Potential adsorption mechanisms of different bio-wastes to remove diazinon from aqueous solution

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Abstract. This paper investigated the isotherms, kinetics, and mechanisms of three types of bio-wastes derived from agro-waste, synthesized as potential adsorbents in diazinon extraction from aqueous solution. The adsorption capacity that differentiates each of the bio-wastes were discussed. Bio-wastes were synthesized for 4 h at a temperature of 600 °C. Bio-wastes were modified by hydrofluoric acid (HF) to enhance the specific area and porosity. The SEM, BET, FT-IR, and pHpzc were used to analyse the characteristics of the bio-wastes. Experimental results showed the different BET specific surface areas ranged from 67.42 to 402.43 m²·g⁻¹ of each bio-waste. Meanwhile, SEM showed that bio-wastes possessed an intricate pore network comprising micropores and narrow mesopores. The pore volume disseminations in the size of the micropores (<2 nm) and narrow mesopores (2-20 nm) of bio-wastes in the range of 16.88-21.24% and 56.57-69.22%, respectively. Solution pH at 4 carried out the highest removal efficiency of diazinon. Langmuir isotherm model showed the best fit to the experimental adsorption data. The maximum adsorption capacities of bio-wastes ranged from 8.60-15.83 mg·g⁻¹. The pore filling and chemical adsorption participated in the adsorption mechanisms of diazinon and other bio-wastes.

1. Introduction
Pesticides are organic chemicals commonly used in agriculture to increase yield, and product quality [1]. Almost 40% of pesticides used internationally are organophosphorus compounds, which were utilized in huge amounts due to their affordability and high efficiency in pest removal [2]. Today, the contamination of surface and ground water by pesticides has become a significant problem [3]. Diazinon is an organophosphorus insecticide, which is commonly used against insects in agriculture. This pesticide can cause damage to humans, animals, and plants due to their consumption of water. Therefore, the presence of pesticides in water would be considered a serious issue that has to be solved. Recently, bio-wastes have become popular absorbents used in pesticide removal from the aqueous environment. With the high porosity, large surface area, ash contents, a mineral component, many functional groups, and great aromatic structure, bio-wastes were treated as an effective absorbent [4]. Many studies reported that bio-wastes are effective absorbents but have different levels of efficiency regarding conditions such as pyrolysis and the synthesis of conditions, porous structure, functional group, and mechanisms [5].

The objective of this study was to investigate the bio-waste materials obtained from three types of agro-waste, synthesized as potential adsorbents for diazinon removal from aqueous solutions and
compare the adsorption capacity of each bio-waste. The adsorption was investigated in the batch adsorption system, including isotherm, kinetics, and mechanisms.

2. Material and methods

2.1 Chemicals and materials
The three types of bio-waste including coconut fibre bio-waste (CF-BW), corn cob bio-waste (CC-BW), and bagasse bio-waste (BG-BW) were collected in Northern Thailand. The diazinon (60% w/v) was provided by the SIMS AGROW CHEME CO., LTD. HF (48.0%) from Loba Chemie Pvt. Ltd, India and deionized water with a resistivity of 18 MΩ.cm.

2.2 Bio-waste preparation
Bio-wastes were sliced into the approximate size (cm$^3$) of 1 x 1 and dried in the oven at 105 °C for a few hours until getting the constant weight. The bio-wastes were burned in a furnace (Nabertherm, Germany) with the temperature slowly increased by 3 °C per minute. The pyrolysis process was conducted under oxygen-limited conditions at 600 °C for 4 hours. The bio-wastes were washed with HF acid by following the method of Minori Uchimiya group [6].

2.3 Bio-wastes characterization
The surface morphology and specific surface area of bio-wastes were analysed by the Scanning Electron Microscope (SEM) and the Brunauer–Emmett–Teller methods (BET), respectively. The FT-IR method was applied to define the functional groups of adsorbents. Mass titration method was utilized to define the point zero charge (pHpzc) of bio-wastes [7].

2.4. Adsorption procedure
The volume of the pesticides and bio-wastes of 1.5 g.L$^{-1}$ was added into 250 ml Erlenmeyer flasks and shaken by MS Orbital Shaker (MS-NOR-30/MS-NOR-3001) for equilibrium time at 120 rpm in dark conditions. A UV–Vis spectrometer (Genesys 10S UV-Vis spectrophotometer, Thermo Scientific, USA) was used to analyse the residual concentration of diazinon by using the wavelength of 247 nm. Whatman filter paper 42 with the retention of 2.5 μm was used to separate the bio-wastes from the diazinon solution. Furthermore, the effect of pH of the solution was prepared in the range from 2.0 to 10.0. HCl and NaOH solutions were used to adjust the pH of the pesticide solutions. The batch adsorption method was applied to the diazinon adsorption experiment.

3. Results and discussion

3.1 Characterization of the bio-wastes
The SEM of the bio-wastes are shown in Figure 1. The pore size of all types of bio-waste had tiny pores and no mineral on the surface areas. The size of the surface morphology of the bio-wastes is the crucial element in the adsorption process.

![Figure 1. SEM pictures of bio-wastes (a,b,c): CC-BW, BG-BW, CF-BW, respectively.](image)
The specific surface area (BET), total pore volume (TPV), and pore volume distributions of bio-wastes were displayed in Table 1. Results show that the specific surface area of CF-BW is higher than CC-BW and BG-BW in the ordering value 402.43 m$^2$.g$^{-1}$, 292.92 m$^2$.g$^{-1}$, and 67.42 m$^2$.g$^{-1}$, respectively. Noticeably, the BET is the main criteria to determine the adsorption capacity of bio-wastes. If the large specific area exists on the surface of the bio-wastes, it has more interfaces for pollution adsorption [8]. Likewise, the total pore volume of CF-BW is also higher than other bio-wastes by distribution into four sizes including, micropores (<2 nm), narrow mesopores (2-20 nm), mesopores (21-50 nm), and macropores (>50 nm). The majority pore volumes of bio-wastes were narrow mesopores and micropores. The TPV is the main factor for the high adsorption of bio-wastes. The pore size of bio-wastes is very important in achieving the uptake of adsorbate.

Table 1. The BET (SSA), TPV, and the pore volume disseminations in pore size of bio-wastes.

| Property             | Unit | BG-BW  | CC-BW  | CF-BW  |
|----------------------|------|--------|--------|--------|
| BET surface area     | m$^2$.g$^{-1}$ | 67.42  | 292.92 | 402.43 |
| TPV                  | cm$^3$.g$^{-1}$ | 0.029  | 0.117  | 0.151  |
| Micropores (< 2 nm)  | %    | 16.88  | 21.24  | 17.40  |
| Narrow mesopores (2-20 nm) | %    | 59.29  | 56.57  | 69.22  |
| Mesopores (21-50 nm) | %    | 15.75  | 10.39  | 6.10   |
| Macropores (> 50 nm) | %    | 8.07   | 11.81  | 7.28   |

The results of the surface functional groups of adsorbents were demonstrated by FT-IR analysis. The FT-IR spectra of the bio-wastes are exhibited in Figure 2.

On the surfaces of the bio-wastes are the eight main functional groups in a different spectrum. The band 3000-3600 cm$^{-1}$ and peak at 3789 cm$^{-1}$ were hydroxyl groups (O-H) stretching vibrations of carboxylic acid, alcohol, and phenol [9]. Moreover, the hydroxyl groups (O-H) are presented with significant H-bonding interaction. Two types of groups C-H such as aromatic C-H and Aliphatic group were found in this adsorption. Aromatic C-H bands were around 744-871 cm$^{-1}$ and Aliphatic C-H bands were 2846-2915 cm$^{-1}$. The bands at 1216 cm$^{-1}$ and 1217 cm$^{-1}$ represented the aromatic C-O stretching of phenolic hydroxyl [10]. The bands at 1045 cm$^{-1}$, 1070 cm$^{-1}$, and 1099 cm$^{-1}$ were recognized to the aromatic C-O stretching of alcohol [11]. The peaks around 1734 cm$^{-1}$ and 1715 cm$^{-1}$ were assigned to the carbonyl group C=O and could show ketone, carboxylic acid, and ester. These groups can cause H-bonding interaction [12]. The bands at 2299-2383 cm$^{-1}$ were ascribed to the ketone group C=O [13]. The bands about 1568-1601 cm$^{-1}$ were ascribed to the aromatic C=C [11]. According to FT-IR spectrum analysis, the major functional groups of the adsorbents include ketone, carbonyl, and aromatic organic molecules which are unsaturated hydrocarbons. The hydroxyl group is
also the main molecule on the adsorbents. All these functional groups can cause H-bonding interaction between adsorbents and pollutants [12]. Furthermore, the aromatic group of the adsorbents has the π-π EDA interaction with the pollutant [12] and alkyl group has hydrophobic properties [14].

3.2. Effect of the pH on diazinon adsorption

The pH of solution influenced the diazinon removal was indicated in Figure 3. From the result, it can be observed that the efficiency of diazinon removal increased when pH values increased to pH 4 but decreased gradually when the pH values are higher than pH 4. However, the electrostatic interaction was engendered by the surface of bio-wastes and diazinon, depending on pH changes in the solution. The percentage of the highest removal of diazinon was succeeded at the pH 4.0, which was not performed by the electrostatic attraction. As a reason, at pH 4, the diazinon was formed as negatively charge d due to the pH of the solution was higher than the pKa (2.6). The surface charges of the bio-wastes were negatively charged when the pH of the solution was adjusted higher than the pHpzc (0.7) value. The adsorption of diazinon by bio-waste occurred without electrostatic attraction. However, the hydrogen bonding, hydrophobic, pore-filling, and π-π EDA interactions can act as factors in this adsorption.

![Graphs showing the influence of pH on diazinon removal](image)

Figure 3. The influence of pH on the efficiency of diazinon removal by bio-wastes (a) CC-BW, (b) BG-BW, and (c) CF-BW.

3.3. The isotherm adsorption models

The adsorption isotherms including Langmuir and Freundlich models of diazinon and bio-wastes were shown in Table 2. The results showed that the Langmuir model of bio-waste adsorption was more appropriate than the Freundlich model due to the R² of the Langmuir model were higher than the R² Freundlich model. These factors demonstrated that the monolayer adsorption of diazinon occurred on the surface of bio-wastes. Regarding R² values in the adsorptions were lower than 1, illustrated the form of the isotherm is favourable for adsorption.

| Models     | Parameters                  | Bio-wastes       |
|------------|-----------------------------|------------------|
|            |                              | CC-BW | BG-BW | CF-BW |
| Langmuir   | Q₀ (mg·g⁻¹)                 | 17.60 | 12.00 | 24.60 |
|            | Kₐ (L·mg⁻¹)                 | 0.050 | 0.210 | 0.190 |
|            | R₁                           | 0.434 | 0.163 | 0.174 |
|            | R₂                           | 0.982 | 0.928 | 0.993 |
|            | Kᵡ (mg·g⁻¹) (mg·L⁻¹)ᵃ       | 1.231 | 3.045 | 4.650 |
| Freundlich | 1/n                          | 0.641 | 0.458 | 0.581 |
|            | R₂                           | 0.956 | 0.917 | 0.966 |

3.4. Effects of the initial diazinon concentration on to the adsorption process
The rate of the adsorption process and initial diazinon concentration had a parallel correlation. The result in Figure 4 showed that increasing the diazinon concentration brought about the increase in adsorption efficiency. The driving force of the concentration gradient was strengthened when the initial diazinon concentration was increased, generating a higher adsorption capacity [15]. Moreover, the adsorption capacity of CF-BW was higher than another two of bio-wastes.

![Graphs showing adsorption capacities of CC-BW, BG-BW, and CF-BW](image)

**Figure 4.** The adsorption capacities of diazinon by bio-wastes (The dosage of adsorbents 1.5 g L⁻¹, pH = 4).

### 3.5. The adsorption mechanism of bio-wastes and diazinon

The hydrogen bonding, electrostatic, hydrophobic, pore-filling, and π-π EDA interactions were the adsorption mechanism between bio-wastes and organic pollutants [16]. In this study, the SSA and the TPV results of bio-wastes before and after diazinon adsorption were different. This validated that the pore-filling mechanism and chemical interaction occurred between adsorbents and diazinon adsorption. According to the pore size data from Table 1, the CC-BW, BG-BW, and CF-BW had a high distribution of micropores (<2 nm) and narrow mesopores (2-20 nm), in the range between 21.24 and 56.57 %, 16.88 and 59.29%, and 17.40 and 69.22%, respectively. The dimension of the molecular structure of diazinon was 1.08 x 0.58 x 1.04 nm (0.65 nm³) analysed by using the ChemBio3D software. The data of the bio-wastes pore size were quite close to the structural size of diazinon. Hence, the diazinon can be adsorbed into micropores and narrow mesopores of the bio-wastes. The pore-filling mechanism happened when the pore size of adsorbent is close to the molecular structure size of adsorbate [17].

The proposed chemical interaction of diazinon and bio-wastes adsorption contain H-bonding, hydrophobic, π-π EDA interactions regarding the results of FT-IR (Figure 5).

![FT-IR graphs of bio-wastes before and after adsorption](image)

**Figure 5.** The FT-IR analysis of bio-wastes before and after diazinon adsorption.

Figure 5 displays the formation of H-bonding and the shift of FT-IR results after diazinon adsorption. The peak and peak area were assigned to the C-O stretching of alcohol (1045 cm⁻¹) and phenolic hydroxyl (1216 cm⁻¹), C=O of carbonyl group (1734 cm⁻¹), C=O of ketone group (2383-2299 cm⁻¹), O-H of alcohol, phenol, and carboxyl (3600-3000 cm⁻¹) which were changed as shown in Figure 5. All of
the peaks suggest that O and H atoms in these functional groups were involved in H-bonding interactions. The π–π EDA interactions of the bio-wastes after diazinon adsorption is shown in Figure 5. The changing of the peaks showed that the aromatic C=C which was related to the π–π EDA interactions. The hydroxyl group of bio-wastes was an electron providing group, this leads to the aromatic rings of bio-wastes to be high in electron density (π). The halogen group had the electron-withdrawing inductive, which caused the nucleus to carry a positive charge (π⁺). So, π–π EDA interactions were formed between diazinon and the aromatic hydrocarbon compound of the bio-wastes. Several functional groups of bio-wastes including, alcohol, phenol, and carboxylic acid groups, showed the H-bonding interaction. Whereas, the alkyl group of bio-wastes presented the hydrophobic interaction and the hydroxyl group of bio-wastes presented the π–π EDA interaction. Therefore, the H-bonding interaction was the major chemical interaction. To conclude, the adsorption mechanism between the bio-wastes and diazinon consisted of the pore-filling sorption mechanism and the chemical interaction. H-bonding was the primary interaction that played an important role in chemical adsorption.

4. Conclusion
This study examined the adsorption mechanism of bio-wastes for diazinon removal. pH 4 was the optimum pH of the solution that engendered the highest removal of diazinon. The adsorption isotherm was followed by the Langmuir isotherm model. When the initial diazinon concentration was increased, this enhanced the adsorption capacity of bio-wastes. The pore-filling adsorption and the chemical interaction were the main factors in the adsorption mechanism. The chemical interaction included H-bonding, hydrophobic, and the π–π EDA interactions; however, the main contributor was H-bonding. Overall, bio-wastes were very useful materials and had a high potential to contribute to the treatment of environmental pollutants.

5. References
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