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EXPLORING MIL-53 (Al) ADSORPTION EFFICIENCY FOR INDIGO CARMINE DYE

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Highlights

- This study focuses on addressing the environmental issue by utilizing MIL-53 (Al) as an adsorbent for removing indigo carmine dye, particularly from textile industries.
- MIL-53 (Al) was synthesized through the hydrothermal method, and different conditions were explored to optimize its effectiveness as an adsorbent for indigo carmine.
- The adsorption study revealed that the Langmuir isotherm model and pseudo-second-order kinetic model provided the best fit to the data.
- The highest adsorption capacity reached 145 mg/g, showcasing the efficiency of MIL-53 (Al) in removing indigo carmine.

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ABSTRACT: Synthetic dyes are extensively used in industrial areas, including plastic, textile, and food. However, they are a major environmental problem due to their negative effects on water quality and living organisms. To address one of these problems, MIL-53 (Al) is served as an adsorbent for removing indigo carmine dye, being widely used in textile industries. The synthesis of MIL-53 (Al) was carried through the hydrothermal method and different synthesis conditions were studied to find the best adsorbent to remove indigo carmine. FTIR, XRD, SEM, and EDS were used to assess materials. Isotherm models and kinetic models were investigated for indigo carmine adsorption, revealing that the Langmuir isotherm model and pseudo-second-order kinetic model provided best fit to data. The highest adsorption capacity was calculated as 145 mg/g. The study contributes valuable insights into the adsorption of indigo carmine by MIL-53 (Al).

Keywords: *Adsorption, Indigo Carmine, Isotherms, Metal Organic Frameworks, MIL-53*

1. INTRODUCTION

Wastewater containing various pollutants is a significant issue today, particularly with the rising population density and the corresponding increase in water consumption rates. As water demand becomes a growing threat daily, it is crucial to transition towards the efficient use of water through wastewater treatment. Industrial waste encompasses numerous pollutants, such as heavy metals, antibiotics, organic chemicals, and dyes. One of the biggest environmental challenges is purification wastewater from dyes, which is growing concern in the textile, food, and leather industries [1].

Metal-organic frames (MOFs) represent a category of porous materials that have garnered a great interest owing to their substantial surface area, adjustable chemical functionality, and structural diversity [2, 3]. In the last three decades, researchers have used MOFs across various applications, such as separation, storage, catalysis, drug delivery, and purification [4]. The suitable properties of MOFs make them well-suited for addressing environmental challenges, particularly in the treatment of organic matter from wastewater.

Indigo Carmine (I.C.), a synthetic dye, is commonly used in dyeing processes especially for silk, wool, and protein fibers [5]. Like many other synthetic dyes, I.C. has adverse impacts on the environment and life forms [6]. The uncontrolled release of I.C. into the environment decreases the quality of water, damages aquatic life and causes permanent damage to human health. Treatment of wastewater is essential before releasing it into nature. In literature, there are different treatment methods for removing I.C. dye, including photocatalytic degradation [7], electrocoagulation [8], membrane filtration [9], and adsorption [10, 11]. Among these methods, adsorption has been worked more since it has many advantages such as easy processing, high efficiency, easy handling, and environmentally friendliness [12]. The selection of an adsorbent is the most important point of the adsorption process due to achieving high removal capacity.

MIL-53 (Al) is a metal organic framework that consist of aluminium metal connected by benzene-1,4-dicarboxylate linkers [13]. MIL-53 (Al) possesses a specific breathing effect, as well as water and thermal stability, making it a suitable for use as an adsorbent [14]. It has been examined for removing specific dyes

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from wastewater. Adsorption of dye by utilizing MOFs is an increasing trend and many researchers have been examined different MOFs to remove various dyes [15-17].

This study aims to examine the indigo carmine adsorption by using MIL-53 (Al), providing valuable information on potential of MOFs as an adsorbent for obtaining clean water. FTIR, XRD, SEM, and EDS were used to characterize MIL-53 (Al). the effects of different synthesis conditions of MIL-53 (Al) on adsorption capacity were studied. Moreover, the typical adsorption parameters such as the effect of adsorbent amount, the effect of initial dye concentrations, the effect of time, and the effect of temperature were examined. Different isotherm and kinetic adsorption models were employed to understand adsorption behavior of indigo carmine dye by MIL-53 (Al).

2. MATERIALS AND METHOD

2.1. Chemicals

Aluminium nitrate nanohydrate (Sigma-Aldrich), 1,4-benzenedicarboxylic acid (Merck), N,N-dimethylformamide (Merck) and methanol (Merck) were used for the MIL-53 (Al) synthesis. Hydrochloric acid (Sigma-Aldrich) and sodium hydroxide (Sigma-Aldrich) were used to arrange the pH of the solutions. Indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$, Sigma-Aldrich) was utilized as a dye.

2.2. MIL-53 (Al) Synthesis

Solvothermal method was used synthesis MIL-53 (Al). Firstly, 0.0023 mol $Al(NO_3)_3{\cdot}9H_2O$ and 0.0023 mol 1,4-benzenedicarboxylic acid was dissolved in 45 ml DMF solvent at separate beakers for 15 minutes. After that solutions were mixed for 15 minutes. Solution was added to stainless steel Teflon autoclave and kept at 120 ^oC for 24 hours [18, 19]. Then, the resulting white solution were centrifuged and washed with DMF and methanol. Lastly, obtained material was dried at 60 ^oC overnight. Further syntheses were conducted with different metal:organic ligand:solvent ratios (1:1:84.6, 1:1:169.2, 1:1:253.8, and 1:1:338.4), temperatures (120, 150, and 220 ^oC), and times (24h, 48h, and 72h).

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out GNR EUROPE 600. Fourier transform infrared (FTIR) analysis was obtained from Thermo Scientific Nicolet iS20 spectrometer. Scanning electron microscopy (SEM) images and Energy dispersive spectrometer (EDS) results were acquired with SM Zeiss LS10.

3. RESULTS AND DISCUSSION

3.1. Synthesis conditions

To see the effect of solvent amount on the synthesized MIL-53 (Al) structure and adsorption capacity, the synthesis was carried out using different ratios of methanol. The molar ratios of metal, organic ligand and methanol were determined as 1:1:84.6, 1:1:169.2, 1:1:253.8, 1:1:338.4. Indigo carmine removal was carried out using MIL-53 (Al) obtained from these syntheses. It was aimed to determine the synthesis conditions for MIL-53 (Al) that show the best adsorption rate. Adsorption experiments were executed a 0.5 g/L adsorbent amount and a 50 mg/L indigo carmine dye solution. The highest adsorption efficiency of 94.6% was acquired with MIL-53(Al) at a molar ratio of 1:1:253.8 (Table 1). Therefore, the next parameter studies will be carried out using this ratio.

Table 1. The adsorption results of MIL-53 (Al) for indigo carmine dye at various solvent amounts

Molar ratio of Al(III)/BDC/metanol	1:1:84.6	1:1:169.2	1:1:253.8	1:1:338.4
% Adsorption	57	85.6	94.6	93.9
q_t (mg/g)	56	84	93.4	92

After investigating the solvent effect, the temperature effect was investigated for the synthesis of MIL-53 (Al). For this purpose, the experiments were performed at temperatures of 120, 150, and 220 ^{o}C. The indigo carmine removal efficiencies and adsorption capacities of MIL-53 (Al) that obtained from these experimental conditions are given in Table 2. According to these results, the highest efficiency of 88.7% was obtained with MIL-53 (Al) synthesized at 120 ^{o}C. Therefore, the temperature value will be 120 ^{o}C in the next steps.

Table 2. The adsorption results of MIL-53 (Al) for indigo carmine dye at various temperatures

Temperature (^{o}C)	120	150	220
% Adsorption	88.7	75.1	48.9
q_t (mg/g)	76.7	61.5	44

Finally, the effect of synthesis time on the structure and adsorption capacity of MIL-53 (Al) was investigated. 24 h, 48 h, and 72 h were selected for synthesis. The highest adsorption capacity was obtained with MIL-53 (Al) synthesized in 24 h, achieving 93% removal (Table 3). When comparing results of all parameters in terms of yields, the experimental conditions were determined as follows; metal, ligand and solvent ratio of 1:1:253.8, temperature of 120 ^{o}C as and synthesis time of 24 h.

Table 3. The adsorption results of MIL-53 (Al) for indigo carmine dye at various synthesis times

Time (hours)	24	48	72
% Adsorption	93.0	88.8	92.6
q_t (mg/g)	86.0	79.1	84.0

3.2. Characterization of MOFs

To understand effect of synthesis conditions on material structure, XRD analysis was used. XRD patterns of MIL-53 (Al) samples obtained by manipulating different metal-to-organic ligand ratios, solvent amounts, and reaction times are presented in Figures 1.a, 1.b, and 1.c. All XRD results of MIL-53 (Al) samples show characteristic peaks at 2θ = 9.6, 10.2, 15.8, and 19.0 with diffraction (101), (200), (011), and (211), respectively [20-22]. As seen from the XRD results, the obtained MIL-53 (Al) samples have sharp intensity and show high crystallinity. However, some samples have lower intensity compared to others, this is due to the lower crystallinity of the samples. The MIL-53 (Al) structure obtained from the synthesis at 150^{o} shows less crystallinity compared to other conditions (Figure 1).

Figure 2. shows FTIR results for MIL-53 (Al) before and after indigo carmine adsorption. The FTIR spectrum of MIL-53 (Al) did not change significantly after adsorption (Figure 2). The strong absorption band at 1603 cm^{-1} is attributed to C=C stretching band in the aromatic group [20]. The peak at 1676 cm^{-1} is ascribed to the stretching vibration of C=O group in terephthalic acid molecules, which are stucked within the pores of MOFs [23]. This peak shifted to 1690 cm^{-1} after indigo carmine adsorption, likely due to interactions between MIL-53 (Al) and indigo carmine dye. The broad peak appeared at 3400 cm^{-1} is belong to the O-H stretching vibration [20], while the peak at 590 cm^{-1} is ascribed to the Al-O group [23], indicating its presence in MIL-53 (Al). Indigo carmine contains C-N bond in its structure and its peak occurs in the

1350-1000 cm^{-1} range. As seen in the FTIR graph, it is thought to form a broad peak around 1320 after adsorption, overlapping with the adjacent peak due to the C-N peak.

SEM images of MIL-53 (Al) for before indigo carmine adsorption (a,c) and after indigo carmine adsorption (b,d) at various magnifications are showed in Figure 3. As depicted in Figure 3, no significant differences were observed between surfaces of MIL-53 (Al) before and after indigo carmine adsorption. The surface of MIL-53 (Al) appears smoother compared to neat MIL-53 (Al) (Figure 3.d). This may be associated to the adsorption of indigo carmine on the surfaces of MIL-53 (Al).

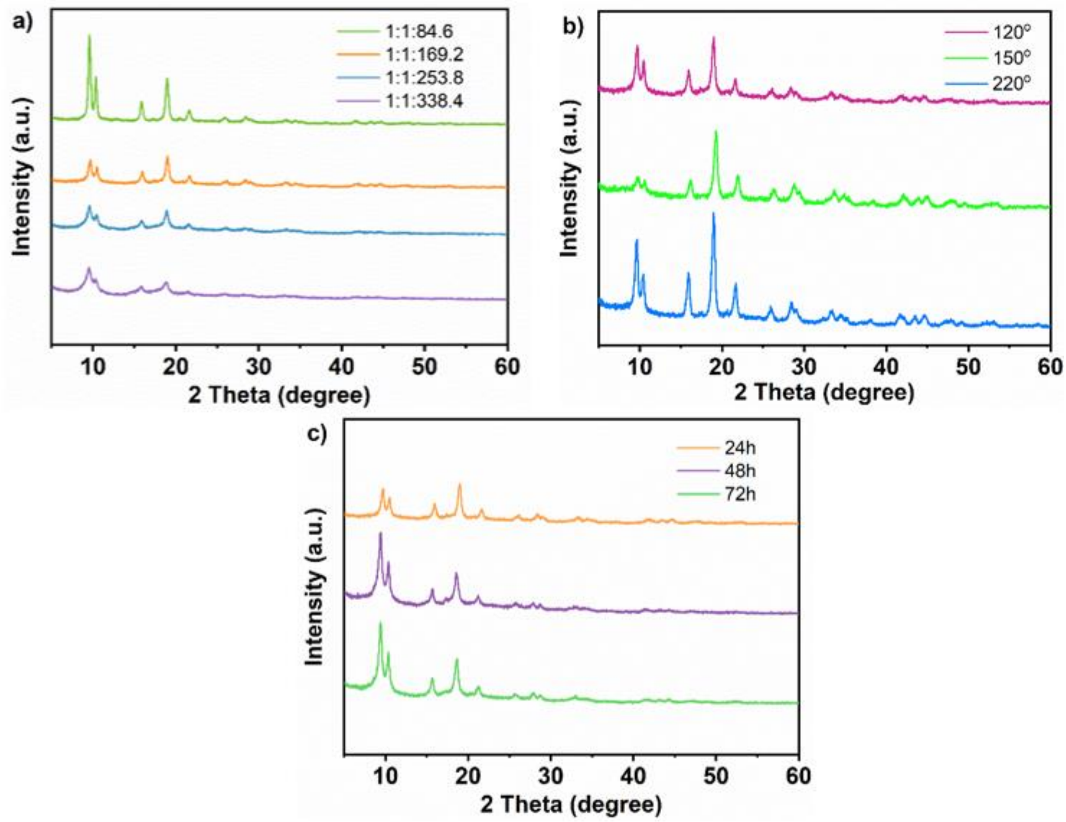

Figure 1. XRD patterns of the MIL-53 (Al) at various solvent amounts (a), temperatures (b), and times (c)

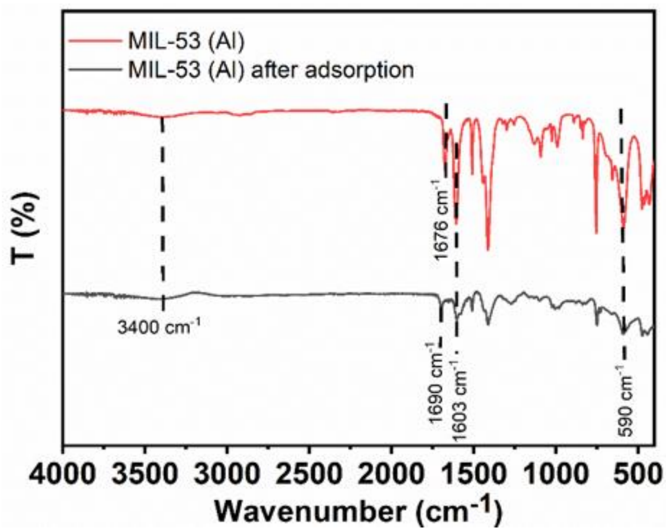

Figure 2. FTIR spectra of MIL-53 (Al).

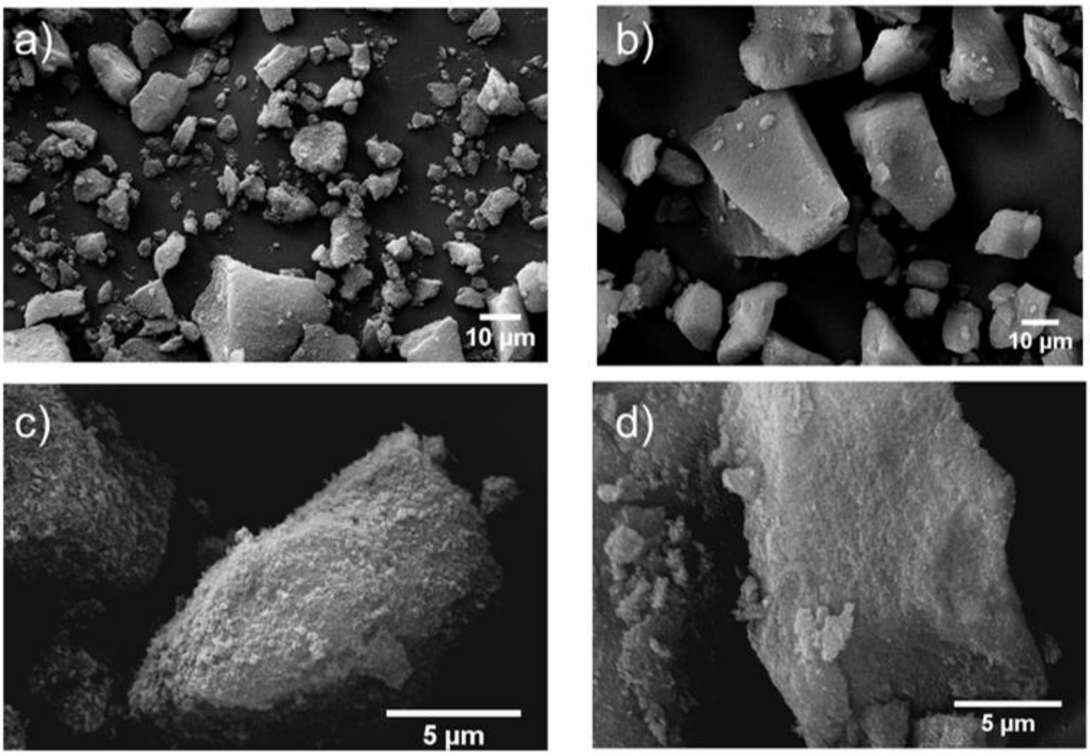

Figure 3. Morphological structure of the MIL-53 (Al) before I.C adsorption (a,c) and after I.C adsorption (b,d).

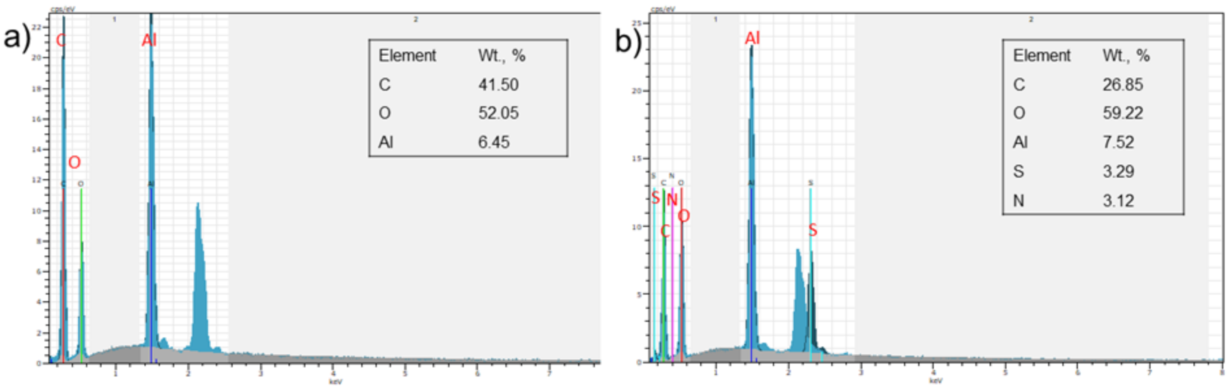

Figure 4. EDS spectrum of the MIL-53 (Al) before I.C adsorption (a) and after I.C adsorption (b).

EDS spectrum of the MIL-53 (Al) before (a) and after (b) indigo carmine adsorption is indicated in Figure 4. As expected, carbon, oxygen, and aluminum peaks (Fig. 4a) were observed at neat MIL-53 (Al). After indigo carmine adsorption, in addition to these peaks, sulfur and nitrogen peaks (Fig. 4b). were also observed since indigo carmine dye includes these elements in its structure. This result clearly shows that indigo carmine dye is adsorbed by MIL-53 (Al).

3.3. Batch adsorption studies

Indigo carmine adsorption by MIL-53 (Al) as adsorbent were conducted with batch studies. Removal percentage of indigo carmine (R, %) and adsorption capacity (q_e, mg g^{-1}) were specified with Equations (1) and (2), respectively.

$$R = \frac{C_0 - C_e}{C_0} \, x \, 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \, x \, V}{m} \, x \, 100 \quad (2)$$

Langmuir isotherm (Equation 3) and Freundlich isotherm equations (Equation 4) are as shown below. In this equations, q_m (mg g^{-1}), K_L (L mg^{-1}), K_F (mg g^{-1}), and n (L mg^{-1}) represent maximum adsorption capacity, Langmuir isotherm constant, Freundlich isotherm constant related to adsorption capacity, and Freundlich isotherm constant associated with adsorption intensity, respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Pseudo-first-order (Equation 5) and pseudo-second-order (Equation 6) models were used to examine indigo carmine adsorption kinetics. In these models, q_t (mg g-1) represents adsorption capacity at time t (min). k_1 (min-1) and k_2 (g mg-1 min-1) are pseudo-first-order and pseudo-second-order rate constants, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

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

Various factors affect the adsorption process, and pH effect is being one of the most crucial ones. In order to find the optimum pH value for indigo carmine removal with MIL-53 (Al), several studies were conducted from pH 2 to 10. The acidity of the dye solutions for pH studies were set up with 0.1 M HCl and NaOH. In these experimental studies, a 50 mg/L, 10 mL I.C dye solution was used for the optimum dosage of adsorbent.

The percentage of I.C adsorption with MIL-53(Al) varied between pH 2 and 10 (Figure 5.a). The pH optimum adsorption efficiency was acquired at pH 3.2, and the adsorption efficiency decreased after this point. In the adsorption process, the pH value of the medium changes the surface charges, providing better information about adsorption. The point of zero charge (pHpzc) value of adsorbent is also studied and given in Figure 5.b. As depicted in the figure, the pHpzc value for MIL-53 (Al) was calculated as 4.1. If the pH of the medium is below 4.1, the net adsorbent charge is positive, while above it is negative [24]. In this case, at the optimum pH value (pH=3.2) the adsorbent charge is positive. Indigo carmine is an anionic dye, and the best adsorption efficiency is achieved at the pH where the adsorbent surface charge is positive. This suggest that effective mechanism can be electrostatic attraction at this point [25]. The reason for decrease in adsorption percentage after after pH 4 can be attributed to surface charges. The adsorbent surface are becomes negatively charged above pHpzc which is 4.1. Since dye is anionic surface interaction between dye and adsorbent are repulsive above pH 4.1 [26].

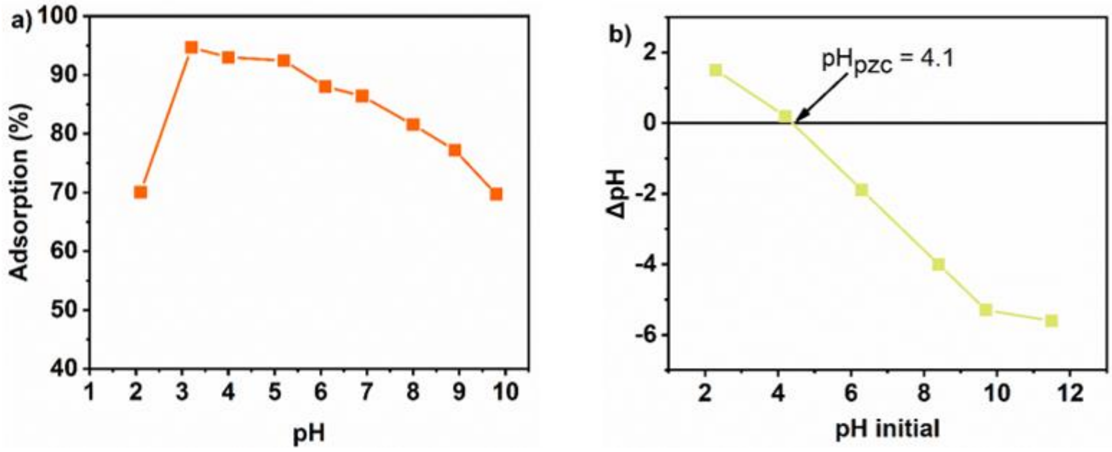

Figure 3. pH effect on the indigo carmine adsorption (a), and pHpzc of the MIL-53 (Al).

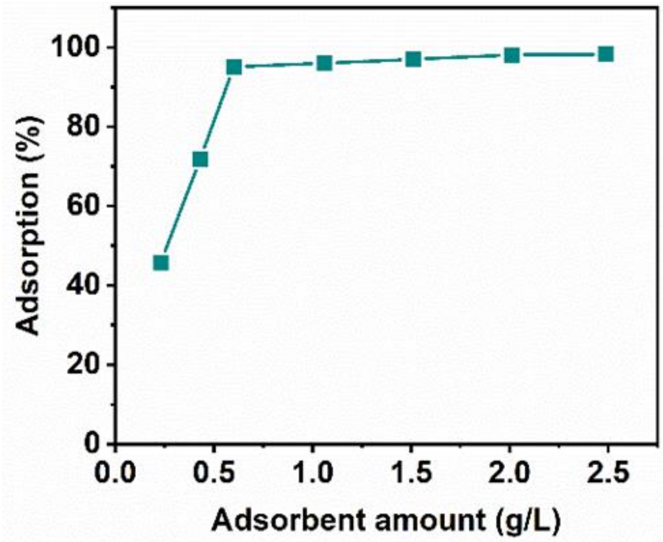

Figure 6. MIL-53 (Al) amount effect on I.C adsorption.

In the study to find the optimum adsorbent amount, experiments were performed with various adsorbent amounts between 0.2 and 2.5 g/L. In the experiments, a 50 mg/L, 10 mL I.C. dye solution was used and carried out at room temperature. The adsorption efficiency increased up to a 0.6 g/L adsorbent dosage and remained constant after this value (Figure 6). The adsorption efficiency increases until the adsorbent amount reaches 0.6 g/L because the adsorbent amount increases the surface area (active sites). However, the adsorption efficiency remains constant after this value since all I.C dye molecules in the medium adsorbed by MIL-53 (Al).

The effect of contact time for I.C dye removal with MIL-53 (Al) was also examined and displayed in Figure 7a. This study was operated at room temperature, employing a 50 mg/L dye solution and an optimum adsorbent amount. As seen in the figure, adsorption efficiency increased up to 120 minutes, and it remained constant after this point. With this study, the optimum contact time was determined as 120 minutes.

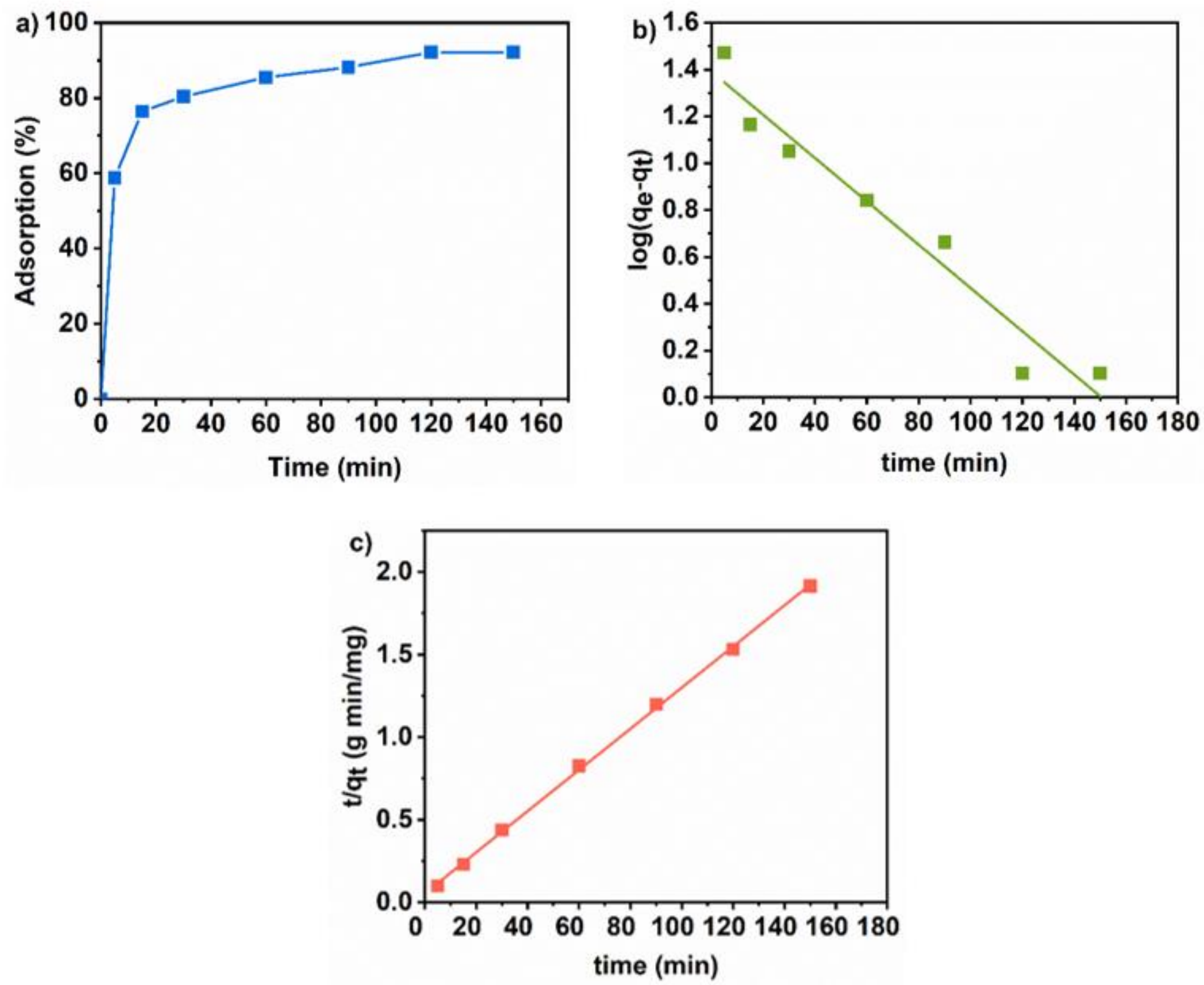

Figure 7. Contact time effect on I.C adsorption (a), pseudo-first-order kinetic (b), and pseudo-second-order kinetic (c) models for I.C adsorption.

The indigo carmine dye adsorption kinetics were examined using both the pseudo-first-order and pseudo-second-order kinetic models [27] (Figure 7b-c). The parameters for these kinetic models for indigo carmine are given in Table 4. The pseudo-second order kinetic model exhibits a superior correlation coefficient ($R^2 = 0.999$) in comparison to the pseudo-first order kinetic model ($R^2 = 0.932$). Thus, the pseudo-second order kinetic model better fits the adsorption data of this work. The assumption of pseudo-second order kinetic model is that rate-limiting step in the process is chemical adsorption [28].

The effect of initial dye concentration is also studied. Different dye solutions varying between 25 and 200 mg/L were used in the study. The studies were performed at the optimum amount of adsorbent at room temperature. The indigo carmine adsorption capacity of MIL-53 (Al) increased with increasing indigo carmine dye concentration (Figure 8.a). The concentration increase provides more chances for the dye molecules to interact with adsorbent. Furthermore, these higher interactions increased adsorption capacity of MIL-53 (Al).

Table 4 displays the capacity of adsorption for the adsorption of indigo carmine dye on various adsorbents. The literature has several research on the adsorption of I.C dye on various adsorbents, and MIL-53 (Al) has a comparatively high adsorption capacity.

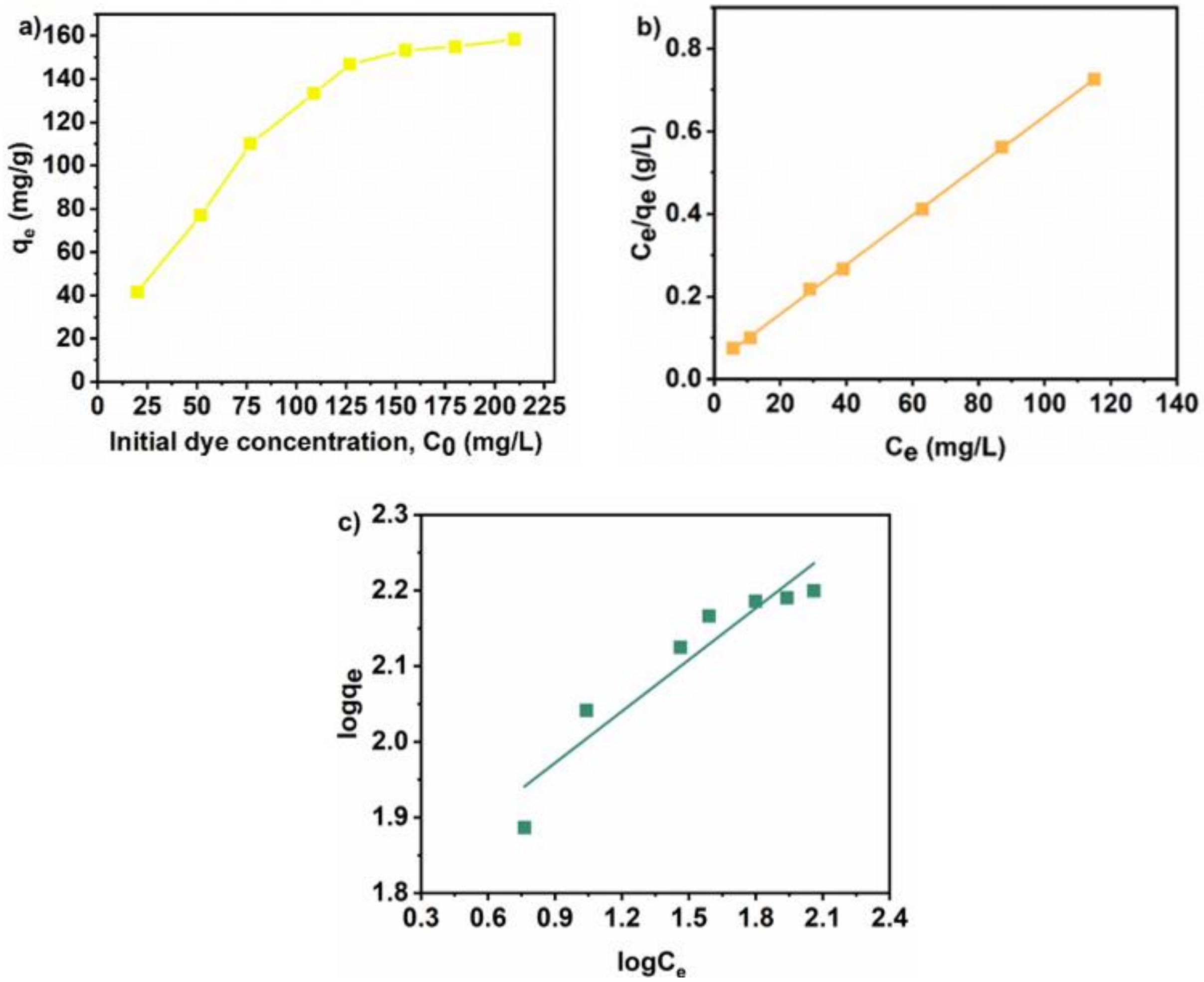

Figure 8. Initial I.C dye concentration effect on adsorption capacity (a), Langmuir (b), and Freundlich (c) isotherm models for I.C adsorption.

Table 4. Comparison of indigo carmine dye adsorption by different adsorbents

No.	Adsorbents	Adsorption capacity (mg/g)	Ref.
1	Activated carbon	79.49	[5]
2	Water treatment residuals (WTR)	30.86	[6]
3	Moringa oleifera seeds	60.0	[10]
4	Chitosan-FAS composite	76.64	[29]
5	Acacia nilotica sawdust activated carbon	24.67	[11]
6	UiO-66	87.2	[30]
7	Maize cob carbon (MCC)	118.48	[31]
8	Pistia stratiotes biosorbent	41.2	[32]
9	Terminalia catappa	106.98	[33]
10	MIL-53 (Al)	156	This work

Table 5. The kinetic models and isotherm models parameters for I.C adsorption.

Models	**Parameter**	**MIL-53 (Al)**
Pseudo-first order kinetic	q_e (mg g^{-1})	24.6
	R^2	0.951
	k_1 (min^{-1})	0.021
Pseudo-second order kinetic	q_e (mg g^{-1})	80
	R^2	0.999
	k_2 (g mg^{-1} min^{-1})	0.0028
Langmuir isotherm	q_m (mg g^{-1})	156
	K_L (L mg^{-1})	4156
	R^2	1
Freundlich isotherm	K_F (mg g^{-1})	58.5
	n (L mg^{-1})	4.41
	R^2	0.897

Isotherm mechanism for indigo carmine adsorption by MIL-53 (Al) were investigated, utilizing Langmuir and Freundlich isotherm models (Figure 8.b and 8.c). Moreover, adsorption isotherms parameters are presented in Table 5. High correlation coefficient (R^2) value of Langmuir isotherm model (R^2 = 1) was shown that this isotherm model was more suitable compared to Freundlich isotherm model. According to Langmuir isotherm model, every point on the adsorbent surface exhibits equivalent adsorption. Furthermore, monolayer, and homogeneous adsorption is observed if data fit to Langmuir isotherm model [34]. The maximum adsorption capacity of MIL-53 (Al) was calculated as 156 mg/g.

4. CONCLUSION

In conclusion, this study demonstrated the effective removal of indigo carmine synthetic dye from water through utilization of MIL-53 (Al). As a result of the adsorption studies, the optimum removal parameters were determined and they are pH: 3.2, adsorbent amount: 0.6 g/L, time: 120 min. In kinetic and isothermal studies, it was observed that the experimental data conformed well to the Langmuir isotherm model (R^2 = 1) and pseudo-second-order kinetic model (R^2 = 0.999), both of which gave a high correlation value. The Langmuir isotherm indicates equal and equivalent adsorption in all regions. The pseudo second-order kinetic model shows the adsorbate binds rapidly to a specified number of adsorption sites on a surface. The maximum adsorption capacity was determined as 156 mg/g. Detailed characterizations and systematic adsorption studies and removal studies of indigo carmine dye using MIL-53 (Al) will contribute to further studies in this field.

Declaration of Ethical Standards

Authors declare to comply with all ethical guidelines including authorship, citation, data reporting, and publishing original research.

Credit Authorship Contribution Statement

D. YANARDAĞ KOLA: Conceptualization, Methodology, Investigation, Writing - Original Draft

S. EDEBALİ: Investigation, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

Declaration of Competing Interest

The authors declared that they have no conflict of interest.

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Data Availability

Data will be made available on request.

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