

REMOVAL OF CHLORAMPHENICOL COMPOUNDS USING HYDROCHAR FROM DRIED LEAVES

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ABSTRACT: Pharmaceutical industries' wastewater contains numerous contaminants including chloramphenicol (CAP) that harm human and aquatic lives which require the wastewater to be treated via adsorption. Hydrothermal carbonization (HTC) aids in producing hydrochar that can be converted into activated carbon at lower operating conditions to increase carbon porosity and decrease production costs. In this study, dry leaves were hydrothermally carbonized to produce hydrochar which was then activated into activated carbon prior to the removal of CAP. For CAP batch adsorption on resultant hydrochar, various operating parameters, including initial CAP concentration (10 mg/L to 50 mg/L) and solution pH (2 to 10) were utilized. Due to the high driving force for efficient mass transfer, the adsorption capacity of the initial CAP concentration increased as an increase in the adsorption capacity with a maximum value of 35.70 mg/g. The presence of the OH⁻ group enables the positive charge of CAP to attach easily to the adsorbent, thus making the basic conditions more favorable as opposed to the acidic conditions with maximum adsorption of 35.82 mg/g at pH 10. It was found that the Freundlich isotherm and pseudo-second order kinetic models suit well with the experimental data. Also, the rate-controlling step in this adsorption is chemical adsorption. According to the results, activated dried leaves derived hydrochar is a promising and cheap adsorbent for the removal of CAP from effluent wastewater.

KEYWORDS: *Adsorption, Characterization, Dried leaves, Hydrochar, Hydrothermal carbonization*

1. INTRODUCTION

In recent years, the potential threat of pharmaceuticals and personal care products to the environment has become a popular issue. Chloramphenicol (CAP), a broad-spectrum antibiotic discovered in 1947 in *Streptomyces Venezuela* is amongst the widely used in medical treatment of human and animals [1-2]. One way to treat the large amount of these compounds in pharmaceutical wastewater is by adopting adsorption techniques as these chemical compounds have high biological activity making biological treatment unsuitable to remove it. There are many sources of adsorbent including hydrochar derived activated carbon. Hydrochar derived from biomass waste via hydrothermal carbonization is an effective adsorbent for pollutant removal because of the abundance of surface oxygen-containing functional groups such as chloramphenicol (CAP) [3]. These functional groups play a crucial role in contaminant adsorption through electrostatic attraction, surface complexes, and ion exchange. Introducing new oxygen-containing functional groups, particularly carboxylate functional groups such as maleate and acetate, into hydrochar's structure and function can considerably increase its performance. As a result, the availability of surface functional groups in hydrochar can improve its adsorption effectiveness and expand the range of applications for which it can be used in

environmental clean-up [2-3]. Dried leaves are one of the potential biomass wastes that can be utilized as raw material for hydrochar as it's available abundantly with no cost. Utilizing dried leaves as source for hydrochar simultaneously solved the environmental issue related to waste management especially in urban area. Previously, Zahari and Hamid recorded 98.25% removal of methylene blue using 2.0 g of absorbent from dried leaves [4]. Meanwhile, Hamid and Thineswaren found that dried leaves that have been hydrothermally carbonized possessed unique characteristics ideally suitable to tuned into adsorbent [5]. Assessing this information earlier, dried leaves hydrochar has been proposed to solve the pharmaceutical wastewater containing chloramphenicol by activating it with phosphoric acid to enhance its surface area and porosity.

2. MATERIALS AND METHODS

Hydrochar was prepared by the hydrothermal carbonization of dried leaves using a stainless-steel reactor. About 25 g of dry leaves and 150 ml of distilled water are placed in the 200 ml reactor, and the treatment was carried out for 2 hours at fixed hydrothermal carbonization temperatures of 200°C. The reactor was then allowed to cool to ambient temperature before the solid char was removed and filtered using filter paper. The char was then cleaned twice with distilled water and dried at 105 °C for 12 hours before being chemically impregnated with phosphoric acid. The dried hydrochar was recovered and dried for 5 hours in an oven at 105°C. The sample is then loaded onto crucible, which are subsequently placed into a quartz tube and placed inside a microwave. The sample was carbonised first in the presence of carbon dioxide (CO₂) using microwave at 511-Watt power for 6 minutes. The activated carbon was cooled to room temperature in the presence of CO₂. The resultant activated carbon (AC) was neutralised with hydrochloric acid (HCl) and sodium hydroxide (NaOH) before being thoroughly rinsed with distilled water until a pH of 7 is attained. Finally, the AC was dried in an oven at 120°C for 24 hours before being characterised and utilized in the adsorption experiment.

2.1. Characterization of Hydrochar

The surface characteristics of samples can be determined by BET surface area analyzer (determine the BET surface area), scanning electron microscopy (image the surface morphology and properties), and FTIR analyzer (determine the functional groups). Two samples of hydrochar were compared in this characterization study which are hydrochar before and after activating with carbon in microwave. Both hydrochar samples were chemically impregnated with phosphoric acid with a 5:1 ratio.

2.1.1. Batch adsorption of Chloramphenicol

A UV-Vis spectrometer is used to determine the concentration of CAP for each interval. Wavelength of 278 nm is used to determine the concentration against time. Eq. (1) and (2) are used to calculate the adsorption capacity and removal efficiency of CAP:

$$\text{Adsorption capacity, } q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where;

Q_e = adsorption capacity (mg/g),

C_0 = initial concentration of CAP solution (mg/L),

C_e = equilibrium concentration of CAP solution (mg/L),

V = volume of solution (L)

W = mass of adsorbent (g)

3. RESULTS AND DISCUSSION

3.1 Surface Electron Microscopy (SEM)

SEM images in Fig. 1(a-d) show that for both precursors, the H_3PO_4 chemical activation leads to a morphological change, developing a porous structure. Based on the SEM images, the pores in hydrochar after activation are more visible and denser compared to before. Moreover, the size of pores can also be seen bigger in after sample due to the char undergoing activation process which increases the porous structure. These pores increase the efficiency of adsorption of CAP solution. Therefore, the larger the number or size of pores will result in better adsorption.

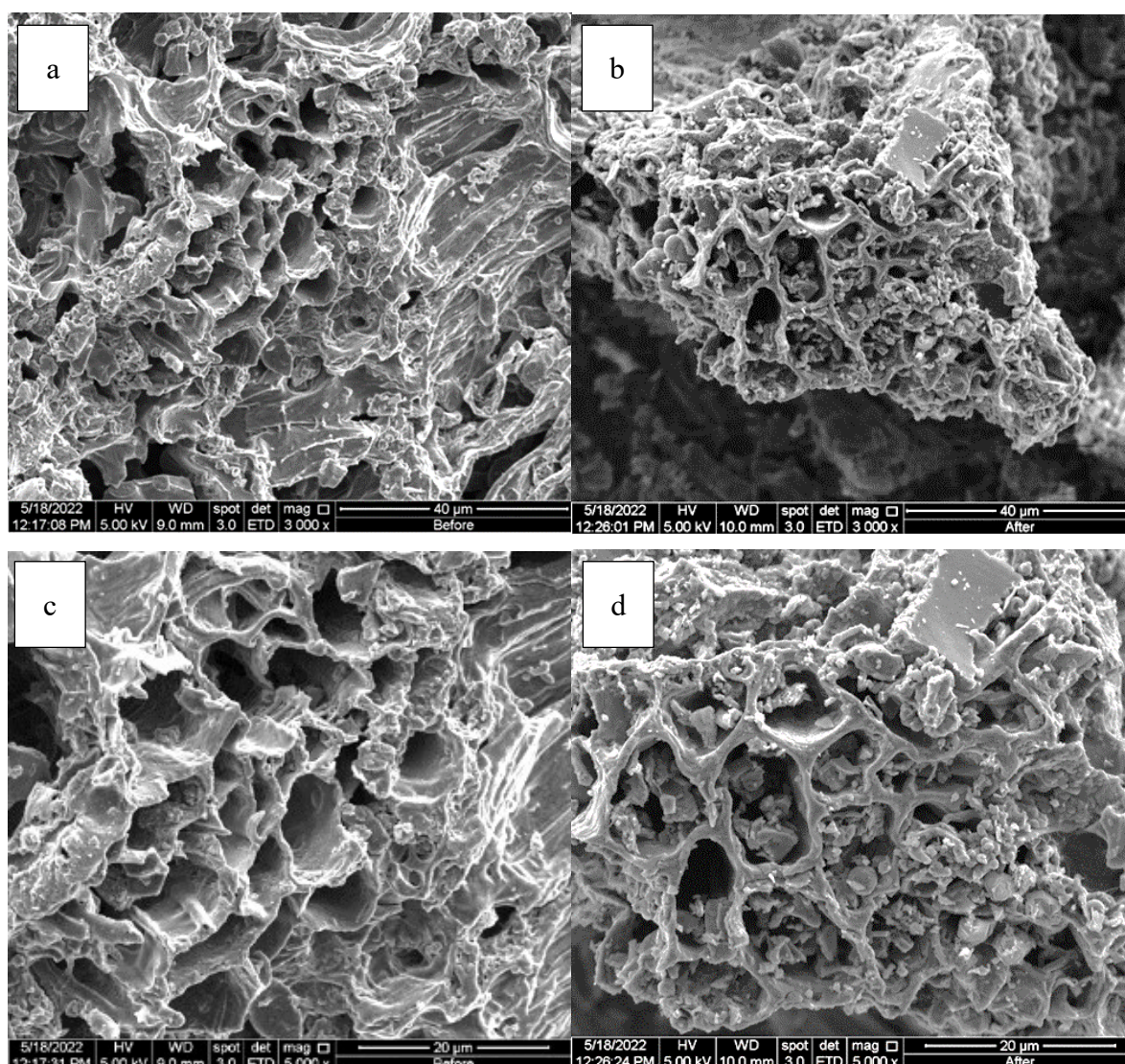


Fig. 1. SEM images before (a) and after (b) at a magnification of 3000x while (c) and (d) are before and after activation at 5000x magnification.

3.2 Fourier-Transform Infrared Spectroscopy (FTIR)

Fig. 2 shows the results of the functional group of hydrochar before and after the activation of carbon. For hydrochar prior to activation, the peaks (3795.91 cm^{-1} and 3402.43 cm^{-1}) indicated the presence of hydrate (H_2O), hydroxyl ($-\text{OH}$), ammonium, or amino, as well as oxygen-related groups such as alcohol and phenol in the plant extract. The broad peak at 2943.37 cm^{-1} was caused by aliphatic compound (C-H) stretching vibration. The peak at 2409.09 cm^{-1} indicated the presence of the triple bond (CC) in the sample. The broad peak at 1649.14 cm^{-1} was caused by the vibration of the double bond carbon ($\text{C}=\text{C}$), an olefinic compound, or an aromatic ring, whereas the peak at 1433.11 cm^{-1} and below was caused by (C-H) vibrations on an aromatic compound. In contrast, the peaks (3992.65 cm^{-1} , 3803.63 cm^{-1} , and 3414 cm^{-1}) observed after activation are due to ($-\text{OH}$) bond stretching vibration. The broad peak at 1583.56 cm^{-1} indicated the stretching of the double bond ($\text{C}=\text{C}$), whereas the peaks at 1409.96 cm^{-1} and below were caused by the vibrations of the (C-H) bond in the aromatic compound.

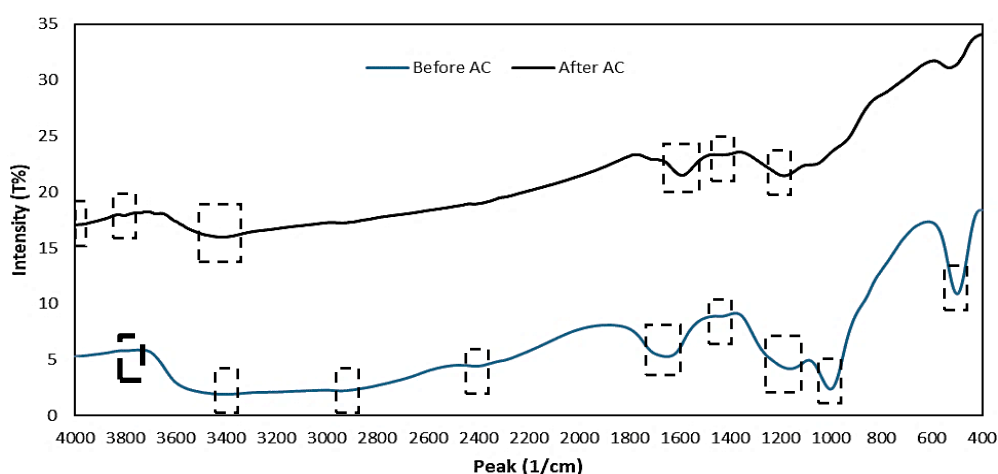


Fig. 2. FTIR result of hydrochar before and after activation.

3.3 Brunauer–Emmett–Teller (BET)

Dried leaves hydrochar derived activated carbon possessed a relatively well-developed pore structure with BET surface area of $647.88\text{ m}^2/\text{g}$, Langmuir surface area of $913.14\text{ m}^2/\text{g}$ and total micropore volume of $0.07\text{ cm}^3/\text{g}$ as illustrated in Table 1. It is obvious that activation using phosphoric acid under carbon dioxide flow has altered the hydrochar significantly. The BET surface area of hydrochar after activation was higher compared to before activation as hydrochar derived activated carbon exerted the larger surface which then allowing for better removal of CAP in degradation studies.

Table 1. The properties of hydrochar before and after activation

Properties	Before (Hydrochar)	After (Activated hydrochar)
BET Surface Area (m^2/g)	5.3966	647.8754
Langmuir Surface Area (m^2/g)	18.2134	913.1442
t-Plot micropore volume (cm^3/g)	-0.0024	0.0676

3.4 Effect of initial concentration of CAP

Removal of CAP using dried leaves hydrochar derived activated carbon was investigated by exposing 0.2 g of adsorbent to CAP solutions with initial concentrations ranging from 10 mg/L to 50 mg/L at neutral pH and 30 °C. Manipulation of initial concentrations aids in determining the suitability of hydrochar applications in different conditions and developing cost-effective processes. At the initial stage of adsorption, the availability of more active sites on the surface of hydrochar promotes a rapid uptake of adsorbates. As shown in Fig. 3, the scenario is well represented by steeper curves observed during the first 5 minutes for each studied initial concentration. The sites are gradually occupied over time due to the competitive adsorption of CAP molecules, and only a few vacant sites are retained. At this stage, the active sites for adsorption have been saturated and difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phase [5]. The possibility of CAP desorbing from adsorbent exists if the amount of CAP absorbed on the adsorbent is in a state of dynamic equilibrium. It is worth noting that three zones were involved in the adsorption of CAP. The first zone represented fast CAP adsorption, implying rapid external diffusion and surface adsorption, while the second zone signified gradual equilibrium and the third zone denoted the equilibrium plateau. As a result, until equilibrium is reached, CAP adsorption becomes slower. Furthermore, the maximum adsorption capacity of hydrochar increased from 6.83 mg/g to 35.70 mg/g as the initial concentration of CAP solution increased from 10 mg/L to 50 mg/L. As shown in Fig. 3, the percentage of adsorption efficiency of hydrochar decreased from 96.41% to 94.89%, as the initial CAP concentration solution increased. At lower concentrations, the initial number of CAP molecules to available surface area ratio is low, and fractional adsorption becomes independent of initial concentration [6]. This could be clarified by the theory that, during the adsorption process, CAP molecules must first encounter the boundary layer effect, then diffuse from the boundary layer film onto the adsorbent surface, and finally diffuse into the porous structure of the adsorbent [7].

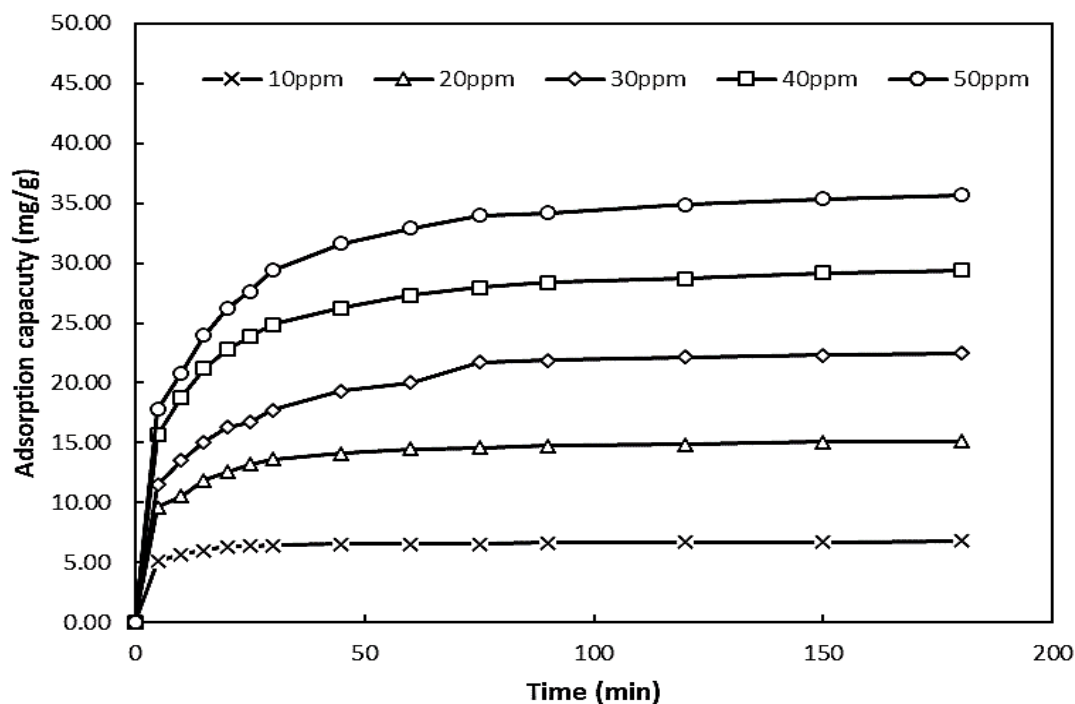


Fig. 3. CAP adsorption uptake versus adsorption time of hydrochar at different initial concentrations.

Furthermore, a longer equilibrium time was required for high initial concentrations. Adsorption equilibrium was reached after 180th minute for the highest initial concentration (50 mg/L), and at the 90th minute for the lowest initial concentration (10 mg/L). This is because, as the adsorbent surface becomes saturated, most of the sorbate molecules diffuse into the porous structure of hydrochar. Because the diffusion mechanism increases the mass transfer resistance to adsorption, higher initial concentrations require a longer contact time to achieve equilibrium with the adsorbent.

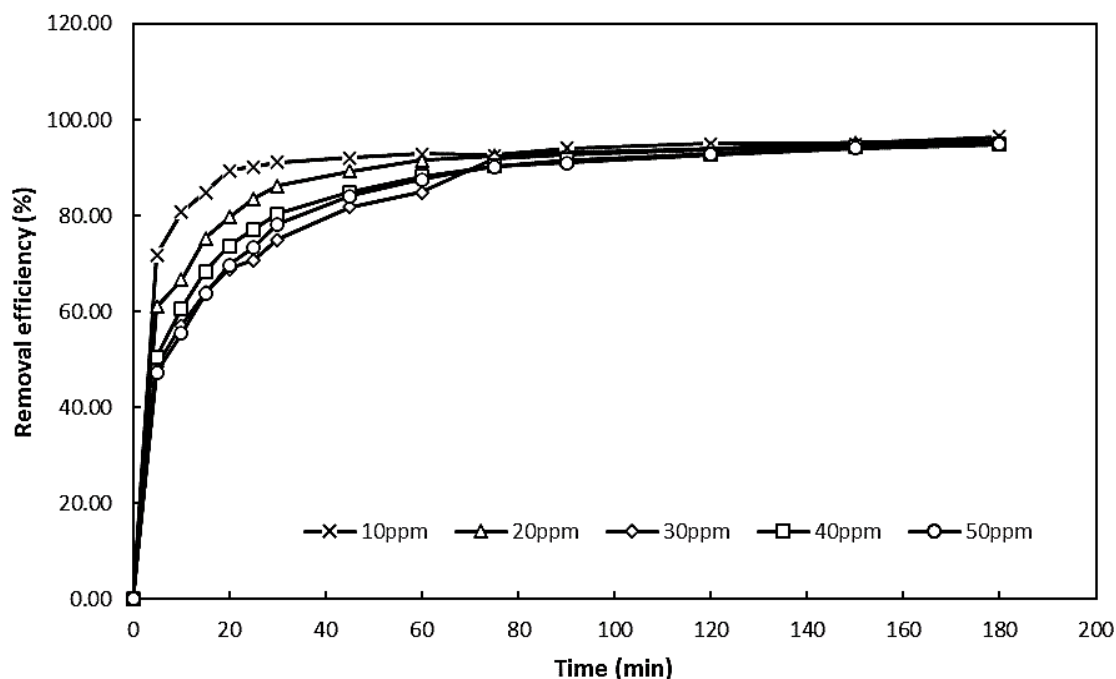


Fig. 4. CAP percentage removal versus adsorption time of hydrochar at different initial concentrations

3.5 Effect of pH of solution

To investigate the effect of solution pH on CAP adsorption, 0.2 g of hydrochar was exposed to 50 mg/L CAP solution at 30 °C at various initial pH levels ranging from pH 2 to pH 10. The pH value was adjusted accordingly by adding hydrochloric acid or sodium hydroxide solution, and the time-dependent adsorption profile is shown in Fig. 3. The adsorption performance improved with contact time until the equilibrium state was reached. Under extremely acidic conditions, CAP molecule uptake was relatively low because hydrochar had the lowest adsorption capacity at equilibrium with a value of 32.74 mg/g. This is because the cationic CAP molecules generate a strong electrostatic repulsion on the surface of hydrochar with a high concentration of H⁺ ions in an acidic environment. Furthermore, according to Islam et al. [4] the presence of OH groups on the surface of hydrochar causes protonation of the OH group and creates a competition between H⁺ ions and CAP molecules to bind with the active sites, resulting in a low affinity. Adsorption capacity-time curves demonstrated that adsorption increased from acidic to basic conditions, with a maximum equilibrium adsorption capacity of 35.82 mg/g at pH 10. Furthermore, the removal efficiency of CAP increases as the pH increases. The removal efficiency at most acidic condition (pH = 2) is 87.29% while at basic condition (pH = 10) is 91.90%. In contrast to acidic solutions, increasing the pH of the solution enhanced the negatively charged active sites on the adsorbent surface in the presence of OH groups and improved adsorption performance. Due to the dissociation of the hydroxyl group,

CAP has a positive charge when dissolved in water. In alkaline solutions, it is more strongly attracted to the negatively charged surface of activated carbon. However, a slight increase in adsorption capacity was observed for solutions ranging from pH 2 to pH 8. It is easily explained that the H^+ and OH^- ions are nearly balanced within these three pH values, resulting in no noticeable competition.

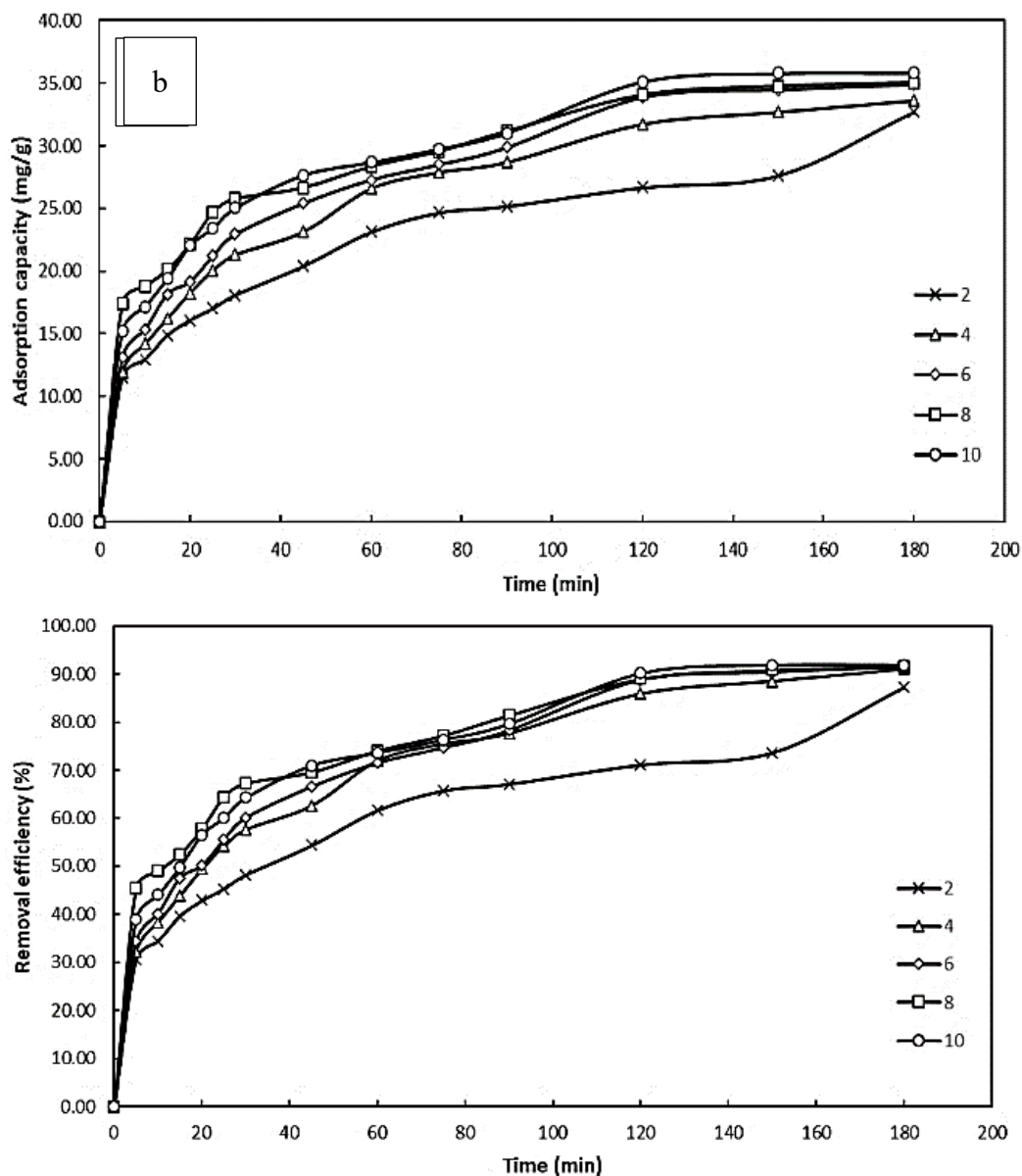


Fig. 5. CAP adsorption uptake (a) and percentage removal (b) versus adsorption time of hydrochar at different pH

3.6 Adsorption Isotherm and Kinetics

Adsorption isotherms describe the relationship between the concentration of CAP (adsorbate) molecules in the aqueous phase and the degree of adsorbed molecules on the adsorbent surface at equilibrium at constant temperature. Langmuir, Freundlich and Temkin isotherms were used as the mathematical model on the experimental data to determine the interaction of adsorbed molecules on the adsorbent surface.

Table 2. Adsorption isotherm parameters for CAP adsorption

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	76.92
	K_L (L/mg)	0.83
	R^2	0.9975
Freundlich	K_F (mg/g)	16.32
	n_F	1.23
	R^2	0.9996
Temkin	B	13.689
	AT (L/mg)	4.12
	R^2	0.9368

From Table 2, it can be summarized that the models showed a good fitting to the experimental data for value R^2 in order of Freundlich > Langmuir > Temkin. The Freundlich isotherm model yielded the best fit with the highest correlation coefficient (R^2) at 0.9996 since they are closer to unity. These results showed that multilayer sorption took place at the heterogenous adsorbent's surface. In addition, the Freundlich constant, n_F is found to be greater than 1, indicating the favourable condition for adsorption. From the tabulated result, it can be noticed that the maximum adsorption capacity, q_m , computed from Freundlich isotherm is close to the experimentally determined value (35.70 mg/g). Hence, the maximum adsorption capacity of CAP by dry leaves hydrochar is estimated to be 16.32 mg/g.

To investigate the adsorption mechanism and the characteristics of CAP adsorption behaviour, pseudo-first order and pseudo-second order kinetic models were fitted to the adsorption kinetics of hydrochar on CAP solution.

Table 3. Kinetic parameters

Parameters	C_0 (mg/L)				
	10	20	30	40	50
q_{exp} (mg/g)	6.83	15.12	22.49	29.39	35.70
Pseudo First Order					
q_{cal} (mg/g)	1.30	5.61	13.14	13.97	18.61
k_1 (min^{-1})	0.02	0.03	0.03	0.03	0.03
R^2	0.7222	0.9273	0.9736	0.9573	0.9634
Pseudo Second Order					
q_{cal} (mg/g)	6.84	15.36	23.31	30.12	36.76
k_1 (g/mg.min)	0.08	0.02	0.01	0.01	0.00
R^2	0.9998	0.9996	0.9979	0.9991	0.9987

Based on the summary of kinetic models in Table 3, pseudo second order kinetic models fit the experimental data better than pseudo first order models, as this model produced higher R^2 values and was closer to unity. For the pseudo-second-order kinetic model, the R^2 values are between 0.9979 and 0.9998, whereas for the pseudo-first-order kinetic model, R^2 values are between 0.7222 and 0.9736 were obtained. Thus, it was determined that the removal of CAP by hydrochar followed pseudo-second order kinetic models. Moreover, the q_e value of the pseudo-second order for both adsorbents was considerably closer to the experimental q_e values than the q_e value of the pseudo-first-order kinetic model. The adsorption of CAP on hydrochar, as described by a pseudo second-order kinetic model, implied a chemical controlling step, indicating that the reactions involved valency forces through the sharing or exchanging of

electrons between the surface functional groups on hydrochar and CAP molecules [8]. Because the kinetic data fitted a pseudo-second-order kinetic model, Qin et al. hypothesised that chemical adsorption was the rate-controlling step of CAP adsorption on porous carbon [9]. Mohd Din et al. reported that CAP adsorption on mesoporous carbons followed a pseudo-second-order kinetic model, with a π - π interaction as a possible CAP adsorption mechanism [10]. Therefore, chemisorption explains the adsorption of CAP on hydrochar prepared in this study.

According to the results presented above, the physical adsorption of CAP by hydrochar was the primary adsorption mechanism. This was because the hydrochar had well-developed porosity and a large surface area that the CAP could occupy. Additionally, chemical interaction existed during the adsorption process. The CAP ketone, nitro, and benzene groups contained π -electron-acceptors with a potent electron-withdrawing capacity. Consequently, CAP had a strong interaction with hydrochar, which possessed graphite surfaces with a high concentration of polarised π -electron via π -electron-donor acceptor (EDA) interaction during the adsorption process. In addition, hydrogen-bond interactions are possible between the N-H, -OH groups in CAP and the O-containing groups (COOH, -CO, etc.) on the AC surface [11]. It was proposed that the ionic/polar groups (such as phenol, amine, and alcohol) present in antibiotic molecules could interact strongly with the corresponding structural components of carbonaceous adsorbents via H-bonding. The functional groups -OH, -CH₃, -NH₂, and N-H in the two antibiotics can act as H acceptors by hydrogen bonding with the O-containing groups -COOH and C=O on the AC surface.

4. CONCLUSION

The CAP removal efficiency of 91.90% was recorded at pH 10 due to the enhancement of the negatively charged active sites on the adsorbent surface in the presence of OH groups and improved adsorption performance. The hydrochar was best characterised by the Freundlich isotherm model, indicating that multilayer CAP sorption occurred on the hydrochar's heterogeneous surfaces. In the meantime, kinetic studies revealed that the adsorbent was best described by a pseudo-second order kinetic model as opposed to a pseudo-first order kinetic model based on the correlation coefficient, R^2 , which was close to unity. This indicates that the rate-controlling step of CAP adsorption on porous carbon was chemical adsorption. Thus, it is implied that dried leaves can be converted into adsorbent to remove CAP from pharmaceutical effluent wastewater.

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