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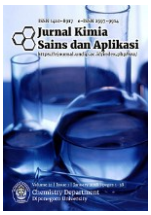

Candlenut Shell and Clay-Derived Monoliths with Molasses Binder: A Sustainable Approach to Water Dye Decontamination

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Abstract

This study presents a sustainable approach to water dye decontamination using monoliths constructed from candlenut shells, clay, and molasses as a binder. The candlenut shells were activated to form carbon and then mixed with natural clay and molasses to create the monolith composite. The dough was pushed through a stainless-steel mold featuring seven circular openings, each measuring 2 cm in width and 2 cm in thickness, to create the monoliths (MCC and MMCC). The monoliths were rigorously tested for adsorption efficiency, isotherm behavior, and kinetic properties. Results showed a high dye removal efficiency, with 92% for methylene blue and 74% for methyl orange, which was attributed to the stronger interaction of methylene blue with the negatively charged surface of the monoliths. The isotherm analysis followed the Langmuir model, indicating monolayer adsorption on uniform active sites. Kinetic studies using linear regression analysis aligned with the pseudo-second-order model, indicating that chemical adsorption was the controlling factor in the rate. Characterization of the monoliths using Scanning Electron Microscopy (SEM) revealed a porous surface morphology, while X-ray Diffraction (XRD) identified the crystalline structures present. Fourier Transform Infrared Spectroscopy (FTIR) confirmed the presence of functional groups essential for dye adsorption, and Brunauer-Emmett-Teller (BET) analysis determined the specific surface area and pore size distribution. In conclusion, this study underscores the viability of using candlenut shell and clay-derived monoliths as efficient and environmentally friendly adsorbents for wastewater treatment, providing a practical solution to dye pollution.

1. Introduction

As population and economic activities have increased in recent years, the demand for clean water has grown significantly. Industrial wastewater containing dyes is a major source of water pollution in the environment. Many dyes are toxic, non-biodegradable, and harmful to aquatic ecosystems and human health. The introduction of dye-polluted discharge into aquatic environments increases color saturation, which blocks sunlight from penetrating the water [1]. Annually, around 2×10^5 tons of dyes are released into water bodies from the dyeing and finishing processes in the textile industry due to inefficient dyeing methods. This discharge contributes to high Chemical Oxygen Demand (COD) levels, which indicate significant organic pollution and pose serious environmental hazards [2].

Many dyes are hazardous and can cause carcinogenic, mutagenic, teratogenic, and other harmful effects on fish species and microbial diversity, disrupting the balance of aquatic ecosystems. In humans, dyes such as methylene blue (MB) can lead to skin sensitivity and cause damage to the brain, central nervous system, and reproductive system, highlighting the severe health risks associated with dye exposure [3]. Therefore, it is crucial to implement effective wastewater treatment strategies for dye-contaminated water to mitigate environmental pollution and safeguard both ecosystems and public health.

Methylene blue (MB) is a synthetic dye extensively used as a colorant for paper, wool, silk, and cotton and is also prevalent in the food, cosmetics, and pharmaceutical industries [4]. While MB has some medicinal properties, it poses environmental concerns due to its widespread use. Similarly, methyl orange (MO) is a common azo anionic dye used in the textile industry, valued for its high solubility, bright orange color in water, and use as a pH indicator in titrations [5]. The release of inadequately treated wastewater containing MB from industrial sources can pose serious health hazards. In humans, exposure to MB can cause various issues, including reduced oxygen levels (cyanosis), tissue damage, formation of abnormal red blood cells, nausea, liver impairment, and cardiovascular distress [6]. Therefore, the adverse impacts of wastewater containing dyes such as MB and MO highlight the need for effective removal strategies before industrial discharge. Both dyes pose significant environmental and health risks, making it crucial to treat wastewater adequately to prevent contamination of water bodies.

Various treatment methods have been employed to remove dyes like MB and MO from the environment, including biological, chemical, and physicochemical techniques. Biological methods, such as the use of enzymes and microorganisms in aerobic and anaerobic degradation, utilize natural processes for dye removal [7, 8, 9]. Chemical methods involve advanced oxidation processes, oxidation, reduction, and electrochemical techniques to break down contaminants [10, 11]. Physicochemical methods, encompassing coagulation, membrane separation, adsorption, filtration, and flotation, offer diverse approaches to treatment, with adsorption being particularly notable [12]. Among these techniques, adsorption stands out as one of the most effective and widely utilized methods for wastewater treatment. Its advantages include cost-effectiveness, simplicity in operation and control, and the potential for regeneration and recycling of adsorbents. The widespread availability of raw materials for adsorbent synthesis further enhances its appeal. Given these benefits, adsorption is recognized for its superior removal capabilities in treating wastewater compared to other methods [13, 14].

Selecting the right adsorbent material is essential for optimizing adsorption efficiency. Various adsorbents have been studied for dye removal, including zeolite [15, 16], MnO_2 nanosorbents [17, 18], activated carbon [15], and bentonite [19, 20]. Activated carbon is particularly valued for its extensive surface area and microporous structure, which enhance its adsorption capabilities. However, the high cost of commercially available activated carbon, primarily due to its expensive raw materials such as coal, limits its widespread use.

Recent research has focused on developing activated carbon from low-cost, renewable agricultural, and industrial byproducts to overcome this challenge. Examples include maize cobs [21], fly ash [22], and sunflower seed hulls [23]. These materials offer a more economical alternative while still providing effective adsorption properties. In Indonesia, particularly in Aceh Province, candlenut shell has emerged as a promising source for activated carbon production. In 2020, the area dedicated to candlenut cultivation in Aceh reached 16,290 hectares, producing 9,051 tons. Traditionally, only the kernel of the candlenut is utilized, with the shells often discarded as waste. However, given that candlenut shells have a shell-to-kernel ratio of 64.57%, much higher than the 30% seen in coconut and oil palm shells, these shells hold significant potential as a source of activated carbon [24].

Raw clays have garnered substantial attention in water purification due to their expansive area, outstanding efficiency in removing impurities at minimal levels, ion-exchange ability, selective attributes, affordability, and widespread availability [25]. Some works have examined the adsorption properties and mechanisms of various types of untreated clays for dye elimination from the solutions [26, 27, 28]. Due to the isomorphous substitution of Al^{3+} with Mg^{2+} in the octahedral layer and Si^{4+} with Al^{3+} in the tetrahedral layer, Untreated clays inherently exhibit a persistent anionic charge. This charge is offset by exchangeable cations (K^+ and Na^+) present in the interlayer spaces, which facilitates the efficient removal of cationic pollutants via ion exchange processes [29].

Powdered adsorbents often necessitate additional separation processes due to sludge formation after adsorption. To address this issue, compact monolithic adsorbents are increasingly being explored as a more streamlined solution [30]. Research has demonstrated the effectiveness of monolithic adsorbents in removing various contaminants, including metal ions, dyes, and volatile compounds. This study introduces a novel monolithic adsorbent made from activated carbon derived from candlenut shells, with clay as a binder and molasses as a filler. The use of molasses not only enhances the binder's effectiveness but also improves the adsorbent's structural integrity and surface area through recrystallization. By focusing on this innovative combination of materials, this work aims to enhance the adsorption efficiency of dyes and other contaminants in water, offering a practical solution for environmental remediation.

2. Experimental

2.1. Materials

This study utilized several materials: activated carbon adsorbent derived from candlenut shell waste, clay from Pidie Regency serving as an adsorbent filler, and commercially obtained molasses, also used as an adsorbent filler. The experimental work involved MB and MO (Merck) and distilled water.

2.2. Activated Carbon Synthesis

The synthesis of activated carbon began with candlenut shells, which were first dried and then ground to a coarse texture using a rice grinder. The ground material was subjected to pyrolysis in a furnace. Subsequently, physical activation was performed at 600°C for 3 hours in the furnace to enhance the adsorptive properties of the carbon.

2.3. Synthesis of Monolithic Candlenut Shell Carbon (MCC) and Modified Molasses Carbon-Clay (MMCC)

The synthesis of MCC was performed using an 80:20 carbon-to-clay ratio to create monolithic carbon blocks with a diameter of 2 cm and a height of 2 cm, featuring seven holes (Figure 1 (a) and (b)). The process involved mixing clay and carbon, both ground to 100 mesh. The resulting mixture was then calcined in a furnace at 600°C for 3 hours. Following this, the construct MMCC was combined with molasses at concentrations of 3% and 5% for each monolithic batch. Distilled water was added to this mixture, which was thoroughly stirred to achieve uniformity. The homogeneous paste was then molded using a stainless steel molder (2 cm diameter, 2 cm height, with 7 holes) to form the monoliths. These were air-dried for 2 days before undergoing a second calcination in the furnace at 600°C.

2.4. Adsorbent Characterizations

An X-ray diffractometer (XRD) was employed to analyze the crystalline structure of the MCC and MMCC monolith. The presence of functional groups in the adsorbents was verified using a Fourier Transform Infrared Spectrometer (FTIR; SHIMADZU P-21), with a wavelength range from 4000 to 400 cm^{-1}. Additionally, a Scanning Electron Microscope with Energy Dispersive X- ray (SEM-EDX; Carl Zeiss Model EVO MA 10) was utilized to examine the surface morphology, structural characteristics, and elemental distribution of the adsorbents. The surface area analysis of the sample was conducted using the BET method to determine its specific surface area, pore volume, and pore size. This analysis provides essential information about the textural properties of the material, which are crucial for understanding its adsorption capacity and overall performance in various applications.

2.5. Preparation of MB and MO Solutions

Stock solutions of MB and MO, each with a concentration of 100 ppm, were prepared from commercial solid dyes and then diluted with distilled water to achieve final concentrations of 12 ppm in 250 mL aliquots. The dilution process involved preparing the working solutions by mixing the stock solution with distilled water. The required volume of distilled water was calculated using Equation 1.

$$M1 \times V1 = M2 \times V2 \quad (1)$$

Where, M1 and V1 represent the concentration and volume of the stock solution, while M2 and V2 represent the concentration and volume of the dilute solution.

Figure 1. (a) Side and (b) top views of the stainless steel molder

2.6. Adsorption Process of MB and MO

To evaluate the performance of MCC and MMCC, the adsorption of MB and MO was conducted using these adsorbents via a batch method. The adsorption process occurred in a reactor equipped with a magnetic stirrer. Monolithic MCC and MMCC adsorbents were introduced into 250 mL of MB and MO solutions, initially at 12 ppm, and the operation was carried out for 150 minutes. At 30-minute intervals, 5 mL samples of the filtrate were taken and analyzed for absorbance using UV-Vis spectroscopy to determine the concentration at each time point. The data collected at 30-minute intervals up to equilibrium provided insights into the percentage removal and foundational kinetics of the adsorption process. To determine the adsorption capacity, the concentration of MB and MO was varied (3, 6, 9, 12, and 15 ppm) and analyzed at an equilibrium time of 150 minutes. The isotherm study was conducted using the Langmuir and Freundlich models, as described in Equations 2 and 3.

$$q_e = \frac{K_L \times C_e}{1+a_L \times C_e} \quad (2)$$

$$q_e = K_f \times C_e^{\frac{1}{n}} \quad (3)$$

Where, K_L (or L) is the Langmuir constant (ppm), K_f is the Freundlich constant (ppm), $1/n$ is the heterogeneity factor of sorption, and C_e is the equilibrium concentration (ppm) [17].

3. Results and Discussion

3.1. Characterization of the Adsorbents

3.1.1. Crystallinity Analysis

The XRD is utilized to assess the crystalline nature of materials, providing a measure of the material's structural order within its crystal lattice. This analysis is crucial for evaluating an adsorbent's potential performance in adsorption applications [31]. Scientifically, XRD reveals the atomic arrangement and degree of structural order in the adsorbent, directly influencing its adsorption capacity and efficiency. A higher degree of crystallinity indicates a more orderly and defined structure, which can influence the availability of active sites for adsorption. Therefore, evaluating the crystallinity of an adsorbent is essential for understanding its suitability and effectiveness in adsorption processes. The crystallinity analysis of MCC and MMCC adsorbents is presented in Figure 2.

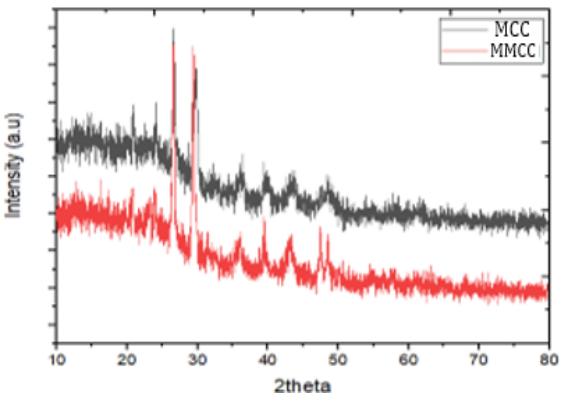

Figure 2. XRD analysis of MCC and MMCC adsorbents

Figure 2 presents the XRD analysis of MCC and MMCC, confirming that both materials exhibit a crystalline structure. This is evident from the sharp peaks observed at 2θ positions of 26.68° and 29.48° for both adsorbents, indicating a well-organized and orderly structure. Such a structure enhances the adsorbent's surface area and pore size, which are crucial for effective adsorption. The XRD spectra of both adsorbents are similar; however, the MMCC adsorbent displays higher peak intensities than MCC, suggesting a more prominent crystalline phase in MMCC. The 2θ values correspond to disordered graphitic carbon, commonly referred to as a "turbostratic structure". Additionally, variations in the full width at half maximum (FWHM) values of the peaks across different carbon samples suggest the presence of distinct micropore wall structures [32, 33, 34].

3.1.2. Infrared Analysis

FTIR spectroscopy was employed to identify functional groups present in the adsorbents, which is crucial for understanding the adsorption process [35]. The FTIR spectra of MCC and MMCC were recorded over the wavelength range of 4000-500 cm^{-1}, as illustrated in Figure 3. The spectra reveal a broad band at 3045 cm^{-1} for the MCC adsorbent and 3018 cm^{-1} for the MMCC adsorbent, indicating the presence of hydroxyl (-OH) groups. This O-H stretching is attributed to hydrogen bonding within and between polymeric substances such as cellulose and lignin, which are components of the candlenut shell.

Additionally, a peak at 2873 cm^{-1} corresponds to C-H stretching vibrations of $-CH_2$ groups in both adsorbents. Peaks at 2513 cm^{-1} for the MCC adsorbent and 2557 cm^{-1} for the MMCC adsorbent are associated with similar vibrations of $-CH_3$ groups. Both adsorbents display comparable FTIR spectra, with no new bands appearing after the addition of molasses. This is expected as the candlenut shell adsorbents already exhibit functional groups such as OH, C-H, and C-O, which are also found in molasses. These findings align with previous research confirming the presence of these functional groups in candlenut shell adsorbents [35, 36].

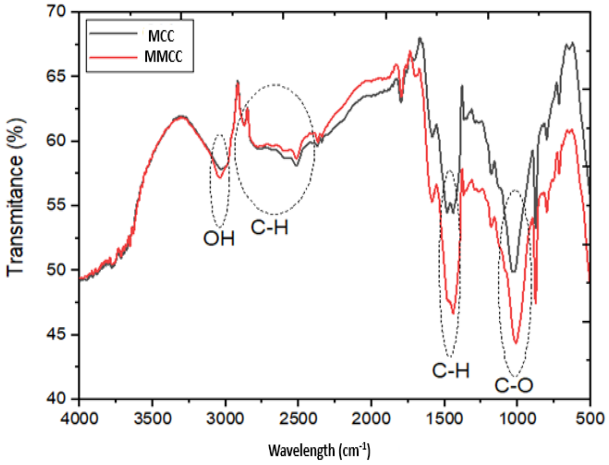

Figure 3. FTIR spectra of MCC and MMCC

3.1.3. Morphological Study

SEM-EDX analysis was conducted to evaluate the structural characteristics, morphology, and chemical composition of adsorbents [37]. Figure 4a displays the morphology of the MCC adsorbent, characterized by a rough and uneven surface with irregular pores and cavities. This texture enhances adsorption efficiency by increasing the available surface area for adsorbate interaction. In contrast, Figure 4b shows the morphology of the adsorbent after the addition of molasses, revealing a more complex surface structure. The presence of molasses may create a binding matrix or layer, altering the surface characteristics of the adsorbent and potentially improving its adsorption properties.

EDX analysis indicates that the MCC adsorbent is predominantly composed of carbon (C) (up to 70%) and oxygen (O) (up to 10%), with the remaining composition consisting of other chemical components listed in Table 1. The addition of molasses to the MMCC adsorbent increases the atomic concentration of calcium (Ca) and reduces the C percentage due to the calcium content in molasses. Consequently, these elements may adsorb onto or bind to the adsorbent surface following the addition of molasses. The detailed elemental composition of the adsorbents is presented in Table 1.

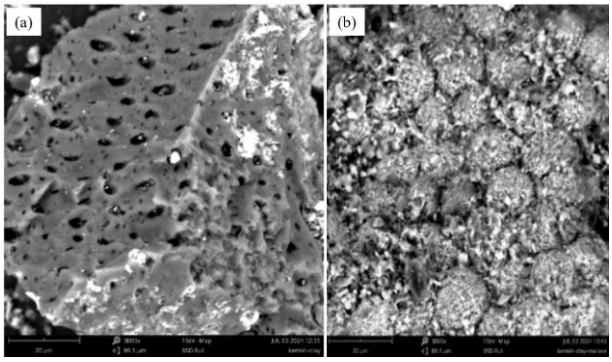

Figure 4. Surface morphology of (a) MCC and (b) MMCC at 3000× magnification

Table 1. Chemical composition of the adsorbents

Element	Atomic concentration (%)	
	MCC	MMCC
C	76.99	70.17
O	19.70	12.26
Ca	1.69	49.17
Si	0.72	1.22
Fe	0.23	1.71
Mg	0.41	0.70
Cl	0.16	0.34
K	0.09	0.66

3.1.4. Pore Distribution Study

BET analysis was performed on MCC and MMCC to determine their specific surface area and pore size distribution. This analysis is crucial for understanding the adsorption properties of the materials, as it provides insights into the available surface area for adsorption and the pore structure that accommodates adsorbates. A larger surface area generally indicates a higher number of active adsorption sites, enhancing the material's efficiency in pollutant removal applications. Additionally, pore size distribution plays a key role in adsorption efficiency, as different pollutants require specific pore sizes for optimal adsorption. For example, larger pores may be more suitable for adsorbing macromolecules, whereas smaller pores are more effective for smaller molecules [38].

The BET results, presented in Table 2, reveal that the specific surface area of MCC is 471.741 m^2/g, whereas MMCC exhibits a slightly higher surface area of 480.454 m^2/g. This increase suggests that the modification of candlenut shell adsorbents with molasses enhances the surface area, potentially improving their adsorption performance. These findings align with previous research on molasses-derived activated biocarbon, which highlighted that the specific surface area of bio-based activated carbon can be significantly enhanced by incorporating molasses as a precursor, followed by chemical activation. This modification likely contributes to the increased porosity and improved textural properties of the adsorbent, making it more effective for various adsorption applications [39].

3.2. Adsorption Performances of MCC and MMC in MB and MO Removal

The adsorption performance of MMC and MMCC in removing MB and MO from aqueous solutions is investigated to assess their potential for wastewater treatment. Both dyes were tested at an initial concentration of 12 ppm, with adsorption studies conducted over 150 minutes and measurements taken at 30-minute intervals. Assessing these adsorbents is crucial for addressing the environmental and health risks associated with dye contamination in wastewater. Understanding their effectiveness over time helps determine their practical applicability and optimize their use in treating dye-contaminated water. The adsorption performance of both MCC and MMCC is presented in Figure 5.

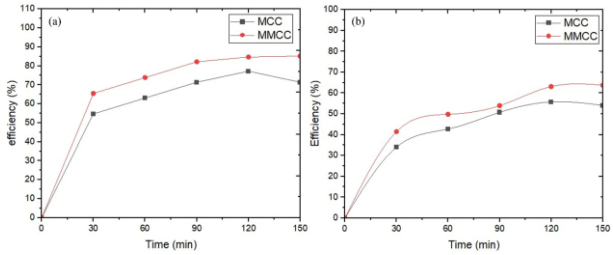

Figure 5. Efficiency removal of (a) MB and (b) MO in adsorption process

Figure 5 shows that the adsorption efficiency of both MB and MO is significantly enhanced when using the MMCC adsorbent. The highest adsorption efficiencies are observed at 150 minutes, with MB reaching 92% and MO at 74%. This difference in performance can be attributed to the nature of the dyes: MB, a cationic dye, interacts more favorably with the negatively charged sites on the MMCC surface, resulting in stronger electrostatic attraction and higher adsorption efficiency. In contrast, MO, an anionic dye, interacts less effectively with the adsorbent, leading to a comparatively lower adsorption efficiency [40].

For the MCC adsorbent, adsorption occurs up to 120 minutes, with an efficiency of 71% for MB and 54% for MO. However, beyond 120 minutes, the adsorption efficiency begins to decline as the MCC adsorbent starts to release the adsorbed dye due to the limited availability of active sites. Notably, desorption of the adsorbate from MCC begins after 90 minutes, emphasizing the critical role of active site availability in sustaining high adsorption performance.

The adsorption mechanism of MB and MO in a binary system is primarily governed by electrostatic interactions, competition for adsorption sites, and the physicochemical properties of the adsorbent. As a cationic dye, MB exhibits a stronger affinity for negatively charged or porous adsorbents due to electrostatic attraction, van der Waals forces, and potential π-π interactions, whereas MO, an anionic dye, lacks this electrostatic advantage. Even without pH adjustment, MB's molecular structure and interaction mechanisms enable it to outcompete MO for available adsorption sites. Adsorption isotherms and kinetic studies further support MB's higher uptake, often following monolayer or multilayer adsorption models depending on the adsorbent's characteristics.

These findings align with Rosanti *et al.* [41], who demonstrated that MB is generally adsorbed more rapidly and effectively than MO. The enhanced adsorption of MB can be attributed to its positive charge, which interacts more favorably with negatively charged adsorbent surfaces, leading to higher adsorption efficiency. In contrast, MO's adsorption is slower and less efficient due to the absence of strong electrostatic interactions. Understanding these mechanisms is crucial for optimizing adsorbent design and application in wastewater treatment, particularly for the selective removal of dyes with varying charge properties [42, 43].

Table 2. BET analysis of MCC and MMCC adsorbent

Adsorbent	Pore area (m^2/g)	Pore volume (cm^3/g)
MCC	471.741	0.369
MMCC	480.454	0.400

Table 3. Isotherm study of MCC and MMCC adsorbents for MB and MO removal

Adsorbent	Adsorbate	Langmuir isotherm			Freundlich isotherm		
		q_m	K_L	R^2	n	K_F	R^2
MCC	MO	1.62	1.14	0.97	2.34	0.79	0.92
	MB	2.06	1.04	0.99	2.24	0.94	0.96
MMCC	MO	1.44	1.53	0.96	2.10	0.83	0.93
	MB	2.80	0.74	0.99	2.55	1.05	0.97

The influence of contact time on the adsorption of MB and MO was investigated to determine the adsorption capacity of MCC and MMCC adsorbents over a period ranging from 30 to 150 minutes. This analysis helps evaluate the effectiveness of the adsorbents in removing MB and MO dyes from the solution [44]. As depicted in Figure 6, the adsorption capacity generally increases with prolonged contact time, which can be attributed to the presence of numerous available active sites on the MCC and MMCC adsorbents that the dye molecules have not yet occupied [45]. However, the adsorption capacity of MCC tends to stabilize at around 120 minutes, followed by the release of some adsorbate. This behavior is likely due to partial saturation of the adsorbent surface, where some active sites are already saturated and no longer able to adsorb additional dye ions [46].

3.3. Isotherm Study

Isotherm studies in adsorption are important for understanding and analyzing the adsorption behavior of MB and MO on MCC and MMCC adsorbents. These studies were conducted by varying the initial concentrations of MB and MO from 3 to 15 ppm, with the adsorption process carried out over 150 minutes. Isotherms provide valuable information about the maximum adsorption capacity of the adsorbent at equilibrium, which helps determine the adsorbent's effectiveness in binding dyes from a solution. Analyzing the isotherms makes it possible to assess whether the adsorption process is monolayer or multilayer. The Langmuir isotherm model describes monolayer adsorption on a homogeneous surface, while the Freundlich model represents adsorption on a heterogeneous surface [47]. The summary of the isotherm study using the Langmuir and Freundlich model is presented in Table 3.

Table 4. Kinetic data summary of PFO and PSO in MCC and MMCC in adsorption

Adsorbent	Adsorbate	PFO		PSO	
		K_1	R^2	K_2	R^2
MCC	MO	0.026	0.987	0.004	0.990
	MB	0.027	0.971	0.006	0.994
MMCC	MO	0.021	0.937	0.008	1.000
	MB	0.037	0.974	0.006	0.994

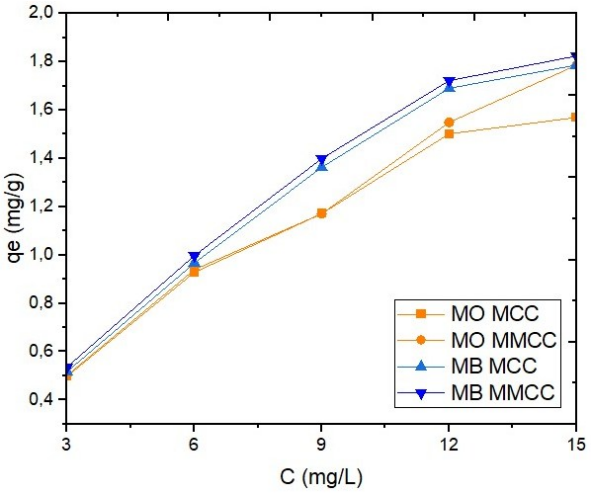

Figure 6. Adsorption capacity vs. time operation in MB and MO adsorption

The isotherm data provide insights into the adsorption characteristics of MCC and MMCC adsorbents for MO and MB, using both the Langmuir and Freundlich models. For the Langmuir isotherm, MCC adsorbing MO shows a maximum adsorption capacity (q_m) of 1.62 ppm, with a Langmuir constant (K_L) of 1.14 ppm and a high correlation coefficient (R^2) of 0.97, indicating a strong fit. When MCC adsorbs MB, the capacity increases to 2.06 ppm, with a K_L of 1.04 L/mg and an even better fit (R^2 of 0.99), suggesting MCC has a greater affinity and capacity for MB than MO. MMCC shows a slightly lower q_m value of 1.44 ppm for MO, with a higher K_L of 1.53 ppm and an R^2 of 0.96, indicating good adsorption potential. For MB, MMCC exhibits the highest q_m value of 2.80 ppm, with a K_L of 0.74 ppm and an excellent correlation (R^2 of 0.99), highlighting MMCC's effectiveness in adsorbing MB due to its modified surface properties.

Regarding the Freundlich isotherm, MCC with MO has a Freundlich constant (K_F) of 0.79 ppm, a heterogeneity factor (n) of 2.34, and an R^2 of 0.92, indicating moderate adsorption on a heterogeneous surface. With MB, the K_F for MCC rises to 0.94 ppm, with n at 2.24 and R^2 at 0.96, suggesting improved adsorption and a better fit to the Freundlich model. For MMCC with MO, the K_F is 0.83 ppm, n is 2.10, and R^2 is 0.93, while for MB, K_F increases to 1.05 ppm, n is 2.55, and R^2 is 0.97, reflecting enhanced adsorption on a heterogeneous surface.

MMCC demonstrates superior adsorption performance for MB, likely due to the additional active sites provided by molasses modification, which increases the adsorbent's affinity for the cationic dye. Both Langmuir and Freundlich models indicate strong adsorption capacities, with the Langmuir model generally showing slightly better fits, suggesting the predominance of monolayer adsorption on the adsorbent surfaces. The Langmuir isotherm model assumes that adsorption occurs on a surface with homogeneous and finite active sites, forming a monolayer. Each site can bind only one MB or MO molecule with uniform energy, and there are no interactions between adjacent adsorbed molecules [18].

3.4. Kinetic Study of MCC and MMCC in MB and MO Adsorption

Adsorption kinetics examines the rate at which solutes adhere to adsorbents, providing insights into the performance of different materials for contaminant removal. This area of study employs different kinetic models, such as the pseudo-first-order (PFO) and pseudo-second-order (PSO) models, to analyze experimental data and understand adsorption processes. The PFO model assumes that the adsorption rate is proportional to the difference between the saturation concentration and the amount adsorbed over time, making it suitable for systems where adsorption occurs rapidly and equilibrium is quickly reached [48].

On the other hand, the PSO model indicates that the adsorption rate is related to the square of the number of available sites, making it particularly relevant for systems dominated by chemisorption. Selecting the appropriate kinetic model is crucial, as using an incorrect model can lead to misinterpretations of the adsorption mechanism and efficiency [49]. A summary of the kinetic study for both adsorbents and adsorbates is presented in Table 4.

The kinetic data for the adsorption of MO and MB on MCC and MMCC reveal that the PSO model provides a superior fit compared to the PFO model. For both adsorbents, the PSO model exhibits higher R^2 values, approaching 1.000, suggesting an excellent correlation between model predictions and experimental data. Additionally, the K_2 value from the PSO model aligns well with the observed adsorption rates, further confirming that this model accurately represents the adsorption process.

Choosing the PSO model as the best fit is justified by its ability to accurately capture the adsorption kinetics, reflecting the significance of chemisorption in the process. The higher R^2 values and more consistent rate constants suggest that the PSO model, which assumes the adsorption rate is proportional to the square of the number of available sites, provides a more reliable representation of the adsorption mechanism. This choice enhances the understanding of the adsorption process and aids in optimizing the adsorbents for effective contaminant removal.

4. Conclusion

This study highlights the effectiveness of monoliths made from activated candlenut shells, clay, and molasses as sustainable adsorbents for water dye removal. The monoliths demonstrated high performance, achieving 92% removal of methylene blue and 74% of methyl orange. The superior performance is attributed to the strong adsorption interactions facilitated by the negatively charged surfaces of the monoliths. Adsorption isotherm analysis followed the Langmuir model, indicating monolayer adsorption on a uniform surface, with a Langmuir constant of 1.53 ppm and an R^2 of 0.96 for methylene blue and a K_L of 1.14 ppm with an R^2 of 0.97 for methyl orange, signifying a high adsorption capacity. Kinetic studies, which fitted the pseudo-second-order model, suggest that the adsorption process is predominantly controlled by chemisorption mechanisms, with a kinetic rate constant (K) of 0.008 for methyl orange and an R^2 of 1.000, indicating a rapid and efficient adsorption process. Characterization techniques, including SEM, XRD, and FTIR, confirmed the presence of a porous structure, identifiable crystalline phases, and functional groups essential for effective dye removal. In summary, the monolithic adsorbents derived from candlenut shells and clay represent a highly effective, environmentally friendly solution for dye removal from wastewater. This approach offers a practical and sustainable method for addressing dye pollution and has significant potential for further development and application in water treatment technologies.

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