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Utilizing Orange Charcoal from Citrus Biomass for Effective Methylthioninium Chloride Dye Removal

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استخدام فحم البرتقال من الكتلة الحيوية للحمضيات لإزالة صبغة كلوريد الميثيلثيونينيوم بشكل فعال

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Abstract:
This study explores the efficacy of orange charcoal, a biochar produced from citrus biomass and activated with hydrochloric acid, for the removal of Methylthioninium Chloride (MC) dye from aqueous solutions. The escalating presence of synthetic dyes in industrial effluents underscores the urgent need for effective remediation strategies. Batch experiments conducted at 25°C demonstrated a remarkable removal efficiency of 97% and an adsorption capacity of 1.56 mg/g, utilizing 0.5 grams of the adsorbent in 50 milliliters of a 16 mg/L dye solution at pH 5. Equilibrium was attained within 20 minutes, signifying rapid adsorption kinetics. The adsorption data were optimally described by the Freundlich isotherm model and conformed to a second-order kinetic model. These findings underscore the potential of orange charcoal as a highly effective adsorbent for Methylthioninium Chloride, thereby significantly enhancing the efficacy of wastewater treatment and advancing sustainable waste management practices.

Keywords: Orange Charcoal; Hcl-Activated Carbon; Methylthioninium Chloride; Wastewater Treatment; Adsorption Capacity.

الملخص
تستكشف هذه الدراسة فعالية فحم البرتقال، وهو الفحم الحيوي الذي يتم إنتاجه من الكتلة الحيوية للحمضيات ويتم تنشيطه بحمض الهيدروكلوريك، لإزالة صبغة كلوريد الميثيلثيونينيوم (MC) من المحاليل المائية. يؤكد الوجود المتزايد للأصباغ الاصطناعية في النفايات السائلة الصناعية على الحاجة الملحة لاستراتيجيات معالجة فعالة. أظهرت تجارب الدفعات التي أجريت عند درجة حرارة 25 درجة مئوية كفاءة إزالة ملحوظة بنسبة 97% وقدرة امتزاز تبلغ 1.56 مجم/جم، باستخدام 0.5 جرام من المادة المازة في 50 ملليلتر من محلول الصبغة 16 مجم/لتر عند درجة حموضة 5. تم تحقيق التوازن خلال 20 دقيقة، مما يدل على حركية الامتزاز السريعة. تم وصف بيانات الامتزاز على النحو الأمثل بواسطة نموذج فروندليك وتتوافق مع النموذج الحركي الزائف من الدرجة الثانية تؤكد هذه النتائج على إمكانات فحم البرتقال كمادة مازة فعالة للغاية لكلوريد الميثيلثيونينيوم، وبالتالي تعزيز فعالية معالجة مياه الصرف الصحي بشكل كبير وتطوير ممارسات الإدارة المستدامة للنفايات.

الكلمات المفتاحية: فحم البرتقال، فحم منشط بحمض الهيدروكلوريك، ميثيلثيونينوم كلوريد، معالجة مياه الصرف الصحي، سعة الامتزاز.

1. Introduction

Water, an indispensable resource fundamental to the survival of all living organisms, occupies a pivotal role in propelling human advancement and is intricately interconnected with both industrial and agricultural sectors (Flilissa et al., 2024). Water pollution constitutes a pervasive global environmental challenge that necessitates urgent attention and the implementation of effective remedial strategies (Tang et al., 2022). A primary contributor to water contamination is the discharge of synthetic dyes from diverse industries, including textiles, paper manufacturing, and dyeing processes (Al-Tohamy et al., 2022). These synthetic dyes, such as Methylthioninium chloride (MC), are extensively employed due to their vibrant coloration and chemical stability. However, their unregulated release into aquatic environments poses significant risks to both aquatic ecosystems and human health (Attarki et al., 2023).

The eradication of dyes from wastewater constitutes a formidable challenge attributable to their intricate chemical architectures and inherent resistance to degradation (Katheresan et al., 2018). Conventional treatment methodologies, encompassing coagulation, flocculation, and biological processes, frequently prove inadequate in efficaciously eliminating dyes from contaminated aqueous systems (Oladoye et al., 2022). Consequently, alternative strategies, notably adsorption, have garnered substantial attention as a promising strategy for eliminating dyes from water-based solutions. Adsorption is a surface-mediated phenomenon in which pollutants are extracted from a liquid or gas phase and subsequently adhere to a solid substrate known as an adsorbent (Sridhar et al., 2022). Activated carbon has become among the most extensively utilized adsorbents owing to its exceptional adsorption capacity, expansive surface area, and well-developed porosity. Typically, activated carbon is synthesized from a diverse range of carbonaceous precursors, including agricultural residues, wood, and coal (Bhatnagar et al., 2013).

In recent times, there has been a burgeoning interest in utilizing agricultural waste and by-products as precursors for the synthesis of activated carbon. This methodology not only addresses the challenges associated with waste management but also provides a cost-effective and sustainable solution for the remediation of pollutants. Orange trees (Citrus sinensis) are cultivated extensively on a global scale, and their biomass residues, including wood and peels, present a valuable resource for the production of activated carbon (Paraskeva et al., 2008). Orange charcoal, derived through the pyrolysis of wood sourced from orange trees, has exhibited promising characteristics for activated carbon production (Danish et al., 2018). Pyrolysis is a thermal decomposition process conducted in the absence of oxygen, resulting in the formation of charcoal with enhanced porosity and surface area (Fahmy et al., 2020). The employment of orange charcoal as a precursor for activated carbon synthesis offers several advantages, including its abundance, low cost, and potential for waste valorization. To further enhance the adsorption properties of orange charcoal-based activated carbon, chemical activation processes are commonly implemented.

Chemical activation encompasses the impregnation of the precursor material with an appropriate activating agent, subsequently followed by a thermal treatment process. Hydrochloric acid (HCl) is one of the frequently utilized activating agents in this context. HCl functions as an oxidizing agent, thereby facilitating the development of a highly porous architecture within the activated carbon and consequently enhancing its adsorption capacity. The primary objective of this study is to examine the adsorption performance of chemically activated carbon derived from orange charcoal, which is synthesized from wood obtained from orange trees, for the removal of Methylthioninium chloride (MC) dye from aqueous solutions. By harnessing locally available waste materials, such as orange tree biomass, and employing a cost-effective activation methodology involving HCl, this approach seeks to provide an environmentally sustainable and economically viable solution for the treatment of dye-contaminated wastewater.

This investigation is dedicated to systematically exploring the impact of various parameters on the adsorption process, including contact time, initial dye concentration, pH, and adsorbent dosage. These variables are pivotal in determining the efficiency and efficacy of the adsorption mechanism. A comprehensive understanding of their effects will facilitate the optimization of process conditions to achieve maximal dye removal (Rápó & Tonk, 2021). The findings of this study are poised to advance the development of sustainable and cost-effective adsorbents for the remediation of dye-contaminated wastewater. The utilization of orange charcoal, derived from wood harvested from orange trees, presents a unique opportunity for waste valorization and promotes environmental sustainability, particularly within the textile industry. By addressing the pervasive challenge of water pollution caused by synthetic dyes, this research aims to significantly contribute to the preservation and protection of our invaluable water resources.

2. Materials and Methods

2.1 Preparation of the Adsorbent

The synthesis of the adsorbent begins with the procurement of orange charcoal. To enhance the purity and quality of the charcoal, impurities are meticulously removed through manual sifting or sieving processes. The subsequent chemical activation procedure involves the impregnation of the charcoal with a 2% hydrochloric acid (HCl) solution, followed by an immersion period of 24 hours to facilitate thorough absorption. Following impregnation, the charcoal is subjected to drying at 80°C to eliminate any residual moisture content. The dried and acid-impregnated charcoal then undergoes high-temperature activation, the parameters of which are determined based on specific experimental conditions. This activation process is conducted by heating the material within a controlled environment, such as a furnace, for a designated duration to develop a highly porous structure .Upon completion of the thermal activation, the chemically activated carbon is meticulously washed with distilled water to remove any remaining activating agents. The purified activated carbon is then dried and subsequently stored in a desiccator to prevent moisture reabsorption, thereby maintaining its optimal adsorption properties. This comprehensive preparation protocol ensures the production of high-quality activated carbon suitable for efficient pollutant removal from aqueous solutions.

2.2 Preparation and Mathematical Modeling of Methylthioninium Chloride Solutions for Adsorption Studies

A concentrated stock solution of Methylthioninium chloride (MC) at a concentration of 1000 mg/L was meticulously prepared by dissolving 1 gram of the MC dye powder in distilled water. This stock solution was subsequently subjected to a series of dilutions to yield working solutions with precisely controlled concentrations Within the framework of this study, a range of mathematical models and equations, frequently employed to characterize and elucidate adsorption phenomena, were systematically applied. The following equations (1) and (2) represent some of the principal models utilized in the analysis of the adsorption processes: (Behlou et al., 2022).

$$q_e = \frac{(C_O - C_e)}{m_s} \times \mathrm{V} \qquad (1)$$

$$R(\%) = \frac{(C_O - C_e)}{C_o} \times 100 \qquad (2)$$

The variables and C_O and C_e denote the initial and equilibrium concentrations of Methylthioninium chloride (MC) in milligrams per liter, respectively. The parameter q_e signifies the equilibrium adsorption capacity of MC, expressed in milligrams per gram, Additionally, V represents the solution's volume in liters (L), and m_s corresponds to the mass of the adsorbent in grams (g).

2.3 Application of Adsorption Isotherm Models to Dye Adsorption

The adsorption isotherm is fundamental for elucidating the interactions between the adsorbent and the adsorbate, providing critical insights into the adsorption capacity. It serves as an indispensable analytical tool for comprehending the mechanisms underpinning the adsorption process. The adsorption interface can be conceptualized as either a monolayer or a multilayer phenomenon. While a multitude of isotherm models have been suggested in the extant scientific literature, the Langmuir and Freundlich isotherm models are the most prevalently utilized frameworks for characterizing adsorption isotherms (Ferkous et al., 2022).The Langmuir isotherm model assumes a homogeneous adsorption surface with a finite number of identical sites, facilitating the formation of a monolayer coverage without any interactions between adsorbed molecules. In contrast, the Freundlich isotherm model accommodates heterogeneous surface energies and multilayer adsorption, thereby providing a more flexible approach to describing adsorption processes on varied surfaces. The application of these models enables the quantitative assessment of adsorption behavior, thereby enhancing the understanding of the efficiency and capacity of the adsorbent in removing Methylthioninium chloride (MC) dye from aqueous solutions. By employing these isotherm models, the study aims to accurately delineate the adsorption characteristics of chemically activated orange charcoal, thereby contributing to the optimization of adsorption parameters and the advancement of effective wastewater treatment methodologies.

2.3.1 Langmuir Adsorption Isotherm Model Applied to Dye Adsorption

The Langmuir adsorption isotherm theory posits that adsorption transpires at discrete, uniform sites distributed throughout the adsorbent material. This paradigm has been extensively employed to elucidate the adsorption process, particularly in the formation of a monolayer, and has consistently demonstrated its efficacy in this context. The linearized representation of the Langmuir isotherm is articulated as follows, delineated in Equation (3):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_a q_m} \tag{3}$$

In the context of the Langmuir adsorption isotherm model, the variables are defined as follows:
q_e : The amount of Methylthioninium chloride (MC) adsorbed per unit mass of adsorbent at equilibrium (mg/g).
C_e: The equilibrium concentration of MC in the solution (mg/L).
q_m: The maximum adsorption capacity, representing the maximum amount of MC that can be adsorbed per unit mass of adsorbent (mg/g).
k_a: The Langmuir isotherm constant, indicative of the affinity between the adsorbent and the adsorbate (L/mg).

2.3.2 Freundlich Adsorption Isotherm Model Applied to Dye Adsorption

The Freundlich adsorption isotherm model posits that the adsorption surface is heterogeneous, characterized by a multitude of adsorption sites with varying energies. This model accounts for the non-uniform distribution of active sites and the multilayer adsorption phenomena, thereby providing a more versatile framework compared to monolayer-based models (Akkari et al., 2023). The linearized form of the Freundlich isotherm is expressed as follows Equation 4:

$$\ln q_e = \ln k_f + \frac{1}{n} \tag{4}$$

In the aforementioned equation (4), q_e signifies the quantity of the adsorbate—in this instance, Methylthioninium chloride (MC)—adsorbed per unit mass of the adsorbent at equilibrium, quantified in milligrams per gram (mg/g). Concurrently, the parameter k_f denotes the Freundlich constant indicative of the adsorbent's adsorption capacity, whereas n characterizes the intensity of the adsorption process, reflecting the heterogeneity of the adsorption sites.

3. Results and Discussion

3.1. Influence of pH on Dye Removal

Figure 1 elucidates the substantial effect of pH on the removal efficiency of Methylthioninium Chloride (MC) dye utilizing orange charcoal activated carbon. Notably, a pH value of 5 emerges as critically significant, achieving a removal efficiency of 96.46%. At this pH level, the protonation of hydroxyl functional groups on the adsorbent surface leads to an increased density of positive charges. This enhanced positive charge density facilitates the electrostatic attraction of the cationic MC dye molecules.

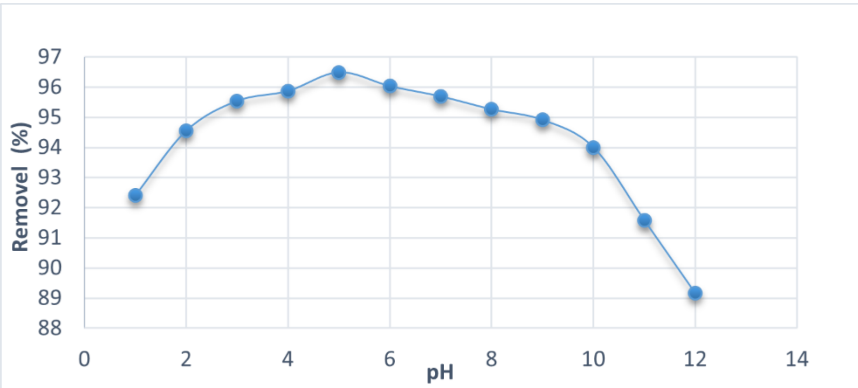

Figure 1: Effect of pH variation on removal percentage of MC.

At pH 5, the system experiences maximal electrostatic repulsion, which effectively inhibits dye aggregation. This inhibition promotes greater contact between the dye molecules and the adsorbent surface, thereby augmenting the adsorption efficiency. The investigation across a broad pH spectrum (ranging from 1 to 12) reveals that acidic conditions generally bolster the adsorption process by enhancing the attraction between the adsorbate and the adsorbent. However, excessively acidic environments may impede adsorption efficiency, potentially due to the saturation of adsorption sites or alterations in the adsorbent's surface chemistry. Conversely, alkaline conditions are observed to diminish adsorption efficiency. In such environments, hydroxide ions (OH^-) compete with the dye molecules for available adsorption sites, thereby reducing the overall adsorption capacity.

The optimal pH of 5 strikes a balance wherein protonation of the adsorbent surface enhances electrostatic interactions without introducing significant competition from hydroxide ions. Consequently, pH 5 provides the most favorable conditions for the removal of MC dye, resulting in the highest observed removal percentage. In this context, this optimal pH condition underscores the importance of surface chemistry and electrostatic interactions in the adsorption mechanism. By fine-tuning the pH to 5, the study demonstrates a significant enhancement in adsorption performance, thereby validating the efficacy of orange charcoal activated carbon as a potent adsorbent for cationic dye removal under controlled pH conditions.

3.2. Influence of Initial Dye Concentration on Adsorption

Figures 2(a) and 2(b) illustrate the effect of varying initial concentrations of Methylthioninium chloride (MC) dye on its adsorption by orange charcoal activated carbon. At an initial concentration of 16 mg/L, the adsorption process achieved a remarkable removal efficiency of 97%, corresponding to an adsorption capacity of 1.55 mg/g. This high level of effectiveness underscores the potent adsorption capabilities of the orange charcoal activated carbon at elevated dye concentrations.

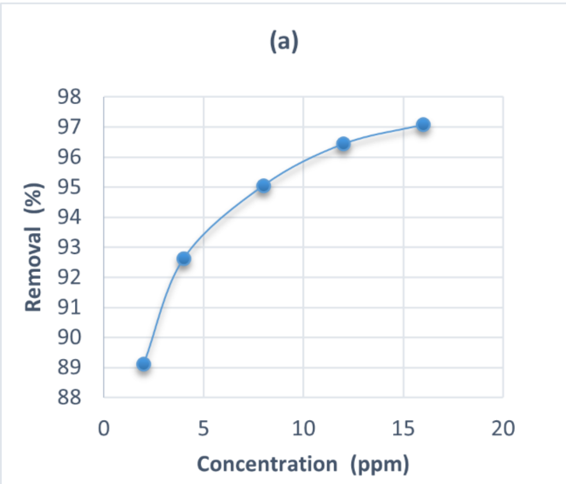

Figure 2 (a): the impact of initial concentration on MC removal percentage.

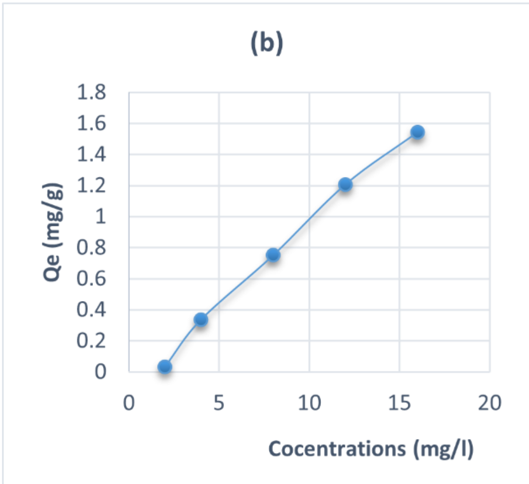

Figure 2 (b): the corresponding adsorption capacity.

The study systematically investigated a range of initial dye concentrations from 2 mg/L to 16 mg/L. Within this concentration spectrum, the adsorption efficiency remained consistently high, demonstrating the adsorbent's robust performance across varying pollutant loads. The observed trend indicates that orange charcoal activated carbon maintains substantial adsorption capacity even as the initial concentration of MC dye increases, which is indicative of its suitability for treating wastewater with diverse dye concentrations. In this direction. The superior performance at 16 mg/L suggests that OCAC is particularly effective in scenarios involving higher dye concentrations, making it a promising candidate for industrial applications where dye loads are typically substantial. The high adsorption capacity at this concentration highlights the adsorbent's ability to accommodate significant amounts of dye, thereby reducing the overall pollutant load in aqueous solutions efficiently. These findings contribute to a deeper understanding of the adsorption dynamics of MC dye onto orange charcoal activated carbon.

The demonstrated effectiveness across a broad range of concentrations not only validates the adsorbent's potential for practical applications but also paves the way for its integration into wastewater treatment protocols. Furthermore, the ability to maintain high adsorption efficiency at elevated concentrations enhances the economic viability and scalability of using orange charcoal activated carbon as a sustainable solution for dye removal in industrial effluents. In summary, the pronounced adsorption performance of orange charcoal activated carbon at an initial MC dye concentration of 16 mg/L affirms its efficacy as a reliable and efficient adsorbent. This study's insights into concentration-dependent adsorption behavior reinforce the potential of orange charcoal activated carbon in advancing wastewater treatment technologies and promoting environmental sustainability.

3.3. Influence of Contact Time on Adsorption Efficiency

Figure 3 delineates the significant impact of contact time on the adsorption efficacy of Methylthioninium chloride (MC) dye utilizing orange charcoal activated carbon (OCAC). Notably, a high removal percentage of 96.57% was attained at a contact duration of merely 20 minutes, underscoring the rapid and efficient adsorption capability of OCAC within this timeframe. The study encompassed a contact time spectrum ranging from 10 to 60 minutes, thereby providing comprehensive insights into the temporal dynamics of the adsorption process.

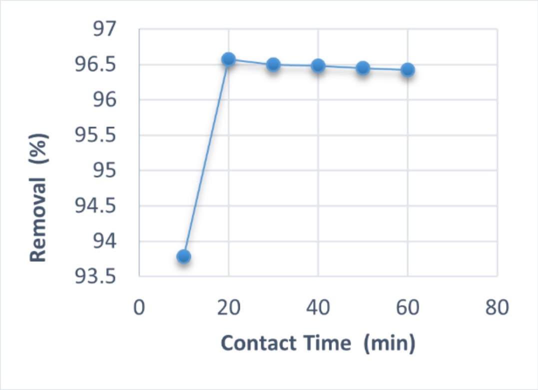

Figure 3: Effect of contact time on the amount of absorption MC.

The observed trend indicates that the adsorption of MC dye onto OCAC is predominantly achieved within the initial 20 minutes, after which the removal efficiency plateaus, suggesting the attainment of equilibrium. This rapid adsorption kinetics highlights the adsorbent's high affinity for the dye molecules and its capacity to facilitate swift pollutant removal from aqueous solutions. The efficiency observed within this relatively short contact period is indicative of the porous structure and surface functional groups of OCAC, which enhance the interaction between the adsorbent and the adsorbate. Furthermore, the extended contact times beyond 20 minutes do not result in substantial increases in removal efficiency, implying that the majority of active adsorption sites are occupied early in the process. This saturation effect is consistent with the formation of a monolayer adsorption as described by the Langmuir isotherm model, where a finite number of adsorption sites are available for dye molecules.

The proficiency of OCAC in achieving high adsorption efficiency within a brief contact time has significant practical implications. It suggests that OCAC can be effectively employed in wastewater treatment systems requiring rapid pollutant removal, thereby enhancing operational efficiency and reducing processing times. Additionally, the ability to reach equilibrium swiftly minimizes the residence time of contaminated water in treatment facilities, contributing to overall cost-effectiveness and scalability of the adsorption process. In summary, the pronounced effect of contact time on the adsorption of MC dye onto OCAC underscores the adsorbent's exceptional performance in facilitating rapid and efficient dye removal. The attainment of near-maximum removal efficiency within 20 minutes highlights the potential of orange charcoal activated carbon as an effective and practical solution for the treatment of dye-contaminated wastewater. These findings reinforce the suitability of OCAC for integration into industrial wastewater management systems, promoting environmental sustainability and enhancing water quality through efficient pollutant remediation.

3.4. Influence of Adsorbent Dosage on Dye Adsorption

Figure 4 illustrates the effect of varying dosages of orange charcoal activated carbon (OCAC) on the adsorption efficiency of Methylthioninium chloride (MC) dye. Specifically, the application of a dosage of 0.5 grams in a 50-milliliter solution yielded an exceptional removal percentage of 97%, underscoring the high efficacy of OCAC at this concentration. The study encompassed a dosage range from 0.1 grams to 1 gram per 50 milliliters; thereby providing comprehensive insights into the adsorption behavior across different adsorbent quantities.

The results demonstrate that the adsorption of MC dye onto OCAC is highly effective within the tested dosage spectrum. As the dosage increases, the availability of active adsorption sites on the OCAC surface correspondingly enhances, facilitating greater dye uptake from the aqueous solution. This positive correlation between adsorbent dosage and removal efficiency highlights the adsorbent's capacity to efficiently eliminate the dye across a broad range of concentrations. Clearly, the optimal performance at a dosage of 0.5 grams is achieved under specific experimental conditions, including a pH of 5, a contact time of 20 minutes, and an initial dye concentration of 16 mg/L. These parameters collectively contribute to the maximization of adsorption efficiency, indicating that OCAC is particularly effective when these conditions are met. The high removal percentage at the optimal dosage reflects the synergistic interplay between the adsorbent's surface properties and the operational parameters, which collectively enhance the adsorption process.

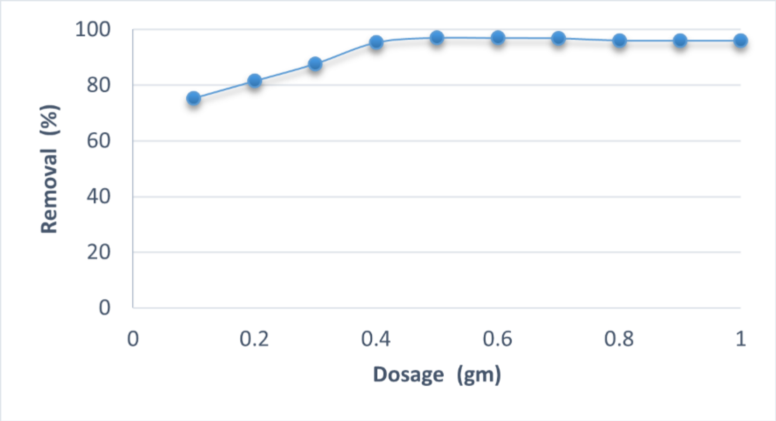

Figure 4: Variation of MC removal versus dosage.

Moreover, the observed trend suggests that beyond a certain dosage threshold, the incremental benefits in removal efficiency may diminish, potentially due to the saturation of adsorption sites or the aggregation of adsorbent particles, which can limit the accessibility of active sites. However, within the studied range, OCAC consistently exhibits robust performance, affirming its suitability as a potent adsorbent for MC dye removal.

3.5. Influence of Adsorbent Particle Size on Dye Adsorption

Figure 5 delineates the profound impact of adsorbent particle size on the adsorption efficacy of Methylthioninium Chloride (MC) dye utilizing OCAC. Specifically, an adsorbent particle size of 100 micrometers exhibited the highest removal efficiency, attaining a removal percentage of 96.96%. The superior performance of smaller particle sizes can be ascribed to several interrelated factors. Primarily, smaller particles offer an increased surface area-to-volume ratio, thereby augmenting the availability of active adsorption sites. This enhancement facilitates more efficient diffusion and mass transfer of dye molecules towards the adsorbent surface.

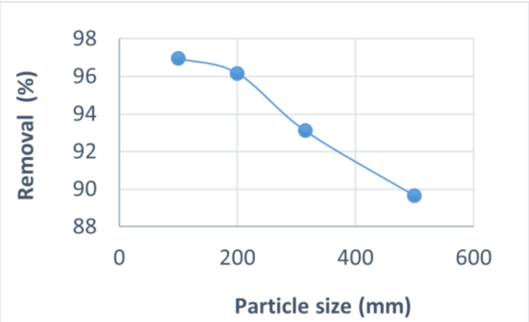

Figure 5: Effect of changing the diameter on the percentage of MC removal.

Furthermore, reduced particle sizes are often associated with a more favorable pore structure, which enhances the accessibility of dye molecules to the internal porosity of the activated carbon. This improved pore accessibility ensures that a greater proportion of dye molecules can be effectively captured and retained within the adsorbent matrix. The high removal percentage observed is consequently the result of the synergistic effect between the diminished particle size and the meticulously optimized experimental conditions, which include a solution volume of 50 mL, a pH of 5, a contact time of 20 minutes, and an initial dye concentration of 16 mg/L.

The optimized particle size not only maximizes the adsorption capacity but also accelerates the adsorption kinetics, enabling rapid attainment of equilibrium. This rapid adsorption is indicative of the enhanced interaction between the adsorbent and the adsorbate facilitated by the smaller particle size. Additionally, smaller particles may exhibit reduced diffusion limitations, thereby ensuring that dye molecules can swiftly traverse the boundary layer surrounding the adsorbent particles and access the active sites more readily. In summary, the reduction in adsorbent particle size to 100 micrometers significantly enhances the removal efficiency of MC dye through increased surface area, improved mass transfer, and optimized pore accessibility. These findings underscore the critical role of particle size in the adsorption process and highlight the potential of finely tuned adsorbent characteristics in achieving superior pollutant removal performance. The elucidation of particle size effects provides valuable insights for the design and optimization of activated carbon-based adsorbents, thereby contributing to the advancement of effective wastewater treatment methodologies.

3.6. Influence of Agitation Speed on Dye Adsorption

Figure 6 elucidates the effect of varying agitation rates on the removal efficiency of Methylthioninium Chloride (MC) dye utilizing orange charcoal activated carbon. Within the investigated range of 100 to 400 revolutions per minute (rpm), the optimal removal efficiency of 96.98% was attained at an agitation rate of 200 rpm. The augmentation of the agitation rate was observed to positively influence the adsorption efficiency by enhancing the interaction between the adsorbent particles and the dye molecules. This enhanced contact facilitates more effective collision and subsequent adsorption of the dye onto the activated carbon surface.

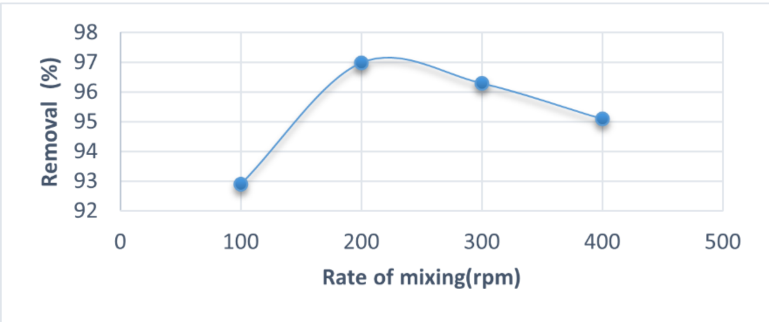

Figure 6: Effect of the initial speed change on the percentage of MC removal.

However, surpassing the optimal agitation rate of 200 rpm resulted in a decline in the removal percentage. This reduction can be attributed to several factors: firstly, excessive agitation may induce desorption of previously adsorbed dye molecules due to increased kinetic energy, disrupting the adsorption equilibrium. Secondly, higher agitation speeds can generate air bubbles and turbulence within the solution, which may hinder the effective interaction between the adsorbent and the adsorbate by creating barriers to mass transfer. Additionally, elevated agitation rates can lead to the formation of a stagnant boundary layer around the adsorbent particles, thereby imposing diffusion limitations that restrict the accessibility of dye molecules to active adsorption sites. Determining the optimal agitation rate is imperative for maximizing removal efficiency while maintaining the integrity of the adsorption process. An agitation rate of 200 rpm emerges as the most favorable condition, balancing sufficient mixing and contact between the adsorbent and adsorbate without introducing adverse effects such as desorption or diffusion limitations.

This optimal agitation speed ensures a homogeneous distribution of dye molecules and adsorbent particles, thereby facilitating efficient and consistent adsorption performance. In conclusion, the agitation speed plays a critical role in the adsorption dynamics of MC dye onto orange charcoal activated carbon. The identification of an optimal agitation rate at 200 rpm underscores the necessity of precise operational control to achieve maximal dye removal efficiency. These findings contribute to the refinement of adsorption process parameters, enhancing the practical applicability and effectiveness of orange charcoal activated carbon in wastewater treatment applications.

3.7 Kinetics Study

The present investigation endeavors to elucidate the adsorption kinetics of Methylthioninium chloride (MC) dye onto OCAC. This study is primarily concerned with comprehending the intricate interactions between the MC dye molecules and the activated carbon matrix. To accomplish this objective, a series of meticulously designed experiments were conducted utilizing various kinetic models, notably the pseudo-first-order and pseudo-second-order equations. These models afforded profound insights into the adsorption mechanisms, facilitating a detailed analysis of the adsorption behavior of MC as it adheres to the carbon surface .Comprehensive documentation of the experimental procedures was undertaken to ensure the precision and reproducibility of each methodological step. The resultant data, which delineate the applicability of the kinetic models and the diffusion processes governing the adsorption of MC dye onto OCAC, are systematically presented in Figure 7. Through this exhaustive and methodical approach, the study aims to advance the understanding of the complex interactions underpinning the adsorption kinetics of organic dyes on activated carbon substrates. The findings contribute to a more nuanced comprehension of the adsorption dynamics, thereby informing the optimization of activated carbon-based remediation strategies for organic dye pollutants in aqueous environments.

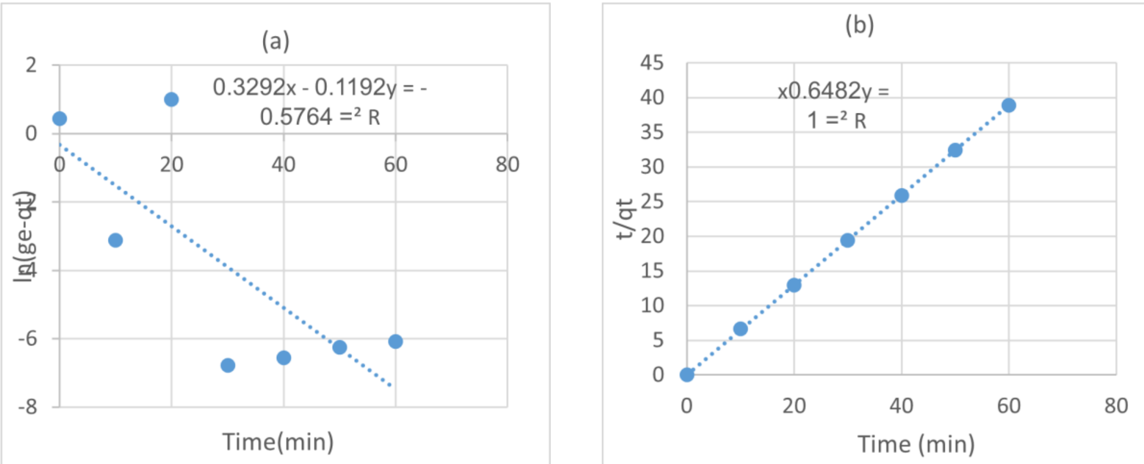

Figure 7: (a) Pseudo-first order kinetic study; b) Pseudo-second order kinetic study, conducted at a dosage of 0.5 g, an initial concentration of 16 mg/L, and a pH of 5.

3.8 Analysis of Adsorption Capacity Utilizing Langmuir and Freundlich Isotherm Models

The examination of adsorption isotherms is pivotal for ascertaining the maximum adsorption capacity of adsorbent materials. To accurately model and interpret the experimental data obtained, it is imperative to employ an isotherm model that aptly represents the adsorption behavior inherent to the system under consideration. The Langmuir isotherm equation is traditionally applicable to scenarios involving adsorption on entirely homogeneous surfaces, where interactions between adsorbed molecules are minimal or negligible. This model postulates monolayer adsorption on a limited number of identical sites, thereby providing a simplified representation of the adsorption process. Conversely, the Freundlich isotherm equation offers a more flexible framework, particularly well-suited for describing adsorption phenomena in heterogeneous aqueous systems.

This model accounts for the variability in surface energies and adsorption site affinities, thereby accommodating multilayer adsorption and providing a more nuanced depiction of the adsorption process. Upon analysis, the correlation coefficients for both the Langmuir and Freundlich models approached unity, thereby indicating a strong conformity between the experimental data and the theoretical predictions of the Freundlich isotherm. This high correlation factor underscores the efficacy of the Freundlich model in accurately representing the adsorption behavior observed in the study, as illustrated in Figures 8 and 9. The superior fit of the Freundlich isotherm suggests that the adsorption process in this system is governed by heterogeneous surface interactions and varying adsorption energies, thereby validating the selection of the Freundlich model for a comprehensive understanding of the adsorption dynamics involved.

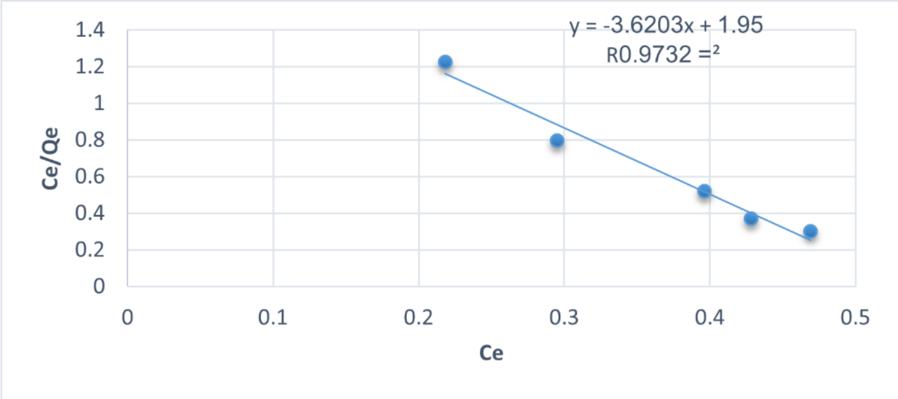

Figure 8: Langmuir isotherm.

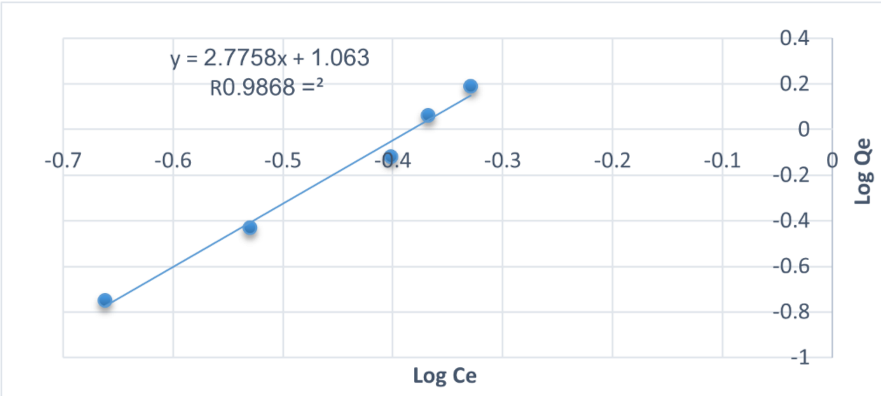

Figure 9: Freundlich isotherm.

These findings elucidate the adsorption characteristics of the OCAC, highlighting its substantial capacity and efficiency in dye removal from aqueous solutions. The successful application of the Freundlich isotherm not only reinforces the model's applicability to complex adsorption systems but also facilitates the optimization of adsorption parameters for enhanced pollutant remediation. Consequently, this analysis contributes to the advancement of sustainable and effective wastewater treatment methodologies through the utilization of tailored activated carbon adsorbents.

4. Conclusions

The present investigation substantiates the efficacy of orange charcoal, derived from the biomass of Citrus sinensis (orange trees), as a potent and sustainable adsorbent for the removal of Methylthioninium chloride (MC) dye from wastewater. This study underscores the significant advantages associated with utilizing agricultural by-products for the synthesis of activated carbon, thereby addressing critical environmental challenges related to water contamination and waste management. The empirical findings advocate for the development of environmentally benign and economically viable solutions for dye-laden wastewater treatment, thereby promoting the valorization of agricultural waste and the adoption of sustainable practices within the textile industry. Furthermore, this research lays a robust foundation for subsequent studies aimed at optimizing the application of orange charcoal, enhancing wastewater remediation techniques, and advancing broader objectives of environmental sustainability. By demonstrating the practical utility of orange charcoal in pollutant removal, this study contributes to the ongoing efforts to mitigate industrial pollution and foster sustainable environmental stewardship.

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