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Removal of Methyl Orange Dye Using Chemically Activated Carbon Derived from Commercial Pine Charcoal

Nooraddein A. Ekrayem[1*], Haitham E. Eshtiwi [2], Abdalsttar A. Benour [3], Abdalnasser M. Abugoffa[4]
[1-4] Department of Chemical Engineering, Alasmarya Islamic University, Zliten, Libya
[*]*Corresponding author: n.ekrayem@asmarya.edu.ly*

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Abstract:
Liquid waste is considered one of the potential sources of water pollution due to its content of toxic dyes. The discharge of azo dyes into the aquatic environment is particularly concerning because of their color, toxicity, and mutagenic effects, which may lead to serious health problems such as cancer. Therefore, this study aims to investigate the removal of methyl orange dye from aqueous solutions using activated carbon prepared from pine branches through a batch adsorption process. Various operational parameters were examined, including solution pH, equilibrium contact time, initial dye concentration, adsorbent dosage, particle size, and temperature. The results indicated that the adsorption of methyl orange decreases with increasing pH, with the optimum value observed at pH = 7. In addition, the adsorption efficiency increased with higher activated carbon dosage and longer contact time, reaching equilibrium within 140 minutes. At dye concentrations ranging from 10 to 30 mg/L, it was found that 0.8 g of activated carbon was sufficient to remove 83.106 % of the dye at an initial concentration of 10 mg/L in 20 mL of solution. The optimum stirring speed was found to be 200 rpm. The optimum particle size and temperature were 0.315 mm and 25°C, respectively. The equilibrium adsorption data were well fitted by both Langmuir and Freundlich isotherm models, showing good agreement between experimental and predicted values based on the correlation coefficient (R^2). The maximum adsorption capacity of the activated carbon was found to be 0.7312 mg/g. These results indicate that activated carbon derived from pine branches can be effectively used as a low-cost and natural adsorbent for the removal of methyl orange from contaminated water.

Keywords: Activated carbon , Methyl orange , Adsorption , Azo dyes , Wastewater treatment.

إزالة صبغة الميثيل البرتقالي باستخدام الكربون المنشط كيميائيًا المشتق من فحم الصنوبر التجاري

نورالدين على اكريم[1]، هيثم اشتيوي[2]، عبد الستار بنور[3]، عبد الناصر أبو قفة [4]
[1-4] قسم الهندسة الكيميائية، الجامعة الأسمرية الإسلامية، زليتن، ليبيا.

الملخص

تُعد المخلفات السائلة أحد المصادر المحتملة لتلوث المياه بسبب احتوائها على أصباغ سامة. ويُعد تصريف أصباغ الآزو في البيئة المائية أمرًا مثيرًا للقلق بشكل خاص بسبب لونها وسُميتها وتأثيراتها الطفرية، والتي قد تؤدي إلى مشاكل صحية خطيرة مثل الإصابة بالسرطان.
لذلك، تهدف هذه الدراسة إلى بحث إزالة صبغة **الميثيل البرتقالي (Methyl Orange)** من المحاليل المائية باستخدام الكربون المنشط المحضر من أغصان الصنوبر من خلال عملية امتزاز بنظام الدفعات **(Batch Adsorption Process)**.
تمت دراسة تأثير مجموعة من العوامل التشغيلية المختلفة، بما في ذلك **الرقم الهيدروجيني للمحلول(pH)** ، وزمن الوصول إلى الاتزان، والتركيز الابتدائي للصبغة، وجرعة المادة المازة، وحجم الجسيمات، ودرجة الحرارة.
أظهرت النتائج أن امتزاز صبغة الميثيل البرتقالي ينخفض مع زيادة قيمة **pH**، حيث تم الحصول على أفضل قيمة عند **pH 7** =كما ازدادت كفاءة الامتزاز مع زيادة كمية الكربون المنشط وزيادة زمن التلامس، حيث تم الوصول إلى حالة الاتزان خلال **140دقيقة**.
وعند تراكيز الصبغة التي تراوحت بين **30–10ملغم/لتر**، تبين أن **0.8غرام** من الكربون المنشط كان كافيًا لإزالة **83.106%**من الصبغة عند تركيز ابتدائي **10ملغم/لتر** في حجم محلول قدره **20ملليلتر**.
بلغت سرعة التحريك المثلى **200دورة/دقيقة(rpm)** ، بينما كان الحجم الأمثل للجسيمات ودرجة الحرارة **0.315مم** و **25°م** على التوالي.
أظهرت بيانات امتزاز الاتزان توافقًا جيدًا مع نموذجي متساوي الحرارة **لانغمير (Langmuir)** و**فريندلخ (Freundlich)**، مع وجود توافق جيد بين القيم التجريبية والقيم المتوقعة اعتمادًا على معامل الارتباط **(R^2)**.
بلغت السعة القصوى لامتزاز الكربون المنشط **0.7312ملغم/غم**. وتشير هذه النتائج إلى أن الكربون المنشط المشتق من أغصان الصنوبر يمكن استخدامه بفعالية كمادة مازة طبيعية ومنخفضة التكلفة لإزالة صبغة الميثيل البرتقالي من المياه الملوثة .

الكلمات المفتاحية: الكربون المنشط؛ الميثيل البرتقالي؛ الامتزاز؛ أصباغ الآزو؛ معالجة مياه الصرف الصحي.

1.Introduction

Environmental pollutants and dyes constitute critical environmental and health issues that are gaining increasing global attention [1]. With rapid industrial advancement and the expansion of human activities, the quantity and quality of chemicals released into the environment have escalated, leading to widespread adverse effects on ecosystems and human health. Chemical compounds of days widely utilized in various industries such as textiles, leather, paper, and other color addition applications [2]. The textile industry constitutes a major contributor to dye pollution; its effluents often contain persistent dye residues and auxiliary chemicals that resist conventional treatment processes effectively. This resultant environmental contamination presents significant ecological risks, primarily through the pollution of aquatic bodies [2]. The presence of these chromophores compounds alters light penetration and transmittance within the water column, thereby affecting the photosynthesis processes of aquatic plants and marine life. Furthermore, these dyes inherently possess a degree of toxicity [2, 3]. For example, Methyl Orange (MO), a widely used azo dye in printing and dyeing applications, has been linked to acute health symptoms upon exposure, including gastrointestinal distress (diarrhea and vomiting) and abdominal pain. Exposure to significantly high concentrations of these toxic substances may, in severe instances, result in mortality [3].

Currently, various techniques have been developed for the removal of dyes from wastewater, including adsorption [4], membrane processes [5], ion exchange [6], biological methods, and electrochemical systems [7], chemical precipitation, filtration [8], evaporation [9]. Among these conventional techniques, adsorption has garnered significant attention for the removal of dyes and pollutants, attributed to its unique advantages, including process simplicity combined with high efficiency, cost-effectiveness, and operation over a wide range of conditions [10]. Furthermore, the flexibility in the selection and design of adequate sorbents is a key feature of the adsorption technique. The adsorption technique has the ability to enrich (or concentrate) trace metals, making it a preferred choice for water purification applications [10].Presently, activated carbon (AC) is deemed one of the most significant and widely used carbonaceous

adsorbents in water treatment and purification, including the removal of dyes and heavy metal ions [11].

Activated carbon exhibits superior efficiency in treating dye-contaminated wastewater, primarily due to its vast specific surface area and complicated pore structure, which provide abundant adsorption sites for diverse contaminant molecules [12, 11]. These properties guarantee high removal efficiency and swift purification across a wide range of chemical conditions. However, its relatively high cost and the difficulty linked to regeneration stimulate the search for more economical alternatives [13, 12]Therefore, current research is focused on capitalizing on inexpensive and renewable agricultural wastes. In this study, the performance of activated carbon derived from Pine Agricultural Wastes was evaluated as a low-cost and efficient biosorbent for the removal of Methyl Orange dye from aqueous solutions [13]. This research aims to optimize the adsorption conditions and investigate the potential of this material as environmentally friendly solution for wastewater treatment.

2. Experimental section

2.1. Materials

Analytical-grade Methyl Orange (MO) was obtained from ACROS Organics, a part of Thermo Fisher Scientific, UK Ltd. MO is classified as a direct, anionic azo dye derived from a benzidine-based structure. Raw pine carbon material was collected from a local market. Hydrochloric acid was supplied by Thomas Baker Chemicals Pvt. Ltd., India (CAS No. 7647-01-0; 37% concentration; density: 1.19 g/mL). This acid was used to prepare a 0.1 M HCl solution. Sodium hydroxide was obtained from the same supplier (CAS No. 1310-73-2; pellets with a minimum purity of 99%) and was used to prepare a 0.1 M NaOH solution. Distilled water (prepared in our laboratory, pH ≈ 7) was used throughout the experiments. All reagents were used without further purification.

2.2. Preparation of Activated Carbon from Pine Charcoal (AC)

The activated carbon (AC) employed in this study was produced from commercially available pine-derived charcoal obtained from a local source. The preparation procedure consisted of a preliminary pre-treatment step followed by chemical activation. Initially, the raw charcoal was attentively washed and then dried in an oven at 120 °C for 24 hours to achieve complete drying of the material. This drying step was essential to guarantee material homogeneity and improve the efficiency of the subsequent activation process. It was then ground and sieved using a mechanical sieve shaker (WiseVen) to obtain a uniform particle size distribution. Subsequently, the resulting powder was chemically activated by impregnation in phosphoric acid (H_3PO_4) solution at a predetermined weight ratio (e.g., 1:1 w/w) for 24 h. After impregnation, the sample was subjected to thermal treatment in a muffle furnace at temperatures ranging from 500 to 600 °C for 1 h under a nitrogen atmosphere to minimize oxidation [14, 15]. The activated carbon was then thoroughly washed with hot distilled water until a neutral pH was achieved. Finally, the material was dried at 105 °C and stored for further experimental use.

2.3 . Batch sorption experiments

Batch adsorption experiments were conducted to To evaluate the performance of varying doses of activated carbon (AC) for the adsorption of Methyl Orange (MO) dye. Samples of AC using various dosages (0.1, 0.2, 0.4, 0.6, 0.8 and 1) g were added to (50) mL conical flasks containing (20) mL of MO solution at various initial concentrations (10, 20 and 30) mg/L. The initial pH of the solution was adjusted to the desired value using aqueous solutions of 1 M Hydrochloric acid (HCl) or 0.5 M Sodium hydroxide (NaOH). Following this, each adsorbent sample was allowed to adsorb the MO dye under an agitation rate of 200 (rpm) for 140 minutes at room temperature. Solution samples were sampled from the MO solution at several time intervals to verify the adsorption efficiency of the AC particles for the MO dye. For each supernatant

aliquot of the samples, distilled water was used to reduce (dilute) the concentration of the MO dye in the solution. Subsequently, a UV-Visible Spectrophotometer was used to determine the concentration of the MO dye in the clarified liquid using a standard calibration curve prepared previously from defined concentrations of MO in aqueous solutions. The equilibrium adsorption capacity (q_e) and the removal percentage (R%) of MO dye from the aqueous solution were determined using Equations (1) and (2), respectively [10].

$$q_e = \frac{V(C_o - C_e)}{m} \quad \text{.....(1)}$$

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

Where: q_e is the adsorption capacity of the adsorbent (mg/g), R% removal efficiency, C_o and C_e (mg/L) is the initial and final concentration of MO dye, V (L) represents the volume of the aqueous solution, and m (g) is the mass of the dry adsorbent.

3. Results and Discussion

3.1 Adsorptive removal of methyl orange dye using activated carbon (AC)

The adsorption behavior of methyl orange dye onto the prepared activated carbon (AC) was investigated using aqueous solutions. This section presents an evaluation of the total efficiency of the adsorbent under various operational conditions. A systematic investigation was conducted to assess the effects of key parameters, namely contact time, solution pH, adsorbent dosage, and initial dye concentration, in order to identify the optimal conditions for efficient dye removal. Detailed discussions of each parameter are provided in the following sections.

3.2 Effect of Contact Time

To evaluate the equilibrium time, a series of experiments was conducted to measure the efficiency of Methyl Orange (MO) dye removal. The following constant conditions were used in these experiments: a solution volume of 20 mL with an initial concentration of 10 mg/L, an adsorbent dosage of 0.8 g, a particle size of 0.315 mm, a stirring rate of 200 rpm, a temperature of 25°C, and a pH value of 7. Sampling was performed at regular intervals throughout the experiment (5, 10, 20, 40, 60, 80, 120, and 140 min). Figure (1) illustrates the results obtained regarding the effect of contact time on the MO removal process across eight experimental batches. The optimal contact time was determined to be 140 minutes, at which point the percentage removal of MO reached its peak, recording 83.106%, and the corresponding adsorption capacity attained 0.202 mg/g.

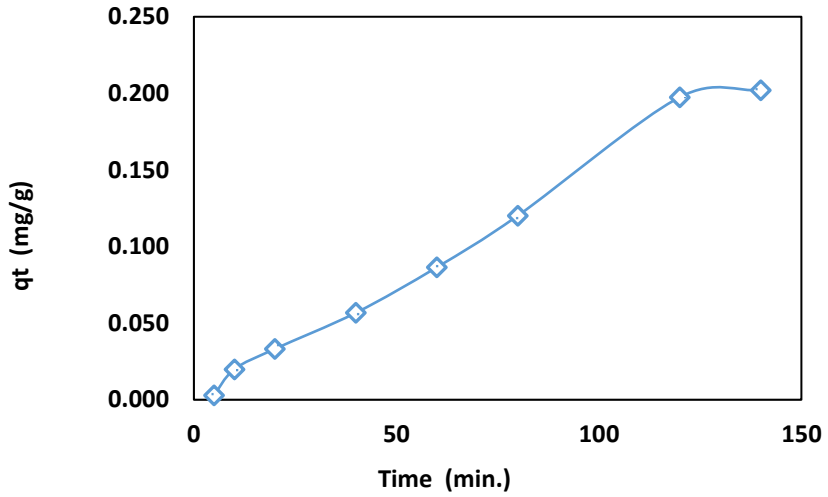

Figure (1). Effect of contact time on the amount of absorption MO .

It was observed that the adsorption capacity of the activated carbon (AC) exhibited a sharp increase during the initial stage, followed by a steady increase to reach an adsorption equilibrium value of (0.200 mg/g) within 120 minutes. This behavior can be attributed to the abundance of available active adsorption sites on the AC surface at the onset of the process. The high concentration gradient between the liquid-solid interfaced promoted the swift uptake of these valid adsorption sites by the MO dye molecules [16, 17].

As a result, there was a significant initial enhancement in the adsorption capacity. As the adsorption with the progression of the process, the number of vacant adsorption sites diminished incrementally. Simultaneously, the driving force derived from the concentration gradient weakened substantially, impeding further dye molecules from overcoming the mass transfer resistance required to migrate to the adsorbent surface, resulting from the depletion of dye molecules in the liquid phase [16, 18]. Therefore, the adsorption rate gradually diminished, and the adsorption capacity finally stabilized until the final adsorption equilibrium was achieved at a contact time of 140 minutes, reaching a maximum adsorption value of 0.202 mg/g.

3.3. Effect of pH

Methyl orange (MO) dye using activated carbon (AC). The experiments were performed at initial dye concentrations of 10, 20, and 30 mg/L, within a pH range of (3–11), at a constant temperature of 25 °C, agitation speed of 200 rpm, adsorbent dosage of 0.8 g per 20 mL solution, and a contact time of 140 min. As shown in Figure (2), the adsorption capacity of AC varied significantly with pH, exhibiting a maximum at pH 3.0, followed by a progressive decline as the pH increased, attaining a minimum at pH 11. This observation suggests that the adsorption process is strongly dependent on the solution acidity, which governs both the surface charge of the adsorbent and the ionic form of the dye in solution. In aqueous media, methyl orange is primarily present in ionic form, where sulfonate groups ($–SO_3^-$) contribute to its negative charge, particularly under acidic conditions where it adopts a quinoid-type structure. On the other hand, the surface of activated carbon becomes positively charged at pH values below 7 due to protonation of functional groups. This charge complementarity promotes strong electrostatic attraction between MO molecules and the adsorbent surface, leading to enhanced adsorption at low PH.

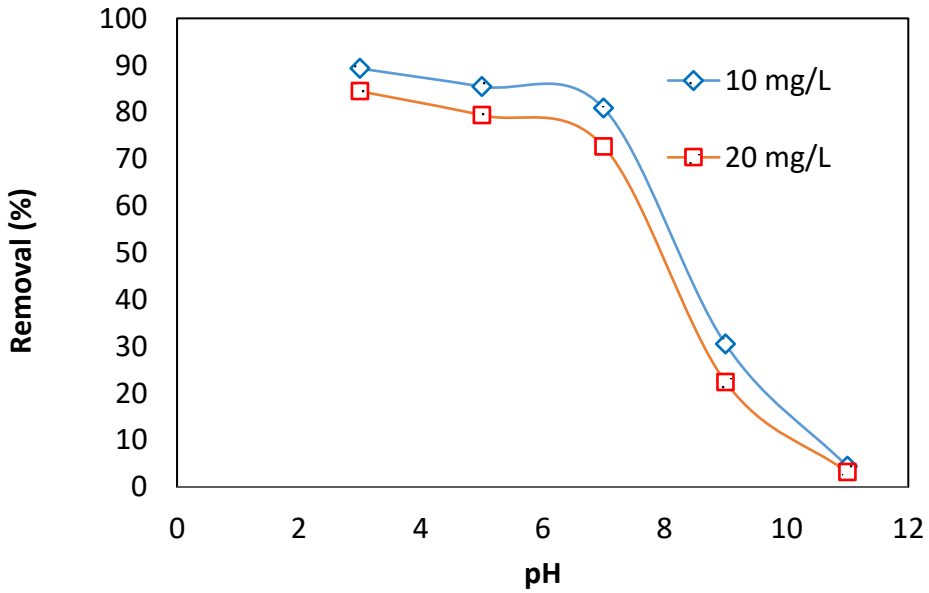

Figure (2). Effect of pH on the removal percentage of methyl orange (MO).

With increasing pH, deprotonation of surface functional groups occurs, resulting in a gradual shift of the AC surface charge toward negative values, as supported by zeta potential measurements. Under these conditions, electrostatic repulsion between the dye molecules and the adsorbent becomes dominant, thereby reducing adsorption efficiency. At higher pH levels, the adsorption mechanism is further influenced by weaker Van der Waals interactions instead of electrostatic forces. In addition, the elevated concentration of OH^- ions competes with dye anions for active adsorption sites, further suppressing MO uptake. Based on these observations, pH 7.0 was selected as the optimum condition for subsequent adsorption experiments to balance surface charge effects and ensure stable adsorption performance [19].

3.4 Effect of Adsorbent Dose

The influence of activated carbon (AC) dosage on the removal efficiency of methyl orange (MO) from aqueous solution is illustrated in Figure (3). All adsorption experiments were conducted under controlled conditions, including an agitation speed of 200 rpm, a particle size of 0.315 mm, a temperature of 25 °C, an initial pH of 7, and a fixed contact time of 140 min, in order to isolate the effect of adsorbent dosage. The results presented in Figure (3) demonstrate a clear dependence of MO removal efficiency on the amount of adsorbent used. In general, an increase in AC dosage leads to a higher percentage removal of MO. This trend can be explained by the fact that increasing the adsorbent dose provides a greater number of available active sites as well as an enlarged total surface area, which enhances the probability of dye molecule interaction with the adsorbent surface and consequently improves adsorption performance [11].

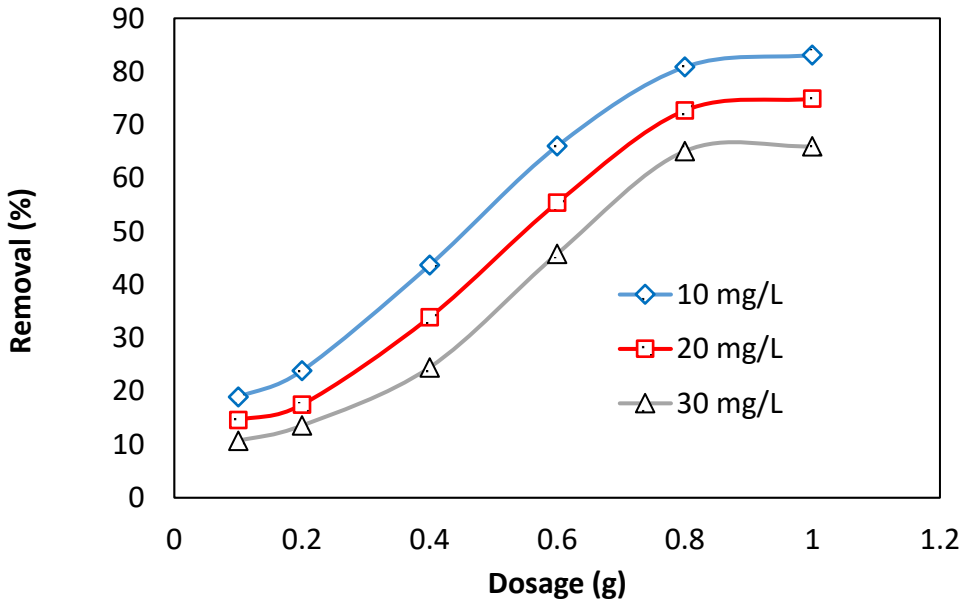

Figure (3). Variation of MO removal versus dosage.

At low adsorbent dosages, the number of available adsorption sites is limited, which may lead to partial surface saturation and incomplete dye removal. As the dosage increases, more active sites become available, allowing a greater number of dye molecules to be adsorbed from the solution. However, beyond a certain dosage, the improvement in removal efficiency becomes less significant. This indicates that the system is approaching a plateau or equilibrium state, where most dye molecules have already been removed. Under these conditions, further addition of adsorbent has little effect on removal efficiency due to the relatively low dye concentration compared to the excess number of available adsorption sites. This observation signifies that the

system has reached a saturation plateau, where the available active sites far exceed the remaining dye molecules in the bulk solution [20, 21]. Overall, the activated carbon exhibited high adsorption performance toward methyl orange under the studied conditions. Based on the experimental results, an adsorbent dosage of 0.8 g/20 mL was identified as the optimum value and was therefore selected for subsequent adsorption studies.

3.5. Effect of Initial Dye Concentration

These batch adsorption studies were conducted for 140 minutes, utilizing varying initial concentrations of Methyl Orange (MO) dye ranging from 10 to 30 mg/L, while other parameters were held constant (adsorbent dosage of 0.8 g per 20 mL solution volume). The objective was to evaluate the impact of this variable on the adsorption efficiency using activated carbon (AC). The results revealed that as the initial concentration of the (MO) dye increased from 10 mg/L to 30 mg/L, the total quantity of adsorbed dye actually increases; however, in contrast, the percentage removal of the dye decreases from 80.84 % t**o** 65.06 %. Figure (4) shows that this increase in the adsorbed quantity is due to the enhancement of the mass transfer driving force (i.e., the increase in the concentration gradient) between the solution and the adsorbent surface. The noticeable drop in the percentage removal, conversely, is attributed to the insufficiency of the available surface area to accommodate the additional quantity of dye molecules in the solution [22].

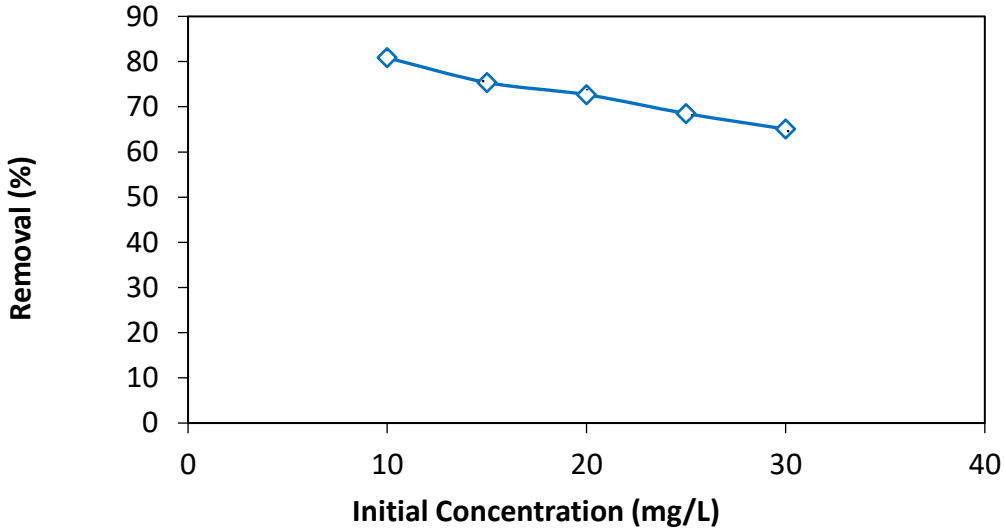

Figure (4). Effect of Initial concentration variation on removal percentage of MO.

At lower initial (MO) concentrations, the vast majority of the (MO) molecules present in the solution can interact with the available active sites on the (AC) surface, leading to a high percentage removal. In contrast, at higher concentrations, competition intensifies among the dye molecules for a fixed and a finite number of available active sites, resulting in faster saturation of the adsorbent material and a subsequent decrease in the overall removal efficiency (percentage).

3.6. Effect of temperature

The effect of temperature on the adsorption of methyl orange (MO) was investigated using 20 mL dye solutions under controlled experimental conditions, including an agitation speed of 200 rpm, 0.8 g of activated carbon (AC) with a particle size of 0.315 mm, an initial pH of 7, and a contact time of 140 min. The adsorption experiments were performed at four different temperatures: 25, 35, 45, and 55 °C, in order to evaluate the thermodynamic behavior of the process. As illustrated in Figure (5), the removal efficiency of MO decreased progressively

with increasing temperature. This trend clearly indicates that the adsorption of MO onto AC is an exothermic process. In exothermic adsorption systems, the uptake of adsorbate molecules is generally favored at lower temperatures, where the interaction between the adsorbate and the adsorbent surface is more stable. The reduction in adsorption efficiency at higher temperatures can be attributed to the weakening of physical interactions, such as electrostatic attraction and Van der Waals forces, between dye molecules and the adsorbent surface. As temperature increases, the kinetic energy of MO molecules increases, reducing their residence time on the adsorbent and increasing the likelihood of desorption. In addition, higher temperatures enhance dye mobility in the solution, which lowers the probability of attachment to active sites and further reduces adsorption capacity due to thermal disruption of weak binding forces. From a thermodynamic viewpoint, the exothermic nature of the adsorption process suggests that it is more favorable at lower temperatures. Consequently, increasing temperature shifts the equilibrium toward desorption, in agreement with Le Chatelier's principle [23, 24].

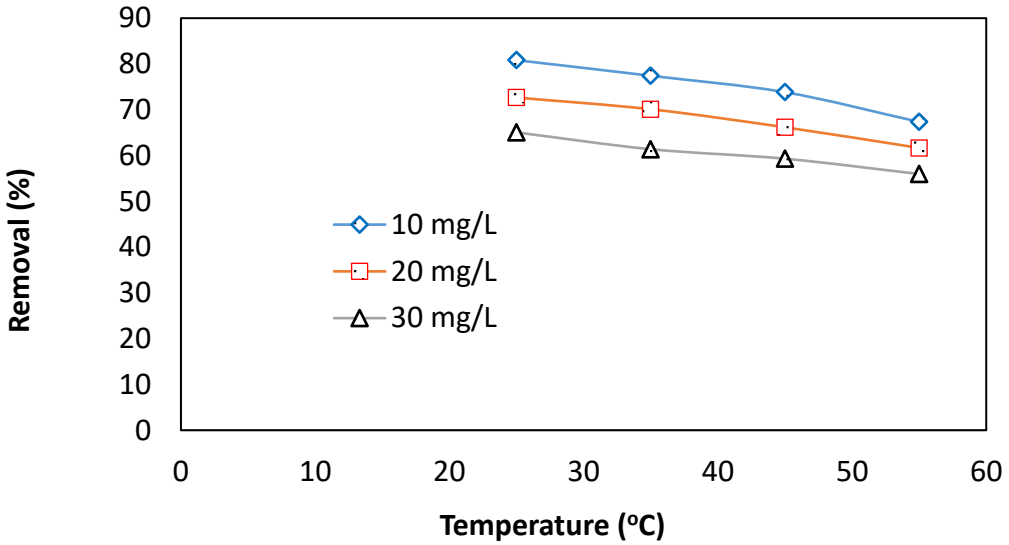

Figure (5). Effect of temperature variation on removal percentage of MO.

Therefore, operating the adsorption system at temperatures above ambient conditions is not only less efficient but also economically unfavorable due to increased energy requirements without significant improvement in removal performance. The results demonstrate that room temperature (25 °C) is sufficient to achieve satisfactory removal efficiency within 140 min, making it the most practical operating condition for this system [23].

3.7. Adsorption isotherms models

Equilibrium data, commonly known as adsorption isotherms, are a basic requirement for the design of adsorption systems. Adsorption isotherms were obtained using the batch method, in which 0.8 g of activated carbon (AC) was added to 20 mL of methyl orange (MO) solution for each experiment. The solutions were agitated at 200 rpm for 140 min at 25 °C and pH 7, using activated carbon with a particle size of 0.315 mm. After equilibration, the supernatant solutions were analyzed for the residual concentration of MO dye. The initial concentration (C_o) and equilibrium concentration (C_e) of MO dye were determined using a spectrophotometer. The equilibrium adsorption of MO dye (q_e vs. C_e) using AC is shown in Figure (6). The isotherm exhibits a sharp increase at the initial stage at low C_e and q_e values, indicating the availability of numerous readily accessible active sites. Eventually, a plateau is reached, suggesting that the adsorbent surface has reached saturation [25].

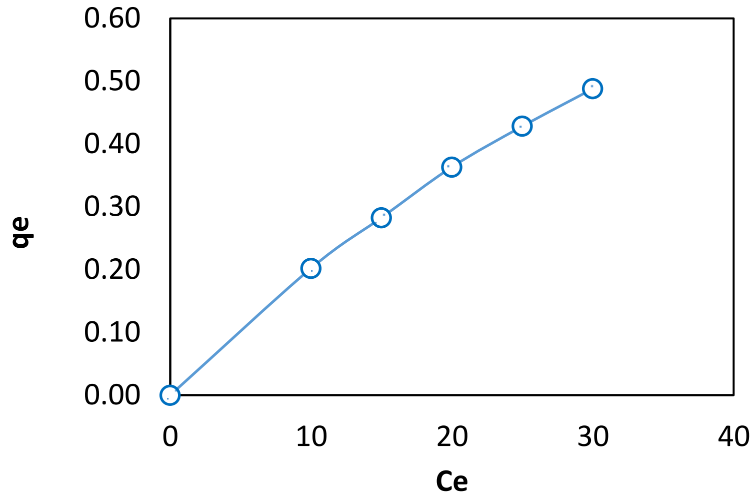

Figure (6). Equilibrium isotherm of MO/AC system, Conditions: (adsorbent dosage = 0.8 g/20 ml, pH =7, contact time = 140 min, agitation rate 200 rpm, particle size 0.315 mm and temperature 25 °C).

To improve the performance of a sorption system for the removal of methyl orange (MO) from aqueous solutions, it is important to determine the most suitable model to describe the equilibrium adsorption behavior. Therefore, two common isotherm models, Langmuir and Freundlich, were applied to fit the experimental data. The Langmuir model assumes monolayer adsorption on a homogeneous surface with a limited number of identical active sites, while the Freundlich model describes adsorption on a heterogeneous surface and allows for multilayer adsorption. The agreement between the experimental data and the model predictions was evaluated using the correlation coefficient (R^2), where values approaching unity indicate a better fit [26].

3.7.1. Langmuir Isotherm

The widely used Langmuir isotherm is proven successful in many real sorption processes, and is expressed in a linear form in Eqn. (3).

$$\frac{C_o}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad \text{..} \quad (3)$$

A plot of C_e/q_e versus Ce is a straight line of a slope a_L/K_L and an intercept $1/K_L$ figure (7). The Langmuir constants K_a and q_m and corresponding correlation coefficient are listed in Table (1) for the MO/AC system where the Langmuir isotherm and experimental data are shown in Figure (7). The correlation coefficient was 0.9907 and the monolayer saturation capacity (q_m) is 0.731 mg/g.

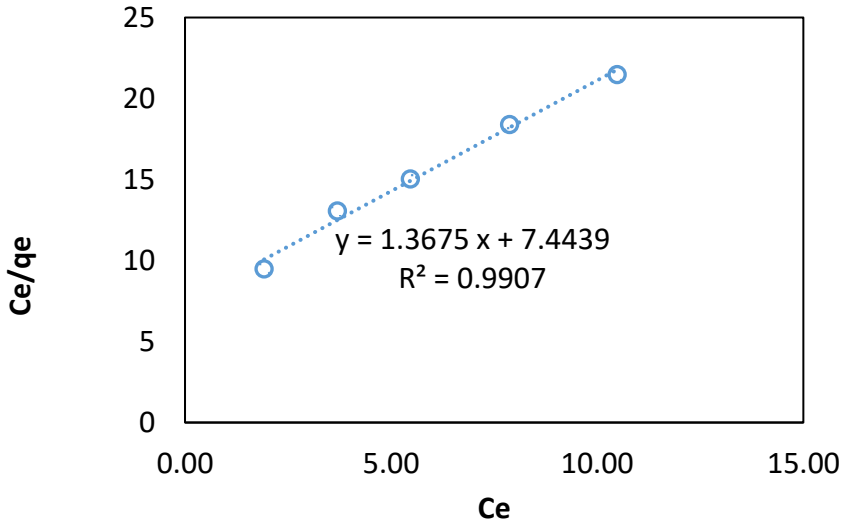

Figure (*7*). Linear form of Langmuir Isotherm of MO/AC system.

The fundamental characteristics of the Langmuir isotherm can be further described using a dimensionless equilibrium parameter known as the separation factor (R_L). This parameter is widely used to evaluate the favorability of the adsorption process [27]. The R_L values obtained at different initial concentrations were found to be in the range of 0 to 1, indicating that the adsorption of methyl orange (MO) onto activated carbon (AC) is favorable under the experimental conditions.

Table (1). Langmuir and Freundlich Isotherm constants.

Langmuir Isotherm			**Freundlich Isotherm**		
K_a (l/mg)	q_m (mg/g)	r^2 ..	K_F (l/g)	n ..	r^2 ..
10.17953	0.7312	0.9907	0.1441	1.9007	0.997

3.7.2. Freundlich Isotherm

The Freundlich isotherm is a widely used model for describing adsorption on heterogeneous surface energy systems [28, 17]. Its linear form is given in Eq. (4). The Freundlich constants, along with the correlation coefficient obtained from Figure(8), are presented in Table (2).

$$q_e = K_F C_e^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where K_F is the Freundlich constant related to sorption capacity in (mg/g). $(L/g)^{1/n}$ and n is related to the adsorption intensity of the adsorbent. Where, K_F and $1/n$ can be determined from the linear plot of ln(qe) versus ln(Ce).

The value of the Freundlich constant n, which lies in the range of 1–10, indicates favorable adsorption. In addition, the correlation coefficient for the Freundlich model is higher than that of the Langmuir model. Therefore, the Freundlich isotherm provides a better fit to the experimental data compared to the Langmuir isotherm [29].

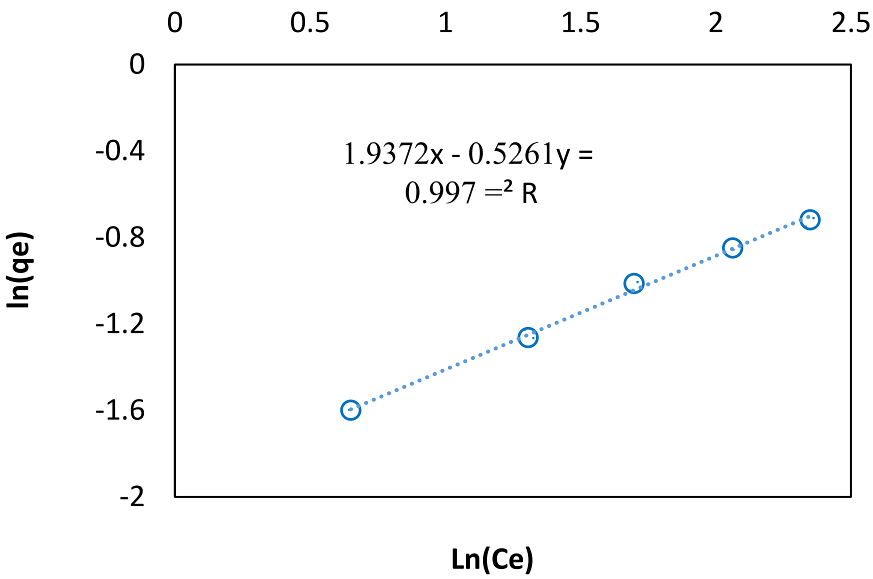

Figure (8). Linear form of Freundlich Isotherm of MO/AC system, Conditions: (adsorbent dosage = 0.8 g/20 mL, pH =7 contact time = 140 min, agitation rate 200 rpm, particle size 0.315 mm and temperature 25 °C).

3.8. Adsorption knietics

Adsorption kinetics is one of the most important parameters in adsorption processes; therefore, it is essential to investigate the adsorption behavior of Methyl Orange onto activated carbon (AC) as an efficient adsorbent. Accordingly, the adsorption kinetics were analyzed using two well-known kinetic models, namely the pseudo-first-order and pseudo-second-order models, to describe and predict the adsorption mechanism. Following linearization, the Lagergren pseudo-first-order and pseudo-second-order kinetic models can be expressed as shown in Eqs. (5) and (6), respectively [29].

$$ln(q_e - q) = ln\, q_e - k_1 t \quad \ldots\ldots\ldots\ldots (5)$$

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

Where the adsorption equilibrium capacity q_e and the rate constants k_1 and k_2 were calculated from the linearized forms of the kinetic models. In the case of the pseudo-first-order model, q_e and k_1 were obtained from the slope and intercept of the linear plot of ln(q_e− q_t) versus time (t). For the pseudo-second-order model, the values of q_e and k_2 were determined from the linear relationship between t/q_t and t. Additionally, the effect of temperature was evaluated using the same t/q_t versus t plots at different temperatures [30]. Kinetic experiments were performed at four temperatures (298, 308, 318, and 328 K) and at initial concentrations of 10, 20, and 30 mg/L in batch mode adsorption,

The parameters of the pseudo-first-order model were obtained from the linear plots of ln(qe −qt) versus t as shown in Figure (9). The results in Table (2) indicate the pseudo-first-order model provides a better fit to the experimental data, suggesting that the adsorption of MO dye onto AC sorbent follows pseudo-first-order kinetics. The adsorption kinetics were also described using the pseudo second-order equation [31]. The linear form of the differential equation is presented in Eqn (6). To calculate the pseudo-second-order rate constant k_2 and q_e the equilibrium adsorption capacity q_e, the slopes and intercepts of the plots of t /q_t versus t Figure(10) were used. . According to the obtained data presented in Table (2) show that the pseudo-second order model is not suitable for the MO/AC system. The results of the comparison between the two models show that the pseudo-first-order kinetic model is the most suitable for describing the adsorption process [18]. This suggests that chemisorption is not the

dominant rate-controlling step, and that adsorption mechanism depends on physical adsorption and boundary layer diffusion [31].

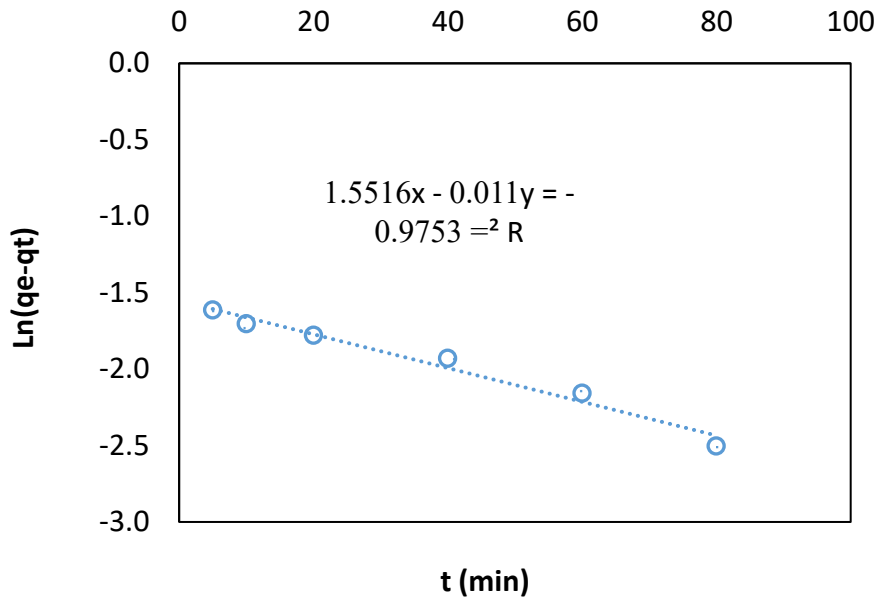

Figure (9). Plot of the pseudo first order adsorption kinetics of MO/AC system .

Table (2). The values of the parameters for different kinetic models fitted to the MO adsorption kinetics on AC at varies initial conditions

Initial concentration C_o (mg/L)	Kinetic model	q_e (mg/g)	k_1 (min^{-1})	k_2 (g/mg·min)	R^2
20	Pseudo-first-order	0.3383	0.0283	—	0.9753
20	Pseudo-second-order	1.4649	—	276.183	0.2117

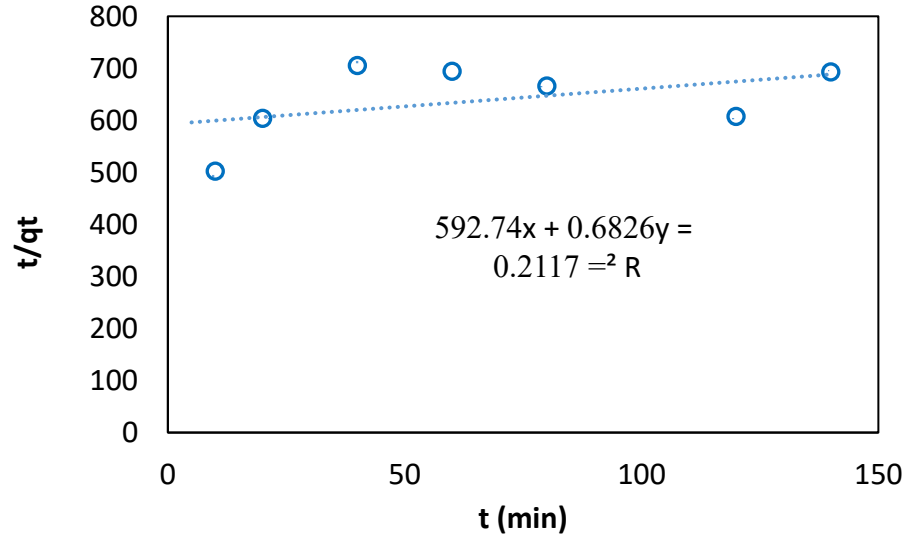

Figure (10). Plot of the pseudo second order adsorption kinetics of MO/AC system. Conditions: (adsorbent dosage = 0.8 g/20 ml, pH =7, contact time = 140 min, agitation rate 200 rpm, particle size0.315 mm and temperature 25 °C) (A-13).

3.9. Thermodynamic Studies

The thermodynamic parameters, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were evaluated to investigate the feasibility and nature of the adsorption process using the following equations [29]:

$$\Delta G^o = -RTlnK_C \quad \text{..... (7)}$$

$$K_C = \frac{C_{Ae}}{C_e} \quad \text{..... (8)}$$

$$lnK_C = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \text{..... (9)}$$

where C_e represents the equilibrium concentration of dye in solution (mg/L), C_{Ae} is the equilibrium concentration of dye on the adsorbent (mg/L), and Kc is the equilibrium constant. The thermodynamic parameters provide valuable information about the spontaneity, heat change, and mechanism of the adsorption process. The ΔG° value indicates the spontaneity of adsorption, where more negative values correspond to a more favorable process. The ΔG° values for MO adsorption onto AC at different temperatures were calculated using Eq. (7). The ΔH° and ΔS° values were obtained from the slope and intercept of the Van't Hoff plot of ln(Kc) versus 1/T, respectively, as shown in Figure (11). The calculated thermodynamic parameters are summarized in Table (3).

The negative values of **ΔG°** confirm that the adsorption process is thermodynamically feasible and spontaneous. However, the increase in ΔG° values with increasing temperature from **298 to 328 K** indicates that the adsorption process becomes less favorable at higher temperatures, suggesting that lower temperatures enhance the adsorption efficiency [32].

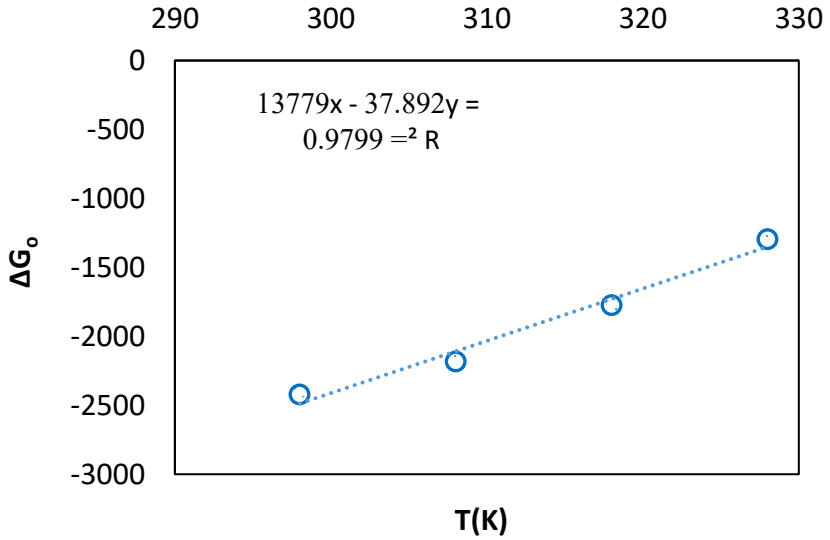

Figure (11). Plot of Gibes free energy vs. *T* for estimation of thermodynamic parameters for the adsorption of MO onto AC.

The negative value of **ΔH°** confirms the exothermic nature of the adsorption process and indicates favorable interactions between MO dye molecules and the AC surface. The negative value of **ΔS°** suggests a decrease in randomness at the solid–solution interface during adsorption, which may be attributed to the removal of water molecules surrounding the dye molecules upon adsorption. The value of **ΔH°** is an important parameter for evaluating the adsorption mechanism. In this study, the calculated **ΔH°** value was **−13.779 kJ/mol**, which falls within the range commonly associated with physical adsorption. Therefore, the adsorption of MO dye onto activated carbon is mainly governed by physical interactions, such as weak intermolecular forces and van der Waals interactions.

Table (3). Thermodynamic parameters for the adsorption of MO onto AC

T(K)	C_e	C_{eA}	K_c	ΔG^o (J/mol)	ΔH^o (J/mol)	ΔS^o (J/mol)
298	5.466	14.534	2.659	-2423.01	-13779	-37.892
308	5.978	14.022	2.346	-2183.23		
318	6.765	13.235	1.957	-1774.59		
328	7.668	12.333	1.608	-1296.15		

Conclusion

This study demonstrates that activated carbon prepared from pine branches is an effective and sustainable adsorbent for the removal of Methyl Orange (MO) dye from aqueous solutions. The adsorption process showed high performance under optimized conditions, including an adsorbent dose of 0.8 g/20 mL, particle size of 0.315 mm, agitation speed of 200 rpm, initial pH of 7, and temperature of 25 °C. The equilibrium was achieved within 140 min, with an adsorption capacity of 0.202 mg/g. The equilibrium data were better fitted by the Freundlich isotherm model compared with the Langmuir model, indicating adsorption onto a heterogeneous surface. Moreover, the pseudo-first-order kinetic model provided the best description of the adsorption behavior, suggesting that physical interactions were the main mechanism involved. Overall, the findings confirm the potential of pine branch-derived activated carbon as a low-cost and environmentally friendly adsorbent, while demonstrating the value of agricultural waste conversion for sustainable wastewater treatment applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.