IJCA

Indonesian Journal of Chemical Analysis

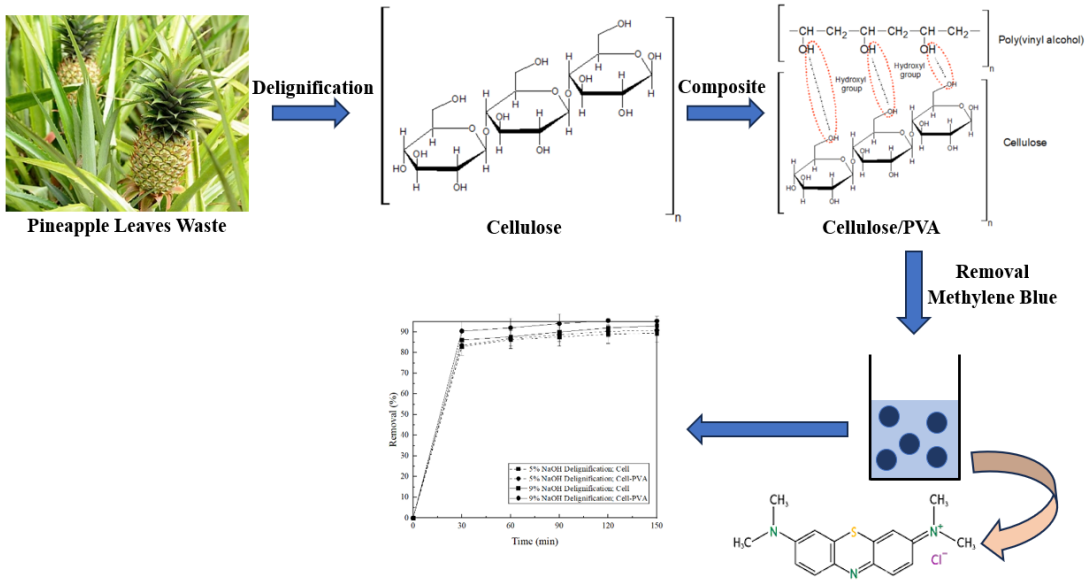
Homepage: https://journal.uii.ac.id/IJCA

Synthesis of a Cellulose/PVA Adsorbent Composite from Pineapple Leaves Waste (Ananas Comosus) for the Degradation of Methylene Blue in Aqueous Solution

Novi Eka Mayangsari[a,c], Tarikh Azis Ramadani[b,c*], Ulvi Pri Astuti[a,c]

[a]Waste Treatment Engineering Study Program, Shipbuilding Institute of Polytechnic Surabaya, Jalan Teknik Kimia, Kampus ITS Sukolilo, 60111, Surabaya, Indonesia
[b]Shipbuilding Engineering Study Program, Shipbuilding Institute of Polytechnic Surabaya, Jalan Teknik Kimia, Kampus ITS Sukolilo, 60111, Surabaya, Indonesia
[c]Waste Treatment Engineering Laboratory, Shipbuilding Institute of Polytechnic Surabaya, Jalan Teknik Kimia, Kampus ITS Sukolilo, 60111, Surabaya, Indonesia
*corresponding author: tarikh@ppns.ac.id
DOI: 10.20885/ijca.vol8.iss1.art6

GRAPHICAL ABSTRACT



ARTICLE INFO

Received : 30 January 2025
Revised : 08 March 2025
Published : 30 March 2025
Keywords : Adsorption, Cellulose, Methylene blue, Pineapple leaves, PVA

ABSTRACT

Methylene blue poses a significant environmental threat due to its high toxicity. Mitigation strategies are imperative to reduce the adverse effects of this compound. Pineapple (*Ananas comosus*) leaves waste can be valorized as a cellulose adsorbent, and cellulose/PVA adsorbent has emerged as a promising solution to minimize the impact of this contaminant. The objective of this study was twofold: first, to assess the efficacy of cellulose/PVA composite in the methylene blue adsorption process, and second, to evaluate its performance with cellulose adsorbent. The findings of the adsorption process demonstrated that the percentage removal of MB reached 94.03% on cellulose/PVA adsorbent with 9% NaOH delignification for 90 minutes. Subsequent kinetics analysis revealed that the adsorption process followed a pseudo-second-order kinetic model. The incorporation of PVA resulted in

a substantial enhancement in the removal of methylene blue by the adsorbent. The findings indicated cellulose and cellulose/PVA composites exhibited superior efficacy as adsorbents compared to cellulose alone in removing methylene blue.

1. INTRODUCTION

Nowadays, the rapid growth of industry has led to an increase in the amount of industrial waste and environmental contaminants. One of the contaminants whose presence is a serious concern is dyes. Dyes, which are often used in the textile industry, can influence the photosynthetic activity of aquatic biota and impact human health, resulting in ecological degradation and numerous diseases [1-3]. Methylene blue (MB) is one of the dyes that can be harmful to the environment and can be responsible for diseases such as dermatitis, skin irritation, leukemia, etc. [3]. Wastewater, which contains this dye, poses significant environmental and societal challenges. This requires effluent treatment to combat these obstacles.

Several techniques have been developed to reduce dyes, such as chemical methods (ozonation), photochemical (electrochemical destruction and Fenton reagents), biological processes (aerobic and anaerobic biodegradation), and physicochemical methods (coagulation/flocculation, adsorption, irradiation, ion exchange, and membrane separation technologies) [2-4]. Adsorption is perceived as the most successful method due to its simplicity, low cost, and high level of efficiency [5, 6]. In the adsorption process, the type of adsorbent has an essential role in enhancing the adsorption capacity. A wide variety of low-cost alternative adsorbents can be utilized for agricultural waste, plantation waste, and industrial solid waste. Adsorbents can be zeolite, clay, sludge, activated carbon, biochar or cellulose derived from diverse biomass [1]. Pineapple leaves (*Ananas comosus*) are waste from plantations that have not been exploited to the maximum. Meanwhile, this waste is mainly generated when the pineapple harvest season arrives, approximately 15-20% of the total pineapple weight [7].

The primary composition of pineapple leaves is cellulose (70-80%), lignin (5-12%), and hemicellulose. Cellulose in pineapple leaves can release hydrogen ions in aqueous solution, thus establishing a negatively charged surface area and can be used as an adsorbent [8]. Cellulose has unique properties, such as hydrophilicity, excellent mechanical properties, non-toxicity, simple modification, recyclability, and environmental harmlessness, making it perfectly safe to discard after use [9, 10]. The transformation of cellulose from lignocellulosic biomass can be facilitated by alkali pretreatment, encompassing various methods such as the application of ammonia in both aqueous and liquid forms, as well as gaseous ammonia. In addition, sodium hydroxide, sodium carbonate, and calcium hydroxide (lime) have been employed in this process. The effectiveness of this method is contingent upon the efficient removal of lignin, which is facilitated by the interaction of alkali with this compound. Among the various alkali agents, sodium hydroxide (NaOH) is particularly effective in delignification processes, achieving up to 60-80% delignification levels within 5-60 minutes and a NaOH concentration of 0.5-10% [11]. Cellulose can be chemically modified with a wide range of substances for wastewater treatment, especially for dye remediation. These cellulose modifications promote sorption efficiency and physical stability, increasing adsorption capacity [4, 12].

Cellulose from bamboo integrated with zinc oxide (ZnO) to reduce methylene blue dye resulted in a removal efficiency of 93.55% [13]. Nanocellulose modified with polypyrrole can deliver an adsorption capacity of up to 298.98 mg/g [14]. Furthermore, cellulose can be modified by enhancing its gel properties by incorporating chitosan, polyvinyl alcohol (PVA), or other polymers [15]. Chitosan exhibits certain drawbacks, including inadequate chemical stability and reduced adsorption capacity of crosslinked chitosan adsorbents [16]. Polyvinyl alcohol (PVA), a semicrystalline polymer, possesses numerous reactive hydroxyl groups, facilitating its interaction with other polymers and enabling the formation of composite blends [17-19]. PVA possesses excellent water solubility and biodegradability, and its long polymer chains, which bind to cellulose, can form a high density, thereby improving cellulose gel's mechanical properties and adsorption capacity [20]. This modification is undertaken to enhance the sorption capacity of cellulose by increasing the hydroxyl groups present, where cellulose already has hydroxy groups from the

presence of inter- and intramolecular hydrogen bonds. The utilization of cellulose derived from agricultural waste (bagasse) and modified with polyvinyl alcohol (PVA) has demonstrated efficacy in the removal of methylene blue (MB) and crystal violet (CV) dyes. The modified cellulose exhibited a removal capacity of 70% for CV and 64.5% for MB, respectively. Furthermore, the degradation rate of cellulose/PVA composite was superior to that of PVA, with a respective rate of 43% and 35% [21]. The mixture of cellulose and PVA will generate a hydrogel homogeneous solution that has promising potential in wastewater treatment [22].

In this study, cellulose gel was fabricated from pineapple leaf waste and Polyvinyl alcohol (Cell-PVA). The gel was characterized by BET analysis, SEM, and XRD. Cellulose gel was applied as an adsorbent to separate methylene blue (MB) dye from an aqueous solution.

2. EXPERIMENTAL METHODS

2.1. Materials

Pineapple leaves were taken from plantations in Menganti, Gresik, East Java. Methylene blue (MB) ($C_{16}H_{18}ClN_3S$; λ_{max}: 663 nm and M_W: 319.85 g mol^{-1}) dye, NaOH, polyvinyl alcohol (PVA) was supplied by Merck.

2.2. Cellulose preparation from pineapple leaves

Pineapple leaves were well washed and dried in the sun for about 3 days, then crushed and homogenized to a size of 60 mesh so it became a powder. The powder was delignified using 5% and 9% (w/v) NaOH in a proportion of 1:30 (w:v) for 90 minutes. After the delignification process, it was rinsed to a neutral pH and dried to a stable weight.

2.3. Composite Fabrication

Polyvinyl alcohol powder of 1 gram was added with 0.1 M HCl. The material was heated at 60ºC with agitation until a gel was obtained. After the gel is formed, 0.5 gram of pineapple leaves adsorbent is added gradually until a homogeneous paste is achieved. The paste was dried at 105ºC to evaporate the water until a water-free mixture was obtained, crushed to powder form, and prepared for characterization.

2.4. Batch Adsorption Process

The study investigated the absorption process of methylene blue by analyzing the effect of contact time (0-150 minutes) with an initial concentration of MB adsorbate of 25 ppm. The adsorption process used two types of adsorbents: cellulose and cellulose-PVA. 1 g of adsorbent was added to 100 ml of MB adsorbate. Afterwards, the mixture is divided between the filtrate and residue. The concentration of MB absorbed in the adsorbent was determined by analyzing the results of the adsorption process using a UV-Vis spectrophotometer (Agilent Cary 60 Spectrophotometer; λ = 665 nm). Eq. 1 can be used to calculate the removal efficiency:

$$\%Removal = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (1)$$

Where C_o and C_e (ppm) represent the initial and final concentrations, respectively.

2.5. Material Characterization

Cellulose and cellulose/polyvinyl alcohol (Cell/PVA) were characterized by XRD (X-Ray Diffraction, with 2θ between 5-50º), BET (Brunauer-Emmett-Teller), and SEM (scanning electron microscopy). The crystal structure of the adsorbent was subjected to X-ray diffraction (XRD) scanning and subsequent analysis. The crystallinity index value was then derived by employing equation 2. The specific surface area of cellulose and cellulose/PVA was identified by BET surface area. The surface properties of the adsorbents were evaluated using SEM.

$$CrI = \frac{I_t - I_a}{I_t} \times 100\% \quad (2)$$

The diffraction intensity of the lattice peak is represented by I_t, and I_a represents the peak intensity of the amorphous fraction. The diffraction angle at about 2θ = 22.5˚ is the lattice peak, and the lowest intensity at the diffraction angle at about 2θ = 18.0˚ is measured as the amorphous part [23].

2.6. Adsorption Kinetic Experiments

Linear adsorption experiment data were analyzed using the pseudo-first-order kinetic model (Eq. 3), the pseudo-second order kinetic model (Eq. 4), the Elovich kinetic model (Eq. 5), and the intra-particle diffusion kinetics parameters (Eq. 6) [24]. The experimental process was conducted at a pH of 6, with an initial concentration of 25 mg/L and a dose of 1 g/100 ml. The temperature was maintained at room temperature, and the duration of the experiment varied as follows: 30, 60, 90, 120, and 150 minutes.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (4)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (5)$$

$$q_t = k_p t^{0,5} + C \quad (6)$$

In the given context, the reaction time (min) is denoted by t, while q_e and q_t represent the adsorption capacity at equilibrium and time t (mg/g), respectively. Furthermore, the rate constants of the pseudo-first-order kinetic model and pseudo-second-order kinetic model are designated by K_1 and K_2. The initial adsorption rate constant, expressed as α (mg/(g min)), the decomposition rate constant (g/mg) denoted by β, and the boundary layer thickness constant C are also of significance in this model.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the Pineapple Leaves

3.1.1. Chesson Analysis

The cellulose extraction process of pineapple leaves uses alkaline, also known as alkaline delignification. Delignification is a process to eliminate lignin compounds in lignocellulosic materials with the assistance of alkali (NaOH solution) [25, 26]. NaOH solution ruined the structure of lignin and disconnected the bond between lignin and cellulose to expand the surface area of cellulose [26]. Table 1 shows the outcome of the cellulose content from the delignification process.

TABLE I. Cellulose content of pineapple leaves before and after the delignification process

Materials	Cellulose content (%)
Pineapple leaves before delignification	34,64
Pineapple leaves after 5% NaOH delignification	46,58
Pineapple leaves after 9% NaOH delignification	60,10

Table 1 presents the cellulose content of pineapple leaves before and after the delignification process. Cellulose content increases in line with the increase in NaOH concentration after the delignification process. The increase in cellulose content is achieved due to a decrease in the level of lignin bound and dissolved with NaOH during the delignification process, and NaOH extracts cellulose, which results in an increase in cellulose content. Cellulose content increased in harmony with the high alkali concentration. This causes more lignin to be stripped and dissolved in the aqueous solution so that the compounds that are the active side of cellulose increase [27].

3.1.2. Scanning Electron Microscope (SEM) Analysis

SEM analysis was used to investigate the morphological changes of pineapple leaves due to the delignification process. Morphological changes of pineapple leaves before and after alkaline

delignification can be seen in Figure 1. The surface morphology of pineapple leaves before the delignification process can be seen in Figure 1 (a), which shows that the surface of pineapple leaves is tight, smooth, and has no hollows. The surface of pineapple leaves is indicated to contain lignin, which functions as a filler for plant cell walls and binds strongly to lignocellulosic compounds, causing the plant cell walls to become firm [28]. Pineapple leaves possess a torn and crushed surface morphology after the delignification process. The surface of pineapple leaves looks rougher and fibrous and has some smooth parts above the surface, as shown in Figure 1 (b). In Figure 1 (c), the surface of pineapple leaves looks more tenuous and smaller and has fewer smooth parts above the surface.

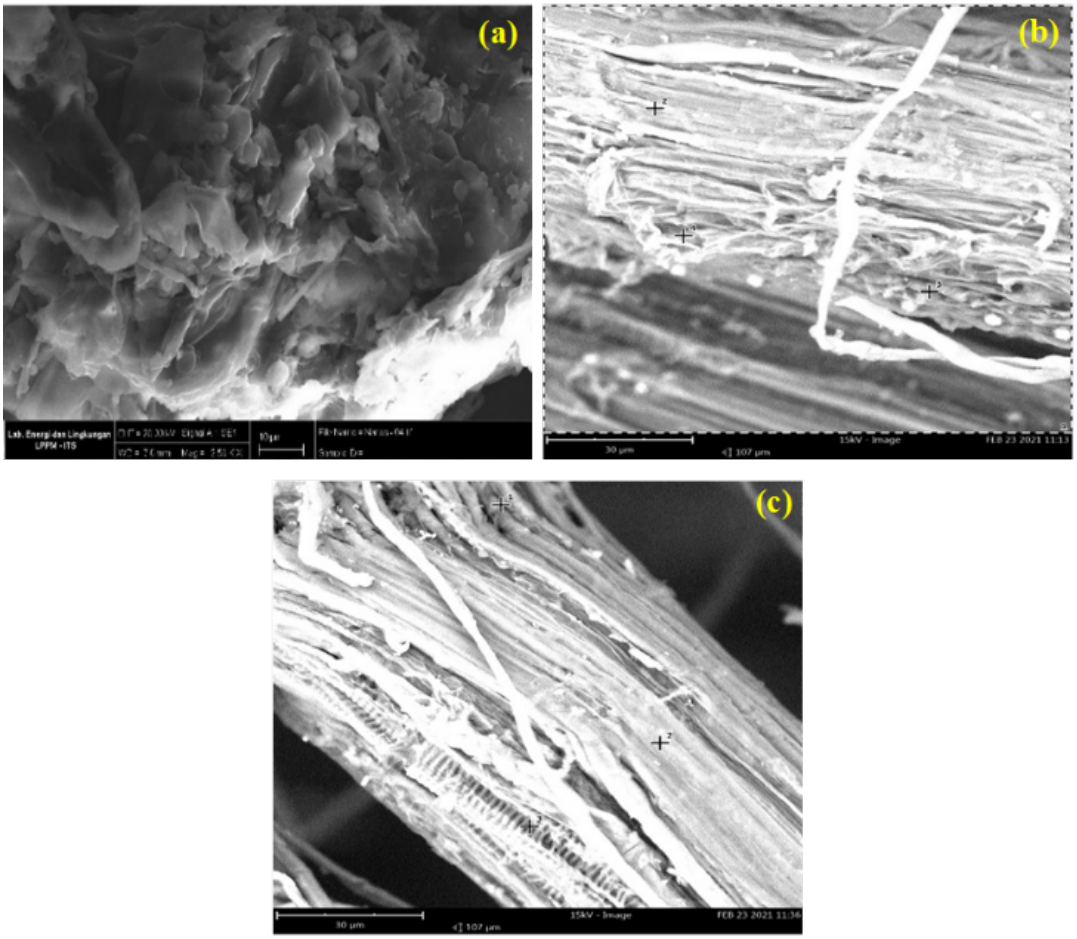


Figure 1. Results of SEM analysis with 2500x magnification (a) Pineapple leaves before delignification (b) Pineapple leaves after 5% NaOH delignification, and (c) Pineapple leaves after 9% NaOH delignification.

Figures 1 (b) and 1 (c) illustrated that the surface of pineapple leaves cellulose after delignification became rougher and larger. This results in the surface area of the pineapple leaves adsorbent becoming larger and more effective for the adsorption process [26]. The difference in surface shape indicated that the higher the NaOH concentration in the delignification process, the more bonds between lignin and cellulose were released. Analysis of cellulose content also found that higher cellulose content occurred at high NaOH concentrations.

3.1.3. X-Ray Diffraction (XRD) Analysis

The crystallinity of the cellulose was investigated using X-ray diffraction (XRD) Analysis. Cellulose has a crystalline structure, while lignin has an amorphous structure. The XRD diffractograms for pineapple leaves before and after the delignification process are shown in Figure 2. Based on Figure 2, it is proved that all diffractograms have a sharp peak at 2θ at around 23º. This

cellulose structure is characteristic of type I cellulose, which has a sharp peak at 2θ around 22º-23º [29]. This indicates the absence of an amorphous component (Lignin) and the increasing crystallinity of the cellulose fiber [30].

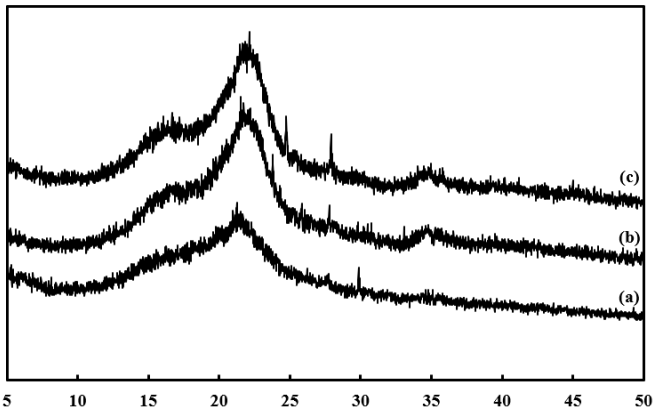


Figure 2. XRD analysis results (a) Pineapple leaves before delignification (b) Pineapple leaves after 5% NaOH delignification, and (c) Pineapple leaves after 9% NaOH delignification.

The results of XRD analysis showed that the degree of crystallinity (CrI) of cellulose before delignification, after delignification with 5% NaOH concentration, and after delignification with 9% NaOH concentration were 51.33%, 56.58%, and 65.98%, respectively. Based on these results, it is known that the degree of crystallinity increases after the delignification process. The increase in crystallinity is due to lignin, an amorphous component, being degraded and causing cellulose to remain. Increased NaOH concentration in the delignification process impacts the degree of crystallinity, which tends to increase and is in line with cellulose content. Adsorbents with clean pores due to the high degree of crystallinity will result in more ions adsorbing [26].

3.2. Characterization of Composite Material

3.2.1. Scanning Electron Microscope (SEM) Analysis

The results of SEM analysis of cellulose-PVA are shown in Figure 3, which is used as the basis for investigating the surface morphology of cellulose-PVA. Based on the morphology results, the cellulose surface appeared rougher and torn due to delignification. The lacerated parts cause cavities and can be filled by PVA. The surface morphology is dominated by the morphology of cellulose fibers that bind together between the fibers. This happens because the cellulose fibers interact physically with PVA to generate a flat, homogeneous composite surface.

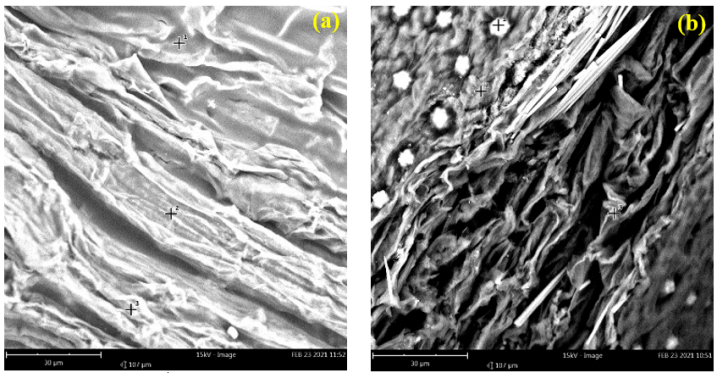


Figure 3. SEM analysis results with 2500x magnification (a) Cellulose (5% NaOH delignification) - PVA and (b) Cellulose (9% NaOH delignification) – PVA

3.2.2. Brunauer-Emmett-Teller (BET) Analysis

The size of the specific surface area of the composites was evaluated using Brunauer-Emmett-Teller (BET) Analysis, which will correlate with the adsorption capacity ability. Table 2 presents the

BET analysis results of cellulose and cellulose/PVA. BET results prove that when cellulose is composited with PVA, it impacts decreasing the surface area of the adsorbent. This is because PVA closes the pore structure of cellulose. However, this modification will make transition pores, which will be close to micropores in size. The specific surface area is also related to the pore structure and distribution, affecting the size in the order of micropores > mesopores > macropores so that adsorption will run optimally [31].

TABLE II. Cellulose surface area before and after being composited with PVA.

Materials	Surface area (m^2/g)
Cellulose after 5% NaOH delignification	168,764
Cellulose after 9% NaOH delignification	300,673
Cellulose (5% NaOH delignification) - PVA	52,674
Cellulose (9% NaOH delignification) - PVA	198,492

3.3. Effectiveness of Adsorbent on Methylene Blue Adsorption

The reduction of methylene blue was evaluated using a variety of contact times and different types of adsorbent materials in the adsorption process. Figure 4 captured the efficiency of methylene blue reduction as influenced by contact time and adsorbent type, namely cellulose and cellulose-PVA. In general, the adsorption of methylene blue progressively increased with increasing contact time. However, the removal efficiency decreased as the contact time exceeded 90 minutes on cellulose/PVA adsorbent with the delignification process using 9% NaOH concentration. This is due to the release of Methylene blue ions from the adsorbent surface. The adsorption rate is accelerated at the beginning of the process and decreases gradually until the equilibrium point. This occurs because many pores are still available as active sites for methylene blue at the beginning of the process, and the number decreases over time. The remaining pores on the adsorbent surface are difficult to occupy due to the repulsive force between the adsorbate molecules in the solid and bulk phases [32].

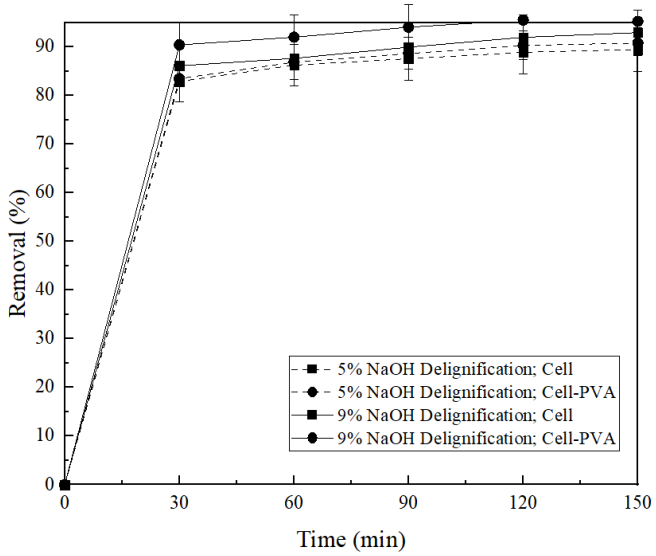


Figure 4. Effect of contact time on methylene blue dye removal.

The efficiency of methylene blue reduction is also related to the type of adsorbent used. Cellulose adsorbent with 9% NaOH delignification produces a more substantial removal efficiency than 5% NaOH delignification. The cellulose adsorbent with 9% NaOH delignification concentration has more cellulose content, forming many hydroxy groups. Cellulose/PVA adsorbent has superior adsorption ability than cellulose adsorbent because it contains a combination of cellulose and PVA,

which has more -OH active groups, so the frequency of bonding with adsorbate is more intense [18]. In addition, the adsorption process is also influenced by the surface area of the adsorbent. According to Table 2, cellulose with 9% NaOH delignification concentration has a more substantial surface area and, after compositing with PVA, produces a smaller surface area. A small surface area produced a small pore size, thus maximizing the adsorption process [31, 33].

3.4. Adsorption Kinetic Studies

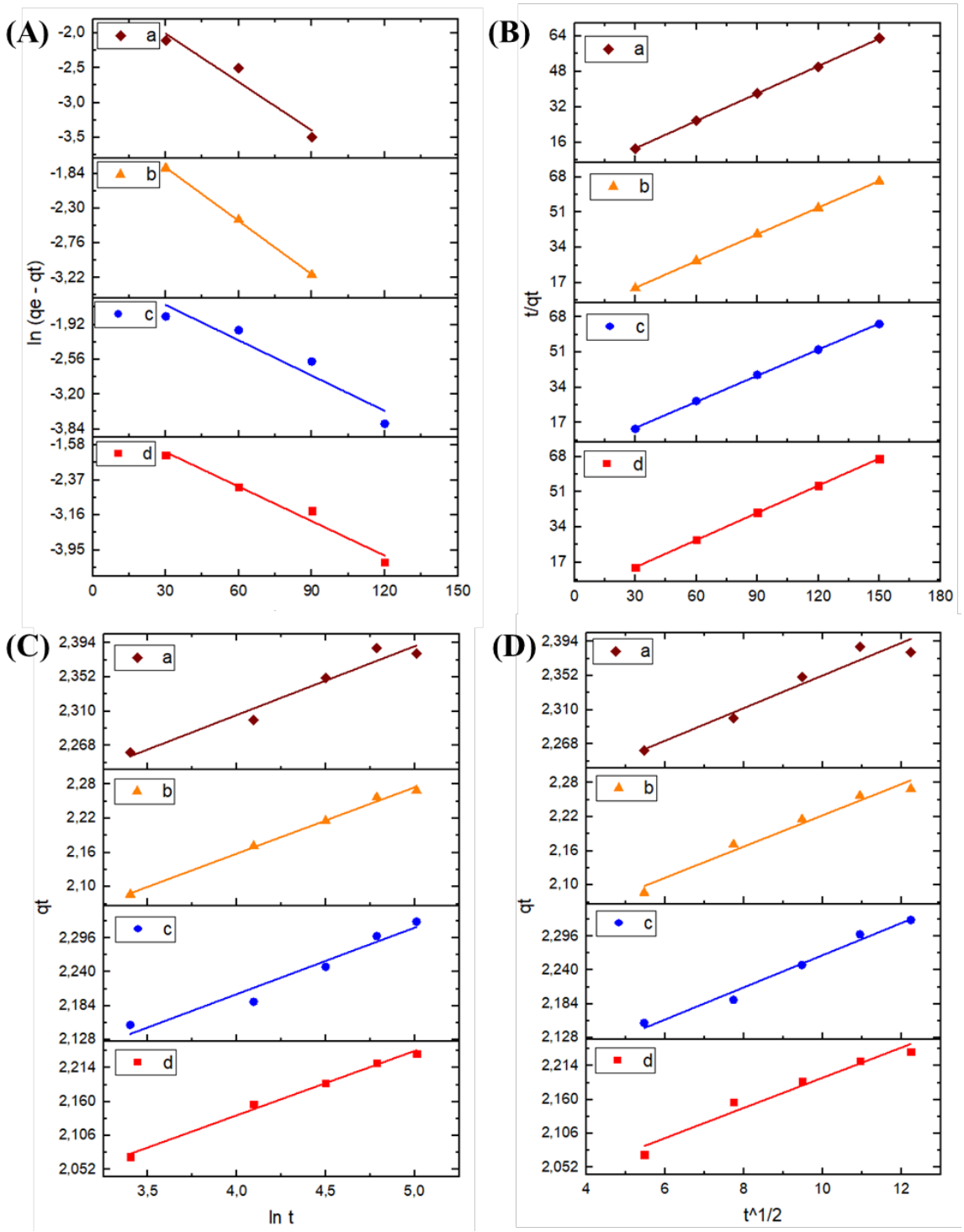


Figure 5. Fitting curves of different kinetic equations of MB adsorption by adsorbent (A) 9% NaOH delignification, cell-PVA; (B) 5% NaOH delignification, cell-PVA; (C) 9% NaOH delignification, cell; (D) 5% NaOH delignification, cell) (inset: a. Pseudo-first-order kinetics

parameters, b. Pseudo-second-order kinetics parameters, c. Elovich kinetics parameters, d. Intra-particle diffusion kinetics parameters).

The effectiveness of the adsorption process is found to be strongly influenced by the adsorption time. As illustrated in Figure 4, the adsorption process exhibits accelerated rates during its initial phase. This phenomenon can be attributed to the abundance of active sites on the surface of the adsorbent. As the duration of the process increases, the equilibrium state of saturation is achieved, leading to a gradual or constant increase in the amount of adsorption.

The present adsorption study utilized four kinetic models: the pseudo-first-order kinetic model, pseudo-second order kinetic model, Elovich kinetic model, and intra-particle diffusion kinetics parameters. As illustrated in Figure 5, the adsorption process exhibits a strong correlation with the pseudo-second-order kinetic model, as evidenced by the high value of the correlation coefficient R^2 (0.999). This observation supports the hypothesis that the adsorption process is driven by chemisorption. The chemisorption process is comprised of three distinct stages. Initially, MB molecules diffuse into the adsorbent surface, undergoing an adsorption process.. Subsequently, once the adsorbent surface reaches its saturation point, MB molecules bind to the active adsorption sites on the adsorbent [24].

The intraparticle diffusion model is a method of controlling the adsorption rate. If the value of C equals 0, it can be deduced that intraparticle diffusion can only control the adsorption rate. However, if the results obtained from this experiment are C≠0, it can be concluded that other diffusion methods control the adsorption rate during the adsorption process [34]. However, it is important to note that, in general, the kinetic model of intraparticle diffusion provides a more accurate representation of adsorption data, as evidenced by its smaller R^2 value. This suggests that the control of the adsorption rate is not determined solely by intraparticle diffusion alone.

3.5. Adsorption Mechanism

Various previous investigations have established the mechanism of methylene blue absorption on the adsorbent surface. Adsorption is achieved in three main steps: transporting the contaminants on the surface of the adsorbent through the aqueous solution, adsorption on the surface of the solid, and transport into the adsorbent particles [35]. The cellulose/PVA composite adsorbent's ability to adsorb methylene blue is demonstrated in Figure 6. The PVA-cellulose adsorbent is manufactured by bonding cellulose with PVA gel, which can enhance the availability of active hydroxyl groups on the adsorbent surface [17]. The negative charge of the hydroxyl group causes electrostatic attraction, resulting in the reduction of methylene blue, which has a different charge [36]. In general, electrostatic attraction will cause methylene blue, a cationic dye, to be adsorbed into the hydroxyl group adsorbent due to its strong affinity [35, 37].

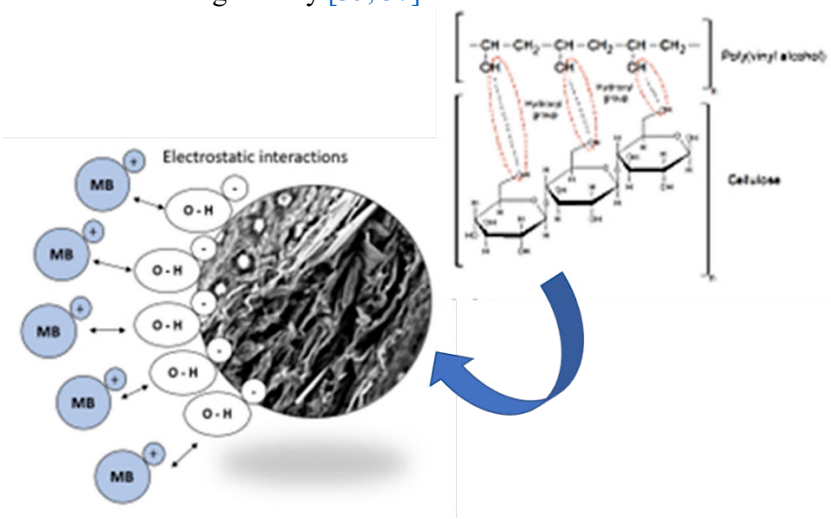


Figure 6. Schematic of adsorption mechanism.

4. CONCLUSIONS

In summary, pineapple leaves have been successfully utilized as a cellulose-PVA absorbent. Based on SEM, XRD, and BET analysis, the characteristics of this adsorbent have an appreciable potential to decrease methylene blue. The maximum methylene blue removal efficiency was 94.03% in the cellulose/PVA composite, with a contact time of 90 minutes. Cellulose/PVA has a smaller surface area than cellulose, which results in a maximum adsorption process.

References

[1] Y. El maguana, N. Elhadiri, M. Benchanaa, and R. Chikri, "Activated Carbon for Dyes Removal: Modeling and Understanding the Adsorption Process," *J Chem*, vol. 2020, p. 2096834, 2020, doi: 10.1155/2020/2096834.

[2] V. X. Nascimento *et al.*, "Adsorptive Features of Magnetic Activated Carbons Prepared by a One-Step Process towards Brilliant Blue Dye," *Molecules*, vol. 28, no. 4, 2023, doi: 10.3390/molecules28041821.

[3] Z. Ren, X. Yang, W. Zhang, and Z. Zhao, "Preparation, characterization and performance of a novel magnetic Fe-Zn activated carbon for efficient removal of dyes from wastewater," *J Mol Struct*, vol. 1274, p. 134407, 2023, doi: https://doi.org/10.1016/j.molstruc.2022.134407.

[4] A. Kausar *et al.*, "Cellulose-based materials and their adsorptive removal efficiency for dyes: A review," *Int J Biol Macromol*, vol. 224, pp. 1337–1355, 2023, doi: https://doi.org/10.1016/j.ijbiomac.2022.10.220.

[5] H. M. El-Bery, M. Saleh, R. A. El-Gendy, M. R. Saleh, and S. M. Thabet, "High adsorption capacity of phenol and methylene blue using activated carbon derived from lignocellulosic agriculture wastes," *Sci Rep*, vol. 12, no. 1, p. 5499, 2022, doi: 10.1038/s41598-022-09475-4.

[6] Y. Kuang, X. Zhang, and S. Zhou, "Adsorption of Methylene Blue in Water onto Activated Carbon by Surfactant Modification," *Water (Basel)*, vol. 12, no. 2, 2020, doi: 10.3390/w12020587.

[7] A. F. Aili Hamzah, M. H. Hamzah, H. Che Man, N. S. Jamali, S. I. Siajam, and M. H. Ismail, "Recent Updates on the Conversion of Pineapple Waste (Ananas comosus) to Value-Added Products, Future Perspectives and Challenges," *Agronomy*, vol. 11, no. 11, 2021, doi: 10.3390/agronomy11112221.

[8] A. A. Kamaru, N. S. Sani, and N. A. N. N. Malek, "Raw and surfactant-modified pineapple leaf as adsorbent for removal of methylene blue and methyl orange from aqueous solution," *Desalination Water Treat*, vol. 57, no. 40, pp. 18836–18850, Aug. 2016, doi: 10.1080/19443994.2015.1095122.

[9] S. Sinha, S. Nigam, S. Solanki, L. Batra, P. Chug, and R. Singh, "Prospects on arsenic remediation using organic cellulose-based adsorbents," *Ind Crops Prod*, vol. 201, p. 116928, 2023, doi: https://doi.org/10.1016/j.indcrop.2023.116928.

[10] Suhas, V. K. Gupta, P. J. M. Carrott, R. Singh, M. Chaudhary, and S. Kushwaha, "Cellulose: A review as natural, modified and activated carbon adsorbent," *Bioresour Technol*, vol. 216, pp. 1066–1076, 2016, doi: https://doi.org/10.1016/j.biortech.2016.05.106.

[11] J. S. Kim, Y. Y. Lee, and T. H. Kim, "A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass," *Bioresour Technol*, vol. 199, pp. 42–48, 2016, doi: https://doi.org/10.1016/j.biortech.2015.08.085.

[12] A. Jamshaid *et al.*, "Cellulose-based Materials for the Removal of Heavy Metals from Wastewater – An Overview," 2017, *Wiley-Blackwell*. doi: 10.1002/cben.201700002.

[13] Y. Guan *et al.*, "Green one-step synthesis of ZnO/cellulose nanocrystal hybrids with modulated morphologies and superfast absorption of cationic dyes," *Int J Biol Macromol*, vol. 132, pp. 51–62, 2019, doi: https://doi.org/10.1016/j.ijbiomac.2019.03.104.

[14] T. Shahnaz, M. M. F. S., P. V.C., and S. Narayanasamy, "Surface modification of nanocellulose using polypyrrole for the adsorptive removal of Congo red dye and chromium in binary mixture," *Int J Biol Macromol*, vol. 151, pp. 322–332, 2020, doi: https://doi.org/10.1016/j.ijbiomac.2020.02.181.

[15] Q. Yi *et al.*, "Preparation and adsorption performance of cellulose nanofibrils/polyvinyl alcohol composite gel spheres with millimeter size," *Carbohydr Polym*, vol. 277, p. 118850, 2022, doi: https://doi.org/10.1016/j.carbpol.2021.118850.

[16] Y. Zhou, S. Fu, L. Zhang, H. Zhan, and M. V Levit, "Use of carboxylated cellulose nanofibrils-filled magnetic chitosan hydrogel beads as adsorbents for Pb(II)," *Carbohydr Polym*, vol. 101, pp. 75–82, 2014, doi: https://doi.org/10.1016/j.carbpol.2013.08.055.

[17] L. Fan, Y. Lu, L.-Y. Yang, F. Huang, and X. Ouyang, "Fabrication of polyethylenimine-functionalized sodium alginate/cellulose nanocrystal/polyvinyl alcohol core–shell microspheres ((PVA/SA/CNC)@PEI) for diclofenac sodium adsorption," *J Colloid Interface Sci*, vol. 554, pp. 48–58, 2019, doi: https://doi.org/10.1016/j.jcis.2019.06.099.

[18] H. Peng, S. Wang, H. Xu, and X. Hao, "Preparation, properties and formation mechanism of cellulose/polyvinyl alcohol bio-composite hydrogel membranes," *New Journal of Chemistry*, vol. 41, no. 14, pp. 6564–6573, 2017, doi: 10.1039/c7nj00845g.

[19] H. Ali, T. M. Tiama, and A. M. Ismail, "New and efficient NiO/chitosan/polyvinyl alcohol nanocomposites as antibacterial and dye adsorptive films," *Int J Biol Macromol*, vol. 186, pp. 278–288, 2021, doi: https://doi.org/10.1016/j.ijbiomac.2021.07.055.

[20] J. Sun *et al.*, "Carboxymethyl cellulose/polyvinyl alcohol composite aerogel supported beta molecular sieve for CH4 adsorption and storage," *Carbohydr Polym*, vol. 321, p. 121246, 2023, doi: https://doi.org/10.1016/j.carbpol.2023.121246.

[21] R. Sarkhel, P. Ganguly, P. Das, A. Bhowal, and S. Sengupta, "Synthesis of biodegradable PVA/cellulose polymer composites and their application in dye removal," *Environmental Quality Management*, vol. 32, no. 3, pp. 313–323, Mar. 2023, doi: https://doi.org/10.1002/tqem.21920.

[22] Q. Yi *et al.*, "Preparation and adsorption performance of cellulose nanofibrils/polyvinyl alcohol composite gel spheres with millimeter size," *Carbohydr Polym*, vol. 277, p. 118850, 2022, doi: https://doi.org/10.1016/j.carbpol.2021.118850.

[23] S. Nam, A. D. French, B. D. Condon, and M. Concha, "Segal crystallinity index revisited by the simulation of X-ray diffraction patterns of cotton cellulose Iβ and cellulose II," *Carbohydr Polym*, vol. 135, pp. 1–9, 2016, doi: https://doi.org/10.1016/j.carbpol.2015.08.035.

[24] Z. Wu *et al.*, "Synthesis of novel magnetic activated carbon for effective Cr(VI) removal via synergistic adsorption and chemical reduction," *Environ Technol Innov*, vol. 30, May 2023, doi: 10.1016/j.eti.2023.103092.

[25] D. Mikulski and G. Kłosowski, "Delignification efficiency of various types of biomass using microwave-assisted hydrotropic pretreatment," *Sci Rep*, vol. 12, no. 1, p. 4561, 2022, doi: 10.1038/s41598-022-08717-9.

[26] J. Zhang, H. Zhou, D. Liu, and X. Zhao, "Chapter 2 - Pretreatment of lignocellulosic biomass for efficient enzymatic saccharification of cellulose," in *Lignocellulosic Biomass to Liquid Biofuels*, A. Yousuf, D. Pirozzi, and F. Sannino, Eds., Academic Press, 2020, pp. 17–65. doi: https://doi.org/10.1016/B978-0-12-815936-1.00002-2.

[27] S. Harun and S. K. Geok, "Effect of sodium hydroxide pretreatment on rice straw composition," *Indian J Sci Technol*, vol. 9, no. 21, 2016, doi: 10.17485/ijst/2016/v9i21/95245.

[28] Q. Liu, L. Luo, and L. Zheng, "Lignins: Biosynthesis and biological functions in plants," Feb. 01, 2018, *MDPI AG*. doi: 10.3390/ijms19020335.

[29] C. Vivian Abiaziem, A. Bassey Williams, A. Ibijoke Inegbenebor, C. Theresa Onwordi, C. O. Ehi-Eromosele, and L. Felicia Petrik, "Preparation and Characterisation of Cellulose Nanocrystal from Sugarcane Peels by XRD, SEM and CP/MAS 13C NMR," in *Journal of Physics: Conference Series*, IOP Publishing Ltd, Oct. 2019. doi: 10.1088/1742-6596/1299/1/012123.

[30] P. B. Subhedar and P. R. Gogate, "Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material," *Ultrason Sonochem*, vol. 21, no. 1, pp. 216–225, 2014, doi: https://doi.org/10.1016/j.ultsonch.2013.08.001.

[31] Z. Wu *et al.*, "Synthesis of novel magnetic activated carbon for effective Cr(VI) removal via synergistic adsorption and chemical reduction," *Environ Technol Innov*, vol. 30, p. 103092, 2023, doi: https://doi.org/10.1016/j.eti.2023.103092.

[32] V. Nejadshafiee and M. R. Islami, "Adsorption capacity of heavy metal ions using sultone-modified magnetic activated carbon as a bio-adsorbent," *Materials Science and Engineering: C*, vol. 101, pp. 42–52, 2019, doi: https://doi.org/10.1016/j.msec.2019.03.081.

[33] C. Peiris, S. R. Gunatilake, T. E. Mlsna, D. Mohan, and M. Vithanage, "Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: A critical review," *Bioresour Technol*, vol. 246, pp. 150–159, 2017, doi: https://doi.org/10.1016/j.biortech.2017.07.150.

[34] J. Chung, N. Sharma, M. Kim, and K. Yun, "Activated carbon derived from sucrose and melamine as low-cost adsorbent with fast adsorption rate for removal of methylene blue in wastewaters," *Journal of Water Process Engineering*, vol. 47, p. 102763, 2022, doi: https://doi.org/10.1016/j.jwpe.2022.102763.

[35] Z. Raji, A. Karim, A. Karam, and S. Khalloufi, "Adsorption of Heavy Metals: Mechanisms, Kinetics, and Applications of Various Adsorbents in Wastewater Remediation—A Review," *Waste*, vol. 1, no. 3, pp. 775–805, 2023, doi: 10.3390/waste1030046.

[36] M. Bilal, I. Ihsanullah, M. Younas, and M. Ul Hassan Shah, "Recent advances in applications of low-cost adsorbents for the removal of heavy metals from water: A critical review," Jan. 01, 2022, *Elsevier B.V.* doi: 10.1016/j.seppur.2021.119510.

[37] K. Bing Tan, A. Zuhairi Abdullah, B. Amini Horri, and B. Salamatinia, "Adsorption Mechanism of Microcrystalline Cellulose as Green Adsorbent for the Removal of Cationic Methylene Blue Dye," 2016.