Removal of Methylene Blue from Aqueous Solution By Polydopamine@Zeolitic Imidazolate-67

Maryam Hajnajafi

University of Guilan

A. Khorshidi (✉ khorshidi@guilan.ac.ir)

University of Guilan <https://orcid.org/0000-0002-8990-8052>

Ali Ghanadzadeh Gilani

University of Guilan

Francis Verpoort

National Research Tomsk Polytechnic University

Research Article

Keywords: Adsorption, ZIF-67, Polydopamine, Methylene Blue, Removal

Posted Date: December 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1162284/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Removal of Methylene Blue from aqueous solution by polydopamine@Zeolitic Imidazolate-67

Maryam Hajnajafi^a, Alireza Khorshidi^{a,}, Ali Ghanadzadeh Gilani^a, Francis Verpoort^{b,c,d}*

^a Department of Chemistry, Faculty of Sciences, University of Guilan, P. O. Box: 41335-1914, Rasht, Iran

^b National Research Tomsk Polytechnic University, Lenina Ave. 30, Tomsk 634050 Russia

^c Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, PR China

^d Ghent University, Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon 406-840, South Korea

* Corresponding author's email: khorshidi@guilan.ac.ir

Abstract

Herein, a facile and low-cost route was used to prepare Polydopamine@Zeolitic Imidazolate Framework-67 (PDA@ZIF-67). The structure, morphology, surface functional groups and particle size distribution of PDA@ZIF-67 were studied using FTIR, FESEM, EDS, and BET analyses. The specific surface area and diameter of PDA@ZIF-67 were equal to be 78.203 m²/g and 4.179 nm, respectively. The PDA@ZIF-67 was used as an adsorbent for the adsorption of methylene blue dye. The results show that the maximum adsorption efficiency of methylene blue on the surface of PDA@ZIF-67 is achieved at pH 2, the temperature of 65°C, 10 mg of adsorbent, and methylene blue concentration of 7.5 ppm.

Moreover, the adsorption process's isothermal, thermodynamic, and kinetics were studied entirely to consider the adsorption mechanism. The methylene blue molecules located in the fine pores of the PDA@ZIF-67 adsorbent determine the adsorption rate. Moreover, the adsorption process of methylene blue at high temperatures is a spontaneous and endothermic reaction. The adsorption efficiency of PDA@ZIF-67, after the recovery, reached 62.21%, which is an excellent advantage for using this adsorbent.

Keywords: Adsorption; ZIF-67; Polydopamine; Methylene Blue; Removal.

Introduction

Rapid growth of chemical industries along with the expansion of agriculture has led to severe pollution of water resources [30]. This topic is considered as a global problem [11]. Among the various types of water pollutants, dyes have emerged as one of the most important pollutants in the scientific community [35].

Methylene blue (MB) with the molecular formula of $C_{16}H_{18}ClN_3S$ is an organic cationic dye, which has been widely used in biology and chemical applications. Large amounts of organic dye effluents are produced annually by related industries such as printing, textiles, dyeing, papermaking, and so on. Colored effluents have undesirable properties such as high BOD, poor biodegradation, toxic nature, etc. These properties are dangerous to living organisms as well as photosynthesis of microorganisms [12].

Up to date, various approaches such as advanced oxidation process (AOP) [41], membrane filtration [39], flocculation [42], ozonation [16], photocatalytic degradation [36], biodegradation[31], membrane technology [1] and coagulation [2] have been used to remove organic pollutants from aqueous phase. However, application of traditional methods still faces two inherent limitations including complexity and economic inefficiency. Therefore, finding an easy, economical and effective method for wastewater treatment has emerged as a hot topic in scientific community. Adsorption on the surface of a suitable adsorbent is another common method for removal of different contaminants. Carbon materials [23, 30], minerals (including kaolinite and montmorillonite) [18], polymers [10] zeolites [37], clays [8], sludge [5], flax fibers [40], and Biochar [33], are some of the most widely used adsorbents in this regard.

However, poor performance of the conventional adsorbents in terms of selectivity and capacity has been emerged as a fundamental problem. In recent years, metal-organic frameworks (MOFs) due to their high porosity and surface area, large adsorption capacity, and desirable guest-host interactions, have been employed as a promising alternative in various applications such as drug delivery, adsorption processes [46], batteries, gas storage, and separation [9, 17, 29, 46]. High adsorption capacity of the MOFs has been attributed to the electrostatic interactions, conjugated π - π interactions and hydrogen bonds. Since the MOFs show good thermal and chemical stability, they have been used in various fields such as gas adsorption, molecular separation and electrochemistry. One of the most studied metal organic frameworks is the Zeolitic Imidazolate-67 (ZIF-67), which consists of Co^{2+} ions linked by 2-methylimidazolate to form a cubic crystal structure with the unit cell parameters of $a = b = c = 16.9585 \text{ \AA}$. Zeolitic Imidazolate-67 offers a three-dimensional (3D) structure with a high tendency to adsorb contaminants in the aqueous media. However, the application of ZIF-67 as an adsorbent still faces three vital problems including low specific surface area, poor structural stability, and difficult separation.

Dopamine (3,4-dihydrophenylamine) is a neurotransmitter that plays a neurological role in the body and brain. This organic compound is naturally synthesized in plants and animals (kidneys and brain) [17]. Dopamine consists of a catechol unit attached to an amine unit by an ethyl chain and will be easily solved in many solvents due to its polar functional groups[29].

One of the derivatives of dopamine is polydopamine (PDA) [25]. The unique properties of PDA (size control, uniform spherical shape, thermal stability, good biocompatibility and non-toxicity) leads to its application in various fields [34]. Moreover, the presence of NH and catechol groups in PDA leads to the application of this compound as an active adsorbent. Recently, scientists have proven that some polymers can be utilized as an effective adsorbent for the absorption of pollutants such as dyes. A porous magnetic carboxylic polymer as an efficient adsorbent for wastewater treatment was reported by Huang et al [21]. Zhang and co-workers modified a cationic magnetic chitosan grain polymer for efficient adsorption of heavy metals and dyes in a wide range of pH [47]. In recent years, scientists have found that the polymer-doped ZIF-67 can be utilized to overcome the above mentioned challenges. Owing to the -OH functionality and its hydrophilic nature, PDA can be easily used as a dopant for ZIF-67, to provide a readily dispersible composite material. It has been shown that the porous structure of the PDA does not block the ZIF-67 holes[32].

In this contribution, preparation and application of a new hybrid material consisting of ZIF-67 and PDA is reported. The PDA@ZIF-67 was used as an efficient adsorbent for removal of MB dye from aqueous solution. Effect of various parameters on the adsorption of MB, including the reaction time, initial dye concentration, absorbent dosage, pH, temperature, and PDA:ZIF-67 ratio was studied, as well as the kinetics and thermodynamics of the adsorption process.

2. Experimental

2.1. Chemicals

All of the chemicals and reagents were purchased as received. $\text{Co}(\text{NH}_3)_2.6\text{H}_2\text{O}$, 2-Methylimidazole, MB, Ethanol, KMnO_4 , and $\text{K}_2\text{Cr}_2\text{O}_7$ were purchased from Merck. Dopamine (DA, 3,4-dihydroxyphenethyl amine) was purchased from Caspian Tamin pharmaceutical Company. Double distilled water was used as solvent in all of the experiments.

2.2. Instrumentation

Ultraviolet–visible (UV–Vis) spectra were recorded at room temperature (RT) by using a Cary 5000 spectrophotometer. Energy-dispersive X-ray spectroscopy (EDS) was performed with a Mira-3 XMu. Morphology of the PDA@ZIF-67 sample was studied by scanning electron

microscopy (SEM, XL30 ESEM; Philips). BET measurements were performed on a BEL SORP mini II. A Milwaukee Mi806 pH-meter was used in all of the experiments.

2.3. Synthesis of ZIF-67

ZIF-67 nanocubes were prepared via a simple method in aqueous solution at room temperature (RT) according to the literature [28].

2.4. Synthesis of PDA@ZIF-67

First, 30 mg of ZIF-67 was dispersed in a solution of 45 mg of polydopamine in 30 mL of double distilled water in an ultrasonic bath. Afterwards, KMnO_4 (in excess, a full spatula) was added and stirred for 6h. Then the white precipitate was washed with water and ethanol several times, and dried at 50 °C overnight. Potassium permanganate was used as a polymerization initiator and the main oxidant to convert dopamine to polydopamine [34]

2-5 Recycling of the PDA@ZIF-67

Recovery and reuse of the PDA@ZIF-67 composite was performed as follows: after the first cycle, the PDA@ZIF-67 composite was separated by centrifugation at 3000 rpm, and washed several times with water and then with ethanol. Finally, the precipitate was dried in an oven at 50 °C overnight. The recycled PDA@ZIF-67 was used consecutively for six cycles.

Batch adsorption studies

To 100 mL of 2.5 ppm solution of MB in double distilled water, 10 mg of PDA@ZIF-67 was added, and the mixture was stirred constantly by a magnetic stirrer. The progress of adsorption was studied at different time intervals by sampling and filtration of the solution, followed by measuring the absorbance of the filtrate at 664 nm.

pH of the solutions was adjusted to the desired value by using Britton–Robinson buffer, which is a universal pH buffer used for the pH range from 2 to 12 [7]. The chemical structure of methylene blue is shown in Figure 1.

Figure 1- Chemical structure of methylene blue

3. Results and discussion

Structural characterization of the adsorbent was carried out by FTIR and FESEM analyses. Figure 2a displays the FTIR spectrum of ZIF-67. Generally, the adsorption peaks in the range of $600\text{-}1500\text{ cm}^{-1}$ are attributed to the stretching and bending vibrations of imidazolate moiety [22]. The observed peak at 1578 cm^{-1} is attributed to the stretching vibration of $\text{C}=\text{N}$ [27]. Also, the adsorption peak at 3135 cm^{-1} is related to the C-H bonds of the aromatic ring of 2-methylimidazole. Figure 2b shows the FTIR spectrum of PDA. The advent of large and wide peak in the range of $3200\text{-}3600\text{ cm}^{-1}$ well corroborates the presence of hydroxyl groups [19]. The adsorption peaks of amine functional groups are not seen in this spectrum due to overlapping of the intense hydroxyl peak [6]. The N-H bending vibrations, however, were observed at 1621 cm^{-1} . The $\text{C}=\text{C}$ vibrations of the PDA structure were appeared at 1504 cm^{-1} . Figure 2c, on the other hand, represents the FTIR spectrum of the PDA@ZIF-67 . One can note that the corresponding peaks of the anticipated functional groups are present in the final product, without considerable changes in their position and intensity.

Figure 2- FT-IR spectra of (a) ZIF-67, (b) polydopamine, and (c) PDA@ZIF-67 composite.

Morphological study of the PDA@ZIF-67 was carried out by FESEM. Surface morphology of the PDA@ZIF-67 composite is shown in Figure 3. Clearly, the PDA@ZIF-67 composite is formed of many ultrafine nanoparticles in the range of 12-18 nm.

Figure 3- FESEM images of the PDA@ZIF-67 composite

EDS analysis was also used to evaluate the composition of the constituting elements of the PDA@ZIF-67. As shown in Figure 4, the corresponding K and L lines of each of the anticipated elements were present, with the C:Co ratio of 26.3:1.3%w/w.

Figure 4- EDS spectrum of the PDA@ZIF-67 composite

BET analysis was used to study the physicochemical properties of PDA@ZIF-67 composite. The corresponding N₂ adsorption-desorption isotherm is shown in Figure 5a, where a type-IV isotherm is clearly visible with a distinct hysteresis loop in the P/P_0 range of 0.3-0.95. The specific surface area of the PDA@ZIF-67 was found to be 203.78 m².g⁻¹. The corresponding BJH pore distribution curve (Figure 5b) was used to evaluate the pore structure of PDA@ZIF-67. As can be seen, two types of pores including micro- (<2 nm) and meso-pores (2-50 nm) were present with an average pore diameter of 4.179 nm.

Figure 5-(a) The N₂ adsorption-desorption isotherm of PDA@ZIF-67, and (b) its corresponding BJH pore distribution curve

With the characterized PDA@ZIF-67 composite in hand, a systematic study was conducted to evaluate its adsorption capacity. First, we compared the adsorption efficiency of MB on polydopamine, Zeolitic Imidazolate-67 and PDA@ZIF-67 composite. To do so, a 2.5 ppm solution of MB in double distilled water was prepared. 10 mg of each adsorbent was added to 100 mL of the aforementioned solution. Up to 99% of MB removal was observed within 45 minutes by using the PDA@ZIF-67 synthesized in presence of potassium permanganate as a polymerization agent (to convert dopamine to polydopamine during the synthesis of PDA@ZIF-67). In comparison, K₂Cr₂O₇ as the polymerization initiator, was not as effective as KMnO₄.

Figure 6 shows the trend of MB adsorption in terms of C/C_0 vs. time for each of the adsorbents, where, C_0 is the initial concentration of dye solution, and C is its concentration at time t . As shown, the PDA@ZIF-67 can remove up to 99% of MB within 45 min using KMnO₄ (as a polymerization initiator) at RT and neutral pH.

Figure 6- The adsorption process of MB (2.5 ppm) over time in the presence of 10 mg of each adsorbent at RT and neutral pH

In order to optimize the polydopamine/ZIF-67 ratio, various proportions of each ingredient was studied. It was found that the optimal ratio of polydopamine to ZIF-67 was 45:30 (mg) as shown in Figure 7.

Figure 7- The adsorption process of MB (2.5 ppm) over time in the presence of 10 mg adsorbent synthesized with different polydopamine: ZIF-67 ratios at RT and neutral pH

One of the key factors in the adsorption processes is the pH of solution. In this study, the Britton-Robinson buffer (Aka BBR or PEM) was used to adjust the pH in the range of 2-12, to study the effect of pH on the adsorption of MB [38]. Figure 8 illustrates the UV-Vis spectra of MB in presence of 10 mg of the composite at different pH values (2, 4, 6, 8, 10, and 12). As shown, the maximum adsorption efficiency was obtained at pH 2, where the solution is almost completely colorless. As predicted, the adsorbent at the negative pH ($\text{pH} < 0$) has a positive charge due to the protonation of the hydroxyl groups, so that the adsorption capacity at high acidic pH cannot be maximum. This observation is due to the fact that electrostatic interactions are not the dominant force in MB at pH 2. In fact, a high adsorption capacity for MB in the MB^+ form in acidic environment is obtained due to the π - π interactions, or formation of hydrogen bonds (Co--OH...NH) between the MB and PDA@ZIF-67 catalyst [45].

Figure 8- Trend of MB (2.5 ppm) adsorption on 10 mg of PDA@ZIF-67 after 10 min at different pH values

Effect of the initial dye concentration on the adsorption process was also studied in presence of 10 mg of PDA@ZIF-67 to determine the optimal concentration of MB. All of the experiments were conducted at RT and pH 2 for 10 minutes. The corresponding UV-Vis spectra are shown in Figure 9, and the results are summarized in Table 1. According to the data of Table 1 and Figure 9, the optimal concentration of MB was determined as 7.5 ppm.

Table 1. The adsorption percentage of different concentrations of MB dye for 10 minutes at pH 2

MB concentration (ppm)	Adsorption efficiency (%)
2.5	94.61
5	93.13
7.5	89.64
10	72.91
15	65.84
20	47.76

Figure 9- The UV-Vis spectra of MB dye solutions with different concentration after 20 min at pH=2

To determine the optimal contact time, the adsorption process of MB (7.5 ppm) was performed at RT and pH=2 in presence of 10 mg of the adsorbent from 2 to 8 min. As shown, the optimal contact time for this situation, was found to be 8 min. with up to 99.98% of dye removal.

Figure 10- Effect of contact time on the adsorption process of MB dye

Eventually, the optimum temperature for the adsorption of MB was determined by studying the adsorption reaction at four different temperatures from 25°C to 65°C. The obtained results are illustrated as Figure 11, where one can see that the adsorption of MB (100 mL, 7.5 ppm) after 8 min is maximum at 65°C in presence of 10 mg of PDA@ZIF-67 at pH 2.

Figure 11- Effect of temperature on the removal of MB (7.5 ppm, pH 2)

Recyclability of the PDA@ZIF-67

The adsorption efficiency of an adsorbent after recycling has emerged as an important and crucial factor. In fact, in the first series, a fresh catalyst was used and the adsorption percentage of methylene blue was measured at pH = 2 and concentration of 7.5 after 8 minutes, which showed red peaks before the adsorption effect and blue peaks after the adsorption effect. As shown in Figure 12, the PDA@ZIF-67 was able to remove up to 62.1% of MB after six successive runs.

Figure 12- Red peak indicates adsorption of methylene blue before adsorbent and blue peaks indicate adsorption of methylene blue after adsorption by PDA@ZIF-67 to 6 times recovery

Adsorption kinetics and isotherms

Study of the adsorption kinetics is very important to predict the adsorption mechanisms that control the pollutants removal and the retention time of adsorbed species. The adsorption kinetics can be explored by some kinetic models such as pseudo-first-order (PFO) [30], pseudo-second-order (PSO) [30], and intra-particle kinetics [20].

The pseudo-first-order equation is described as equation (1);

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad \text{Equation 1}$$

where, the unit of rate constant (k_1) is 1/min., and t is the adsorption time.

The Pseudo-second-order equation can be explained by equation (2);

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{Equation 2}$$

where, k_2 represents the rate constant of the pseudo-second-order equation (g/mg.min). The initial absorption velocity can be obtained using the values of k_2 and q_e in the top equation.

The intramolecular diffusion model follows the equation 3;

$$q_t = k_i t^{0.5} + C$$

Equation 3

where, C is related to the thickness of the boundary layer. The rate constant of intramolecular diffusion (k_i) is min/1. Table 2 shows the calculated parameters for the adsorption of MB by PDA @ ZIF-67.

Table 2. Kinetic parameters obtained from traditional models for MB adsorption (5 mg L⁻¹)

Pseudo first-order			Pseudo second-order			Intra-particle diffusion		
q_e	K_1	R^2	q_e	K_2	R^2	K_{diff}	C	R^2
33.861	0.464	0.9541	81.3	0.018	0.9997	9.8578	48.258	0.9661

The obtained q_e values from the pseudo-first-order kinetics model for MB adsorption is not consistent with the experimental data. The q -theoretic data values follow the pseudo-second-order model. According to the model, the intra-particle diffusion of the adsorption process creates a linear diagram for q_t vs. $t^{0.5}$ implying that if the lines pass through the origin, the speed control step is shown with this model (Figure 13).

Figure 13--(a-c) Pseudo-first order, pseudo-second order, and intra-particle model for dye adsorption on PDA@ZIF-67 utilizing linear equation

The highest and lowest R^2 values belong to the pseudo-second-order and pseudo-first-order kinetics, respectively. Therefore, the adsorption of MB on PDA@ZIF-67 best fits to the pseudo-second order model. The results indicate that the rate-limiting phase of MB adsorption is the chemical adsorption phase of capacitance forces through the exchange or sharing of electrons between the adsorbent and the adsorbent. To better understand the mechanism of the adsorption process, adsorption isotherms were used. Therefore, Langmuir, Freundlich, and Temkin isotherms were selected as the three most important isotherm models in this study.

The adsorption process was studied at a constant temperature. Adsorption isotherms are mathematical relationships that show the amount of adsorbed molecules on the surface of the adsorbent. The adsorption properties of PDA@ZIF-67 toward MB at different concentrations of 2.5 to 20 mg/L was investigated.

A) Langmuir adsorption isotherm:

The Langmuir adsorption isotherm is one of the adsorption isotherms, which was developed by Irwin Langmuir in 1916 [9].

The Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}k_L} \quad \text{Equation 4}$$

Where, k_L denotes Langmuir constant (mg/L) and it means adsorption capacity at a pure level.

According to the Langmuir equation, the obtained values for K_L and q_{max} were 2.0833 L/mg, and 100 mg/g, respectively.

B) Freundlich adsorption isotherm

The Freundlich equation is as follows [23]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad \text{Equation 5}$$

where, K_f is the Freundlich constant (mg/g), which represents the approximate index of Freundlich surface adsorption, and $1/n$ is the factor of surface adsorption strength during the adsorption process. The value of K_f based on the Freundlich equation was found to be 56.053 mg/g.

C) Temkin adsorption isotherm

The equation of Temkin described in the literature [25] is as follows:

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e \quad \text{Equation 6}$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of MB (mg/L), R , A , T and b are the Temkin constants. According to the obtained parameters, the Langmuir, Freundlich and Temkin diagrams are drawn and

interpreted. According to the diagrams (Figure 14), it can be concluded that the adsorbent follows the Langmuir adsorption isotherm (with high values of R^2).

Table 3. The Langmuir, Freundlich and Temkin isotherms model constants and their correlation coefficients R^2 for the sorption of MB on PDA@ZIF-67.

Langmuir			Freundlich			Temkin		
Q_0 (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (g/L)	R^2	K_t (mg/g)	B	R^2
101.3772	0.2460	0.9328	5112.109	4.8247	0.9066	0.8665	13.3558	0.8029

Figure 14-(a-c) Langmuir, Freundlich, and Temkin isotherms for MB adsorption onto PDA@ZIF-67 (Initial concentration of 7.5ppm, 65 oC).

Thermodynamics

The thermodynamic parameters were taken into account to characterize the adsorption operation on account of the 1 mole transfer of a solute from an aqueous solution on the solid-liquid interface. The empirical outcomes for adsorption of MB dye on PDA@ZIF-67 catalyst were applied at five various temperatures (298, 308, 318, 328, and 338 K) to evaluate the thermodynamics parameters like Gibbs free energy (ΔG° , kJ/mol), entropy change (ΔS° , J/mol K), and enthalpy change (ΔH° , kJ/mol). The aforementioned parameters were calculated utilizing Van't Hoffs equation.

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Equation 8}$$

$$\Delta G^{\circ} = -RT \ln K_d$$

Equation 9

Table 3. Thermodynamic parameters of MB adsorption on PDA@ZIF-67

Temperature (K)	Thermodynamic parameters		
	$\Delta G^{\circ}_a(\text{KJ mol}^{-1})$	$\Delta H^{\circ}_a(\text{KJ mol}^{-1})$	$\Delta S^{\circ}_a(\text{J mol}^{-1} \text{ K}^{-1})$
298.15	-11.0567	30.6512	140.132
308.15	-12.6887		
318.15	-13.8791		
328.15	-15.2529		
338.15	-16.7788		

Where, R, T, and K_L refer to the gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), temperature (K), and Langmuir isotherm constant (L g^{-1}), respectively. By plotting $\log K_L$ against T^{-1} the values of ΔS° and ΔH° whereas ΔG° were determined utilizing the Equation 9. Table 5 reveals the obtained thermodynamic parameters.

$\Delta S^{\circ} > 0$ implies that the MB molecules adsorption is randomly increased at the solid/solution border of the adsorbent. Consequently, throughout the enhancement of MB adsorbed on the adsorbent surface, the amount of MB in solution decreases, and the freedom of solvent particles and PDA@ZIF-67 interface accelerates. Therefore, there is a strong affinity between the PDA@ZIF-67 particles and MB molecules [26].

Additionally, the endothermic reaction can be corroborated with the improving adsorption capacity correlated with the increase in temperature. $\Delta G^{\circ} < 0$ indicates that the process of adsorption is practical at RT and the increase of ΔG° values with growing temperature signifies which the adsorption process of MB on the PDA@ZIF-67 is more spontaneous at higher temperatures [38].

On the other hand, the ΔH° magnitude can provide an idea about the kind of adsorption. The evolved heat during physical adsorption is of the same magnitude order as the heats of condensation, for instance, $2.1 - 20.9 \text{ kJ mol}^{-1}$, whereas the heats of chemisorption generally fall between $80-200 \text{ kJ mol}^{-1}$ [38]. In this research, the ΔH° value was $30.6512 \text{ kJ mol}^{-1}$ that signifies that the adsorption of MB should be considered as chemisorption [39]. It has been observed that

the adsorbent capacity was mainly a function of the initial concentration of MB, and q_m generally increases with increasing initial concentration of MB [38].

Table 4. A comparison of the obtained results for PDA@ZIF-67 with other common adsorbents reported in the literature.

Adsorbent	q(mg/g)	Experimental Condition	Reference
PDA@ZIF-67	100	pH 2 CA=7.5mg/L Contact time=8min Temprature=65°C m=10mg	Present work
MOF1	102.4	pH 7 CA=10 Contact time=2h Temprature =25°C	[44]
Laboratory paper	24	pH Nature CA=40 Contact time=2h Adsorbent=0.25g Temprature=30°C	[14]
Fe ₃ O ₄ @MIL-100(Fe)	73.80	pH 9 CA=60mg/L Contact time=120min m=100mg Temprature=45°C	[43]
Magnetite@silica @pectin hybrid nanocomposite	85.18	pH 8 CA=100 Contact time=120min Temprature=25°C	[4]
Parthenium hysterphorus	39.7	pH 7 CA=0.4g/100mL Contact time=60min	[24]
CuO loaded Activated Carbon 1	10.54	pH 6 CA=50mg/L Contact time=4.5min Adsorbent=1.1g/L Temprature=room	[13]
Fly ash geopolymers powder	50.7	pH higher CA=75mg/L Contact time=2h Adsorbent=40mg Temprature=25°C	[15]
Fe-BDC MOF	8.65	pH 9 CA=5mg/L Contact time=24h Adsorbent=2.5g/L Temprature=323 K	[3]

4. Conclusion

In the present work, a new hybrid crystalline porous material was synthesized by doping ZIF-67 with PDA. The resultant composite was used as an adsorbent to remove MB dye from aqueous solution. The PDA@ZIF-67 exhibited an excellent adsorption performance in removal of MB dye. The optimal conditions for the maximum adsorption efficiency was found to be dye concentration of 7.5 ppm, pH 2, 10 mg of PDA@ZIF-67 dosage, at 338 K. The Langmuir isotherm with a maximum adsorption of MB mg/g was identified as a more favorable model to describe the adsorption process. Based on the results, it can be concluded that the PDA@ZIF-67 can be used as an effective adsorbent to remove MB from aqueous solutions.

Declarations: The authors of this manuscript declare no conflict of interest.

References

1. Albatrni H, Qiblawey H, El-Naas MH (2021) Comparative study between adsorption and membrane technologies for the removal of mercury. *Sep Purif Technol* 257:117833
2. Aleem M, Cao J, Li C et al. (2020) Coagulation-and adsorption-based environmental impact assessment and textile effluent treatment. *Water Air Soil Pollut* 231:1-8
3. Arora C, Soni S, Sahu S et al. (2019) Iron based metal organic framework for efficient removal of methylene blue dye from industrial waste. *J. Mol. Liq.* 284:343-352
4. Attallah OA, Al-Ghobashy MA, Nebsen M et al. (2016) Removal of cationic and anionic dyes from aqueous solution with magnetite/pectin and magnetite/silica/pectin hybrid nanocomposites: kinetic, isotherm and mechanism analysis. *RSC Adv* 6:11461-11480
5. Atun G, Ortaboy S, Tüzün E et al. (2021) A comparison of anionic and cationic dye removal efficiency of industrial bauxite waste red-mud. *J Dispers Sci Technol*:1-13
6. Batul R, Bhave M, J Mahon P et al. (2020) Polydopamine nanosphere with in-situ loaded gentamicin and its antimicrobial activity. *Molecules* 25:2090
7. Bioumy SA, Ahmed RA, Fekry AM (2020) Electrochemical corrosion behavior of graphene oxide/chitosan/silver nanoparticle composite coating on stainless steel utensils in aqueous media. *J Bio Tribocorros* 6:1-14
8. Chai J-B, Au P-I, Mubarak NM et al. (2020) Adsorption of heavy metal from industrial wastewater onto low-cost Malaysian kaolin clay-based adsorbent. *Environ Sci Pollut Res* 27:13949-13962
9. Chen L, Zhang X, Cheng X et al. (2020) The function of metal-organic frameworks in the application of MOF-based composites. *Nanoscale Adv* 2:2628-2647
10. Chen M, Shen Y, Xu L et al. (2020) Synthesis of a super-absorbent nanocomposite hydrogel based on vinyl hybrid silica nanospheres and its properties. *RSC Adv* 10:41022-41031

11. Choi Y, Lee J-H, Kim K et al. (2021) Identification, quantification, and prioritization of new emerging pollutants in domestic and industrial effluents, Korea: Application of LC-HRMS based suspect and non-target screening. *J Hazard Mater* 402:123706
12. Dahiya D, Nigam PS (2020) Waste management by biological approach employing natural substrates and microbial agents for the remediation of dyes' wastewater. *Appl Sci* 10:2958
13. Dashamiri S, Ghaedi M, Dashtian K et al. (2016) Ultrasonic enhancement of the simultaneous removal of quaternary toxic organic dyes by CuO nanoparticles loaded on activated carbon: Central composite design, kinetic and isotherm study. *Ultrason Sonochem* 31:546-557
14. Durairaj A, Sakthivel T, Ramanathan S et al. (2019) Conversion of laboratory paper waste into useful activated carbon: a potential supercapacitor material and a good adsorbent for organic pollutant and heavy metals. *Cellulose* 26:3313-3324
15. Ghaedi M, Hajjati S, Mahmudi Z et al. (2015) Modeling of competitive ultrasonic assisted removal of the dyes – Methylene blue and Safranin-O using Fe₃O₄ nanoparticles. *Chem Eng J* 268:28-37
16. Guillossou R, Le Roux J, Brosillon S et al. (2020) Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents. *Chemosphere* 245:125530
17. Hassanpour A, Zamanfar M, Ebrahimiasl S et al. (2021) Dopamine Drug Adsorption on the Aluminum Nitride Single-Wall Nanotube: Ab initio Study. *Arab J Sci Eng*:1-8
18. Hızal J, Yılmazoğlu M (2021) Montmorillonite clay composite for heavy metal removal from water. In: *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water*. Springer Sci. Rev. 93-112
19. Ho C-C, Ding S-J (2013) The pH-controlled nanoparticles size of polydopamine for anti-cancer drug delivery. *Journal of Materials Science: Mater Med* 24:2381-2390
20. Hooshyar SP, Panahi HA, Moniri E et al. (2021) Tailoring a new hyperbranched PEGylated dendrimer nano-polymer as a super-adsorbent for magnetic solid-phase extraction and determination of letrozole in biological and pharmaceutical samples. *J. Mol. Liq.* 338:116772
21. Huang L, Miao J, Shuai Q (2020) Carboxyl-functionalized magnetic porous organic polymers as efficient adsorbent for wastewater remediation. *J Taiwan Inst Chem Eng* 109:97-102
22. Khan A, Ali M, Ilyas A et al. (2018) ZIF-67 filled PDMS mixed matrix membranes for recovery of ethanol via pervaporation. *Sep Purif Technol* 206:50-58
23. Kuśmierk K, Świątkowski A, Skrzypczyńska K et al. (2021) Adsorptive and Electrochemical Properties of Carbon Nanotubes, Activated Carbon, and Graphene Oxide with Relatively Similar Specific Surface Area. *Materials* 14:496
24. Lata H, Garg VK, Gupta RK (2007) Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: An agricultural waste. *Dyes Pigm* 74:653-658
25. Lee HA, Park E, Lee H (2020) Polydopamine and its derivative surface chemistry in material science: a focused review for studies at KAIST. *Adv Mater* 32:1907505
26. Li M, Sun P, Wu Q et al. (2018) Core-shell magnetic metal-organic framework molecularly imprinted nanospheres for specific adsorption of tetrabromobisphenol A from water. *Environ Sci: Nano* 5:2651-2662
27. Li Y, Jin Z, Zhao T (2020) Performance of ZIF-67-Derived fold polyhedrons for enhanced photocatalytic hydrogen evolution. *J Chem Eng* 382:123051
28. Lü Y, Zhan W, He Y et al. (2014) MOF-templated synthesis of porous Co₃O₄ concave nanocubes with high specific surface area and their gas sensing properties. *ACS Appl Mater Interfaces* 6:4186-4195

29. Luo H, Gu C, Zheng W et al. (2015) Facile synthesis of novel size-controlled antibacterial hybrid spheres using silver nanoparticles loaded with poly-dopamine spheres. *Rsc Adv* 5:13470-13477
30. Mohammadinezhad A, Marandi GB, Farsadrooh M et al. (2018) Synthesis of poly(acrylamide-co-itaconic acid)/MWCNTs superabsorbent hydrogel nanocomposite by ultrasound-assisted technique: Swelling behavior and Pb (II) adsorption capacity. *Ultrason Sonochem* 49:1-12
31. Piai L, Blokland M, Van Der Wal A et al. (2020) Biodegradation and adsorption of micropollutants by biological activated carbon from a drinking water production plant. *J. Hazard. Mater* 388:122028
32. Qiu M, He C (2019) Efficient removal of heavy metal ions by forward osmosis membrane with a polydopamine modified zeolitic imidazolate framework incorporated selective layer. *J. Hazard. Mater.* 367:339-347
33. Sahu S, Pahi S, Tripathy S et al. (2020) Adsorption of methylene blue on chemically modified lychee seed biochar: Dynamic, equilibrium, and thermodynamic study. *J Mol Liq* 315:113743
34. Shahbakhsh M, Noroozifar M (2018) Poly (dopamine quinone-chromium (III) complex) microspheres as new modifier for simultaneous determination of phenolic compounds. *Biosens. Bioelectron.* 102:439-448
35. Shindhal T, Rakholiya P, Varjani S et al. (2021) A critical review on advances in the practices and perspectives for the treatment of dye industry wastewater. *Bioeng. Bugs* 12:70-87
36. Sohrabnezhad S, Pourahmad A, Karimi MF (2020) Magnetite-metal organic framework core@ shell for degradation of ampicillin antibiotic in aqueous solution. *J Solid State Chem* 288:121420
37. Tony M (2020) Zeolite-based adsorbent from alum sludge residue for textile wastewater treatment. *Int J Environ Sci Techno* 17:2485-2498
38. Utsev J, Iwar R, Ifyale K (2020) Adsorption of methylene blue from aqueous solution onto delonix regia pod activated carbon: Batch equilibrium isotherm, kinetic and thermodynamic studies *agricult. wastes* 4:18-19
39. Vieira WT, De Farias MB, Spaolonzi MP et al. (2020) Removal of endocrine disruptors in waters by adsorption, membrane filtration and biodegradation. A review. *Environ Chem Lett* 18:1113-1143
40. Vučković N, Nikodijević M, Đorđević D (2021) The study of direct dye sorption on flax fibers during dyeing. *Chem. Ind. Chem. Eng. Q* 27:255-263
41. Wang J, Wang S (2020) Reactive species in advanced oxidation processes: Formation, identification and reaction A. *J Chem Eng*:126158
42. Wang K, Wei T, Li Y et al. (2021) Flocculation-to-adsorption transition of novel salt-responsive polyelectrolyte for recycling of highly polluted saline textile effluents. *J Chem Eng* 413:127410
43. Yang Q, Zhao Q, Ren S et al. (2016) Fabrication of core-shell Fe₃O₄@MIL-100(Fe) magnetic microspheres for the removal of Cr(VI) in aqueous solution. *J. Solid State Chem* 244:25-30
44. Yi F-Y, Li J-P, Wu D et al. (2015) A Series of Multifunctional Metal–Organic Frameworks Showing Excellent Luminescent Sensing, Sensitization, and Adsorbent Abilities. *Chem – A Eur J* 21:11475-11482
45. Yi FY, Li JP, Wu D et al. (2015) A series of multifunctional metal–organic frameworks showing excellent luminescent sensing, sensitization, and adsorbent abilities. *Chem – A Eur J* 21:11475-11482
46. Yu F, Bai X, Liang M et al. (2021) Recent progress on metal-organic framework-derived porous carbon and its composite for pollutant adsorption from liquid phase. *Chem Eng J* 405:126960
47. Zhang M, Zhang Z, Peng Y et al. (2020) Novel cationic polymer modified magnetic chitosan beads for efficient adsorption of heavy metals and dyes over a wide pH range. *Int J Biol Macromol* 156:289-301