 8. Values of thermodynamic parameters for BPB removal with AC.

Temperatures (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
303	5.97		
323	6.37	0.2	19
335	6.61		
348	6.86		

**Figure 10.** (a) Effect of temperature on the BPB adsorption by AC and (b) Plot of ΔG° versus T for the estimation of the thermodynamic parameters.

4. Conclusions

A cost-effective activated carbon was used as adsorbents for the removal of BPB from aqueous solution by adsorption process. The effects of some parameters (contact time, temperature, pH, and ionic strength) on adsorption were evaluated. The adsorption increased with increasing adsorbent dose, while it was decreasing with increasing pH, temperature and ionic strength. The experimental adsorption capacities of the AC for the adsorption of BPB determined as 98% in acidic media. The Langmuir adsorption capacity of the BPB was found to be 7.52 mg·g⁻¹. The adsorption was in consistent with the Langmuir, Freundlich and Temkin isotherm models and with the pseudo-second order kinetic model. The adsorption was of non-spontaneous and endothermic nature. The CBAC could be also used for the process design and it could be used as a potential adsorbent for the removal of various compounds from wastewaters.

The coconut shells used in this present work are considered as waste and abundantly available with promises affordable adsorbent for the removal of BPB from aqueous solution that is suitable for the wastewater treatment.

Conflict of interest

The authors declare no competing financial interest.

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