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Effect of pH on Adsorption of Amoxycillin Trihydrate using Activated Charcoal from Maerua Decumbens

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Abstract

Most pharmaceutical wastewaters contain amoxycillin trihydrate in trace or significant amounts. These compounds are toxic to aquatic life; and by extension to humans. Adsorption is one of the successful methods used to remove these pollutants from water. However, most pharmaceutical effluents occur in a wide range of pH which is a key parameter of adsorption process. This study aimed at evaluating the most feasible pH value for optimized adsorption of amoxycillin trihydrate using Maerua decumbens activated charcoal. *M.* decumbens charcoal and activated charcoal were prepared and characterized for functional groups. 500ml of 5g/L amoxycillin trihydrate sorbate was then subjected to batch adsorption at 300rpm for 2 hours. The sorbent weight used was 2.25g for both normal and activated charcoal. Parallel studies were conducted at 20^0C and 25^0C at varying pH values from 2.0 to 10.0. The initial (C_o) and final concentrations (C_t) were analyzed by spectroscopic absorbance at 334.5nm. The activated sorbents had more functional groups compared to that of the normal M. decumbens. This led to more adsorption efficiency of up to 77% for the activated sorbent compared to 67% for the normal sorbent. Increase in pH values increased adsorption efficiency up to pH 8.0 after which adsorption efficiency decreased. The adsorption isotherms conducted revealed formation of both monolayers and multiple layers. These findings will greatly impact on wastewater purification strategies to eradicate water pollution globally.

Keywords: Amoxycillin trihydrate; Adsorption; M decumbens; pH

Introduction

Pharmaceuticals products have shown adverse effects on aquatic and human life. Presence of estrogen from birth control pills and post-menopausal hormone treatment have feminizing effect on male fish which alter the male-to-female ratios [1]. There are appreciable risks to health of humans arising from exposure to trace levels of pharmaceuticals. The presence of antibiotic-contaminated effluents in water lead to bacteria that are antibiotic-resistant [2]. Residues of hypertensive-inducing drugs such as penicillin and their degradation products may also elicit allergic reaction in humans [3]. Penicillin antibiotics were among the first medication to be effective against many bacterial infections caused by Staphylococci and Streptococci [4]. Penicillin make up for four groups that belong to the B lactam class of antibiotics [5]. Within this group, the most consumed subgroup is amino penicillin which include ampicillin, amoxicillin, epicillin and bacampicillin [6]. Amoxicillin is a broad-spectrum semisynthetic aminopenicillin antibiotic with bactericidal activity. Amoxicillin binds to and inactivates penicillin binding protein (PBP) located on the inner membrane of the bacterial cell wall. Inactivation of PBPs interferes with cross linkage of peptidoglycan chains necessary for bacterial cell wall synthesis [7]. This results in weakening bacteria cell wall and cause cell lysis [7]. Amoxicillin trihydrate is a broad spectrum semisynthetic antibiotic similar to ampicillin [8]. Its resistance to gastric acid permits high serum levels with oral administrator. Amoxicillin and ciprofloxacin antibiotics are excreted in significantly large quantities in pharmaceutical areas or production industries [9]. They are therefore likely to end up in domestic wastewater in significant quantities. Presence of these compounds in water bodies thereafter cause harm to marine and human life. Amoxicillin trihydrate has a broad structure with expansive sites [6]. Due to its structure, adsorption is the most suitable means for its removal. The expansive sites of carbon (especially charcoal) make it a prime adsorbent material. Activation of the charcoal by heating with salts at high temperatures is used to optimize on adsorption efficiency of charcoal [10]. Activated charcoal is an odorless and tasteless powder. It is able to absorb thousands of times its own weight in gases, heavy metals, poisons and chemical often making them ineffective [11]. Activated charcoal has been used in adsorption of several drugs [12]. Some of these drugs include acetaminophen, digoxin, theophylline, tricyclic and antidepressants [13]. The type of tree used in preparation of charcoal and activated charcoal is also fundamental in the ultimate adsorption efficiency of the activated charcoal. Charcoal from *Maerua decumbens* tree has been characterized to have numerous adsorption sites [14]. Maerua decumbens is a shrub or a woody herb species in the Capparaceae family [15]. It grows to a height of 0.5m to 3m with a large swollen root. It mainly occurs naturally in arid and semi-arid areas in Kenya. This plant was traditionally used by rural communities in Kenya for medicinal purposes. Its charcoal was used for water purification. This study aimed at investigating the effects of adsorbate pH on the efficiency of adsorption of amoxycillin trihydrate using *M. decumbens* activated charcoal. This is because most pharmaceutical effluents containing amoxycillin trihydrate occur in a wide pH range. A lot of effort is used in adsorption of these effluents without knowing the exact adsorbent pH for efficient removal of the pollutants.

Materials and Methods

Design of experiment

Activated charcoal was obtained from mixing *M. decumbens* charcoal with concentrated sulfuric acid. *M. decumbens* charcoal was characterized for change in adsorptive functional groups before and after activation. Adsorption studies of amoxycillin trihydrate were carried out at varying adsorbate pH (i.e from pH 2.0 to 10.0). UV VIS spectroscopy was used to quantify the levels of the adsorbate removed. Thereafter, adsorption modelling studies were carried out to determine the nature of the processes at different temperature conditions. Monitoring of the adsorption columns was done at Maasai Mara University, Narok, Kenya while UV VIS analysis was conducted at Lab and Allied pharmaceuticals Co., and Nairobi, Kenya.

Methods

Chemicals and reagents used

Sulfuric acid (98% pure), nitric acid (65% pure) and sodium hydroxide (95% pure) were all obtained from Sigma (St Louis, USA). Amoxycillin trihydrate solution and standards (all 98% pure) were obtained from Lab and Allied Pharmaceuticals (Nairobi, Kenya).

Preparation of adsorbate

M. decumbens was collected from Narok region in Kenya. Its charcoal powder was mixed with concentrated sulfuric acid (10ml of the acid for every 100g of the charcoal powder). The mixture was left for 48 hours then washed with enough distilled water. The mixture was then concentrated to remove any moisture and acid mists present before re-crushing to fine powder. The activated carbon was dried in an oven at 120°C for 6 hours and stored in a desiccator until use. A sample of the powder was characterized for functional groups before and after activation. Shimadzu-119 FT-IR was used for this characterization. The dry powder was then adjusted to varying pH levels using dilute nitric acid and sodium hydroxide solutions. pH levels of 2.0 to 10.0 were prepared. A pH meter, Hanna G-114 model was used.

Preparation of adsorbent and adsorption process

A batch model reactor with 2.25g of the adsorbent and 500ml of amoxycillin trihydrate in a 1000ml flask. The reactors were agitated using a magnetic stirrer at 300rpm. 5g/L amoxycillin trihydrate solution (C_0) was used for adsorption. Adsorption was carried out at room temperature with a constant contact time of 2 hours. Analysis of the adsorbate concentration before and after analysis was carried out using UV VIS spectrometer (model UV 25-1950). The absorbance was checked at the wavelength 334.5nm. A calibration curve was obtained from which the sample concentrations were calculated. Distilled water was used as the blank in the analyses.

Data analysis

Data was represented as mean ± standard deviation; for each quadruple analysis. The level of significance was set at 0.05. 3 degrees of freedoms were used. Statistical analysis was done using Ms Excel and OriginLab (version 6.5).

Results and Discussions

Characterization of Functional groups in M. decumbens charcoal

Activation of *M. decumbens* charcoal imprinted more functional groups onto the adsorbent. As a rule of thumb, the more the organic functional groups present, the more the adsorption sites increase. A good adsorbate should have many active sites for the mobile adsorbate to attach to. Activation of *M. decumbens* increased the peak at 3805.4cm^{-1}, resulting from adsorbed water as a result of the activation process. A peak due to alcoholic -OH at 3184.4cm^{-1} was slightly shifted to 3199.2cm^{-1} with slight increase in its intensity. This peak is crucial in attracting and binding protons in the adsorbate which are in solution. The sp acetylenic triple carbon bond at 2550.6cm^{-1} in the normal charcoal was shifted to 2651.0cm^{-1}. Acetylenic groups are quite unstable and thus form a site of reaction in their compounds. A similar peak shift was observed for amide groups in the adsorbent (from 2198.7cm^{-1} in the normal charcoal to 2089.0cm^{-1} in the activated charcoal) (Figure 1). Pyrrole, which has this functional group have frequently been used to enhance the adsorption efficiency of cellulose [16]. Other compounds containing amide groups have also been used to functionalize various adsorbents (with varying success rates) [17]. These peaks are seen to result from amino groups due to unburnt biomass in the charcoal. Activation of the charcoal also introduced some peaks which were absent in the normal M. decumbens charcoal. There were peaks between 1500-2000cm^{-1} as a result of carbonyl groups, aromatic and aliphatic double bonds. These peaks further increase the reactivity of the adsorbent. Presence of the carbonyl peak (at 1733.3cm^{-1}) as well as -C-O-H peak (at 1031.2cm^{-1}) in the activated charcoal indicate presence of carboxylic groups [18]. Found out that aliphatic and phenolic hydroxyl groups as well as -COOH groups in adsorbent surfaces promote more reactions with the adsorbate leading to higher efficiency rates. One of the major adsorption reactions mentioned is esterification [19]. Several aromatic groups have also been used to functionalize adsorbents in wastewater purification [20]. These functionalizing and modifier groups also increase the re-usability potential of the adsorbent. An adsorbent with these groups embedded on its surface (like activated *M. decumbens* charcoal powder) is thus likely to have a longer life span. The activated charcoal powder had peaks between 650-1000cm^{-1} due to benzylic groups, organometallic and organohalide compounds. These groups are attributable to impurities in the sulfuric acid used for activation. The peaks are however crucial in enhancing more ion-exchange reactions with the adsorbate.

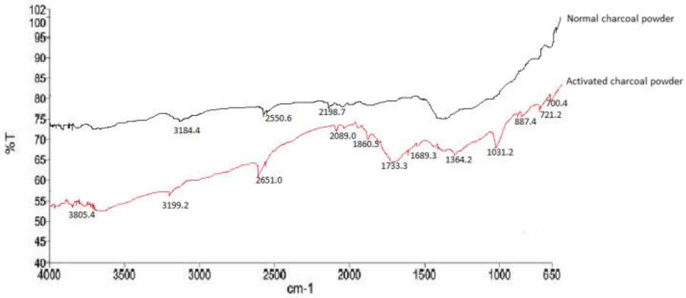

Figure 1: *FT-IR spectra of M. decumbens charcoal and activated charcoal powder.*

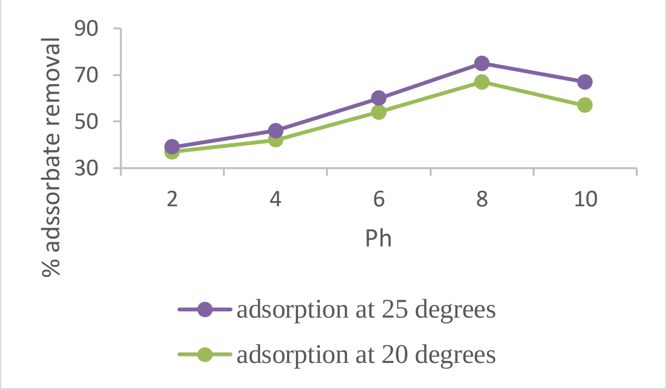

Figure 2: *Percentage removal of amoxycillin trihydrate using normal M. decumbens charcoal powder.*

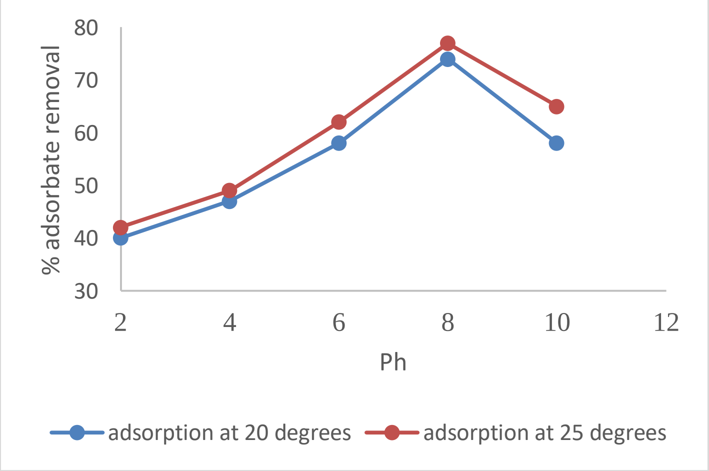

Figure 3: *Percentage removal of amoxycillin trihydrate using activated M. decumbens charcoal powder.*

Effect of pH on adsorption process

The activated charcoal powder was found to have a higher adsorption efficiency compared to the normal one (Tables 1 and 2). The samples exposed to a higher temperature (25^{0}C) were also found to be slightly more efficient in the adsorption process. The optimum adsorption efficiencies were found at pH 8.0. Adsorption efficiency increased with increasing pH from pH 2.0 up to pH 8.0 and decreased after this pH value. These findings concur with those of Boukhelkhal [21]. Who observed efficient removal of amoxycillin using wheat bran at pH 7.0 and 25^{0}C. From the table, there was a significant increase in adsorption efficiency from the normal to the activated charcoal. This can be attributed to the increase in the active adsorption sites imprinted onto the charcoal during activation process. Increase in adsorption with pH values results from the ionization of amoxycillin trihydrate compound in solution. The structure of amoxycillin trihydrate contain ionizable protons, amine and hydroxyl groups. At neutral pH, the zwitterionic form of this compound exist. The structure is thus quite polarized and can easily bind onto the adsorbent material. Organic acids and bases, like amoxycillin compounds depend on the correlation between pH and pKa values. At pH 8.0, the pKa of amoxycillin is less than its pH increasing the dissociated amoxycillin compounds. This has a positive effect on the rate of adsorption. (Figures 2 and 3) below shows the extent of amoxycillin trihydrate adsorbed at varying pH values. At low pH values, the dissolution constant, pKa of amoxycillin trihydrate is quite high limiting ionization of this compound. Therefore, the compound is less polar and interactions with the adsorbent are limited. This trend decreases gradually and at pH 8.0, the pH value is more than the dissolution constant. The compound easily ionizes and is charged leading to more interactions with the adsorbent. However, at high pH values above 9.0, there is more competition for the active sites between the adsorbate and hydroxyl ions from the buffering reagent (sodium hydroxide). This competition limits the chances of adsorption of amoxycillin trihydrate. The samples subjected at 25^{0}C experienced a higher adsorption efficiency compared to those at 20^{0}C. This is attributed to increased polarization of the adsorbate with temperature leading to more interactions with the adsorbent.

Effect of temperature on the adsorption isotherms

Langmuir isotherms of the adsorbents showed that the adsorption processes gave monolayers. A homogenous type of adsorption had occurred in all the adsorbents. The R^{2} values for the isotherms was unity (one) (Figures 4 and 5) thus ascertaining homogenous adsorptions [22]. Found out similar adsorption isotherms in adsorption of amoxycillin from pharmaceutical wastewater. Increase in temperature did not have a significant effect on the R^{2} value of the models. However, temperature increase reduced the adsorption capacities (from the y-intercept values) of both normal and activated *M. decumbens* charcoal. The adsorption isotherms were confirmed for formation of multiple layers by Freundlich and Temkin isotherms.

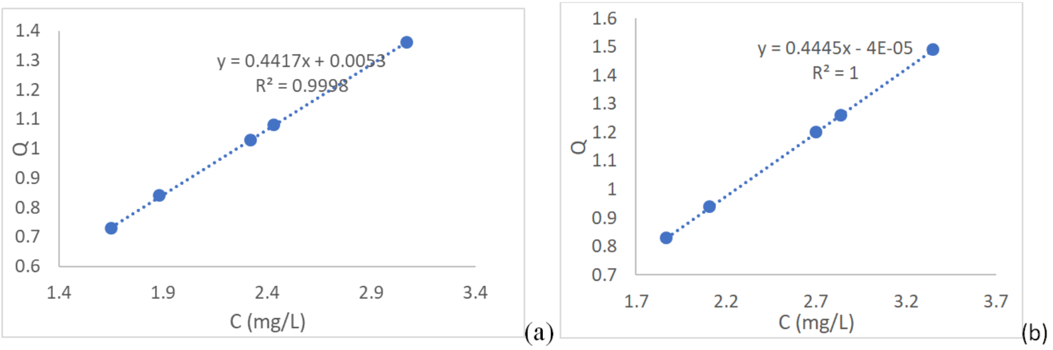

Figure 4: *Langmuir isotherms for adsorption of amoxycillin trihydrate using normal charcoal at 20^{0}C (a) and 25^{0}C (b).*

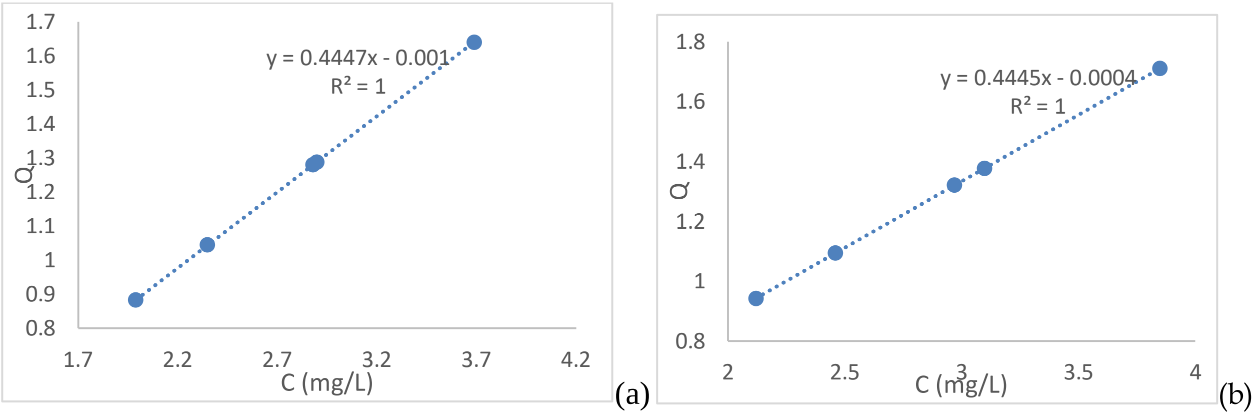

Figure 5: *Langmuir isotherms for adsorption of amoxycillin trihydrate using activated charcoal at 20^{0}C (a) and 25^{0}C (b).*

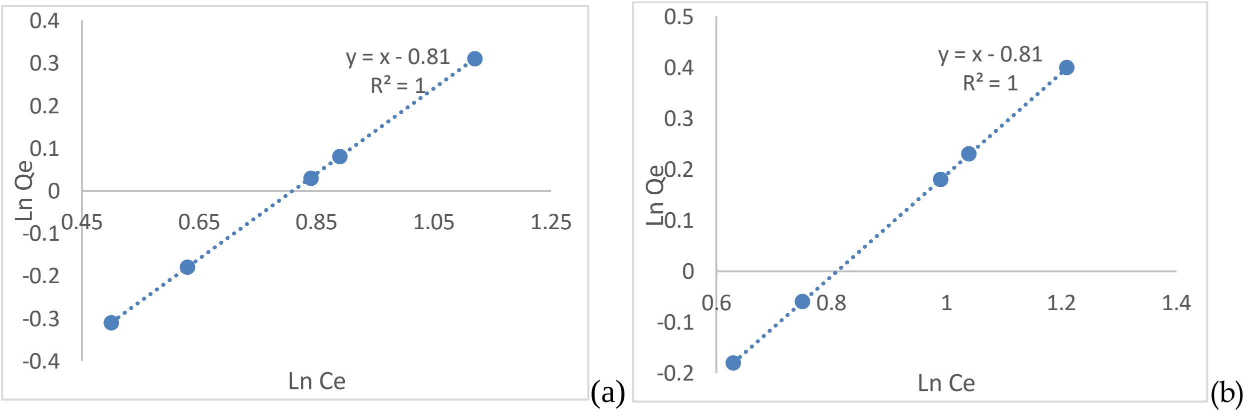

Figure 6: *Freundlich isotherms for adsorption of amoxycillin trihydrate on normal M. decumbens charcoal at 20^{0}C (a) and 25^{0}C (b).*

The adsorption process was found to linearly fit Freundlich isotherm model of both normal and activated adsorbents. The temperature of adsorption process did not play any significant role in determining the formation of heterogenous layers. The slopes of all the adsorbent models were relatively similar (0.44 ± 0.005). However, the y-intercepts were quite negligible citing less adsorbate intensity in the models (Figures 6 and 7) below illustrates the Freundlich models plotted. Since both the Langmuir and Freundlich isotherms linearly fitted in almost all the sorbents used, it is feasible to conclude that the adsorbents had different particle sizes to enable both homogenous and heterogenous layers [22]. Such an adsorbent is efficient for optimized removal of pollutants in pharmaceutical wastewater. The y-intercept of the activated and normal sorbents were quite similar (0.81± 0.005). However, the slopes of the activated sorbents were significantly higher than those of the normal sorbents ($\alpha \geq 0.05$, n= 3). This implies that while the minimum adsorption capacity of *M. decumbens* charcoal powder was similar for normal and activated charcoal, their adsorption intensities varied. There were also indirect adsorbent/adsorbate interactions arising from interactions between the adsorbent and sorbates. This information was confirmed by the Temkin models in (Figures 8 and 9) below. The R^2 values of the models were found to increase with temperature for the two sets of adsorbents (i.e normal and activated *M.* decumbens). Increase in temperature led to more interactions due to increased kinetic motion of the adsorbates around the adsorbent. The heat of adsorption (ΔH_{ads}) of the molecules in the adsorption processes decreased with increase in temperature since adsorbent coverage is increasing [22].

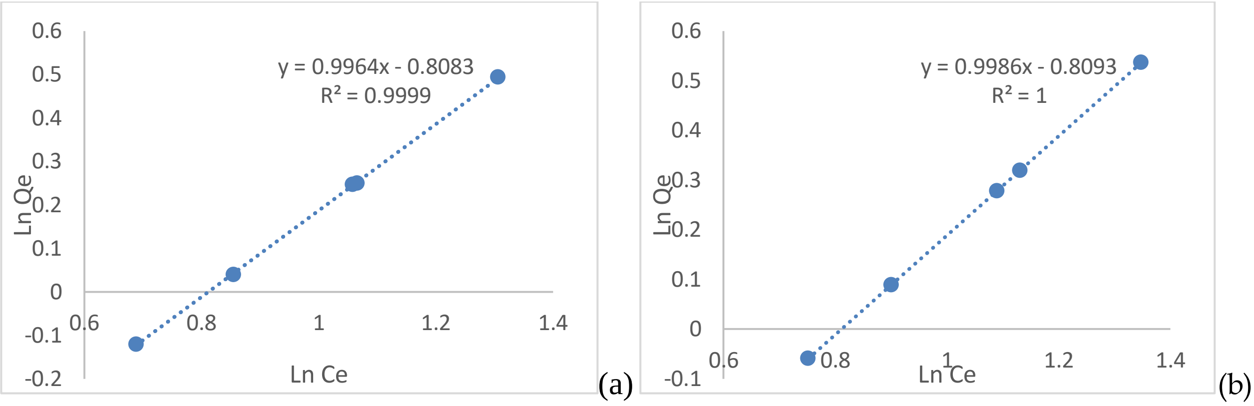

***Figure 7:** Freundlich isotherms for adsorption of amoxycillin trihydrate on activated M. decumbens charcoal at 20^{0}C (a) and 25^{0}C (b).*

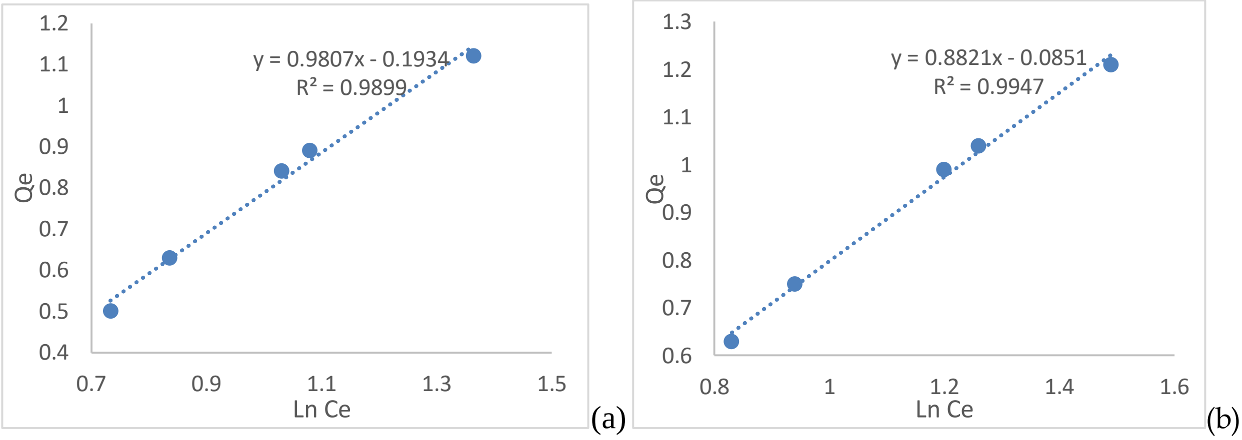

***Figure 8:** Temkin adsorption models of amoxycillin trihydrate on normal M. decumbens charcoal powder at 20^{0}C (a) and 25^{0}C (b).*

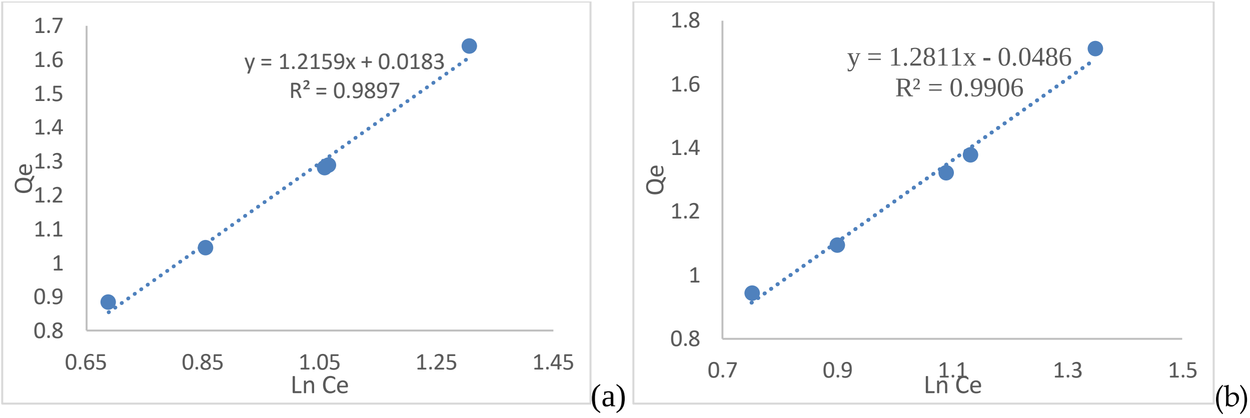

***Figure 9:** Temkin adsorption models of amoxycillin trihydrate on activated M. decumbens charcoal powder at 20^{0}C (a) and 25^{0}C (b).*

***Table 1:** Effect of pH on adsorption of Amoxycillin trihydrate using normal M. decumbens charcoal.*

Adsorbate pH	Initial concentration (C_o) (g/L)	Final concentration (C_t) (g/L)	
		20^{0}C	25^{0}C
2.0	5.0	3.35	3.13
4.0	5.0	3.12	2.89
6.0	5.0	2.68	2.30
8.0	5.0	1.93	1.65
10.0	5.0	2.57	2.16

***Table 2:** Effect of pH on adsorption of Amoxycillin trihydrate using activated M. decumbens charcoal.*

Adsorbate pH	Initial concentration (C_o) (g/L)	Final concentration (C_t) (g/L)	
		20^{0}C	25^{0}C
2.0	5.0	3.01	2.88
4.0	5.0	2.65	2.54
6.0	5.0	2.10	1.90
8.0	5.0	1.31	1.15
10.0	5.0	2.12	2.03

The slopes of the models of sorbents with activated charcoal were significantly higher than those of normal *M. decumbens* charcoal ($\alpha \geq 0.05$, $n = 3$). The slope of the models can be equated to RT/b where R is universal gas constamt, T is absolute temperature and b is Temkins heat of sorption. It can therefore be concluded that the activation process reduced the heat of sorption (thus enabling more adsorption process). There was no specific trend in the adsorption capacities from the y-intercept values of the models obtained.

Conclusions

Activation of *M. decumbens* charcoal powder increased the number of adsorption peaks in the sorbent. This led to an increase in the adsorption efficiency of up to 77% in the activated charcoal compared to 67% in the normal charcoal. The adsorption efficiency increased with pH increase from pH 2.0 to pH 8.0 before reducing in pH 10.0. Optimum adsorption was thus achieved at pH 8.0. According to Langmuir and Freundlich adsorption isotherms, both homogenous and heterogenous adsorptions were obtained. From the Temkin isotherms, an increase in temperature from 20^0C to 25^0C decreased the interactions of amoxycillin trihydrate and *M. decumbens* sorbent.

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Conflicts of Interest

The authors declare to have no conflicts of interest.

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No funding was received for this work.

Data availability Statement

All the data used is enclosed within this manuscript or any supplementary sheets attached.

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