Adsorption mechanism of dichlorvos onto coconut fibre biochar: the significant dependence of H-bonding and the pore-filling mechanism
Quach An Binh and Puangrat Kajitvichyanukul

ABSTRACT
The adsorption mechanism of dichlorvos onto coconut fibre biochar (CFB) was investigated by the batch adsorption technique. Coconut fibre waste material was synthesised at 600 °C for 4 h under oxygen-limited conditions. The biochar was modified by HCl acid to enhance the specific surface area and porosity. The characteristics of the biochar were analysed by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) specific surface area, and Fourier transform-infrared (FT-IR). The results showed that the BET specific surface area of biochar was 402.4 m²/g. Experimental data presented a good fit to Langmuir isotherm and the pseudo-second-order model. Langmuir isotherm illustrated that monolayer adsorption of dichlorvos occurred on the surface of CFB, with a maximum adsorption capacity of 90.9 mg/g. The diffusion model confirmed that the liquid film diffusion was the rate-limiting step, and the major diffusion mechanism of dichlorvos onto biochar. The BET result after dichlorvos adsorption demonstrated that pore-filling occurred and occupied 58.27%. The pore-filling and chemical interactions, performed important roles in the adsorption of dichlorvos onto CFB. Chemical adsorption is comprised of two interactions, which are hydrophobic and H-bonding, but the prime is H-bonding. CFB is a very potential material for the removal of dichlorvos and environmental pollutants.

Key words | adsorption, biochar, dichlorvos, diffusion, mechanism, pesticide

INTRODUCTION
Dichlorvos (2,2-dichlorovinyl dimethyl phosphate) is an organophosphate insecticide that was generally used to control flies, mosquitoes, ticks, cockroaches, clover mites, crickets, cutworms, grasshoppers, and webworms. This insecticide was applied to exterminate insects in domestic, agricultural and industrial areas (Edwards 2006).

Dichlorvos can act as a contact and stomach poison by way of skin penetration, swallowing and respiration (Richter & Corcoran 1997). Dichlorvos was classified by the Environmental Protection Agency (EPA) as highly toxic compound and assigned class I-toxicity. Human contact with dichlorvos over a short period of time can generate symptoms such as megrim, nausea, blurred vision, regurgitation, excessive sweating, and pupil constriction. Chronic exposure to dichlorvos can lead to narcotism or even death (Sahithya et al. 2015).

Biochar has been widely applied in the adsorption method. Biochar obtained rich carbon that was synthesised from the biomass pyrolysis process with limited oxygen. Biochar has a great potential to efficiently adsorb contaminants in wastewater. Biomass is available to produce biochar at a lower cost. Additionally, biochar has some special properties that include a large surface area, a porous structure, functional groups, and mineral components (Saleh et al. 2016).

After the pyrolysis process, minerals appeared on the surface and blocked the surface pores of the biochar. Hence, acid washing treatment is very necessary to enhance the specific surface area of biochar (Uchimiya et al. 2012). If the main contributions on the surface area of the biochar are micropores (<2 nm) and small mesopores (2–20 nm), these pore sizes were suggested to be the primary factor to participate in the uptake of the organic compounds by pore-filling adsorption (Inyang & Dickenson 2015). There were several interactions that occurred between biochar and the organic compounds, including hydrophobic adsorption,
H-bonding, electrostatic, $\pi$–$\pi$ electron-donor–acceptor (EDA) interactions, and cation–$\pi$ bonding (Inyang & Dickenson 2015).

Recently, several adsorbents were used in the adsorption method to resolve the dichlorvos pollutant such as biopolymer modified MMT–CuO composites (Sahithya et al. 2015), Super paramagnetic poly (styrene-co-acrylic acid) hydrogel (Alka & Anita 2014), TiO$_2$ (Lu et al. 1996), and activated carbon from groundnut shell (Gimba et al. 2010). However, the information of the dichlorvos removal by biochar was rare and the adsorption mechanism of dichlorvos onto the biochar was not reported. This inspired us to explore the adsorption mechanism between dichlorvos and biochar.

The purpose of this study was to investigate the adsorption mechanism of dichlorvos and modified coconut fibre biochar (CFB). The CFB was synthesised under oxygen-limited conditions and modified by HCl acid. The characteristics of CFB were investigated using different analytical techniques including Brunauer–Emmett–Teller (BET) method, scanning electron microscope (SEM), and Fourier transform-infrared (FT-IR). The batch adsorption method was applied to study the kinetics adsorption model, the adsorption isotherm, the intraparticle diffusion model, and the diffusion mechanism of dichlorvos and CFB. Especially, the adsorption mechanism between the CFB and dichlorvos pollutant were explored and explained in depth.

**MATERIALS AND METHODS**

**Chemicals and materials**

In this study, dichlorvos (50% w/v) was provided by Big Giant Company, Thailand. HCl (36.46%, ACI Labscan, Thailand). The dilution of all the solutions was carried out using deionized water that had a resistivity of 18 MΩ.cm. The CFB to produce biochar was collected in Northern Thailand. This material was chosen in this work due to its characteristic as fibrous material with high specific surface area (402.4 m$^2$/g) and porous structure.

**Synthesis and washing of CFB**

The CFB was chopped into cubiform of approximately 1 cm$^2$. In order to extrude the low moisture content that was in the CFB, it was dried in an oven at 105 °C for a few hours until a constant weight was achieved. Subsequently, the biomass was transferred to a ceramic crucible and burnt in a furnace (Nabertherm, Germany). The operating temperature in the furnace was slowly increased by 3 °C per minute (Krzesińska & Zachariasz 2007). The pyrolysis process was conducted under oxygen-limited conditions at 600 °C for 4 h.

To perform the characterization and the adsorption experiments of the biochar, a pestle and mortar was used to crush the CFB, then the biochar was passed through a 0.8 mm sieve. The 0.1 M HCl acid was used to remove minerals from the CFB according to the method of Uchimiya et al. (2012).

**Characterization of biochar**

The surface morphology of the biochar was explored by SEM (LEO 1455 VP model, Carl Zeiss Microscopy GmbH, UK). The BET method was used to determine the specific surface area (SSA) and total pore volume (TPV) of the CFB (TriStar II 3020, Micromeritics Instrument Corporation, USA). The functional groups of biochar were explored by the FT-IR method (Frontier, PerkinElmer, Germany). The Boehm titration method was used to determine the surface chemistry of the biochar (Chun et al. 2004; Mukherjee et al. 2011). Mathematical formulae according to Goertzen et al. (2010) were used to calculate its quantity. The batch experiment was used to determine the pH$_{pzc}$ of biochar and followed the method of Tan et al. (2016).

**Adsorption experiment**

The batch adsorption method was applied to the dichlorvos adsorption experiment. The stock of dichlorvos solution was 1,000 mg/L and diluted in deionized water, because the dichlorvos hydrolysis shows a pH higher than 4, HCl acid was used to adjust the pH of the solution (pH < 4) to control the hydrolysis of the dichlorvos (Oncescu & Oancea 2007). The solutions used in the experiment were in the range of 10–30 mg/L and were diluted from the stock dichlorvos solution. The adsorption experiments were conducted using 250 mL sealed conical glass, and the dosage of CFB was 1.5 g/L.

In this experiment, Erlenmeyer flasks were shaken (MS Orbital Shaker, MS-NOR-30/MS-NOR-3001) for 6 h at 120 rpm in dark conditions. For the duration of the adsorption experiment, the filtrate of dichlorvos solution was passed through Whatman filter paper 42 and the residual concentration was analysed by UV-Vis spectrometer.
Mathematical models of adsorption kinetics and adsorption isotherm

The adsorption kinetics and adsorption isotherm were applied to determine the experimental data:

\[ q_t = \frac{V \left( C_0 - C_t \right)}{W} \]  
\[ q_e = \frac{V \left( C_0 - C_e \right)}{W} \]  

where \( q_t \) (mg/g) and \( q_e \) (mg/g) are the amount of dichlorvos adsorption at \( t \) and equilibrium time, respectively; \( C_0 \) and \( C_e \) (mg/L) are the initial and the equilibrium dichlorvos concentration, respectively; \( W \) (g) is the mass of biochar; \( V \) (L) is the volume of the dichlorvos solution (Liu et al. 2013a; Tan et al. 2016).

Two kinetic models, the pseudo-first-order (PFO) (Equation (3)) and pseudo-second-order (PSO) (Equation (4)) were applied to analyse the adsorption kinetics of dichlorvos and CFB. The PFO and PSO showed mononuclear and binuclear sorption, respectively (Tan et al. 2016), in the equations shown below:

\[ \ln \left( \frac{q_e}{q_t} - \frac{q_t}{q_e} \right) = k_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  

where \( k_1 \) (h\(^{-1}\)) and \( k_2 \) (g.mg\(^{-1}.h^{-1}\)) are the sorption rate constants of the pseudo-first-order and the pseudo-second-order models, respectively (Tan et al. 2016).

To evaluate the adsorption capacities of the dichlorvos on the CFB, Langmuir and Freundlich isotherm models were used to calculate the adsorption experiment data.

Langmuir adsorption isotherms presented monolayer sorption onto a homogeneous surface and are shown in Equation (5)

\[ q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \]  

where \( Q_0 \) (mg/g) is the maximum monolayer coverage capacity; \( K_L \) (L/mg) is the Langmuir isotherm constant (Tan et al. 2016).

\( R_L \) is the separation factor (Equation (6)) and is calculated from the Langmuir isotherm. This value showed the favourable adsorption between adsorbent and adsorbate (\( R_L > 1 \): unfavourable, \( R_L = 1 \): linear, \( 0 < R_L < 1 \): favourable, and \( R_L = 0 \): irreversible) (Essandoh et al. 2017).

\[ R_L = \frac{1}{1 + K_L C_0} \]  

Freundlich adsorption isotherm was applied to define the heterogeneous adsorption on the surface, Freundlich adsorption isotherms are presented in Equation (7).

\[ q_e = K_f C_e^n \]  

where \( K_f \) (mg.g\(^{-1}\).mg.L\(^{-1}\).L\(^{-1}\)) is the Freundlich isotherm constant and is related in the adsorption capacity; \( n \) is the intensity of the adsorption (Tan et al. 2016).

Diffusion study

The film diffusion model and the particle diffusion model were applied to identify the rate-limiting step of the adsorption process. The film diffusion model expresses the liquid film that surrounds the biochar surface. The particle diffusion model expresses the diffusion of dichlorvos molecules that enter the biochar pores (Liu et al. 2016).

The mathematical model of the particle diffusion model shows as follows:

\[ \ln \left( \frac{1 - X^2 \left( t \right)}{X_0} \right) = k_p t \]  

where \( X(t) = q_t/q_e \); \( D_p \) (m\(^2\)/s) is the particle diffusion coefficient; \( r_0 \) (m) is the biochar radius; \( k_p \) (min\(^{-1}\)) is the effective intraparticle diffusivity.

\[ k_p = \frac{D_p r_0^2}{r_0^2} \]  

The \( k_p \) (min\(^{-1}\)) was the slope on the graph, and was made by plotting \(-\ln \left( 1 - X^2 \left( t \right) \right) \) versus \( t \).

The mathematical model of the film diffusion model is as follows:

\[ \ln \left( 1 - X \left( t \right) \right) = k_f t \]  

where \( k_f \) is the slope on the graph, and was made by plotting \(-\ln \left( 1 - X \left( t \right) \right) \) versus \( t \).
where $k_f$ (min$^{-1}$) was the slope on the graph, and was made by plotting the $-\ln(1-X(t))$ versus $t$; $D_f$ (m$^2$/s) is the film diffusion coefficient.

$$D_f = \frac{k_f\delta C_r}{3C_e}$$ (11)

$C_e$ (mg/L) is the equilibrium concentration of the dichlorvos in the solution, and $C_r$ (mg/L) is the dichlorvos concentration that is adsorbed by the biochar. $\delta$ ($10^{-5}$ m) is the thickness of the liquid film (Liu et al. 2016).

## RESULTS AND DISCUSSION

### Characterization of the CFB

The SEM micrograph of modified CFB synthesised at 600 °C for 4 h is shown in Figure 1(a). The surface morphology of the CFB had tiny heterogeneous and longitudinal pores with diameters in the range of 2.90–10.48 μm. These structures likely manifest a high capacity adsorption of biochar with pollutants, whereas minerals were found on the surface of a non-modified CFB (Figure 1(b)). The presence of minerals on the biochar surface can cause blocking of the pores, and decreases the specific surface area of the biochar (Uchimiya et al. 2015). This phenomenon would significantly affect their adsorption ability. Therefore, mineral removal is very important to improve the porosity of biochar (Uchimiya et al. 2012).

The adsorption capacity of biochar depended significantly on the specific surface area. The specific surface area (BET) of CFB was 402.4 m$^2$/g, the large specific surface area of biochar interfaced well with the adsorption of pollutants (Tan et al. 2016). The TPV is one of the main factors for the high adsorption of biochar. The TPV and pore volume distributions of the CFB were calculated using the Barrett-Joyner-Halenda (BJH) model. The pore volume distributions in pore size of CFB of micropores (<2 nm) and narrow mesopores (2–20 nm) were 17.40, 69.22%, respectively. The pore size of biochar is very important in achieving the uptake of adsorbate (Wang et al. 2018).

The values of the surface functional groups of the CFB were estimated by the Boehm titrations method. The CFB surface functional groups are 0.375 mmol/g carboxyl, 0.250 mmol/g lactonic, 0.625 mmol/g phenolic, 1.250 mmol/g total acidity, and 0.285 mmol/g total basicity. Both acid and base functional groups acted as efficient adsorption sites for the removal of adsorbate. The pHpzc of biochar, determined by the batch experiment, was 0.7.

The FT-IR spectrum of the CFB are indicated in Figure 2 which manifests the presence of eight main functional groups on the surfaces of the CFB. The band at 1,217 cm$^{-1}$ represented the aromatic C-O stretching of phenolic hydroxyl (Chun et al. 2004). The band at 1,070 cm$^{-1}$ was assigned to the aromatic C-O stretching of alcohol (Saffari et al. 2015). Peaks around 878 and 750 cm$^{-1}$ were ascribed to the aromatic C-H out-of-plane bending mode (Tran et al. 2017). The 2,915 and 2,845 cm$^{-1}$ peak area represented C-H stretching of the alkyl group (Kinney et al. 2015). The 3,000 to 3,600 cm$^{-1}$ peak areas, and one that peaked at 3,789 were assigned to the hydroxyl groups (O-H) stretching vibrations of carboxylic acid, alcohol, and phenol (Tran et al. 2017). The peak at 1,715 cm$^{-1}$ was assigned to the carbonyl group C–O, and could show ketone, carboxylic acid, and ester (Liu et al. 2015). The bands at 2,354 and 2,299 cm$^{-1}$ were ascribed ketone group C = O (Nuithitikul et al. 2010). The band at

![Figure 1](https://iwaponline.com/wst/article-pdf/79/5/866/561908/wst079050866.pdf)
1,571 cm$^{-1}$ was ascribed to the aromatic C = C (Saffari et al. 2015). The functional groups of the CFB are hydroxyl, ketone, carbonyl, C-O stretching of phenolic hydroxyl and alcohol, can form an H-bonding interaction with pollutants (Liu et al. 2015a). Additionally, the alkyl groups of biochar with hydrophobic properties (Kinney et al. 2002) and can cause the hydrophobic interaction with pollutants.

**Adsorption isotherm models of dichlorvos adsorbed on CFB**

The adsorption isotherms of dichlorvos and CFB was explored in this study. Table 1 showed that the Langmuir, and the Freundlich models fitted the experimental data. However, the Langmuir model was more pertinent than the Freundlich model. The $R^2$ of the Langmuir, and the Freundlich models were 0.992 and 0.987, respectively. This demonstrated that monolayer adsorption of dichlorvos occurred on the surface of CFB. From the data indicated in Table 1, the $R_L$ value was 0.0004, and proved to be the favourable adsorption of CFB and dichlorvos (Essandoh et al. 2017).

**Table 1** Isotherm parameters for dichlorvos adsorption onto coconut fibre biochar

<table>
<thead>
<tr>
<th>Parameters of Langmuir isotherm</th>
<th>Parameters of Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_0$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>90.9</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The kinetics adsorption models of dichlorvos adsorption onto CFB

The kinetic parameters of CFB and dichlorvos were assessed including the adsorption capacity, the rate constants, and $R^2$, and are shown in Table 2. The $q_e$ value calculated from the PFO was significantly dissimilar to the $q_e$ value of the experimental data. The $q_e$ values were calculated from the PSO were confirmed as fitting the experimental data, and the $R^2$ values of the PSO were 0.999 to 1.000, whereas the $R^2$ values of the PFO were lower than the $R^2$ values of the PSO, which were 0.806 to 0.998. The two values of $q_e$ and $R^2$ that were analysed above, the adsorption kinetic of dichlorvos was adsorbed onto CFB, totally fitted the PSO.

Effects of the initial dichlorvos concentration on the adsorption process of CFB

The rate of the adsorption process depended on the initial adsorbate concentration. The correlation of the initial dichlorvos concentrations and the adsorption rate constant of the PSO showed an inverse relation. Table 2 demonstrates the adsorption rate constant $k_2$ (PSO) of dichlorvos concentration at 10 mg/L was faster than the other dichlorvos concentrations. At high dichlorvos concentrations, the intense competition between them fixed the activated surface sites on the biochar, leading to slow diffusion (Weng...
et al. 2009). The high initial concentration is the reason that causes a low rate constant $k_2$ (PSO) and the high rate constant $k_2$ is the result of a low concentration.

In addition, the experimental data illustrated that the adsorption capacities of dichlorvos were increased, when the initial concentration increased (Table 2 and Figure 3) leading the driving force of the concentration gradient was strengthened, it generated a higher adsorption capacity (Weng et al. 2009). Therefore, increasing the initial dichlorvos concentrations brought about the increase in the adsorption capacity.

### Intraparticle diffusion (IPD) model of dichlorvos adsorbed onto CFB

To study the diffusion process of dichlorvos adsorption onto CFB, the IPD diffusion model was applied to this experiment. The IPD model signifies the rate of the adsorption process, which depends on the diffusion rate of the adsorbate to move towards the adsorbent (Hafshejani et al. 2016). The IPD model (Weber-Morris model) is used to describe the empirically explored functional relationship of $q_t$ versus $t^{1/2}$. The IPD model is presented below.

$$q_t = k_{id} t^{1/2} + C_i$$  \hspace{1cm} (12)

where $k_{id}$ (mg g$^{-1}$ h$^{-1/2}$) includes $k_{id1}$, $k_{id2}$, $k_{id3}$ and are the diffusion rates. $k_{id1}$, $k_{id2}$, and $k_{id3}$ are the rate constant of the external surface, the gradual adsorption, and the equilibrium adsorption stage, respectively. $C_i$ (mg/g) is the intercept, and shows the thickness of the boundary layers effect (Lu et al. 2015).

In this study, the parameters of $k_{id1}$, $k_{id2}$, $k_{id3}$ for dichlorvos adsorption onto CFB are indicated in Table 3. Figure 4 (qt versus t$^{1/2}$) of dichlorvos adsorption onto CFB was not a linear line over the whole of the time range, showing the event of more than one kinetic stage in the dichlorvos adsorption process. From the IPD graph of CFB, the dichlorvos adsorption process consists of three stages: the instant adsorption (1), the slow adsorption (2), and the equilibrium adsorption stage (3). In the three stages, the second and third participated in the IPD process (Lu et al. 2015). Figure 4 indicated the linear lines of stages 2 and 3 did not pass

### Table 2 | Kinetic parameters for dichlorvos adsorption onto coconut fibre biochar

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$q_e$, exp. (mg/g)</th>
<th>$q_e$, calc. (mg/g)</th>
<th>$k_1$ (h$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_e$, calc. (mg/g)</th>
<th>$k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.15</td>
<td>0.57</td>
<td>0.85</td>
<td>0.998</td>
<td>6.17</td>
<td>4.40</td>
<td>1.000</td>
</tr>
<tr>
<td>15</td>
<td>9.25</td>
<td>0.72</td>
<td>0.72</td>
<td>0.806</td>
<td>9.30</td>
<td>2.95</td>
<td>1.000</td>
</tr>
<tr>
<td>20</td>
<td>12.28</td>
<td>1.05</td>
<td>0.60</td>
<td>0.916</td>
<td>12.34</td>
<td>1.87</td>
<td>1.000</td>
</tr>
<tr>
<td>25</td>
<td>15.23</td>
<td>1.71</td>
<td>0.58</td>
<td>0.944</td>
<td>15.33</td>
<td>1.12</td>
<td>0.999</td>
</tr>
<tr>
<td>30</td>
<td>18.12</td>
<td>2.16</td>
<td>0.48</td>
<td>0.951</td>
<td>18.24</td>
<td>0.81</td>
<td>0.999</td>
</tr>
</tbody>
</table>

### Table 3 | Intraparticle diffusion model data for the dichlorvos adsorption onto coconut fibre biochar

<table>
<thead>
<tr>
<th>Dichlorvos concentration</th>
<th>Instant adsorption stage</th>
<th>Slow adsorption stage</th>
<th>Equilibrium adsorption stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{id1}$ (mg g$^{-1}$ h$^{-1/2}$)</td>
<td>$k_{id2}$ (mg g$^{-1}$ h$^{-1/2}$)</td>
<td>$k_{id3}$ (mg g$^{-1}$ h$^{-1/2}$)</td>
</tr>
<tr>
<td>10 mg/L</td>
<td>11.30</td>
<td>0.37</td>
<td>0.07</td>
</tr>
<tr>
<td>15 mg/L</td>
<td>16.41</td>
<td>0.80</td>
<td>0.05</td>
</tr>
<tr>
<td>20 mg/L</td>
<td>21.91</td>
<td>0.87</td>
<td>0.24</td>
</tr>
<tr>
<td>25 mg/L</td>
<td>26.79</td>
<td>1.42</td>
<td>0.32</td>
</tr>
<tr>
<td>30 mg/L</td>
<td>31.73</td>
<td>1.72</td>
<td>0.52</td>
</tr>
</tbody>
</table>
through the origin, which proved that the rate of the entire dichlorvos adsorption process was not controlled by the intraparticle diffusion (Lu et al. 2015).

In the various concentration of the dichlorvos, the kid1 were higher than the kid2 and kid3 (Table 3). This demonstrates that the rate constant of the instant adsorption (kid1) was faster than the rate constant of the gradual adsorption stage (kid2) and the equilibrium adsorption stage (kid3) of the IPD. This determined that the IPD was involved in the dichlorvos adsorption process. However, the IPD was not the only rate-limiting step of the whole adsorption process of dichlorvos. The rate-limiting step of the diffusion mechanism, is a major contribution in the adsorption of dichlorvos and CFB, and was followed by film diffusion, which is clarified in the next section.

**Diffusion study**

The CFB particle radius ($r_0$) used in this study was in the range of 100–270 μm. Hence, the average radius of the CFB particles were applied to the particle diffusion and the film diffusion models, was 185 μm.

From the formulae of the film diffusion, and the particle diffusion models, the $D_f$ and $D_p$ values were evaluated to explore the rate-limiting step of dichlorvos adsorption onto CFB. The $D_f$ values of the film diffusion model in this experiment were in the range of 1.01 × 10^{-12}–8.42 × 10^{-12} (m²/s) and $D_p$ values of the particle diffusion model were in the range of 6.01 × 10^{-13}–1.16 × 10^{-12} (m²/s). The particle and film diffusion were the rate-limiting steps, when the $D_p$ values of the particle diffusion model were 10^{-15} to 10^{-18} (m²/s), and the $D_f$ values of the film diffusion model were 10^{-10} to 10^{-12} (m²/s) (Michelsen et al. 1975). The comparisons show that the values of $D_f$ in this experiment were in the range of the $D_f$ values that Michelsen suggested, but the values of $D_p$ were not. Therefore, the rate-limiting step of the dichlorvos adsorption process onto CFB was the film diffusion. The film diffusion was the main contribution and the major mechanism of the dichlorvos adsorption process onto CFB.

**The adsorption mechanism of CFB and dichlorvos**

The adsorption mechanism of biochar and organic pollutants comprises of H-bonding, hydrophobic, electrostatic, π-π EDA interactions, and pore-filling (Tan et al. 2015). From the evidence in this study, the intensities of FT-IR on the CFB surface and TPV in the CFB before and after the dichlorvos adsorption were different. The proposed adsorption mechanism of the CFB and dichlorvos consists of the pore-filling mechanism and chemical adsorption (Figure 6).

The CFB had a high distribution of pore volume in micropores (<2 nm) and narrow mesopores (2–20 nm), which were in the range of 17.40 and 69.22%, respectively. The geometry of the molecular structure of dichlorvos was calculated by using the ChemBio3D software (Liu et al. 2015) with the result of 0.73 × 0.26 × 0.61 nm. The molecular structure size of dichlorvos was in the range of the pore size (micropores and narrow mesopores) of the CFB. Therefore, dichlorvos can be adsorbed into the micropores and narrow mesopores of CFB by pore-filling mechanism. The micropores and narrow mesopores of biochar were the major factors for diffusion of adsorbate (Wang et al. 2018).

In this research, the SSA and the TPV results of the CFB showed before and after dichlorvos adsorption changes. Before and after adsorption, the SSA of the CFB was 402.4 m²/g and 161.8 m²/g, and the TPV of the CFB was 0.151 and 0.063 cm³/g, respectively. The TPV of the Figure 4 | Intraparticle diffusion graph shows the different dichlorvos concentrations onto coconut fibre biochar (kid1: the instant adsorption stage, kid2: the slow adsorption stage, kid3: the equilibrium adsorption stage).
CFB after dichlorvos adsorption was significantly decreased by 58.27%. The reduction of the SSA and the TPV of the CFB after dichlorvos adsorption, the pore size of biochar and the molecular size of dichlorvos are explained above. This indicates that the pore-filling mechanism was performed in the adsorption process between the CFB and dichlorvos.

The formation of the chemical adsorption was formed by the interactions of the functional groups of biochar and the dichlorvos molecules. Based on the results of FT-IR of the CFB before and after dichlorvos adsorption (Figure 5 and Table 4), suggest that the chemical interaction of the CFB and dichlorvos consisted of H-bonding, and hydrophobic interactions.

For the formation of H-bonding, the shift of FT-IR results after dichlorvos adsorption were observed and presented in Figure 5 and Table 4. The FT-IR changes at the peak where C-O stretching of alcohol (1,070 cm\(^{-1}\)), C-O stretching of phenolic hydroxyl (1,217 cm\(^{-1}\)), O-H of alcohol, phenol, and carboxyl (3,600–3,000 and 3,789 cm\(^{-1}\)) suggested that hydrogen in these functional groups of biochar, participated in H-bonding interaction with oxygen from dichlorvos. According to a report by Essandoh et al. (2017), carboxylic acid, phenolic group of biochar can act as a hydrogen donor or acceptor, which can perform the H-bonding interaction with the oxygen of pollutants. Additionally, oxygen atoms from the phosphates group of dichlorvos carry a negative charge (Gamoke et al. 2009). Hence, H-bonding interaction could be formed between hydrogen from the functional groups of biochar, including carboxylic acid, alcohol, phenolic groups, and oxygen from the phosphate group (P = O) of dichlorvos.

![Figure 5](https://iwaponline.com/wst/article-pdf/79/5/866/561908/wst079050866.pdf)

**Figure 5** | FT-IR analysis of coconut fibre biochar before and after dichlorvos adsorption.

**Table 4** | Intensity change (% transmittance) of FT-IR of coconut fibre biochar before and after dichlorvos adsorption

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Ascribed to the type of vibration</th>
<th>The functional group</th>
<th>The intensity changed (% Transmittance)</th>
<th>The proposed interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,070</td>
<td>C-O</td>
<td>C-O stretching of alcohol</td>
<td>0.84</td>
<td>H-bonding</td>
</tr>
<tr>
<td>1,217</td>
<td>C-O</td>
<td>C-O stretching of phenolic hydroxyl</td>
<td>0.50</td>
<td>H-bonding</td>
</tr>
<tr>
<td>2,915–2,845</td>
<td>C-H</td>
<td>Aliphatic C-H</td>
<td>0.92</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>3,600–3,000 and 3,789</td>
<td>O-H</td>
<td>Alcohol, phenol, carboxylic acid</td>
<td>1.04</td>
<td>H-bonding</td>
</tr>
</tbody>
</table>
The intensity of the peak areas were 2,915–2,845 cm\(^{-1}\) that changed after dichlorvos adsorption, they were ascribed to the alkyl group. The alkyl groups of biochar presented hydrophobic properties (Kinney et al. 2012). Hence, the hydrophobic bond can be formed from alkyl side chains (aliphatic) from dichlorvos, and alkyl groups from the CFB.

From the FT-IR results, the functional groups in CFB included alcohol, phenol, and carboxylic acid group which participated in H-bonding interaction. H-bonding interaction occurs between the O atom and H atom. H atom have a positive charge and can attach to O atom which have a higher electronegativity. The O atom bearing negative charge (Gamoke et al. 2009) of dichlorvos can have H-bonding interaction with H atom bearing positive charge of phenol, alcohol, and carboxylic groups of biochar. From surface functional groups of the CFB estimated by the Boehm titrations method and the transformation intensity in FT-IR after the dichlorvos adsorption, several functional groups of biochar, including, alcohol, phenol, and carboxylic acid groups, showed the H-bonding interaction, whereas only the alkyl group of biochar presented the hydrophobic interaction (Figure 6). Therefore, the H-bonding interaction was the major chemical interaction. To conclude, the adsorption mechanism between the CFB and dichlorvos consists of the pore-filling sorption mechanism and the chemical interaction. H-bonding was the primary interaction that played an important role in the chemical adsorption.

**CONCLUSIONS**

Acid washing removed minerals from the biochar surface and achieved the perfect porosity of the CFB. Adsorption isotherm of dichlorvos and the CFB was followed by the Langmuir isotherm model. The adsorption kinetics data were a good fit to the pseudo-second-order model. The liquid film model was the rate-limiting step of the adsorption process. The pore-filling and the chemical interaction were the main adsorption mechanism of dichlorvos onto the CFB. The chemical interaction included H-bonding and the hydrophobic interactions, however, the main contributor was H-bonding. Based on the overall results of this study, CFB had a high efficiency in the removal of dichlorvos. It is a very useful material for the removal of environmental pollutants.

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