

(pH_{pzc}) of the activated carbon adsorbent is illustrated in Fig. 3. pH_{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 pH_{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 pH_{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 pH_{pzc} (pH 6) and affects the hydroxyl surface groups (H^+) on the activated carbon surface to become positively charged [19, 20].

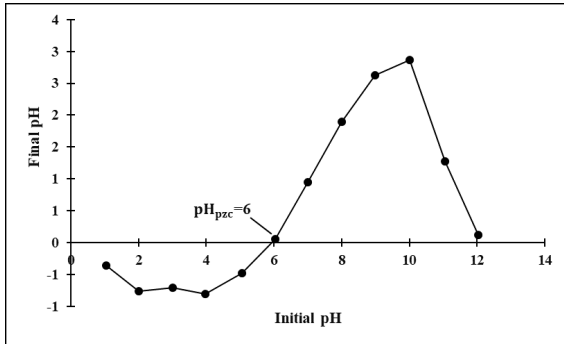


Fig. 3. pH_{pzc} of activated carbon in this experiment.

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.

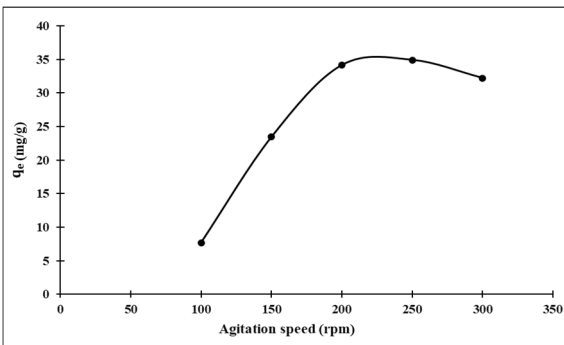


Fig. 4. Effect of the agitation on methomyl adsorption via activated carbon.

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.

$$q_t = \frac{q_e}{(1 - \exp^{-kt})} \quad (3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

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

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (6)$$

where k_1 (min^{-1}) is the pseudo-first order adsorption rate constant, k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) 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 (R^2) 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

Concentration (mg/L)	$q_{e,exp}$ (mg/g)	pseudo-first order			pseudo-second order		
		K_1 (min^{-1})	q_c (mg/g)	R^2	K_2 (g/mg·min)	q_e (mg/g)	R^2
20	36.3111	0.0138	41.908975	0.9687	9.05627E-05	64.1026	0.8885

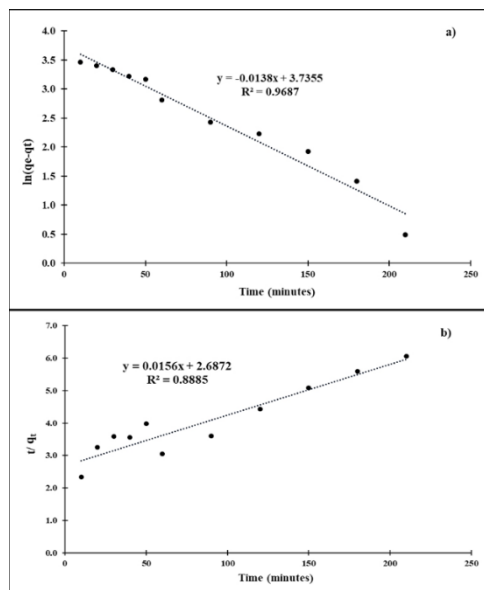


Fig. 5. Adsorption kinetics of methomyl on AC by fitting a) pseudo-first order and b) pseudo-second order.

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 drawn 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

Concentration (mg/L)	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mg/g)	K_L (mg/g)	R^2	K_f (mg/g)	n	R^2
20	89.6906	1.23E+15	1	6.4047	1.234	0.7117

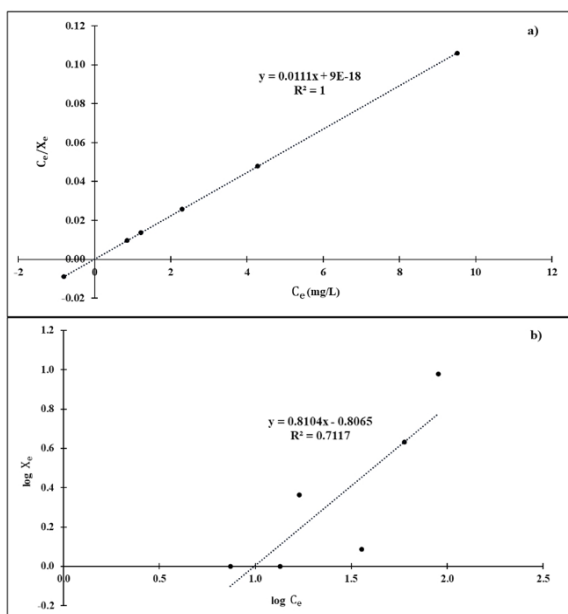


Fig. 6. Adsorption isotherm of methomyl on AC using a) the Langmuir model and b) the Freundlich model.

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.

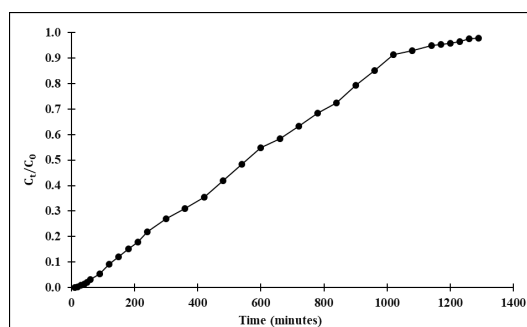


Fig. 7. Breakthrough curve of methomyl adsorption by AC from fixed-bed column experiments.

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_{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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REFERENCES

- [1] A. Singh, A. Malik, and R. Singh, "Pesticide residues in the environment and their potential health impacts," *Journal of Environmental Biology*, vol. 40, no. 4, pp. 839–858, 2019.
- [2] S. A. Nsibandé and P. B. C. Forbes, "Fluorescence detection of pesticides using quantum dot materials—A review," *Analytica Chimica Acta*, vol. 945, pp. 9–22, 2016.
- [3] S. M. Taha, M. E. Amer, A. E. Elmarsafy, and M. Y. Elkady, "Adsorption of 15 different pesticides on untreated and phosphoric acid treated biochar and charcoal from water," *Journal of Environmental Chemical Engineering*, vol. 2, pp. 2013–2025, 2014.
- [4] A. Sharma *et al.*, "Worldwide pesticide usage and its impacts on ecosystem," *SN Appl. Sci.*, 2019, vol. 1, p. 1446.
- [5] L. Zhou, Y. Zhang, R. Ying, G. Wang, T. Long, J. Li, and Y. Lin, "Thermoactivated persulfate oxidation of pesticide chlorpyrifos in aquatic system: kinetic and mechanistic investigations," *Environ. Sci. Pollut. Res.*, vol. 24, 2017, pp. 11549–11558.
- [6] J. Meijide, S. Rodriguez, M. A. Sanromán, and M. Pazos, "Comprehensive solution for acetamiprid degradation: Combined electro Fenton and adsorption process," *J. Electroanal. Chem.*, 2018, vol. 808, pp. 446–454.
- [7] Y. Zhang, Y. Li, X. Li, J. Miao, C. Liu, and H. Li, "Methomyl-induced oxidative stress and apoptosis in human liver carcinoma (HepG2) cells," *Environmental Science and Pollution Research*, vol. 26, no. 6, pp. 6150–6158, 2019.
- [8] X. Wu, X. Sun, C. Zhang, C. Gong, and J. Hu, "Micro-mechanism and rate constants for OH-initiated degradation of methomyl in atmosphere," *Chemosphere*, 2014, vol. 107, pp. 331–335.
- [9] A. A. Seleem, "Induction of hyperpigmentation and heat shock protein 70 response to the toxicity of methomyl insecticide during the organ development of the Arabian toad, *Bufo arabicus* (Heyden, 1827)," *J. Histotechnol.*, 2019, vol. 42, pp. 104–115.
- [10] W. Wang, X. Li, Y. Wang, W. Liu, and X. Qiao, "Photocatalytic degradation of methomyl by AgBr/TiO₂ under visible light irradiation: Kinetics, mechanism and response surface optimization," *Chemical Engineering Journal*, vol. 343, pp. 383–391, 2018.
- [11] C. Lin, "Methomyl poisoning presenting with decorticate posture and cortical blindness," *Neurol. Int.*, vol. 6, p. 5307, 2014.
- [12] A. Derylo-Marczewska *et al.*, "Phenoxyacid pesticide adsorption on activated carbon—Equilibrium and kinetics," *Chemosphere*, vol. 214, pp. 349–360, 2019.
- [13] A. Mojiri *et al.*, "Pesticides in aquatic environments and their removal by adsorption methods," *Chemosphere*, vol. 253, 126646, 2020.
- [14] X. Yan, Y. Li, X. Li, Y. Zhang, H. Zhang, and H. Li, "Adsorption of methomyl from water by modified corn straw biochar: Kinetics, isotherms, and thermodynamics," *Ecotoxicology and Environmental Safety*, vol. 188, 109893, 2020.
- [15] J. McGinley *et al.*, "Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon," *Journal of Environmental Management*, vol. 323, 116102, 2022.
- [16] Y. Wang, S. L. Wang, T. Xie, and J. Cao, "Activated carbon derived from waste tangerine seed for the high-performance adsorption of carbamate pesticides from water and plant," *Bioresource Technology*, vol. 316, 123929, 2020.
- [17] P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjana, P. Vijayalshmi, and S. Sivanesan, "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions," *Desalination*, vol. 261, no. 1–2, pp. 52–60, 2010.
- [18] K. Sun and J. C. Jiang, "Preparation and characterization of activated carbon from rubber seed shell by physical activation with steam," *Biomass Bioenergy*, vol. 34, no. 4, pp. 539–544, 2010.
- [19] R. C. Ferreira, O. M. C. Junior, K. Q. Carvalho, P. A. Arroyo, and M. A. S. D. Barrosa, "Effect of solution pH on the removal of paracetamol by activated carbon of dende coconut mesocarp," *Chemical and Biochemical Engineering Quarterly*, vol. 29, no. 1, pp. 47–53, 2015.
- [20] T. A. H. Nguyen, T. L. Nguyen, T. V. Nguyen, and T. L. Tran, "Adsorption of methomyl pesticide in aqueous solution using activated

carbon derived from agricultural wastes: Equilibrium, kinetic, and thermodynamic studies,” *Environmental Science and Pollution Research*, vol. 27, no. 33, pp. 41330–41342, 2020.

- [21] F. Jemal, T. Nurelegne, W. H. Stijn, and H. Van, “Adsorption of distillery spent wash on activated bagasse fly ash: Kinetics and thermodynamics,” *Journal of Environmental Chemical Engineering*, vol. 5, pp. 5381–5388, 2017.
- [22] J. M. Salman, V. O. Njoku, and B. H. Hameed, “Adsorption of pesticides from aqueous solution onto banana stalk activated carbon,” *Chemical Engineering Journal*, vol. 174, pp. 41–48, 2021.
- [23] T. Wan-Chi, D. G. L. Mark, L. P. B. A. Hanna, M. F. Cybelle, I. C. James, and W. Meng-Wei, “Competitive fixe-bed adsorption of Pb(II), Cu(II), and Ni(II) from aqueous solution using chitosan-coated bentonite,” *International Journal of Polymer Science*, vol. 16, no. 11, 2016.
- [24] H. Patel, “Fixed-bed column adsorption study: A comprehensive review,” *Applied Water Science*, vol. 9, no. 3, p. 45, 2019.

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