Lifting removal of cationic dye (methylene blue) from wastewater by improving Zr-MOFs via second metal Al coordination

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ABSTRACT: Metal organic frameworks (MOFs) are frequently used as adsorbents in adsorption processes to remove dyes from effluent produced by the textile industry. Today, dye contaminants have become an important environmental problem. One of these dyes is methylene blue (MB) and its removal from wastewater is a priority because it is persistent and non-degradable. MB is used in many industries although it has potential harmful effects on human and aquatic life and can be considered a hazardous chemical when in wastewater. The present study shows the potential applications for enhanced forms of UiO-66 MOFs, such as UiO-66, UiO-66-10%Al and UiO-66-30%Al. These forms were prepared to remove MB from wastewater using batch experiments. Characterisation of adsorbents were accomplished successfully using Fourier transform infrared, X-ray powder diffraction, Brunauer–Emmett–Teller surface area and thermogravimetric analysis techniques. To investigate equilibrium adsorptive behaviour, Langmuir and Freundlich isotherm models were tested against the experimental data. Based on linear regression correlation coefficient (R²), the Freundlich model described the equilibrium isotherm of MOF/MB better than the Langmuir model. Of all forms of UiO-66 MOF, UiO-66-10%Al had the maximum Langmuir adsorption capacity at 49.26 mg/g. A kinetics study examined pseudo first-order, pseudo second order and Elovich models to determine which could explain the sorption mechanism. While the pseudo second order and Elovich models showed a good fit with the experimental data, the correlation coefficient of the pseudo second-order model was the highest. These results indicate that adsorption of MB is controlled by a chemisorption mechanism. Further, intraparticle diffusion was utilised to describe the adsorption mechanism and determine the rate-limiting steps in the adsorption process.

Keywords: Metal Organic Frameworks (MOFs), dye, methylene blue, pollutants removal, adsorption

1. INTRODUCTION

Despite government regulations, ensuring environmental compliance with established terms of wastewater release and chemical handling is difficult [1]. Today, dye contaminants have become one of the most important environmental problems in the world. Effluent with organic dyes discarded into natural watercourses endanger living creatures and the environment because of their toxicity and carcinogenic effects [2]. In addition, dye content in water prevents sunlight penetration which decreases plant photosynthesis [1].

Significant amounts of dyes are employed in a wide range of industries involved in producing paper, textile, leather, pharmaceauticals, food, cosmetics, print products, iron-steel products, coke, petroleum, pesticides, paints, solvents, wood-preserving chemicals. Further, their manufacturing plants consume large volumes of water that in turn generate large volumes of wastewater [3]. Almost 100,000 dyes and pigments have been tabulated to exist, consisting of 7000 kinds of chemical structures, that are used to produce $7 \times 10^4$ tonnes per year worldwide [4-8]. The majority of these dyes are resistant to biodegradation and oxidation processes [9]. About 10–15% of the dyes is discharged into the effluent during the dyeing process [10, 11]. Recently, studies have reported that around 12% of synthetic dyes are wasted through colouring processes and operations [12]; 20% of lost dyes enter industrial wastewaters [13, 14].

Dyes can be divided into two main groups, anionic (acidic) and cationic (basic) colour dyes. Methylene blue (MB) is a basic dye that is a focus of this study. Although MB is used in some medical applications, it is also widely used in colouring paper, dyed cottons, wools, coating for paper stocks, etc. Though MB is not strongly hazardous, it has some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [15].
Environmental, it is essential to remove dyes from industrial wastewater because of their toxicity and high visibility [7, 16-18]. Consequently, there is a continuous urgent need to ensure the removal these pollutants from industrial effluent and to comply with government legislation [19]. Many techniques have been attempted to discolour industrial discharge that involve chemical, biological and physical removal methods; however, most are unsuccessful because of their limitations and disadvantages [20].

Adsorption is a well-known and favourite technique because of its feasibility, simplicity and efficiency in the removal of such contaminants [21]. Many adsorbents have been employed to treat industrial wastewater containing dye. They include activated carbon derived from different sources of raw materials [22-33], agricultural solid waste [34-47], biosorbents [17, 18, 48-60], zeolites [61-66], industrial solid wastes [15, 67-74], natural clay minerals [75-83], resins [84-87], metal oxides [88, 89], metal organic frameworks (MOFs) [2, 90-93].

Activated carbon from various sources has been the most investigated adsorbent in laboratories and most used by industries to remove basic dyes from their wastewaters [87, 94-97]. However, its cost has limited its commercial use as a sorbent. As a result, many studies have been undertaken in the last decade to identify a cost-effective sorbent [98].

MOF [99-106], or hybrid inorganic and organic framework [107], is a 21st-century material with tunable options, organic functionality, open metal sites in its skeleton, large-sized pores, high surface areas (1000 to 10,000 m²/g) as well as high thermal, water, chemical, architectural and mechanical stability [2, 108]. It is a class of ultra-high porous material constructed with secondary building units (SBUs) [109] and synthesised by reticular chemistry [110, 111] that connect the inorganic part with the metal ion to the organic part with polytopic carboxylate group to form vertices and linkers with strong bonds [112]. The variety of geometry, size and functionality of the constituents of MOFs has enabled scientists around the world to synthesise more than 84,185 MOF structures [102]. Their variety and multiplicity, as well as permanent porosity, make them favourable materials in many applications, such as CO₂ capture, hydrogen and methane storage, sensors, photocatalysis, drug delivery, catalysis applications and the adsorptive removal of contaminants from aqueous solutions [90, 112-117].

The objective of the present study is to describe the synthesis and characterisation of single-metal Zr-MOF (UiO-66) and bimetal Zr-MOFs (UiO-66-10%Al and UiO-66-30%Al), and examine their potential as sorbents to remove MB, a cationic basic dye, in wastewater. The kinetics and equilibrium of the adsorption process were fitted to kinetics models and equilibrium theoretical models. Further, the mechanism that limits the rate of sorption reaction was investigated using an intraparticle diffusion method to improve understanding of the dynamics in the adsorption process.

2. METHODOLOGY

2.1 Synthesis and activation

All chemicals were supplied by Sigma-Aldrich (Australia) without further purifications.

A scaled-up procedure of a previously reported method [59] of synthesising Zr-MOF was successfully undertaken, using a modified ratio of ZrCl₄:BDC:DMF (2.27 mmol ZrCl₄, 2.27 mmol 1,4-benzenedicarboxylic acid [BDC]). The abovementioned chemicals were mixed with continuous agitation with 405.38 mmol N, N-dimethylformamide (DMF) solvothermally. The resulting mixture was placed in an autoclave at 393 K for 1 d. The product Zr-MOF was filtered, dried and immersed in chloroform for 5 d. After activation by chloroform was completed, the solid was filtered and dried using vacuum and heated at 463 K for 48 h.

The following method was used to synthesise UiO-66-10%Al. Terephthalic acid (1.1 g, 98%; Sigma-Aldrich) and DMF (73 mL, 99%; Sigma-Aldrich) were mixed together and stirred until the acid dissolved. Within 10 min of the clear solution forming, ZrCl₄ (1.5 g; Sigma-Aldrich, 99%) was added to the solution with continued stirring for another 5 min. Al (NO₃)₃ 9H₂O (0.15 g) was then added, along with 2 mL of H₂O, to the mixture and stirred for another 15 min. The solution was transferred to a 125-mL Teflon-lined autoclave, which was tightly sealed and then placed in a preheated oven at 132 °C for 24 h. The white powder product of UiO-66-10% Al was collected using a centrifuge machine and washed in DMF three times. The resultant product was dried in an oven and activated by immersing it in absolute methanol (100%; Sigma-Aldrich) for 5 d. Before using the MOF as an adsorbent, it was filtered, dried and heated at 473 K overnight.

To synthesise UiO-66-30%Al, ZrCl₄ (1.5 g) was mixed with terephthalic acid (1.3 g) in DMF (60.2 mL). After mixing for 15 min, Al (NO₃)₃ 9H₂O (0.45 g) was added and then 5 mL of H₂O was added to the mixture. The solution was mixed for approximately 30 min. It was then moved to a 125-mL Teflon-lined autoclave, which was tightly sealed and then placed in a preheated oven at 157°C for 1 d. The white powder product of UiO-66-10% Al was collected using a centrifuge machine and washed in DMF three times. The resultant product was dried in an oven and activated by immersing in absolute methanol (100%; Sigma-Aldrich) for 5 d. Before using the MOF as an adsorbent, it was filtered, dried and heated in a vacuum at 473K overnight.

2.2 Characterisation

Thermogravimetric analysis (TGA) of the single-metal and bimetal Zr-MOFs was done using a TGA instrument (TGA/DSC1 STARe system; Mettler-Toledo). All MOF samples were placed in crucibles and transferred to the machine and heated at a rate of 5K/min until 1173K when the air gas flow rate was maintained at 10 mL/min.

The stability of the functional groups on the organic linkers were assessed using Fourier transform infrared spectroscopy (FTIR; Spectrum 100 FT-IR spectrometer, PerkinElmer). A scanning process was undertaken by an attenuated total reflectance technique to obtain the FTIR
spectra range 600 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

To check the integrity of the MOF structure, X-ray powder diffraction patterns were obtained using an X-ray diffractometer (D8 Advance, Bruker AXS) with Cu Ka radiation (\(\lambda = 1.5406\) Å), accelerating voltage 40 kV and current 40 mA.

\(N_2\) adsorption/desorption isotherms were performed using a Quantachrome instrument (Autosorb-I), and textural properties of the Zr-MOFs were determined, such as pore size, pore volume and surface area. All MOFs were prepared by heat and vacuum for 1 d before loading to the machine to determine their adsorption properties.

### 2.3 Adsorption Process

An aqueous stock solution of MO (1000 ppm) was prepared by dissolving MB (C\(_{16}\)H\(_{18}\)ClN\(_2\)S, molecular weight 319.85 g.mol\(^{-1}\); Sigma-Aldrich) in deionised water. Aqueous solutions with different concentrations of MB (5–100 ppm) were prepared by successive dilution of the stock solution with water, and MB concentrations were determined using absorbance at 668 nm wavelength of the solution after obtaining the UV spectra of the solution with a spectrophotometer (UV spectrophotometer). A calibration curve was obtained from spectra of the standard solutions (5–100 ppm). Prior to adsorption, the adsorbents were dried overnight in a vacuum at 373 K. Several glass containers were cleaned, dried and filled to 20 mL with MB of different concentrations ranging from 5 to 50 ppm. Following this, an exact amount of an MOF adsorbent (20 mg) was put in each glass container.

The dye solutions containing the adsorbents were mixed well by a magnetic stirrer and maintained for 5 min to 24 h at 298 K. The samples for analysis were collected by syringe filter at different sampling intervals. A UV spectrometer was used to investigate the dye content in the supernatant.

### 2.4 Adsorption Study

The adsorption mechanism and rate of diffusion were estimated using three kinetic models: pseudo second-order [119], pseudo first-order [120] and intraparticle diffusion models [121]. Adsorption behaviours were simulated using the Langmuir [122] and Freundlich [123] adsorption isotherms.

#### 2.4.1 Kinetic Study

Batch adsorption laboratory techniques were used to design the experiments. All practical kinetics experiments were conducted by preparing the specified initial concentrations (5–50 mg/L) and adding a predetermined dose of the adsorbent into a definite volume of MB solution at room temperature. Agitation was performed with a magnetic stirrer machine at 200 rpm to optimise mass transfer and contact with the interfacial area for a predetermined time interval. MB concentration was measured using the supernatant at each predetermined time interval using a UV spectroscopy machine.

The amount of MB adsorbed ontoUiO-66, UiO-66-10% Al and UiO-66-33% Al MOFs at any time was calculated using Equation 1 [124]. However, the percentage removal of MB was computed by Equation 2 [125].

\[
q_t = \frac{(C_0 - C_t)V}{m} 
\]

\[
R\% = \frac{(C_0 - C_t)}{C_0} \times 100 
\]

Where:
- \(q_t\) : the amount of MB adsorbed per unit weight of MOF at any time t (mg/g)
- \(C_0\) : initial concentration of the MB solution at time zero (mg/L)
- \(C_t\) : the concentration of MB solution at time t (mg/L)
- \(V\) : volume of the MB solution in the batch adsorption process (L)
- \(R\%\) : percentage removal of MB
- \(m\) : MOF mass used in the adsorption batch process (g).

- **Pseudo first-order model**
  The MOF removal of MB from simulated wastewater can be represented by a linear pseudo first-order model of adsorption [120, 126] expressed below:

\[
l n(q_e - q_t) = l n(q_e) - k_1t 
\]

Where:
- \(q_e\) : the amount of MB adsorbed per unit weight of MOF at equilibrium (mg/g)
- \(q_t\) : the amount of MB adsorbed per unit weight of MOF at any time t (mg/g)
- \(k_1\) : pseudo first-order rate constant (min\(^{-1}\))
- \(t\) : time (min).

The linear relationship between values of \(\ln(q_e - q_t)\) and t can be plotted as a straight line, from which \(q_e\) and \(k_1\) can be found easily from the intercept and slope, respectively.

- **Pseudo second-order model**
  The sorption kinetics of the MOF/MB system may also be described by a linearised form of the pseudo second-order model [119], based on adsorption equilibrium capacity expressed in the following form:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t 
\]

Where:
- \(q_e\) : the amount of MB adsorbed per unit weight of MOF at equilibrium (mg/g)
- \(q_t\) : the amount of MB adsorbed per unit weight of MOF at any time t (mg/g)
- \(k_2\) : pseudo second-order rate constant (g/mg min).

The values of \((t/q_t)\) are linearly correlated with t, and the plot of \((t/q_t)\) against t should be a straight line. The determination of \(q_e\) and \(k_2\) can be done from the slope and intercept, respectively.

- **Elovich kinetic model**
  The Elovich equation is generally used for chemisorption applications and can be written as follows:
Where:
\( q_t \): the amount of MB adsorbed per unit weight of MOF at any time \( t \) (mg/g)
\( \alpha \): a constant representing the initial rate of adsorption
\( \beta \): constant during any one experiment
\( t \): time (min).

It appears that the initial adsorption rate at the beginning of contact time is not controlled by exponential law because when \( q_t \) approaches zero, \( \frac{dq_t}{dt} \) equals \( \alpha \). Integrating Equation 5 by assuming \( q_t = 0 \) at \( t = 0 \), the result will be:

\[
q_t = \left( \frac{1}{\beta} \right) \ln(1 + \alpha \beta t)
\]
(6)

If \( \alpha \beta t > 1 \), the simple form of Equation 5.6 can be expressed as follows:

\[
q_t = \left( \frac{1}{\beta} \right) \ln(\alpha \beta) + \left( \frac{1}{\beta} \right) \ln(t)
\]
(7)

In a plot of the straight-line equation of \( q_t \) as a function of \( \ln(t) \), the slope and intercept will be \( (1/\beta) \) and \( (1/\beta) \ln(\alpha \beta) \), respectively. Equation 7 can facilitate the determination of the applicability of the Elovich kinetic equation on MOF/MB systems [128].

- **Intraparticle diffusion model**

  The intraparticle diffusion–based model is commonly used to test the mechanism of adsorption of pollutants onto a sorbent. This model is employed to identify the adsorption mechanism of MB onto MOF, and can be written as follows:

\[
q_t = k_{pt} t^{1/2} + C
\]
(8)

Where:
\( q_t \): the amount of MB adsorbed per unit weight of MOF at any time \( t \) (mg/g)
\( k_{pt} \): intraparticle diffusion rate constant (mg/g min\(^{0.5}\))
\( t \): time (min)
\( C \): intercept.

Based on this model, which is a linear relationship, the loading capacity is proportional to \( t^{1/2} \) as well as the intraparticle diffusion rate constant \( (k_{pt}) \); \( k_{pt} \) and \( C \) can be determined from the slope and intercept of the intraparticle diffusion equation plot, respectively.

**2.4.1 Equilibrium Study**

Equilibrium studies were also performed in the same experiments carried out for kinetics studies. Agitation was done using a magnetic stirrer machine at 200 rpm until the process reached equilibrium.

The amount of MB adsorbed onto UiO-66, UiO-66-10%Al and UiO-66-30%Al MOFs at equilibrium can be expressed by Equation (2)[129]:

\[
q_e = (C_0 - C_e) \frac{V}{m}
\]
(9)

Where:
\( q_e \): the amount of MB adsorbed per unit weight of MOF at equilibrium (mg/g)
\( C_0 \): initial concentration of MB solution at time zero (mg/L)
\( C_e \): concentration of MB solution at equilibrium (mg/L)
\( V \): volume of MB solution in batch adsorption process (L)
\( m \): MOF mass used in the adsorption batch process (g).

- **Isotherm models**

  Identifying an adsorption isotherm is essential for describing the interaction of the pollutant (MB) with the adsorbent (MOF), so that the adsorbent can be optimised [130]. The two common isotherms are the Langmuir [131] and the Freundlich [123] isotherms.

  - **The Langmuir models**

    A nonlinear form of the Langmuir isotherm model can be expressed as:

\[
q_e = \frac{q_m k_L C_e}{1 + k_L C_e}
\]
(10)

It is possible to linearise the Langmuir isotherm equation to give the following:

\[
\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{k_L q_m}
\]
(11)

Where:
\( q_m \): Langmuir maximum loading capacity (mg/g)
\( K_L \): Langmuir constant related to the energy of adsorption and affinity of binding sites (L/mg)
\( C_e \): the equilibrium concentration of adsorbate (mg/L)
\( q_e \): adsorption capacity at equilibrium (mg/g).

A plot of \( C_e/q_e \) versus \( C_e \) should obtain a linear relationship. Therefore, \( q_m \) and \( K_L \) can be determined from the slope and intercept of the plot.

The dimensionless constant separation factor \( R_L \) is an important characteristic of the Langmuir isotherm that can be represented by the following equation [96, 132-134]:

\[
R_L = \frac{1}{(1 + K_L C_0)}
\]
(12)

Where:
\( C_0 \): initial concentration of MB (mg/L)
\( K_L \): Langmuir constant (L/mg).

The value of \( R_L \) plays a very important role in the shape of the isotherm because it indicates the adsorption process is: unfavourable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favourable (\( 0 < R_L < 1 \)), irreversible (\( R_L = 0 \)).

- **The Freundlich models**

  The nonlinear model of the Freundlich isotherm [123] can be expressed as:

\[
q_e = k_F C_e^{1/n}
\]
(13)

The linear equation of the Freundlich isotherm can be expressed as [15, 135]:
\[ \ln (q_e) = \ln (k_f) + \frac{1}{n} \ln (C_e) \quad (14) \]

Where:
- \( k_f \): the calculated Freundlich equilibrium constant ([mg/g] [L/mg])\(^{1/n} \) as an indicator of adsorption capacity
- \( n \): a measure of the deviation from linearity of adsorption (g/L).

A plot of \( \ln (q_e) \) versus \( \ln (C_e) \) should obtain a linear relationship; therefore, \( n \) and \( k_f \) can be determined from the slope and intercept of the plot. If the value of \( n \) > 1, it is good indication that the adsorption process is favourable.

3. RESULTS AND DISCUSSION

3.1 Characterisation

As shown in Figure 1(a), the XRD pattern for the modified bimetal Zr-MOF (UiO-66-10%Al and UiO-66-30%Al), in contrast to the parent single-metal Zr-MOF (UiO-66) before and after use, verify the phase purity and structural integrity of the MOF samples. Therefore, they are good signs of successful synthesis and activation of MOFs with pores free of oxide contaminants. Furthermore, Figure 1(a) show also the XRD patterns of the same above-mentioned MOFs after use in adsorption process.

Figure 1(b) illustrates FTIR spectra of parent (UiO-66) and modified bimetal Zr-MOF (UiO-66-10%Al and UiO-66-30%Al) before and after use. According to FTIR spectra of the three Zr-MOFs (single-metal and bimetal samples) shown in Figure 1(b), the application of the same vibration bands resulted in a slight deviation in the position of some peaks for the bimetal samples, with broader peaks verifying a difference in the dipole between ground state and excited state of bimetal Zr-MOFs due to incorporation of the second metal centre [136, 137]. The extension of the vibration bands of bimetal MOFs was 1590 to 1525 cm\(^{-1} \); it was originally in the range 1615 to 1580 cm\(^{-1} \) because of C=O-C stretching in the aromatic ring of terephthalate salts [138]. In addition, the FTIR spectrum shows the stretching vibration of asymmetric COO\(^{-} \) and asymmetric COO\(^{-} \) in organic linkers at bands 1500 and 1390 cm\(^{-1} \). However, bands at 881, 812 and 785 cm\(^{-1} \) were assigned to Zr-O stretching. In addition, stretching vibration of C-H at 730 cm\(^{-1} \) was attributed to the out-of-plane bending of aromatic ring of UiO-66, in comparison with that at 744 cm\(^{-1} \) attributed to the spectrum of bimetal Zr-MOF [137, 139] and the stretching vibration of C-H at 1017 cm\(^{-1} \) to Zr-MOF.

Thermal stability of UiO-66, UiO66-10%Al and UiO66-30%Al was investigated using a TGA machine (TGA/DSC1 STArE system; Mettler-Toledo). The results of thermogravimetric analysis of all Zr-MOFs (single-metal and bimetal) are shown in Figure 1(c). They validate the thermal stability and structural robustness up to 725 K with a continuous mass loss of 15% and 25% for bimetal and single-metal MOFs, respectively. However, the variation in the weight loss of the samples is due to pre-treatment (dehydrated and hydrated) and solvent molecules in the pore interior of the material [140].

![Fig. 1. Characterisation of metal organic framework samples: (a) PXRD patterns, (b) FTIR spectra and (c) TGA profiles of pristine and modified UiO-66 samples.](image-url)
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Table 1 Textural properties of adsorbents based on N\textsubscript{2} adsorption/isotherms.

| Adsorbents       | Specific surface area (S\textsubscript{BET}) (m\textsuperscript{2} g\textsuperscript{-1}) | Pore volume (cc g\textsuperscript{-1}) | Pore diameter (nm) |
|------------------|---------------------------------|-------------------------------------|-------------------|
| UiO-66           | 1585.5                          | 0.82                                | 1.04              |
| UiO-66-10% Al    | 1145.953                       | 1.34                                | 2.33              |
| UiO-66-30% Al    | 769.011                         | 0.39                                | 1.01              |

adsorption at approximate relative pressure equal to 0.999, indicating improving mesopore and macropore size. Based on the N\textsubscript{2} adsorption--desorption isotherms, the values for the surface area, pore volume and pore size (textural properties) of Zr-MOF were calculated and listed in Table 1. These values indicate decreases in the specific surface area ($S_{\text{BET}}$) with increases in the percentage of the second metal. That is, the $S_{\text{BET}}$ gradually decreased from 1585.5 m\textsuperscript{2} g\textsuperscript{-1} in UiO-66 to become 1145.953 m\textsuperscript{2} g\textsuperscript{-1} in UiO-66-10% Al, and reached 769.011 m\textsuperscript{2} g\textsuperscript{-1} in UiO-66-30% Al.

In contrast, the pore volume and diameter were enlarged in UiO-66-10% Al, at 1.34 cc g\textsuperscript{-1} and 2.33 nm, respectively. The reason for such augmentation is attributable to the replacement of methanol molecules by the second metal in the first activation process involving solvent exchange and discarding it in the second activation process by heating and vacuum.

3.2 Kinetic Studies

Studies of kinetics are an essential part of a sorption process to enable the researchers to determine the rate and mechanism of adsorption [141]. To investigate the adsorption mechanism, including the mass transfer and chemical reaction [2], experimental data were examined using pseudo first-order, pseudo second-order and Elovich models. All the information and parameters relating to mechanism of adsorption can be obtained via adsorption kinetics, which are vital in treatment of aqueous effluent [142].

The adsorption process of the three solid /liquid (MOF/MB) systems were examined using pseudo first-order, pseudo second order [143-145] and Elovich models [128, 141, 146]. The key feature of these equations is the ease with which adsorption properties (e.g., adsorption capacity, rate constant) can be assigned, and the initial

Fig. 2. N\textsubscript{2} adsorption/desorption isotherm of UiO-66 (a), N\textsubscript{2} adsorption/desorption isotherms of UiO-66-Al samples (b), micro pore distribution (c) and mesopore distribution (d) of UiO-66, UiO-66-10% Al and UiO-66-30% Al.
adsorption rate can be easily found from the linear equations of these models without previous knowledge of any parameter.

As adsorption processes involve chemisorption, they can be described by pseudo-second-order rate expression [143-145] and Elovich model [128, 141, 146]. Moreover, the pseudo-second-order model showed the highest linear correlation coefficient ($R^2$) and therefore, the highest agreement with the kinetics experimental data than did the Elovich model, for all MB/Zr-MOF systems.

The pseudo-first-order equation did not fit well for the entire range of reactions in all MOF/MB systems. In general, the equation was only applicable to the first 20 or 30 min of the adsorption interaction process this is consistent with the reported literature [147-160]. Consequently, the MOF/MB systems did not fit the pseudo-first-order equation for the whole range of contact time.

Kinetics adsorption studies are crucial indicators of a criteria of adsorbent efficiency (i.e., the rate of adsorption) and provide a clear picture of the mechanism of adsorption. Figure 3 below explains the variation in the amount of adsorbate on adsorbent ($q_t$) as a function of contact time. The rate of MB adsorption was high at the beginning of the sorption process before slowing as the reaction progressed until reaching an equilibrium saturation. That the rate of adsorption was faster at the start may be due to the accessibility of adsorptive sites of the MOFs [161, 162]. The adsorption of MB by UiO-66-10%Al took less time than by the other two MOFs, which indicate that the rate of dye sorption by UiO-66-10%Al was the quickest among the three MOFs examined.

Figure 3 also illustrates the dependency of MB uptake on contact time given different initial concentrations of MB. It confirms that higher initial concentrations of MB lead to increases in adsorption capacity for MB dye. Consequently, MB uptake per unit mass of MOF, or adsorption density, also increases. Specifically, higher initial concentrations of MB may reduce accessibility of adsorption sites, which can increase the amount of adsorbate on adsorbent [163]. The increase in adsorption density or capacity with higher initial concentrations of MB is generally due to the availability of unsaturated adsorption sites on the surface of MOFs during the sorption batch process [164, 165].

To analyse the adsorption kinetics of the dye/MOF system, pseudo first-order [120], pseudo second-order [166] and Elovich equations [127] were examined. Tables 2 and 3 present the resultant values of the parameters fitted to the pseudo second order and Elovich models, respectively.

There pseudo-first-order equation was not a good fit for the entire range of reactions in all MOF/MB systems; however, it can be generally applied to the first 20 or 30 min of the adsorption interaction process. This is consistent with the reported literature [147]. Consequently, the MOF/MB systems did not obey the equation during the whole of the contact time through the equation was mostly valid for the initial stage of the sorption process. In addition, the experimental $q_t$ values, which can be obtained from the intercept of the linear relationship between ln($q_t$ - $q_e$) and time, did not agree with the computed values. These results are proof that the adsorption of MB onto Zr-MOFs (single-metal and bimetal) is not based on first-order kinetics [94].

The obtained experimental data were further fitted to the pseudo second-order equation. The values for $q_e$ and $k_2$ were obtained from the slope and intercept of the linear plots of ($t$/($q_t$ - $q_e$)) versus t, respectively, and listed in Table 2. Figure 3(b), (d) and (f) show that MB uptake by Zr-MOF increased with increasing in contact time for each of the different initial MB concentrations, as well as at higher initial MB concentrations. The correlation coefficients of the plots showed that the pseudo-second-order equation had the best fit with the experimental data, with the range of $R^2$ values (0.9953–0.9999) listed in Table 2. These results verify the agreement of this kinetic model and the second-order behaviour of the adsorption process of MB by Zr-MOFs. Based on the linear regression correlation coefficient values ($R^2$), the nature of the sorption process over the whole range of contact time for all solid/liquid systems in this study can be considered a chemisorption mechanism, as the rate-controlling step related to valence forces of sharing or exchanging electrons between Zr-MOFs and MB.

The results of the correlational analysis of the amount of dye adsorbed (mg/g) against contact time for four initial MB concentrations (5, 15, 30 and 50 ppm) are shown in Figure 3. The results indicate that the amount of dye loading, $q_e$ (mg/g), increased with contact time for each concentration separately.

The Elovich model can be applied to the chemisorption reaction; it is a model reasonably employed in chemisorption processes and to a wide range of slow adsorption processes. Specifically, this model may facilitate those systems for which the adsorption surface is heterogeneous.

Experimental data of MOF/MB batch adsorption systems were incorrectly described using the pseudo first-order model. Further, these systems can be represented by a combination of two or three sequential and instantaneous pseudo first-order reactions. The basic form of the Elovich equation described the experimental data well; however, the Elovich equation can be easily fitted to the experimental data using one straight line to describe the whole progress of contact time [128].

The experimental data were also examined with respect to the Elovich model, with the values of all parameters derived and the slope and intercept of the linear relationship indicating the constants $\alpha$ and $\beta$, respectively. In addition, these constants can be comparison parameters of reaction rates of MB adsorption in the various kinds of Zr-MOF; the values of $\alpha$ and $\beta$, derived from the linear plots of $q_t$ versus ln ($t$), are listed in Table 3. According to the Elovich model, the increase in $\alpha$ and/or the decrease in $\beta$ should increase the adsorption rate, which in turn increases MB uptake. Therefore, the relative loading of the three Zr-MOFs are UiO-66-10%Al > UiO-66-30%Al > UiO-66 [128].

Figure 3(a), (c) and (e) illustrate the changes in Zr-MOFs capacities at different initial MB concentrations with time. Loading capacities are increased with increasing contact time at each initial concentration, and with higher initial MB concentrations. Based on the values of the correlation coefficient ($R^2$) and the fact that higher $R^2$ values reflect better bit with the adsorption kinetics model, the best
fit for the experimental data was exhibited by the Elovich equation model for all MB/MOF systems (single-metal and bimetal). The range of R² values (0.9242–0.9986) is listed in Table 3. These results indicate and emphasise that all the investigated sorption systems obey chemisorption kinetics.

Table 2. Calculated kinetics constant (k₂) and correlation coefficient (R²) of the pseudo second-order model for Cᵰ = 5, 15, 30 and 50 mg/L.

| Adsorbent       | Adsorbate | Pseudo second-order kinetics constant k₂ (g/[mg.min]) | 5 ppm | 15 ppm | 30 ppm | 50 ppm |
|-----------------|-----------|------------------------------------------------------|-------|-------|-------|-------|
|                 |           | k₂        | R²   | k₂    | R²   | k₂    | R²   |
| UiO-66          | MB        | 0.01050   | 0.9989 | 0.00546 | 0.9992 | 0.00273 | 0.9992 | 0.00147 | 0.9990 |
| UiO-66-10% Al   | MB        | 1.34913   | 0.9999 | 0.01560 | 0.9997 | 0.00653 | 0.9995 | 0.00158 | 0.9953 |
| UiO-66-30% Al   | MB        | 0.00520   | 0.9977 | 0.00212 | 0.9984 | 0.00060 | 0.9975 | 0.00074 | 0.9990 |

Fig. 3. Fitting of experimental data using Elovich and second-order kinetics models of MB adsorption MB onto UiO-66 (a, b), UiO-66-10%Al (c, d) and UiO-66-30%Al (e, f).
3.3 Intraparticle diffusion studies

In addition, the intraparticle diffusion model suggested by Weber and Morris [121] was utilised to recognise the diffusion mechanism. Based on this model, the loading q against the square root of the contact time varies almost proportionally. Further, intraparticle diffusion models are vital to identifying the steps involved in the adsorption process to facilitate understanding of the adsorption mechanism [167].

![Intraparticle diffusion studies](image-url)

**Table 3** Calculated kinetics constants ($\alpha$ and $\beta$) and correlation coefficient ($R^2$) of Elovich model for $C_i = 5, 15, 30$ and $50$ mg/L.

| Adsorbent       | Adsorbate | $\alpha$ | $\beta$ | $R^2$ | $R^2$ | $R^2$ |
|-----------------|-----------|----------|---------|-------|-------|-------|
| MB              | 1.02294   | 1.9857   | 0.9903  | 0.9738| 0.9896| 0.9884|
| MB              | 1.02294   | 1.9857   | 0.9903  | 0.9738| 0.9896| 0.9884|
| MB              | 1.02294   | 1.9857   | 0.9903  | 0.9738| 0.9896| 0.9884|
| MB              | 1.02294   | 1.9857   | 0.9903  | 0.9738| 0.9896| 0.9884|

**Fig. 4.** Fitting of experimental data using intraparticle diffusion models of MB adsorption onto UiO-66 (a), UiO-66-10%Al (b) and UiO-66-30%Al (c).
The lack of descriptions of the adsorption mechanism and rate-controlling step of the adsorption process are some of the limitations of the pseudo first-order, pseudo second order and Elovich kinetic models. In response to these limitations, Weber and Morris created the intraparticle diffusion model [169]. The migration of the pollutant (MB) from bulk phase to the surface of the sorbent (Zr-MOFs) can be either by film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one of these steps [169].

Figure 4 plots the q against $t^{1/2}$ rather than t, for the various initial MB concentrations. Linear variations in uptake with $t^{1/2}$ is gained for a certain initial fraction of the reaction. The straight-line plot of $q_t$ versus $t^{1/2}$ may provide the values of the intraparticle diffusion rate constant $k_p$, $k_c$ and C can be found from the slope and intercept of the model, respectively. Table 4 lists these values as well as the correlation coefficients ($R^2$) for the initial MB concentrations 5, 15, 30 and 50 mg/L. The focus of the intraparticle diffusion model is on the second linear portion of the plot, in which the slope characterises the rate constant ($k_p$) while the intercept (C) is related to the thickness of the boundary layer [15].

Figure 4 illustrates the three stages of the adsorption mechanism, which are represented by the three linear relationships. The first part of the plot is inclined sharply, indicating rapid sorption or external surface adsorption. The second part represents the rate-controlling step which is intraparticle diffusion, the slowest stage of adsorption [170]. The last part is the equilibrium where the processes of adsorption of MB onto Zr-MOFs reach a plateau because either the active adsorptive sites on MOFs have been occupied or the concentration of MB in the solution is extremely low [95]. Specifically, Figure 4 shows that the second straight line does not pass through the origin or initial point of adsorption because of variations in mass-transfer rate between the saturation and equilibrium steps of sorption [171-174]. In addition, this kind of deviation from the origin is proof that pore diffusion is not the only rate-limiting factor [175].

### 3.4 Equilibrium studies

A set of batch experiments was conducted with various initial MB concentrations: 5, 15, 30 and 50 mg/L. The one factor allowed us to vary concentrations of MB while maintaining other process factors like MOF dose, stirrer speed, volume of the solution and temperature unchanged. Data from the equilibrium experiments were investigated using Langmuir [131] and Freundlich [123] isotherms.

The assumption of the Langmuir isotherm theory is described as monolayer coverage of adsorbate (MB) onto a homogenous absorbent (Zr-MOFs) surface [131]. Hence, its basic assumption is that sorption takes place at specific homogeneous sites on the adsorbent. As soon as an adsorbent site is occupied by an MB molecule, no additional adsorption can occur at that site again.

The equilibrium data were examined using a Langmuir model. The values of the parameters and constants, together with the $R^2$ values, were obtained from the slope and intercept of the linear plot and listed in Table 5. Figure 5(a), (b) and (c) illustrate the experimental equilibrium data and the predicted theoretical Langmuir isotherm for the adsorption process of MB onto Zr-MOF (single-metal and bimetal).

The fundamental characteristics of the Langmuir model can be expressed in terms of a dimensionless constant

| Adsorbent  | Initial concentration of MB solution (mg L$^{-1}$) | $k_p$ (mg g$^{-1}$ min$^{-1/2}$) | C (mg g$^{-1}$) | $R^2$  |
|------------|--------------------------------------------------|---------------------------------|----------------|--------|
| UiO-66     | 5                                                | 0.0991                          | 0.5017         | 0.9999 |
|            | 15                                               | 0.22                            | 2.1455         | 0.9918 |
|            | 30                                               | 0.3955                          | 3.5763         | 0.9884 |
|            | 50                                               | 0.638                           | 3.8144         | 0.9959 |
| UiO-66-10%Al | 5                                                | 0.4314                          | 3.8489         | 0.9850 |
|            | 15                                               | 0.5717                          | 7.9333         | 0.9552 |
|            | 30                                               | 1.011                           | 15.226         | 0.9797 |
|            | 50                                               | 1.1428                          | 24.123         | 0.9720 |
| UiO-66-30%Al | 5                                                | 0.2536                          | 1.0889         | 0.9994 |
|            | 15                                               | 0.2958                          | 5.8863         | 0.9947 |
|            | 30                                               | 0.4446                          | 7.9245         | 0.9901 |
|            | 50                                               | 0.4402                          | 15.395         | 0.9775 |

Table 4 Calculated kinetics constant ($k_p$), C and correlation coefficient ($R^2$) for $C_i = 5,15,30$ and 50 ppm.
The separation factor, $R_L$, or Equation 12 [133]. The value of $R_L$ is an indication of the shape of the isotherm. Basically, the $R_L$ value determines the favourability of the adsorption process, which can be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The equilibrium analysis revealed that the $R_L$ values were between 0 and 1, indicating a favourable adsorption process for all MB/Zr-MOF (single-metal and bimetal) systems.

The Freundlich model [123] is an empirical equation that assumes the adsorption process can occur on heterogeneous surfaces and that the adsorption capacity depends on the concentration of MB. According to Equation 13, equilibrium adsorption properties such as $K_F$ and $(1/n)$ are rough indicators of the adsorption capacity and the adsorption intensity, respectively. The favourability of the adsorption process can be determined from the magnitude of the exponent $(1/n)$; the criterion for a favourable adsorption is that the values of $n$ must be greater than one [176].

The equilibrium data were further tested by the Freundlich isotherm model. Freundlich isotherm constants and correlation coefficient ($R^2$) values are tabulated in Table 5. As shown in Table 5, the correlation coefficient of the Freundlich isotherm for all MB/MOF systems were higher than those based on the Langmuir model, proving strong linearity. The analysis verified that the values of $n$ for all systems were greater than one, as tabulated in Table 5. Such a result is solid confirmation of favourable adsorption and easy loading of MB onto Zr-MOFs from aqueous solutions [177].

The maximum Langmuir adsorption capacity was exhibited by UiO-66-10%Al, with $q_m$ of 49.26 mg/g. Furthermore, the comparative adsorption capacity of Zr-MOFs for MB in this study, relative to that of other adsorbents reported in the literature, is provided in Table 6.

### Table 5 Calculated equilibrium constants ($k_L$, $k_F$, $q_m$, $n$ and correlation coefficient ($R^2$)) of MB adsorption onto UiO-66, UiO-66-10%Al and UiO-66-30%Al for $C_i = 5, 15, 30$ and 50 mg/L.

| Adsorbent  | Adsorption isotherm model | Parameter      | Value (mg/g) | $R^2$ |
|------------|----------------------------|----------------|--------------|-------|
| UiO-66     | Langmuir                   | $q_m$          | 14.52        | 0.9889|
|            |                             | $K_L$ (L/mg)   | 0.02447      |       |
|            | Freundlich                 | $K_F$ ([mg/g] [L/mg]^{1/n}) | 0.98157 | 0.9979|
|            |                             | $n$ (g/L)      | 1.2918       |       |
| UiO-66-10%Al| Langmuir                   | $q_m$          | 49.26        | 0.9396|
|            |                             | $K_L$ (L/mg)   | 29           |       |
|            | Freundlich                 | $K_F$ ([mg/g] [L/mg]^{1/n}) | 53.53 | 0.9711|
|            |                             | $n$ (g/L)      | 4.05         |       |
| UiO-66-30%Al| Langmuir                   | $q_m$          | 27.85        | 0.9777|
|            |                             | $K_L$ (L/mg)   | 1.10         |       |
|            | Freundlich                 | $K_F$ ([mg/g] [L/mg]^{1/n}) | 16.71 | 0.9888|
|            |                             | $n$ (g/L)      | 7.52         |       |

### Table 6 Comparison of monolayer equilibrium capacity for methylene blue onto different sorbents.

| Adsorbent            | Condition | $q_m$ (mg/g) | Reference |
|----------------------|-----------|--------------|-----------|
| UiO-66-10%Al         | Normal    | 49.26        | This study|
| UiO-66-30%Al         | Normal    | 27.85        | This study|
| UiO-66               | Normal    | 14.52        | This study|
| Tobacco stem ash     | Normal    | 35.70        | [185]     |
| Oak sawdust          | Normal    | 29.94        | [187]     |
| ZnCl$_2$ activated POME sludge | Normal    | 22.40        | [189]     |
| Salvadora persica stem ash | Normal    | 22.78        | [190]     |
| Activated fly-ash    | Normal    | 14.28        | [192]     |
| Fly-ash A            | Normal    | 6.0          | [72]      |
| Coir pith carbon     | Normal    | 5.87         | [194]     |
| Neem sawdust         | Normal    | 3.62         | [195]     |
The most efficient adsorbent among the three Zr-MOFs was UiO-66-10%Al, with the largest pore volume (1.34 cc·g⁻¹) and pore diameter (2.33 nm), verifying that the addition of up to 10% Al enhanced the textural properties of the prototype Zr-MOF. For all MB/MOF systems, high initial concentrations of MB were found to facilitate adsorption capacity.

It can be concluded that the pseudo first-order model does not fit the experimental data well. While it can be generally applied to the initial period of the first step of the adsorption consistent with reports of most sorption studies in the literature the applicability of pseudo first-order mechanisms are restricted to a limited fraction of the beginning of the contact time [147]. The Elovich and pseudo second-order models showed the highest correlation in all MOF/MB systems studied over a longer period of adsorption. Besides, adsorption kinetics obeyed the pseudo second order kinetics model nicely, based on the fact that the highest correlation coefficients (R²) were achieved with this model.

Equilibrium data were tested using the Langmuir and Freundlich models, and were found to be best defined by the Freundlich isotherm. The maximum adsorption capacity of the most efficient adsorbent was 49.26 mg/g for UiO-66-10%Al. This performance was compared with that of other porous adsorbents in previous studies.

The gained parameters from this study support the design and lay the foundations for establishing a continuous treatment process that removes MB from wastewater.

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