Activated Carbon in Methomyl Adsorption and Its Capabilities: Batch and Fixed-Bed Column Experiments

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Abstract—This study aimed to assess the effectiveness of activated carbon (AC) in removing methomyl from water. Batch and fixed-bed column experiments were conducted to investigate the potential of AC for methomyl adsorption and to identify the optimal conditions for its application in water treatment. The batch experiments determined that activated carbon could adsorb methomyl at a rate of 32.70 mg/g after 300 m of contact. The highest adsorption capacity of 35.35 mg/g was observed at pH 2. Further agitation speed experiments revealed that turbulence is critical in controlling the solid–liquid mass transfer mechanism. The result from the pseudo-first-order adsorption kinetic equation was consistent with the experimental data, and the Langmuir adsorption isotherm better described the methomyl adsorption of activated carbon. The fixed-bed column experiments showed that the adsorption efficiency was depleted after continuous use after 19 hours (1,140 m), corresponding to the adsorption equilibrium point.

Keywords—activated carbon, adsorption, fixed-bed column, methomyl

I. INTRODUCTION

Pesticides are commonly used in agriculture to protect crops from pests and diseases, but their excessive use has led to environmental contamination and health risks [1]. These pesticides affect the target organisms and the environment, including the groundwater, surface water, soil, and atmosphere through flow, leaching, and pulverization processes, thus contaminating the ecosystem [2, 3]. An annual average of 2 million tons of pesticides is used globally to tackle weeds, insects, and pests. Herbicides and insecticides are the most common forms of pesticides, dominating total pesticide consumption at 47.5% and 29.5%, respectively. Primary pesticide-consuming countries include China, the USA, Argentina, India, Japan, Canada, Brazil, France, Italy, and Thailand [4]. Pesticide contamination is environmentally harmful, constituting an essential global public topic [5]. Neonicotinooids and carbamate pesticides are commonly used for agricultural and household activities, as they are highly soluble in water [6]. Methomyl, a broad-spectrum insecticide, is one of agriculture’s most widely used pesticides [7]. Methomyl, i.e., S-methyl-N-[(methylcarbamoyl) oxy] thiaoacetimidate, with the formula C₉H₁₀N₂O₃S, is a broad-spectrum oxime carbamate pesticide. Due to its high water solubility (57.9 g·L⁻¹, 25 °C), methomyl in the environment cannot be fixed in the soil. The half-life of methomyl ranges between 3 and 50 days in soil, between 6 and 262 days in water, and between 160 and 224 days in air [8]. Long-term exposure to methomyl can result in hepatotoxicity, cytotoxicity, and neurotoxicity in animals [9]. However, methomyl harms human health and the environment, as it can penetrate the soil and contaminate groundwater [10]. It has been found in humans’ and animals’ blood, liver, kidneys, and brain [11]. Therefore, the removal of methomyl from contaminated water is of great importance. To remove these pollutants from water, advanced processes such as gamma irradiation, bioremediation, membrane filtration, advanced oxidation processes, ozonization, and adsorption [12]. Throughout the last few years, research has focused on eliminating organic pollutants in water using low-cost adsorption, which can resolve the contamination problem effectively. Carbon-based sorbents show high efficiency (nearly 100%) in removing pesticides from water bodies [13]. Activated carbon (AC) is extensively used as an adsorbent for removing various pollutants from water [14]. Due to its low initial cost; excellent performance due to its large surface area (300–2500 [m²/g]); and high porosity, activated carbon (AC) has attracted interest as an adsorbent for insecticides in water treatment plants [15].

An example of activated carbon used to adsorb pesticides is tangerine seed-activated carbon (TSAC), used to remove pesticides. Carbamates (CMs) were eliminated from the complex solution. It was found that TSAC had a specific surface area of 659.62 m²/g and a total pore volume of 0.6203 cc/g. The Langmuir isotherm is more appropriate for the adsorption process of CMs on TSAC [16].

Most of the past works have studied the removal of methomyl from the water via activated carbon using batch experiments to find the optimum conditions and kinetics. However, the adsorption of methomyl via fixed-bed column experiments has not been studied. This information could improve more efficient methods for removing methomyl from water sources.

This study investigated the potential of AC in methomyl adsorption through batch and fixed-bed column experiments. This study aimed to evaluate AC’s efficiency in removing methomyl from water and determine the optimal conditions for its application in water treatment.

II. MATERIALS AND METHODS

A. Materials and Reagents

In this study, activated carbon (Iodine Number 1000) was taken from the Filter Supply Co., Ltd., Thailand, and was used without further purification. A model organic pollutant
was methomyl in an aqueous solution, which was synthesized using commercial grade methomyl \((\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2\text{S})\) with 90% purity. The DI water type II (conductivity < 1 \(\mu\)s/cm, resistivity > 1 M\(\Omega\)-cm, and total organics < 50 ppb) was used to prepare the solution. Furthermore, 99% sodium hydroxide (Micropearl) (RCI Labscan, AR grade) or 96% sulfuric acid (RCI Labscan, AR grade) was used for pH adjusting.

B. Batch Experiment

Batch experiments were conducted using an orbital shaker at an agitation speed of 250 rpm at room temperature (25–30 \(^\circ\)C). To an Erlenmeyer flask filled with 200 mL of 20 mg/L methomyl (aq), a specific mass of AC (0.1 g/L) was added. Equilibrium studies were performed by shaking the suspension-containing AC and methomyl for a specific time interval, up to a maximum of 780 min or 13 h. Samples were collected periodically at the designated time. Before methomyl analysis, the sample was filtered through a 0.45-\(\mu\)m nylon filter. Varying methomyl pH solutions (2, 3, 5, 7, 9, and 11) and varying agitation speeds (100, 150, 200, 250, and 300 rpm) were also investigated in separate experiments. Methomyl removal efficiencies were measured in triplicates following a specific protocol for each condition. Initially, each aqueous methomyl solution’s UV–Vis absorption spectrum was measured using a UV–Vis spectrophotometer (GENESYSTM 20, Japan). The methomyl had a maximum wavelength of 234 nm. The aqueous methomyl concentrations before and after experiment were assessed by forming a calibration curve based on the Beer–Lambert law and using the calibration relationships of absorbance and concentration data.

C. Fixed-Bed Column Experiment

The AC used in this experiment was sieved using 18 Mesh trays (1.000 mm) for size selection. The fixed-bed column was built from a 20 mL plastic syringe (inside diameter 19.13 mm) and was packed with 2.46 g sieved AC. The initial concentration of methomyl aqueous solution at pH 7 was 20 mg/L. The 3 mL/min flow rate was applied using a BT100M peristaltic pump. The breakthrough experiment was conducted until 95% exhaustion occurred and continuously monitored for up to 21.5 hours.

Two equations were employed to evaluate the effectiveness of activated carbon (AC) in methomyl removal. The first equation calculates the removal efficiency of methomyl, expressed as a percentage. It uses the original concentration \((C_0)\) and the equilibrium concentration \((C_e)\) of methomyl in milligrams per liter (mg/L) before and after adsorption, respectively, as shown in Equation (1) as follows:

\[
\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}
\]

The second equation quantifies the amount of methomyl adsorbed at equilibrium, measured in milligrams per gram (mg/g). It uses the same variables as the first equation but also includes the volume \((V)\) of the solution and the mass \((m)\) of the AC used, as shown in equation (2) as follows:

\[
q_e = \frac{(C_0 - C_e)}{V} \times \frac{m}{m} \tag{2}
\]

III. RESULTS AND DISCUSSION

A. Batch Adsorption Test

1) Equilibrium study

The ability of methomyl adsorption using activated carbon increased with increasing contact time, and the rate of adsorption increased rapidly during the first 120 min (Fig. 1). However, over time, the adsorption rate caused by the movement of methomyl molecules from the outside into the pores within the adsorbent particles starts to slow down. As a result, the adsorption will decrease until it reaches equilibrium at the contact time of 300 minutes. The adsorption capacity is most remarkable from 300 to 780 min, during which the adsorption rate equals the desorption speed. This study found that at a contact time of 300 min, it had the highest adsorption capacity of 32.70 mg/g.

An activated carbon adsorbent’s adsorption capacity tends to decrease when the pH is increased from 2 to 11, because pH values are directly related to the amount of hydroxide ions (OH\(^-\)) and hydrogen ions (H\(^+\)), and high pH values contain more OH\(^-\) than low pH values. The point of zero charges
When the pH value of the solution is lower than the pH\text{pzc} exchange is in equilibrium at the surface of the adsorbent. Becomes positively charged [19, 20].

\text{pH\text{pzc}} of the activated carbon adsorbent is illustrated in Fig. 3. \text{pH\text{pzc}} is the point at which the pH of the anion–cation exchange is in equilibrium at the surface of the adsorbent. When the pH value of the solution is lower than the \text{pH\text{pzc}} value, it causes the surface of the adsorbent to demonstrate a positive charge, which results in the good adsorption of negatively charged methomyl. The study results of the surface charge expression of the activated carbon adsorbent showed that the \text{pH\text{pzc}} value was 6. At a pH of 2, the activated carbon had the highest methomyl adsorption capacity because a pH of 2 is less than \text{pH\text{pzc}} (pH 6) and affects the hydroxyl surface groups (H⁺) on the activated carbon surface to become positively charged [19, 20].

**3) Effect of agitation speed**

This study used 200 mL of methomyl solution with an initial concentration of 20 mg/L at a pH of 2 and 300 min. The speed range of 100 to 300 rpm was studied. As a result of the study shown in Fig. 4, when the agitation speed increased from 100 to 250 rpm, the adsorption capacity increased from 7.68 mg/g to 34.92 mg/g. However, rising the agitation speed to upon 250 rpm causes the absorbing ability to decrease since the turbulence effect is a critical factor that plays an essential role in controlling the solid–liquid mass transfer mechanism.

The diffusion rate of methomyl molecules from the liquid to the liquid boundary layer surrounding the adsorbent particles increases with the system’s speed, because the mass transfer rate is higher when the thickness of the liquid boundary layer is diminished. In contrast, if the liquid boundary layer is very thick, it hinders the movement of molecules toward the adsorbent. Therefore, it is essential to maintain a suitable speed to ensure efficient mass transfer. The adsorption rate is subject to film diffusion and pore diffusion, which in turn depends on the turbulence of the system. If the water turbulence is low, the water film surrounding the adsorbent is very thick. As a result, it acts as an obstacle to the movement of molecules into the adsorbent, causing the film diffusion to determine the adsorption rate. On the other hand, if the water turbulence is high, the water film surrounding the adsorbent is thinner, and pore diffusion thus determines the adsorption rate.

Conversely, if the water exhibits high turbulence levels, the solution’s pore diffusion determines the adsorption velocity, leading to a faster adsorption rate. The findings from the study, as depicted in Fig. 4, denote that increasing the speed from 250 to 300 rpm results in a decrease in adsorption capacity. This phenomenon occurs due to the absorption turbulence reaching its limit. If the limit is exceeded, the adsorption capacity will not increase further. When turbulence is very high, the kinetic energy of the substance molecules is absorbed, causing the sorbent particles to collide rapidly, causing the adsorbed molecules surrounding the adsorbent to separate due to a weak suction force [21].

**B. Adsorption Kinetics**

The adsorption kinetics of methomyl adsorption on the AC were studied using the initial methomyl concentration of 20 mg/L, pH of 2, and sorbent dosages of 0.5 g/L to examine the speed of the methomyl adsorption reaction of activated carbon. To gain a deeper understanding of how methomyl interacts with AC, two non-linear kinetic models (the pseudo-first order and pseudo-second order models) were utilized to analyze the results of batch experiments. This approach allowed for a more thorough examination of the mechanisms involved in methomyl adsorption onto AC.

The pseudo-first order is given in Eq. (3) and in Eq. (4) as a linear form.

\[
\begin{align*}
q_t & = \frac{q_e}{1 - \exp(-k_1t)} \\
\ln(q_e - q_t) & = \ln q_e - k_1t
\end{align*}
\]

The pseudo-second order is given in Eq. (5) and in Eq. (6) as a linear form:

\[
\begin{align*}
q_t & = \frac{q_e^2k_2t}{(1+q_ek_2t)} \\
\frac{t}{q_t} & = \frac{1}{(k_2q_e^2)} + \frac{t}{q_e}
\end{align*}
\]

where \(k_1\) (min⁻¹) is the pseudo-first order adsorption rate constant, \(k_2\) (g/(mg-min)) is the pseudo-second-order adsorption rate constant, and \(q_e\) and \(q_t\) (mg/g) is the amount adsorbed at equilibrium and the amount adsorbed at the time “t”, respectively [22].

In Fig. 5, the pseudo-first order adsorption kinetic equation has a correlation coefficient (R²) value of 0.9687, which is closer to 1 than that of the pseudo-second order adsorption kinetic equation. Suggests that the pseudo-first order adsorption kinetics equation is consistent with the experimental data. In Table 1, the rate constant of the pseudo-first rate reaction is 0.0138 min⁻¹. The experiments showed great adsorption capacity, reaching 36.3111 mg/g. This high adsorption capacity indicates that activated carbon could be used to absorb methomyl from actual wastewater. Additionally, comparing the adsorption capacity calculated using the first-order adsorption kinetic equation \(q_e\) with the experimental adsorption capacity \(q_e,\text{exp}\) was closer than when using the pseudo-second order adsorption kinetic equations.
### Table 1. Kinetic parameters of the pseudo-first order and pseudo-second order models for the adsorption of methomyl on AC

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>( q_{e,exp} ) (mg/g)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( q_e ) (mg/g)</td>
</tr>
<tr>
<td>20</td>
<td>36.3111</td>
<td>0.0138</td>
<td>41.908975</td>
</tr>
</tbody>
</table>

Fig. 5. Adsorption kinetics of methomyl on AC by fitting a) pseudo-first order and b) pseudo-second order.

### C. Adsorption Isotherm

This study used a 200 mL solution containing 20 mg/L of methomyl at a pH of 7. The solution was shaken at 250 rpm for 300 min at room temperature while activated carbon weights of 0.02, 0.05, 0.10, 0.20, 0.30, and 0.50 g were tested in the experiments. The results of the study are shown in Table 2. The adsorption isotherm equation used in the study was Langmuir’s model. The relationship between the \( C_e/X_e \) and the \( C_e \) value was plotted in Fig. 6 (a) to analyze the study results. The slope and intercept values of the y-axis were employed to calculate the system constant (\( K_L \)) and the maximum capability (\( q_{max} \)), respectively. Freundlich’s adsorption isotherm equation was also used in the study. The relationship between \( \log X_e \) and \( \log C_e \) was drew in Fig. 6 (b), and the slope and intercept values on the y-axis were used to calculate the system constant (\( K_f \)) and the adsorption density (\( n \)), respectively.

According to the findings presented in Table 2, it is evident that the Langmuir adsorption isotherm has a correlation coefficient (\( R^2 \)) of 1, which is higher than that of the Freundlich adsorption isotherm (0.7117). This result suggests that the methomyl adsorption of activated carbon is better explained using Langmuir’s adsorption isotherm. The results of this study are consistent with the research of Wang et al. 2020 [16], which found that the Langmuir isotherm model was more suitable for the carbamate pesticides adsorption process onto the tangerine seed activated carbon. Furthermore, the maximum adsorption capacity \( q_{max} \) was 89.6906 mg/g. Since the Langmuir adsorption isotherm is a single-layer adsorption, it can be inferred that the methomyl molecules are attached to the surface of the activated carbon, and each location on the surface can only capture one molecule of methomyl. Overall, these results suggest that the Langmuir adsorption isotherm is more suitable for explaining the methomyl adsorption on activated carbon than the Freundlich adsorption isotherms.

### Table 2. Parameter of adsorption isotherms for the adsorption of methomyl on AC

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>( q_{max} ) (mg/g)</th>
<th>( K_L ) (mg/g)</th>
<th>( R^2 )</th>
<th>( K_f ) (mg/g)</th>
<th>( n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>89.6906</td>
<td>1.23E+15</td>
<td>1</td>
<td>6.4047</td>
<td>1.234</td>
<td>0.7117</td>
</tr>
</tbody>
</table>

D. Fixed-Bed Column Experiments

A continuous-flow fixed-bed column system was employed for this study, given its common use in industrial wastewater treatment [23, 24]. The breakthrough curve of methomyl adsorption was investigated using a downflow column and conducted the experiment at an initial methomyl concentration of 20 mg/L, a methomyl flow rate of 3 mL/min, and 4.62 g of activated carbon in the column.

Fig. 6. Adsorption isotherm of methomyl on AC using a) the Langmuir model and b) the Freundlich model.

Fig. 7. Breakthrough curve of methomyl adsorption by AC from fixed-bed column experiments.
Based on the findings presented in Fig. 7, this study determined that activated carbon effectively adsorbed methomyl at the onset and exhibited a relatively linear adsorption pattern in the middle phase. However, adsorption began to decline thereafter, and the adsorption efficiency was depleted at 19 h (1,140 min), corresponding to the adsorption equilibrium point. By examining the breakthrough curve, it is possible to derive the sorbent’s adsorption capacity and predict the system’s service life.

IV. CONCLUSION

The findings from this study on methomyl adsorption via activated carbon have significant implications in environmental remediation. Methomyl is a toxic pesticide commonly used in agriculture, and its presence in water bodies can harm aquatic life and human health. AC for adsorption is a promising method for removing methomyl from water sources. Batch and fixed-bed column experiments were conducted to investigate the potential of AC for methomyl adsorption and to identify the optimal conditions for its application in water treatments. This study’s results suggest that pH and contact time are crucial factors affecting methomyl adsorption efficiency via AC. The batch experiments determined that AC can adsorb methomyl at a rate of 32.70 mg/g after 300 minutes of contact. The highest adsorption capacity of 35.35 mg/g was observed at pH 2. The Langmuir adsorption isotherm was found to describe better the methomyl adsorption process, which could guide future research on developing effective adsorption technologies. The maximum adsorption capacity q\text{max} was 89.6906 mg/g. A fixed-bed column experiment was completed with an initial methomyl concentration of 20 mg/L, a methomyl flow rate of 3 mL/min, and 4.62 g of activated carbon in the column. The adsorption efficiency was exhausted at 19 hours. This information could lead to the developing of more efficient and cost-effective adsorption systems for removing methomyl from water sources. In terms of potential applications and extensions, this study’s findings could be applied to developing adsorption-based water treatment technologies for removing other pesticides or toxic contaminants from water sources. Further research could also explore using AC in combination with other adsorbents or treatment methods to enhance the efficiency of methomyl removal.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHOR CONTRIBUTIONS

Conceptualization, A.W., and A.K.; data curation, A.K., O.F., S.H.; formal analysis, A.W.; funding support, A.W.; investigation, A.W., A.K., K.K. P.S., L.K.; methodology, A.W., and A.K.; project administration, A.W.; resources, A.W.; supervision, A.W.; validation, A.W.; visualization, K.K.; writing—original draft, A.W.; writing—review and editing, A.K., A.W.; all authors had approved the final version.

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