ภาคผนวก ก
ผลการดูดซับสารเมโธมิลของไบโอชาร์

ตารางที่ ก. 1 ผลของระยะเวลาสัมผัสที่มีต่อการดูดซับสารเมโธมิล

ระยะเวลาสัมผัส (นาที)	C/C0		
	BCA	BNS	BHP
0	0.00	0.00	0.00
5	0.14	0.61	1.69
15	0.20	0.73	1.76
30	0.26	1.39	1.91
60	0.35	1.64	1.98
120	0.41	1.76	2.04
180	0.53	1.84	2.22
240	0.63	1.92	2.30
300	0.67	2.06	2.39
360	0.72	2.40	2.40
1440	0.92	2.87	2.41

ตารางที่ ก. 2 ผลของค่าความเร็วรอบที่มีต่อการดูดซับสารเมโธมิลที่ความเร็วรอบ 50 RPM

RPM 50	C/C0		
Time(min)	BCA	BNS	BHP
0	1	1	1
5	1.00	0.99	0.98
15	1.00	0.97	0.97
30	0.97	0.97	0.96
60	0.97	0.95	0.96
120	0.96	0.95	0.95
180	0.96	0.95	0.94
240	0.96	0.95	0.94
300	0.96	0.94	0.94
360	0.95	0.93	0.94
1440	0.95	0.91	0.93

ตารางที่ ก. 3 ผลของค่าความเร็วรอบที่มีต่อการดูดซับสารเมโธมิลที่ความเร็วรอบ 100 RPM

RPM 100	C/C0		
Time(min)	BCA	BNS	BHP
0	1	1	1
5	0.99	0.97	0.96
15	0.98	0.96	0.96
30	0.97	0.95	0.95
60	0.96	0.95	0.95
120	0.96	0.94	0.93
180	0.96	0.93	0.92
240	0.95	0.92	0.91
300	0.95	0.92	0.91
360	0.93	0.91	0.90
1440	0.93	0.90	0.90

ตารางที่ ก. 4 ผลของค่าความเร็วรอบที่มีต่อการดูดซับสารเมโธมิลที่ความเร็วรอบ 200 RPM

RPM 200	C/C0		
Time(min)	BCA	BNS	BHP
0	1	1	1
5	0.99	0.94	0.83
15	0.98	0.93	0.82
30	0.97	0.86	0.81
60	0.96	0.83	0.80
120	0.96	0.82	0.79
180	0.95	0.81	0.78
240	0.94	0.81	0.77
300	0.93	0.79	0.76
360	0.93	0.76	0.76
1440	0.91	0.71	0.76

ตารางที่ ก. 5 ผลของค่าพีเอชต่อการดูดซับสารเมโธมิลด้วยไบโอชาร์

พีเอช	**C/C0**		
	BCA	**BNS**	**BHP**
3	0.86	0.75	0.83
5	0.89	0.87	0.88
7	0.87	0.88	0.9
9	0.85	0.93	0.93
11	0.71	0.65	0.75

ตารางที่ ก. 6 ผลของน้ำหนักวัสดุดูดซับต่อประสิทธิภาพการดูดซับ

น้ำหนัก (mg)	**Concentration (mg/l)**		
	BCA	**BNS**	**BHP**
30	9.51	8.01	8.52
60	8.95	7.13	7.91
120	7.53	4.50	5.53
240	5.59	2.09	3.23
300	4.85	1.80	2.79
600	3.12	0.92	1.54

ภาคผนวก ข
รูปประกอบการสังเคราะห์ไบโอชาร์จากเหง้ามันสำปะหลัง


นำเหง้ามันสำปะหลังไปล้างด้วย
น้ำปราศจากไอออน (deionized water) เพื่อกำจัดสิ่งสกปรก


นำเหง้ามันสำปะหลังไปตากแดดเป็นเวลา 48 ชั่วโมง เพื่อให้เหง้ามันสำปะหลังแห้ง


นำไปอบไล่ความชื้นที่อุณหภูมิ 80 องศาเซลเซียส เป็นเวลา 24 ชั่วโมง

นำมาตัดให้มีขนาดเล็กประมาณ 1-2 เซนติเมตร

รูปที่ ข.1 การเตรียมวัสดุชีวมวลจากเหง้ามันสำปะหลัง

 

เหง้ามันสำปะหลัง 10 กรัม

ไพโรไลซิสที่อุณหภูมิ 300 400 500 องศาเซลเซียส
เป็นระยะเวลา 0.5, 1, 1.5, 2, 2.5 ชั่วโมง

ภาคผนวก ค
บทความทางวิชาการที่ได้รับการตีพิมพ์เผยแพร่ในระหว่างศึกษา

Synthesis of Cassava Rhizome Biochar for Methomyl Adsorption

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ABSTRACT

This research aims to study the synthesis of biochar from cassava rhizomes and the factors involved in the absorption of methomyl. The factors of interest in the synthesis of biochar include the pyrolysis temperatures of 300, 400, and 500 °C and the pyrolysis time of 2.5 hours under nitrogen gas conditions, and the obtained biochar was modified with phosphoric acid to increase the efficiency of adsorption. The biochar obtained from the synthesis will be examined using various techniques, including CHN/O, BET, SEM, FTIR, XTM, etc. The factors in the study of adsorption that are of interest include contact time agitation speed and pH value, etc. The study found that the temperature and duration of pyrolysis affect the quality of biochar. The selected biochar was obtained at 500 °C for 2.5 hours with the highest %C of 78.149 and the lowest H/C of 0.026, which is similar to other research studies. The biochar is of high quality and will have a stable C ratio, and low H/C. A higher carbon content will result in a more stable biochar. Modifying biochar with phosphoric acid results in increasing the physical and chemical goods. The specific surface area from BET measurement and average pore diameter from XTM analysis (from Synchrotron Light Research Institute (SLRI)) both increased from 2.29 to 3.39 (m^2/g) and 1.57 to 6.54 (Å), respectively. For methomyl adsorption experiments, it was found that equilibrium was reached after 180 minutes. The rotational speed and pH value affected the adsorption efficiency. The optimum condition for methomyl adsorption was with an agitation speed of 200 rpm at pH 3 with an efficiency of 27.90 %.

Keywords : biochar; cassava rhizomes; methomyl; pesticides; phosphoric acid

INTRODUCTION

At present, the agricultural sector uses pesticides in farming, resulting in the accumulation of pesticides in the environment. When pesticide accumulation exceeds saturation, it will cause the soil to desorption. Pesticides are washed away along with the leaching process of rain that falls into natural water sources [1]. Pesticides contaminating natural water sources can accumulate in the food chain of living things in water sources. This results in an increased risk to human health. Methomyl has been found in groundwater and surface water. It was found at 10 µg/l in groundwater and 30 µg/l in surface water, respectively. The standards for pesticides in soil and surface water should not be more than 0.1 µg/l as regulated by the EU and US EPA [2]. However, the amount of methomyl found was still higher than the standard.

This research is interested in methomyl treatment. From past research studies, various technologies have been used to treat methomyl, such as absorption, photodegradation, and advanced oxidation processes. Adsorption is widely used in removing pesticides because it is easy to use and inexpensive [2]. Biochar is a carbon-rich product used as an adsorbent to remove contaminants in water supplies by the physical surface and chemical properties of biochar. Biochar production is also relatively low-cost. Most of the starting materials are waste materials from industrial and agricultural industries. This led to interest in the synthesis of biochar from biomass. In this research, the starting raw material for producing biochar is cassava rhizome because cassava is one of the economic crops of Thailand. From the study of Aup-Ngoen in 2020, it was found that the highest percentage of carbon content was cassava rhizome compared with durian peel, pineapple peel, and corncob, so it was considered a starting material that can be used to produce biochar [3]. Adsorption of the atrazine and imidacloprid using phosphoric acid modified-biochar from agricultural waste showed the maximum adsorption efficiency of atrazine was 70.7% and imidacloprid was 77.8%, respectively. The phosphoric acid treatment increased the absorption of both pesticides Type [4].

METHODOLOGY

Preparation and modification of biochars

Preparation of biochars: 10g of cassava rhizomes were pyrolysis at temperatures of 300, 400, and 500 °C for 2.5 hours with an increasing rate of temperature at 5°C/minute under nitrogen gas conditions.

Modification of biochars: Briefly, 10 g were immersed in 100 mL 14% H_3PO_4 solution for 24 hours. at 25°C. After that, the phosphoric-modified biochars were washed with distilled water until the pH of the supernatants was stable. Subsequently, the supernatants were discarded and the biochars were oven-dried overnight at 105°C.

Characterization of biochars

A total elemental composition such as carbon, hydrogen, nitrogen, and oxygen was measured by the elemental analyzer. Brunauer–Emmett–Teller (BET) was used to detect specific surface areas of biochars. Fourier transform infrared (FTIR) spectra of biochars were conducted by an FTIR instrument. The morphology of the biochar was determined via scanning electron microscopy (SEM) and Synchrotron X-ray tomographic microscopy (XTM) at beamline 1.2W was operated at 1.2GeV, 150 mA in Synchrotron Light Research Institute (SLRI) were characterized the porosity by Octopus Analysis software and rendered in 3D tomographic reconstruction by using Drishti software. A laser scattering particle size distribution analyzer was used to measure the size and particle distribution of the material. Point of zero charge with salt addition technique To determine the charge on the surface of biochar.

Adsorption experiments

Varying methomyl pH solutions (3, 5, 7, 9, and 11) and varying agitation speeds (100, 150, 200, and 250 rpm) were also investigated in separate experiments. Batch experiments were conducted using an orbital shaker at an agitation speed of 200 rpm at room temperature. To an Erlenmeyer flask filled with 10 mg/L methomyl (aq), a specific mass of biochar (1 g/L) was added. Equilibrium studies were performed by shaking the suspension containing biochar and methomyl for a specific time interval, up to a maximum of 360 min. Samples were collected periodically at the designated time and filtered through a 0.45-μm Nylon filter before methomyl analysis. Methomyl removal efficiencies were measured in triplicates following a specific protocol for each condition. The filtrate was analyzed for pesticide concentrations using high-pressure liquid chromatography (HPLC) techniques.

RESULTS AND DISCUSSIONS

Characterization of biochars

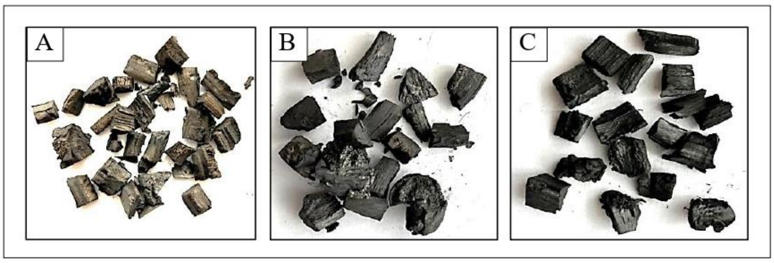

Figure 1. Photograph of physical characteristics of biochar synthesis from cassava rhizomes. (A) Biochar cassava rhizomes 300 °C/2.5 hr., (B) Biochar cassava rhizomes 400°C/2.5 hr., (C) Biochar cassava rhizomes 500°C/2.5hr.

From Figure 1. It is found that the physical characteristics of biochar at a temperature of 300 °C are somewhat brownish, similar to wood. Therefore, it is assumed that there is incomplete combustion. For biochar at 400 and 500 °C, the color is completely black. Therefore, it is assumed that it becomes complete biochar. Therefore, only biochar at 400 and 500 °C was selected to be analyzed with CHN/O to analyze the composition.

Table 1 Organic elemental compositions

Sample Biochar	% C	% H	% N	Ratio H/C
400 °C / 2.5 hr.	75.132	3.7878	1.7910	0.0504
500 °C / 2.5 hr.	78.149	2.0398	0.6919	0.0261

Table 2 Physiochemical characteristics of biochars from BET analysis.

Sample	Surface Area (m^2/g)	Average pore diameter (Å)	Total pore volume (cc /g)
Biochar CA	2.29E+00	1.57E+02	1.76E-02
Biochar+ H_3PO_4	3.39E+00	6.54E+02	1.33E-02

From Table 1. It was found that biochar synthesized at a temperature of 500 °C 2.5 hr. had the highest carbon content of 78.149 % and the H/C ratio was 0.026, which was like other research studies. High-quality biochar has a stable C ratio and a low H/C ratio. The selected biochar is then treated with phosphoric acid. From Table 2., the modification of phosphoric acid can increase the specific surface area of biochar produced from cassava rhizomes as proved by BET analysis. Even if the change in specific surface area is small. The phosphoric acid-modified biochar showed a higher average pore diameter similar to Peng's studies [5].

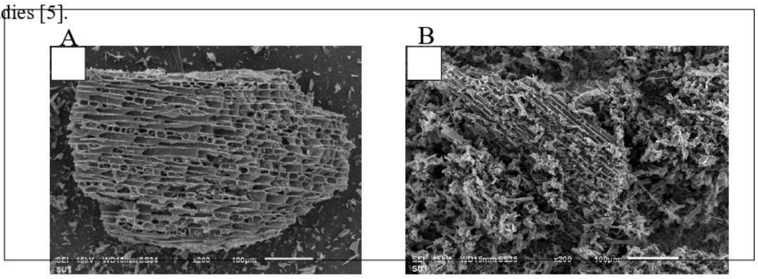

Figure 2. SEM images of (A) Biochars CA.
(B) BiocharCA + H_3PO_4.

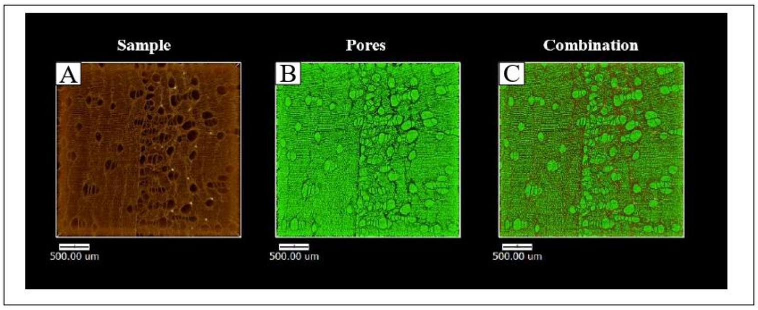

Figure 3. Results of the X-ray Tomographic Microscopy (XTM) technique of the synthesized biochar cassava rhizomes 500°C/2.5 hr.

From Figure 2, the modification results in adhesion occurring between the phosphoric acid and the pore structure on the biochar surface. Until you can barely see the pore structure. This corresponds to the BET and FTIR result values with an increase in the specific surface area and functional groups. The 3D X-ray characteristics and porosity (%) of biochar were studied using the X-ray Tomographic Microscopy (XTM) technique from Synchrotron Light Research Institute (SLRI). XTM results in Figure 3 show a 3D X-ray image in which Figure 3A shows only biochar solid structure (brown color), Figure 3B shows only the pore in the biochar sample, and Figure 3C shows both biochar solid structure combined with pore in structure. From XTM measurement, a porosity of 28% was obtained, which means that the remaining 72% was solid biochar.

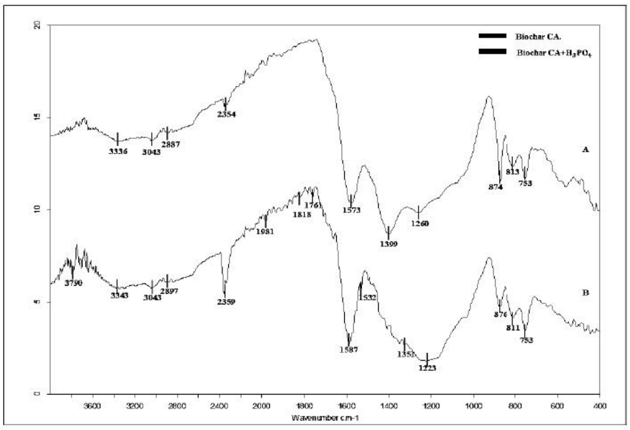

Figure 4. FTIR spectra of BiocharCA. and BiocharCA + H_3PO_4.

The results of the Fourier transform infrared spectrophotometer (FTIR) are shown in Figure 4. A peak at 3200-3800 cm^{-1} was found in both biochar and modified biochar, which were found to be O-H bonds [6], A peak at 2850-3000 cm^{-1} was found in both biochar and modified biochar, which were found to be C-H stretching, A peak at 1400-1600 cm^{-1} was found in both biochar and modified biochar, which were found to be C=C stretching [7], it can be seen that both types of biochar changes can be seen in the wavenumber range of 1200-1400. Phosphoric acid treatment shows an increase in the formation of P=O, P=OOH groups, which is similar to Peng's studies [5] where P=O, P-OOH groups were detected after treatment with phosphoric acid. Research has studied the size of biochar for adsorption. It was found that small biochar had increased adsorption. Therefore, biochar is crushed before use [8]. The size and distribution were then measured using a laser scattering particle size distribution analyzer. For the particle size distribution analysis technique using laser scattering, it was found that the particle size distribution of biochar was in the range of 10 – 300 μm and the average particle size was 54 μm. As shown in Figure 5.

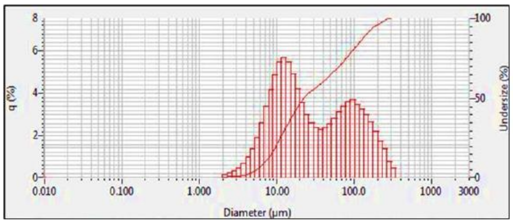

Figure 5. Measurement of size and distribution of biochar particles

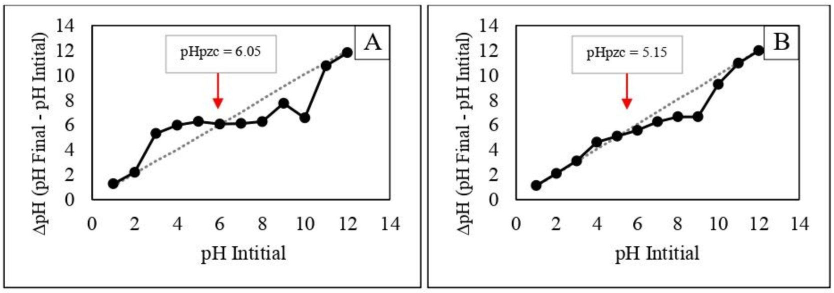

Figure 6. Points of Zero Charge (pH_{pzc}) of biochar.
(A) biochar from cassava rhizomes (B) biochar from cassava rhizomes modified with phosphoric acid.

By studying the pH value at zero surface charge, points of zero charge of the adsorbent are shown in Figure 6, where the value refers to the pH at which the sum of the surface charges of the adsorbent is equal to zero. When the pH value of the solution is lower than the value, it will cause the surface of the adsorbent to display a positive charge. When the pH value of the solution is higher than the value, it will cause the surface of the adsorbent to display a negative charge [9]. The results of this study found that the point of zero charge of biochar from cassava rhizomes is 6.05, meaning that at pH of 6.05, the surface charge of cassava rhizome biochar is zero and the of cassava rhizome biochar modified with phosphoric acid is 5.15 shown in Figure 6B.

Adsorption Experiment

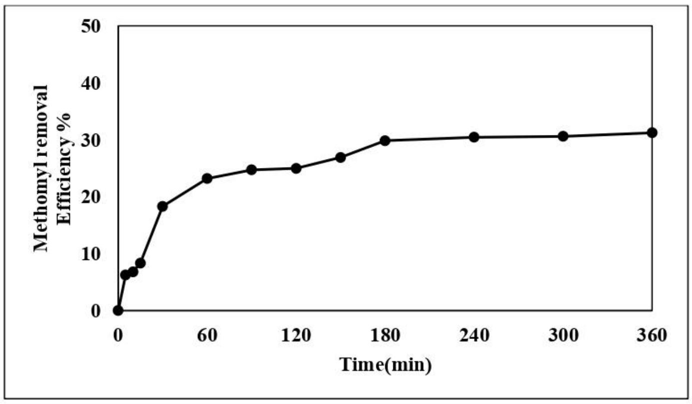

Figure 7. Effect of the contact time
Initial concentration methomyl 10 mg/l, biochar 1 g, Initial pH 6.20, agitation speed 200 rpm.

The ability to absorb methomyl by biochar from cassava rhizomes modified with phosphoric acid increases with increasing contact time and the adsorption rate increases rapidly during the first 180 minutes as shown in Figure 7. But over time, the adsorption rate caused by the movement of methomyl molecules in the adsorbent particles begins to slow down until equilibrium is reached at a contact time of 180 minutes. The adsorption capacity is most remarkable from 180 to 360 minutes, during which the adsorption rate is equal to the desorption speed. This study found that during the contact period of 180 minutes, the efficiency was 29.84%.

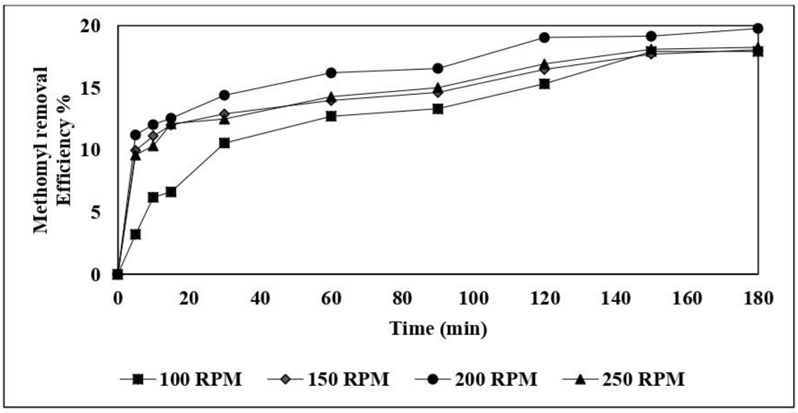

Figure 8. Effect of the agitation speed
Initial concentration methomyl 10 mg/l, biochar from cassava rhizomes modified with phosphoric acid 1 g, Initial pH 6.00.

From Figure 8, it can be seen that when increasing the agitation speed, the methomyl adsorption efficiency by biochar was increased. But when the speed is increased to more than 200 rpm, the adsorption efficiency starts to decrease. This is because the effect of turbulence is one of the key factors that are important in controlling the solid-liquid mass transfer mechanism [10]. Figure 9 shows that the pH of the solution has an important influence on the adsorption behavior of methomyl. The adsorption efficiency of methomyl decreased with increasing pH, but when the pH increased to 11, methomyl decomposed into other compounds. Resulting in the remaining methomyl value is less than it should be [9]. From research of Akl, M. A., *et al.* (2016), in the pH range of 2-8, methomyl is relatively stable. In contrast, when the pH increased to 10, the residual methomyl content was only 12% of the original value. Moreover, at pH values as high as 12, methomyl was completely degraded into other compounds. This means that methomyl is relatively degraded in the basic solution. Therefore, the effect of pH on the adsorption capacity was investigated in the range of pH 2-8 [11].

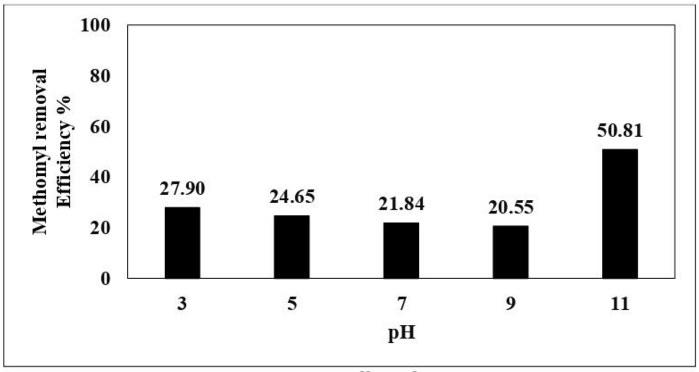

Figure 9. Effect of pH
Initial concentration methomyl 10 mg/l, biochar from cassava rhizomes modified with phosphoric acid 1 g, agitation speed 200 rpm.

CONCLUSION

In this study, biochar was produced from cassava rhizomes. It was found that the best condition for the synthesized biochar was 500°C for 2.5 hours, resulting in a 78.149% carbon content and an H/C ratio of 0.026. The biochar is of high quality and will have a stable carbon ratio, low H/C ratio, and a higher carbon content, which will result in a more stable biochar, respectively. Therefore, we chose to further study it by modifying it with phosphoric acid. XTM measurements revealed a porosity of 28%, meaning that the remaining 72% was solid biochar. Modifying the biochar with phosphoric acid increased physical and chemical properties. The specific surface area measured by BET and the average pore diameter both increased from 2.29 to 3.39 m^2/g and 1.57 to 6.54 Å, respectively. Additionally, there were more functional groups present than before. Phosphoric acid treatment showed an increase in the formation of P=O and P=OOH groups, which is similar to Peng's studies [5]. From the results of the adsorption experiment, it can be seen that the adsorption capacity is most remarkable from 180 to 360 minutes, during which the adsorption rate equals the desorption speed. The agitation speed and pH affect the adsorption efficiency. The optimal conditions are a stirring speed of 200 rpm, and a pH of 3, resulting in an efficiency of 27.90%. In the pH range of more than 10, methomyl will be decomposed into other compounds, which is not a mechanism of adsorption.

ACKNOWLEDGEMENT

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