Synthesis and Characterization of a Contemporary Type of Metal-Organic Framework and its Application for Purification Wastewater from Toxic Methylene Blue Dye

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ABSTRACT

This paper describes the synthesis of a promising material and evaluates the suitability of a metal-organic framework (MOF-199) for purifying toxic methylene blue (MB) dye wastewater via an adsorption process. (MOF-199) is considered much better than traditional adsorbents. The research focused on determining the adsorption characteristics and dye removal effectiveness with MOF-199, where several factors were studied, including dye concentration, contact time, amount of adsorbent, and pH. The highest observed dye removal efficiency was 97.21% when the pH was 7.5, and the reaction duration was 90 minutes. This was achieved by adding 0.2 g of MOF-199 to a dye solution containing 20 mg/L methylene blue. The adsorption process was evaluated by Langmuir, and the Freundlich isotherm models. As the strong correlation factor ($R^2 = 0.9989$) indicates a pseudo-second-order kinetic model describes the adsorption methylene blue by MOF-199 the best. This indicates that the main mechanism of dye removal is chemisorption. Finally, the MOF-199 material can have remarkable reusability as an adsorption material for MB and subsequent efficiency of MOF-199 exhibited a reduction of 14.43% after undergoing four cycles, compared to its initial state. Yet, it remained at a commendably high level.

Keywords: MOF-199, metal-organic framework, methylene blue dye, wastewater.

INTRODUCTION

Synthetic dye chemical processes are used in a variety of sectors, including paper, textiles, plastic, cosmetics, and printing. Unfortunately, these dyes are frequently discarded as untreated waste, contaminating water resources [1]. Dyes have been found to have significant adverse impacts on both the environment and biological organisms. Numerous colors exhibit hazardous and carcinogenic properties [2, 3]. In addition to possessing detrimental characteristics, most dyes exhibit inertness and non-biodegradability [4]. Hence, eliminating dyes from effluents before their release into natural ecosystems is of utmost significance. There has been a notable increase in the quantity of hazardous chemicals discharged into surface water over recent decades. According to the current data, the production of commercially accessible dyes exceeds 100,000 varieties, with an annual output of around 7×10^5 tons/year. Around two percent of these dye products are typically released into water systems as waste [5]. Typically, the presence of dye in water becomes perceptible when its concentration exceeds (1 mg/L) [6]. The combination of dye effluent in wastewater has the potential to pose environmental hazards. Various conventional methods as well as physical, chemical and biological processes have been established to address dyes to safeguard the environment [7]. Various materials, including coal, wood, low-cost adsorbents, rice husk, zeolite, activated carbon, cotton waste, clay, and other porous substances, have been documented in literature as potential adsorbents for eliminating dye from aqueous solutions [8, 9]. Metal-organic frameworks (MOFs) possess the characteristics that make them promising candidates for eliminating organic dyes from industrial effluents. This can be primarily ascribed to the

strong adsorptive characteristics and enormous surface area exhibited by the material. MOFs are well-defined crystalline substances comprising metal ions or groups that function as nodes, interconnected by organic ligands that serve as linkers [10]. The materials under consideration possess notable characteristics that render them suitable for many applications in separation process, gas storage, drug administration, sensors catalysis, and catalysis [11]. This suitability arises from the ability to adjust the pore size, shape, and composition of the material, as indicated by references [4, 12]. The adsorptive elimination of different dyes has also been observed for Fe-MOF-235 [13]. The batch technique is a straightforward method that offers a convenient approach to understanding the factors influencing the adsorption process [14].

Methylene blue is a heterocyclic aromatic chemical containing a sulfur atom with $C_{16}H_{18}N_3SCl$ molecular formula and 319.9 g mol^{-1} molecular weight. It finds application in the textile industry for dyeing fabrics and various materials. This particular cationic dye can induce hemolytic anemia, high blood pressure, jaundice, quadriplegia, Heinz body formation, skin discoloration, and necrosis at the injection site [15–17].

EXPERIMENTAL PART

Materials

Cupric nitrate tri hydrate that is a highly water soluble $(Cu(NO_3)_2 \cdot 3H_2O)$ (Merck, 99%), ethanol (C_2H_5OH) (Merck, 95%,), and Trimesic acid (H_3BTC) (Merck, 95%) have been used in the preparation process and does not required purification because all this material is of analytical grade. All the solutions have been prepared using distilled water with an ionizer > 0.001.

Preparation of MOF-199

Metal-organic framework (MOF-199) is manufactured through laboratory approach using hydro/solvothermal techniques. This harmonic formulation of MOF-199 was based on previous work developing this framework with some modifications [18, 19]. The solution was prepared by liquefying 1.75 g (7.24 mmol) of copper (II) trinitrate $(Cu(NO_3)_2 \cdot 3H_2O)$ and 0.84 g (4 mmol) of trimesic acid (H_3BTC) in 48 ml of ethanol (EtOH). The suspension was introduced into a

Teflon container and then into an autoclave, the experimental procedure involved performing the reaction for 14 h at a temperature of 120°C while maintaining self-pressure. Then, the autoclave was permitted to gradually decrease in temperature until it reached the surrounding environmental conditions. The blue powder was acquired and afterwards subjected to filtration, rinsed several times, and soaked with 60 mL (1:1 vol. %) deionized water and ethanol to remove unreacted materials and side products such as CuO and Cu_2O. Then, it was dried for 5 hours at 60°C. Finally, MOF-199 was activated for 16 h at 100°C in vacuum. The sample was kept until further use in a container inside the desiccator.

Laboratory tests showed the surface area 1119.469 m^2/g and pore volume 0.655 cm^3/g. Moreover, it is necessary to perform other analyses, such as Fourier Transforms Infrared Spectroscopy (FTIR), X-ray deflection meter (XRD) (Shimadzu SRD 6000) with tube voltage of 40 k$_v$, a 5–60° scan range, and A tube current of 35 mA tube current, and the shape of MOF-199 was determined using a 2000X scanning electron microscope (SEM Inspect™ F50 type) after being coated with gold to protect the sample, as described below. This study, the MOF-199 adsorbent was used to perform a batch adsorption process aimed at purifying wastewater contaminated with dyes, with a special focus on methylene blue dye. The wastewater used in this study will be an aqueous solution designed to simulate wastewater.

Methylene blue dye removal study

Spectrophotometric techniques were employed to investigate the elimination of dye in several studies. The experimental procedures for removing methylene blue (MB) dye using MOF-199 were conducted only under batch settings. The experimental parameters included in this study encompassed contact time, amount of the adsorbent (MOF-199), pH, and initial concentration of the target compound MB. The methylene blue dye standard solution was made, resulting in a 1000 mg/L concentration. Lower concentrations of methylene blue in aqueous solutions were generated by amalgamating the standard solution with deionized water. The concentration of the dye solution was determined by employing a UV-VIS spectrophotometer [UV-2900, Manufacturer: UK] and measuring the absorbance at the full wavelength of MB (λ_{max} = 664 nm). The standard

solutions were prepared at various concentrations (20 to 250 ppm) under a fixed pH of 7.5, as determined using a pH-Cond-Salinity meter. Table 1 presents the experimental details of Methylene Blue (MB) adsorption using MOF-199. The calculation of the dye absorption capacity (q_e), namely the quantity of dye adsorbed (measured in milligrams) on the surface per gram of MOF-199 and the removal efficiency (expressed as a percentage) of Metal-Organic Framework (MOF), was performed using Eq. 1 and 2, respectively [20].

$$Uptake\ capacity\ q_e\ (mg/g) = (C_i - C_e)\frac{V}{M} \quad (1)$$

$$Removal\ efficiency\ \% = (C_i - C_e\ /\ C_i) \times 100 \quad (2)$$

where: the variables C_i [mg/L] and Ce [mg/L] represent the initial and balance concentrations of the dye solution, respectively. V [L] – the volume of solution, while m [g] represents the mass of MOF-199.

Adsorption isotherm

Under constant temperature conditions, the phrase "adsorption isotherm" refers to the correlation established among the quantity of liquid adsorbed onto an adsorbent material and its corresponding equilibrium concentration within the solution. The Langmuir, Temkin, and Freundlich models are widely acknowledged and utilized in numerous scientific investigations. The Freundlich isotherm model is derived from examining the adsorption behavior of dye molecules onto a heterogeneous adsorbent surface. In contrast, The Langmuir isotherm examines the process of adsorption of dye molecules onto a uniform adsorbent surface, with particular emphasis on the formation of a monolayer. The forms of the Langmuir, and Freundlich isotherms are mathematically denoted by Eq. 3, and 4, respectively [21, 22]:

$$Langmuir\ isotherm\ \frac{1}{qe} = \frac{1}{KL \times qmax}\frac{1}{ce} + \frac{1}{qmax} \quad (3)$$

$$Freundlich\ isotherm\ lnq_e = lnK_f + [Ce \times (1/n)] \quad (4)$$

where: q_{max} – the upper limit of adsorbate quantity per unit of mass adsorbent needed to achieve complete covering of the surface with a monolayer [mg/g], K_L – denotes the equilibrium constant for adsorption according to the Langmuir isotherm (l/mg), q_e – refers to the adsorption uptake at balance [mgg⁻¹], Ce – represents the concentration of adsorbate at balance [mgl⁻¹], K_f – an unspecified variable, the Freundlich constant is a parameter that quantifies the adsorption uptake [measured in mg/g] and adsorption intensity (represented by n).

Adsorption kinetics

The kinetics of methylene blue removal on MOF-199 were determined by the use of pseudo-first-order and pseudo-second-order equations. The procedure of selecting the best appropriate model entails evaluating the correlation coefficient, represented as R^2, within the context of linear regression analysis [23, 24].

Pseudo-first-order kinetic model

The adsorption phenomenon occurs inside a monolayer situated on the interface where the liquid and solid phases contact. Equation 5 represents the mathematical formulation of the kinetic model.

$$log\ (q_e - q_t) = log\ qe - (K_1/2.303)t \quad (5)$$

where: K_1 – represents the pseudo-first order rate constant (min⁻¹), q_t – denotes the quantity of adsorbed solute, whereas q_e – refers to the adsorption uptake at balance (mg/g), lastly, the variable t time (min).

Pseudo-second order kinetic model

The rate of the reaction is proportionate to the quantity of adsorbate molecules that have been adsorbed onto the surface of the adsorbent material, once equilibrium has been attained. Equation 6 represents the mathematical model.

Table 1. Experimental details for adsorption MB by MOF-199

Effect of system	Range	Unit
Contact time effect	30, 60, 90, 120, 150, 180 , 210	Min
Adsorbent dose effect	0.05, 0.1, 0.15 , 0.2, 0.25, 0.3, 0.35	g/100 mL
Acidic function (PH) effect	2, 4, 6, 7, 8,10, 12	
Initial concentration methylene blue effect	20, 60, 100, 140, 180, 220, 250	ppm

$$\frac{t}{qt} = \frac{t}{qe} + \frac{1}{K2 \times qe^2} \qquad (6)$$

where: K_2 – rate constant [g.mg $^{-1}$.min^{-1}].

RESULTS AND DISCUSSION

Characterization of MOF_199

X-ray diffraction (XRD) is widely recognized as a highly effective technique for the examination of the crystal building and phase purity of metal-organic frameworks (MOFs), such as MOF-199. The XRD pattern characterization of the MOF-199 material in Figure 1 shows several sharp peaks of the standard model. Figure 2 represents the as-synthesized MOF-199, where the peaks are observed at 2θ values of 9.5°, 11.6° and 13.5°, which correspond to the levels Crystallography of (211), (222) and (400) [19]. Calculations of the relative crystallinity of the MOF-199 crystal were performed using equation 7, which was found to be equal to 100%.

$$Relative\ crystallinity\ \% = \frac{\sum Intensities\ of\ the\ peaks\ of\ MOF-199\ sample}{\sum Intensities\ of\ the\ peaks\ of\ reference\ sample} \times 100 \qquad (7)$$

Fourier Transform Infrared Spectroscopy (FTIR) shows that the coordination of an organic ligand with a metal ion to create MOF-199 leads to alterations in the functional groups present within the organic ligand. The infrared analysis of the sample revealed a prominent stretching vibration of carboxylate anions in the range of 1400–1600 cm^{-1}, providing evidence for the occurrence of a reaction between the organic ligands –COOH groups and metal ions. A band observed at the wave count range of (3400–2800 cm^{-1}) was detected, suggesting the existence of water molecules and hydroxyl (OH) groups within the structure of the material. The MOF-199 sample was confirmed free of CuO and Cu$_2$O without absorption peaks at 412, 500, 620, and 620 cm^{-1}. The FTIR analysis for MOF-199 is shown in Figure 3 [25]. The scanning Electron Microscopy (SEM) is a crucial test for analysis the morphological
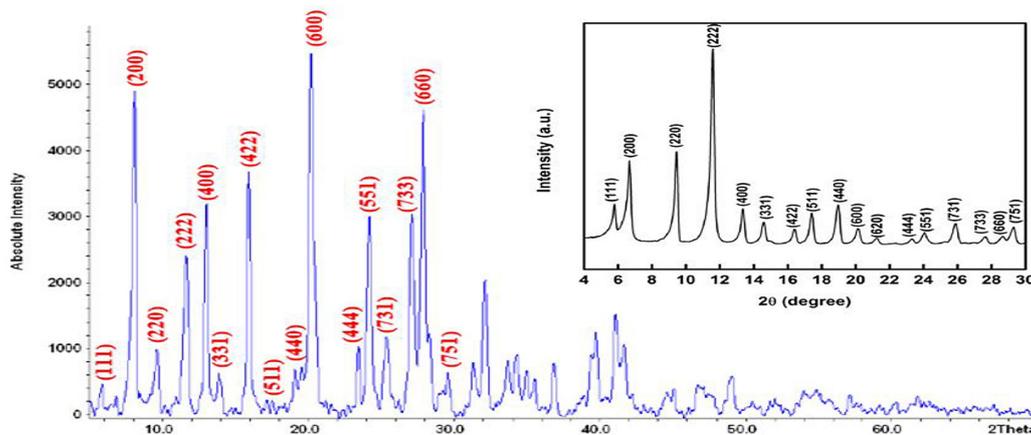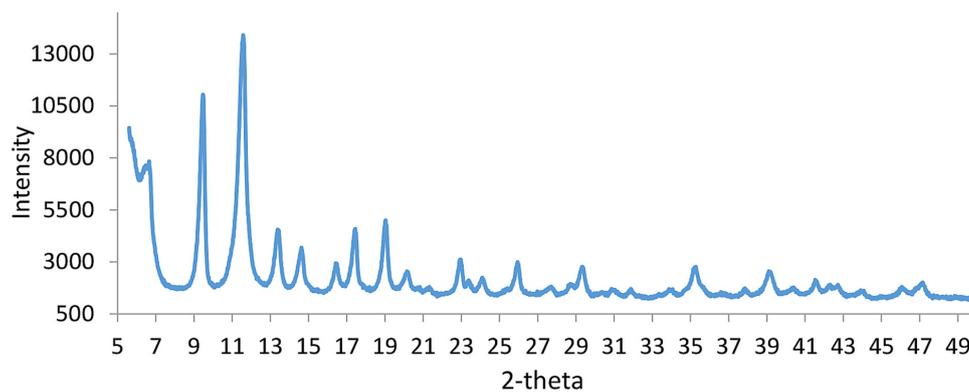

Figure 1. XRD for MOF-199 typical pattern [19]

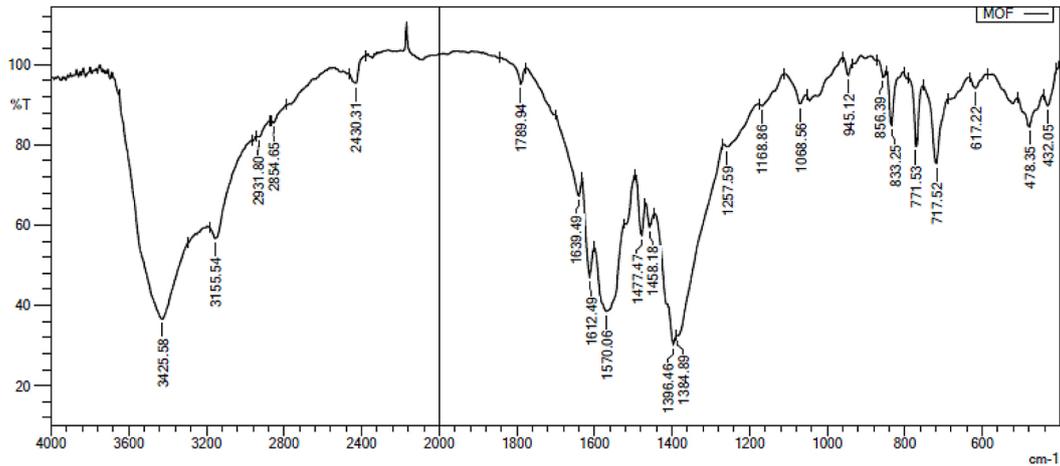**Figure 2.** XRD for the MOF-199 preparation

Figure 3. FTIR for the MOF-199 preparation

characteristics of materials. Figure 4 displays SEM images of the prepared MOF-199 showing generally, larger and easily recognized octahedral or cuboidal crystals shapes.

Investigation of the methylene blue removal by MOF-199

The impact of interaction time

The main aim of this work was to investigate adsorption characteristics of methylene blue utilizing MOF-199 throughout various time intervals spanning from 30 to 210 minutes. The study implemented the measures to maintain constant values for all other variables, PH (7.5), dose (2 g/L), laboratory temperature (25°C), C_i concentration (250 mg/L), and mixing speed (200 rounds per minute). A period of 90 minutes was found as a balance point for this study, and the removal rate reached 96.65%. Figure 5 shows the results of methylene blue adsorption experiments performed

on MOF-199, with special emphasis on the effect of the percentage of dye removal using Equation 2. It is important to realize that the degree of removal of methylene blue dye increases when the contact time is extended. The adsorption process of methylene blue dye has an initial rapid rate, which then slows down as vacant spots on the surface of the adsorbent are gradually occupied. The observed decrease in velocity can be attributed to the repulsive interactions occurring between the methylene blue molecules present in the solution phase and those molecules that were adsorbed on the surface of MOF-199. The complexity of this technique increases as the number of dye molecules fills these unoccupied sites increases, consistent with the results of previous investigations [19, 26].

The impact of MOF-199 dose

The influence of the initial MOF-199 dosage holds significant importance for applications on a larger scale. As depicted in Figure 6,
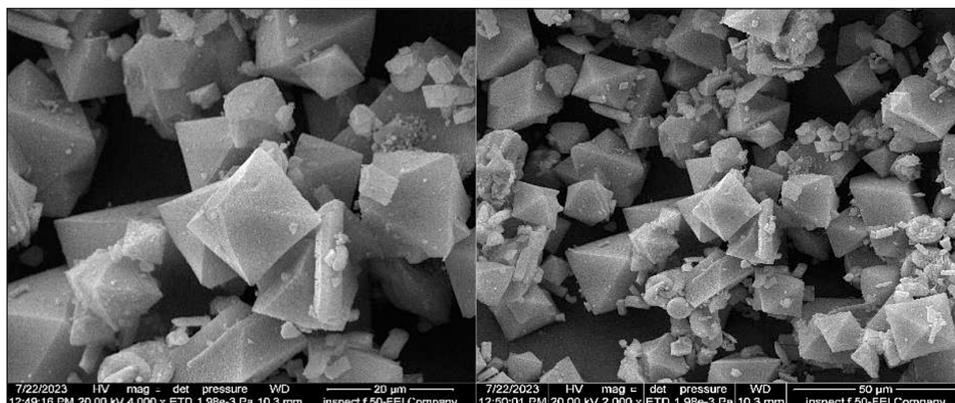

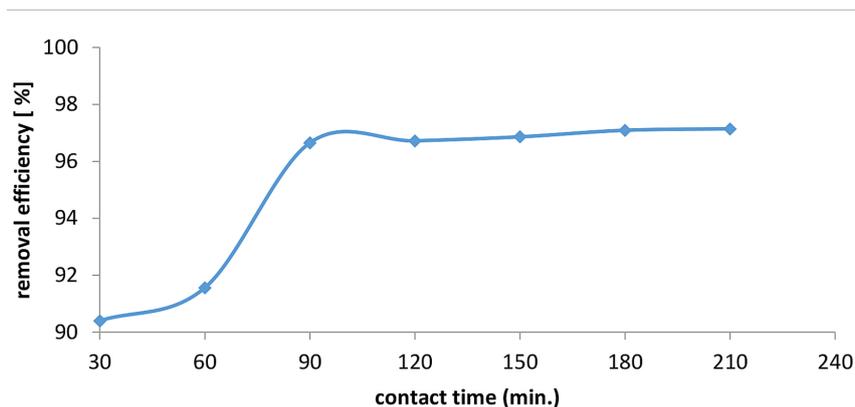**Figure 4.** SEM for the MOF-199 preparation

Figure 5. Contact time effect on methylene blue dye removal of by MOF-199
(C_i of MB = 250 mg/L, adsorbent dose = 2 g/l, PH = 7.5, and temp. = 25°C)

various quantities of MOF-199 were employed, alternating from 0.5–3.5 g/l. the other variables were maintained at their optimal operational values (pH = 7.5, time = 90 minutes, temperature = 25°C, C_i = 250 mg/l, As = 200 rpm). The removal efficiency (%) exhibits a rapid increase with ascending doses of the adsorbent until equilibrium is achieved at 2 g/l, showing a peak removal efficiency of 96.53%. The increased efficacy in the elimination of methylene blue can be due to the heightened exposure of adsorption sites, hence boosting the effectiveness of MB dye molecule elimination. This observation aligns with the findings from prior research [26].

The impact of Acidic Function (pH)

The impact of Acidic Function holds paramount importance in the adsorption process, prompting an exploration of its impact on adsorptive behavior across the pH spectrum of 2 to 12 was attuned by drop-wise addition of diluted HCl and NaOH solution. While maintaining the other parameters under

optimal operational conditions (time = 90 minutes, As = 200 rpm, temperature = 25°C, MOF-199 dose = 2 g/l, C_i of MB = 250 ppm), the removal exhibited an increase within the pH range of 2 to 7, followed by a decrease within the pH range of 8 to 12, as shown in Figure 7. This behavior predominantly arises from the heightened association of dye ion's, attributed to the electrostatic attraction forces between the MB dye and MOF-199. Adsorption of methylene blue on MOF-199 is generally more favorable at pH values above the zero charge point PHpzc. On the contrary, the adsorption process is inhibited at pH values lower than PHpzc, noting that the PHpzc for MOF-199 was 4.5, consistent with the literature [27].

The impact of initial MB concentration

The impact of initial dye concentrations on the removal of MB% is demonstrated in Figure 8, encompassing initial dye concentrations within the variety of 20 to 250 mg/l. This investigation retained the remaining parameters at their optimal
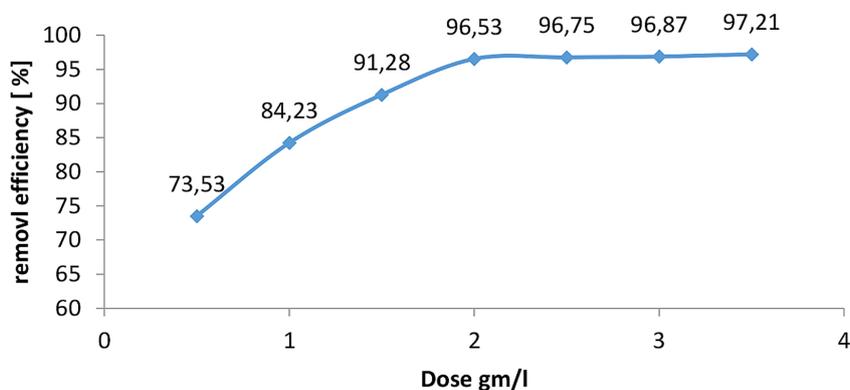

Figure 6. The effect of adsorbent dose on the MB dye removal efficiency
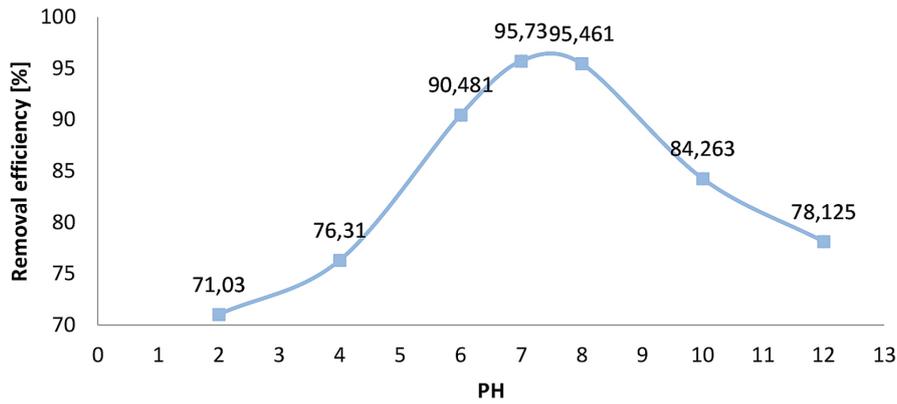(C_i of MB =250 mg/L, contact time = 90 min, PH = 7.5, temp = 25°C)

Figure 7. The pH effect on MB dye removal efficiency (c_i of MB = 250 mg/L, contact time = 90 min, dose = 2g/L, temp. = 25°C)

operational values (time = 90 minutes, as = 200 rpm, temperature = 25°C, MOF-199 dose = 2 g/l, c_i of MB = 250 ppm). Notably, the removal percentage of methylene blue reached high values across varying concentrations, approximately equal to 97%. This finding suggests that the quantity of MOF-199 utilized provides a sufficient adsorption surface and active sites for this concentration range. The decline in the dye removal% can be described by the fact that all adsorbents have a limited number of active sites, which become saturated once a specific concentration threshold is reached. Once the dye concentration in the solution exceeds a certain threshold, the total of active sites available becomes restricted, resulting in a reduction in the efficacy of the removal process. The findings of this study are in line with prior research [19,24]. On the basis of previous results, the best operating conditions for the best adsorption process using MOF-199 adsorbent can be predicted where the dose of adsorbent = 2 g/l, contact

time = 90 minutes, pH = 7.5 and concentration of methylene blue =20 ppm.

Adsorption isotherms

Langmuir isotherm

The equilibrium documents pertaining to the adsorption of methylene blue on the adsorbent MOF-199 were analyzed using the linear Langmuir equation, as denoted by equation 3. Figure 9 depicts a line plot that showcases the correlation between specific adsorption [$1/q_e$] vs. [$1/C_e$]. The values of R^2, q_{max} (maximum adsorption capacity), and K_L [Langmuir constant] found in Tables 2 and 3. The K_L values provide evidence that this model effectively characterizes the phenomenon of equilibrium adsorption [27].

Freundlich isotherm

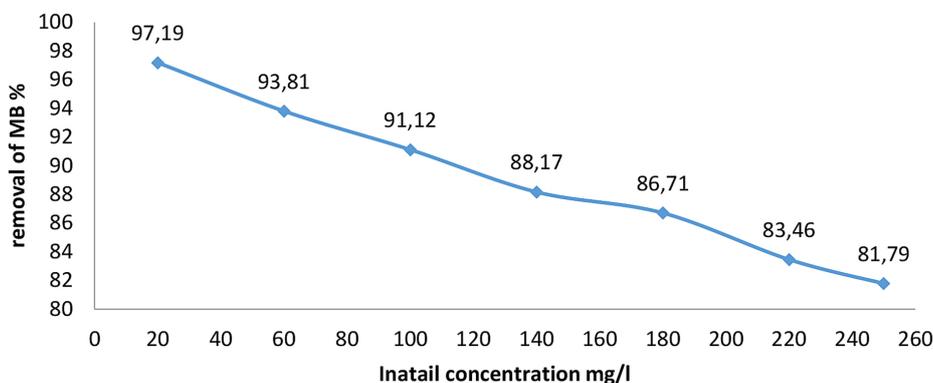A comprehensive examination of the equilibrium records about the adsorption of methylene

Figure 8. Initial MB concentration effect on MB dye removal efficiency (dose of mof-199 = 2 g/l, contact time= 90 min, pH= 7.5, temp. = 25°C)
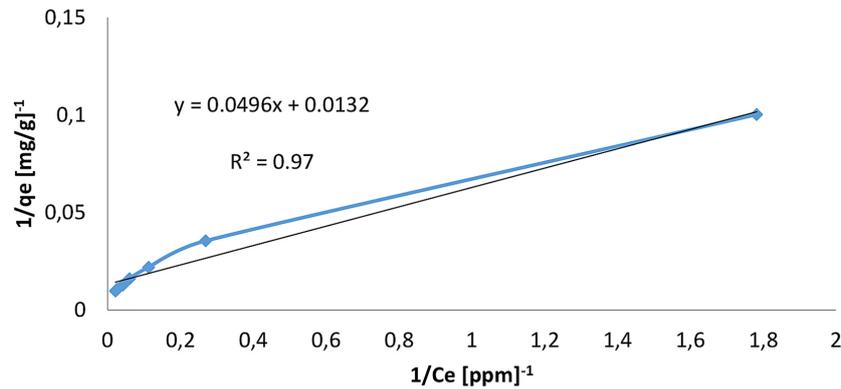
Figure 9. Langmuir isotherm for methylene blue at Ci 20, 60,100,140,180,220 and 250 ppm
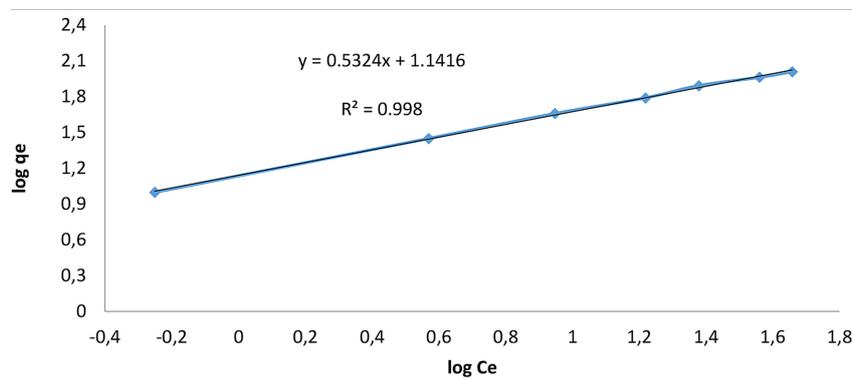

Figure 10. Freundlich Isotherm for methylene blue at C_i 20, 60, 100, 140, 180, 220 and 250 ppm

blue was undertaken utilizing the Freundlich isotherm model by equation 4, as depicted in Figure 10. The isothermal data demonstrates a significant agreement with the Freundlich equation, as indicated by a high correlation coefficient of 0.9989. To obtain a thorough overview of the estimated values, it is recommended to consult Tables 2 and 3. The results obtained from the adsorption isotherm models, as presented in Tables 2 and 3, it is crucial to acknowledge that the coefficient of determination (R^2) reveals that the Freundlich model yields a significantly higher value ($R^2 = 0.9989$) in comparison to the

Langmuir ($R^2 = 0.979$) isotherm models. The observation above implies that the process of methylene blue dye adsorption onto MOF-199 exhibits a non-uniform multilayer adsorption pattern, which aligns with the Freundlich isotherm model, as reported in a previous study [28].

Kinetic study

Pseudo-first-order model

Figure 11 depicts a linear graph representing the time vs. log (q_e-q_t). Within this particular

Table 2. The results of adsorption capacity that obtained from the isotherm models

Initial concentration, *Ci* [mg/l]	Finial concentration *Ce* [mg/l]	Uptake capacity *qe* [mg/g]
20	0.561	9.971
60	3.711	28.144
100	8.871	45.564
140	16.562	61.719
180	23.921	78.039
220	36.375	91.812
250	45.523	102.238

Table 3. The results obtained from the adsorption isotherm models

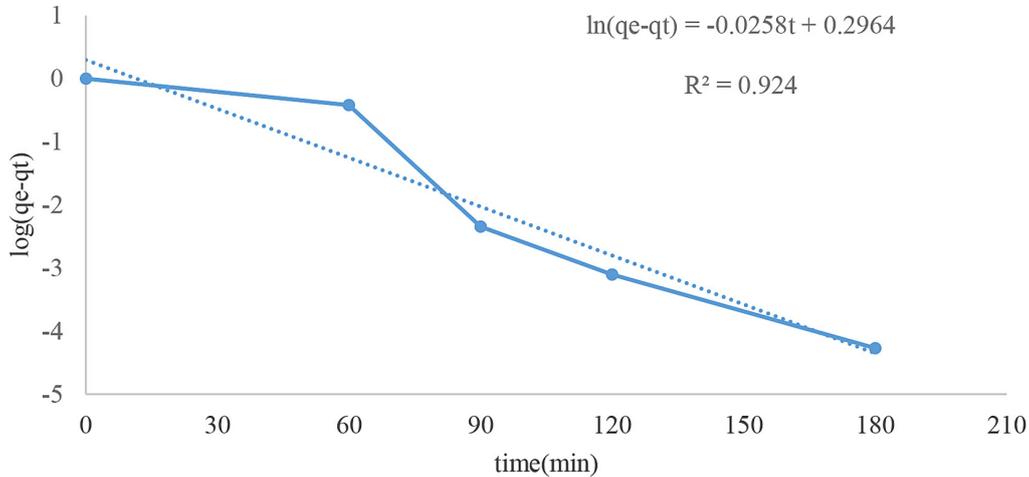| Langmuir isotherm			Freundlich isotherm		
q_m [mg/g]	K_L [l/mg]	R^2	K_f ([mg/g][l/mg] $^{1/n}$)	n	R^2
75.757	0.2661	0.979	13.854	1.878	0.9989

$$\ln(qe-qt) = -0.0258t + 0.2964$$

$$R^2 = 0.924$$

Figure 11. Pseudo-first-order kinetic model for methylene blue adsorption at Ci of 20 ppm at time 30, 60, 90,120,150 and 180 minutes

context, the symbol q_t represents the quantity of methylene blue that is adsorbed at a specific moment in time, denoted as t. The experimental data do not exhibit a strong alignment with the pseudo-first-order model. Please see Table 4 for comprehensive data on the rate constant (k_1), equilibrium concentration (q_e), and correlation coefficient.

Pseudo-second-order kinetics

Figure 12 depicts a linear portrayal of the correlation between the variable t/qt and the variable time (t) within the specified context. The contract between the pseudo-second-order model and the experimental data is robust, as indicated by a significantly high correlation coefficient of (R^2 = 0.9998). The performance exhibited by this fit exceeds that of the alignment obtained by utilizing the pseudo-first-order model. The findings of this

investigation suggest that the predominant mechanism via which methylene blue dye is removed from its aqueous solution, utilizing MOF-199, is by means of a chemisorption phenomenon. Table 4 presents the computed parameters of the pseudo-first order and pseudo-second order [29].

Reusability of adsorbent MOF-199

It is imperative to ascertain the reactivation and reusability potential of the adsorbent due to its economic implications. Following the adsorption procedure under certain conditions (temperature of 298°K, initial concentration of 20 ppm for MB, and a contact period of 90 minutes), a sample of MOF-199 weighing 0.2 g is extracted using the washing method. Subsequently, the adsorption process is repeated after regenerating the MOF

Table 4. Parameters of pseudo-first order and pseudo-second order

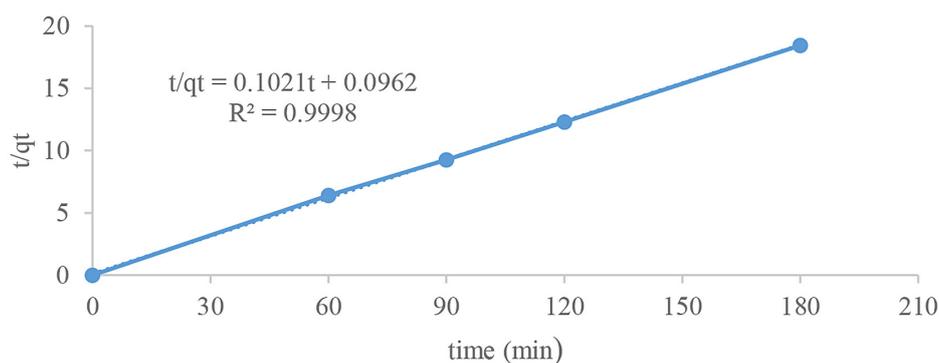| Model	Parameters	Values
Pseudo-first order	K_1 (min^{-1})	-0.0001
	qe, *cal* (mg/g)	0.805
	R^2	0.9246
Pseudo-second order	$qe.exp$ (mg/g)	9.705
	K_2 (g/mg·min)	10.395
	R^2	0.9998

Figure 12. Pseudo-second-order kinetic model for methylene blue at 20 ppm C_i at time points 30, 60, 90, 120, 150, and 180 minutes
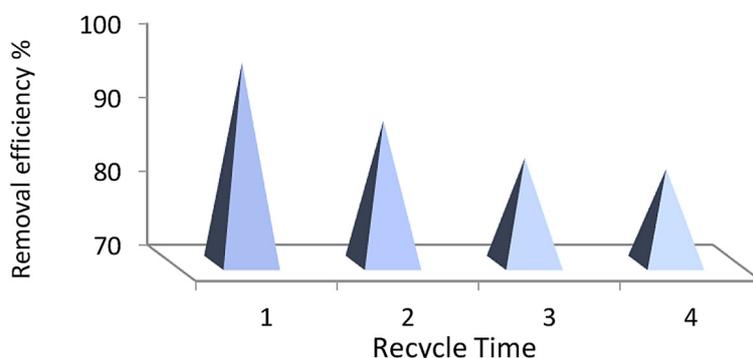

Figure 13. MOF-199 reusability at (adsorbent dose of 2 g/l, contact time 90 min, and ci of MB Initial 20 ppm)

under the same parameters above. The adsorbent that has reached its saturation point is subjected to an elution process, which entails immersing it in a vial (125 ml) containing 60 ml of ethanol at room temperature for 12 hours. After the adsorbent has been separated from the solution and subjected to alcohol washing. The experiment was run thrice using a 60 ml alcohol for each attempt. Subsequently, the washing procedure was repeated. The adsorbent in a vacuum drier is subjected to a drying process lasting 16 hours, with a temperature of 373 kelvin. Notably, the effectiveness of MOF-199 declined by 14.43% later four cycles compared with new MOF-199. The effects of the reusability cycles were detailed in Figure 13, and the efficiency remained commendably high. This outcome underscores the remarkable reusability of MOF-199 as an adsorption material for wastewater treatment involving methylene blue [18].

CONCLUSIONS

The present study showcases the effective synthesis of MOF-199 utilizing the hydrothermal technique. The application of MOF-199 in a batch operation has shown significant efficacy in eliminating the methylene blue dye from wastewater. Multiple experiments were carried out to determine the influence of many factors, including contact time, adsorbent dosage, pH, and initial dye concentration, on the efficacy of MB removal. These studies yielded a removal rate of 97%. The results obtained from the experiment on equilibrium adsorption demonstrated a strong correlation with the Freundlich adsorption isotherm, occurring via chemisorption mechanisms. Finally, the MOF-199 in this study was effectively regenerated through alcohol washing and thereafter reused for four cycles.

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