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Iron based metal organic framework for efficient removal of methylene blue dye from industrial waste

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ABSTRACT

The present investigation assesses the applicability of Fe-BDC metal organic framework for the removal of the toxic dye methylene blue from industrial waste. The adsorption characteristics and dye removal efficiency of Fe-BDC MOF has been determined by investigating factors such as effect of contact time, concentration of the dye, amount of adsorbents, and temperature. Upto 94.74% dye removal was attained by increasing the dose of adsorbent and temperature. Maximum 94.74% dye removal was achieved after 24 h, on adding 25 mg of Fe-BDC MOF to dye solution of MB having concentration 5 mg/L. Langmuir, Freundlich and Tempkin, isotherm models have been used to evaluate the ongoing adsorption. Freundlich adsorption isotherm was found to be best fitted for the adsorption process. On the basis of pseudo-first-order, pseudo-second-order and intra particle diffusion kinetic equations, different kinetic parameters have been obtained. Pseudo second order kinetic model with rate constant (k_2) 4.9×10^{-2} g/mg·min, is found to be best fitted for adsorption of methylene blue on Fe-BDC MOF indicating that removal of dye takes place dominantly through chemisorption process.

1. Introduction

Several industries such as paper, textiles, plastic, cosmetics, printing etc. use chemical processes involving synthetic dyes which are often thrown out as untreated waste and get mixed with water resources [1]. Synthetic dyes have severe effects on environment as well as living beings. Many dyes are toxic and carcinogenic in nature [2,3]. Along with these harmful properties most dyes are inert and non-biodegradable [4]. It is therefore extremely important to remove dyes from effluents before discharging into natural bodies. A variety of materials such as coal, wood, rice husk, fly ash, activated carbon, cotton waste, clay and other porous materials were reported as adsorbent for the removal of dye from its aqueous solutions [5–9]. Metal organic frameworks (MOFs) can be potential agent for the removal of organic dyes from industrial effluents due to their adsorptive properties and high surface area. Metal-organic frameworks (MOFs) are crystalline materials composed of metal ions or clusters as nodes and organic ligands as linker. The pore size, shape and composition of MOF's can be controlled. These interesting materials have potential applications in gas storage, separation, drug delivery, catalysis and sensors due to their tuneable pore size, shape and composition of the material [1,4,10]. Some MOFs such as Ti-MIL-125 [11], Zn-MOF [12], Cr-MIL-101 [13], Fe-MOF-235 [14] have also been reported for the adsorptive removal of various dyes.

Two techniques, based on adsorption methodology, i.e. batch or column, are used to remove pollutants from water. The batch technique is a simple technique and it provides a simple way to elucidate the parameters influencing adsorption process [15–17]. Column technique is helpful in deciding the amount of adsorbent required for removal of pollutants from wastewater. In column technique the adsorbent is constantly in contact with spanking fresh solution. Columns have been reported to have better removal efficiency over batch in some cases [18,19]. In present work, capacity of batch process is found to be higher in comparison to column.

In the present work we have synthesised iron – benzene dicarboxilic acid MOF (Fe-BDC MOF) and used this material for the removal of methylene blue dye. Methylene blue is a heterocyclic aromatic compound containing sulphur used in textile industries for dyeing various types of fabric and materials. This cationic dye causes haemolytic anaemia, hypertension, skin staining, precordial pain and injection site necrosis [20].

Abbreviations: MOF, metal organic framework; BDC, benzene dicarboxylic acid/terephthalic acid; MB, methylene blue; PXRD, powder X-ray diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; DMF, dimethyl formamide; DMSO, dimethyl sulphoxide; TEA, triethyl amine.

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2. Experimental section

2.1. Materials

All reagents and chemicals for synthesis and analysis are commercially available and used as received. Methylene blue (MB) is a sulphur-containing heterocyclic aromatic dye used in textile industries for dyeing cotton, silk and wool [20]. The crystalline structure was proved by powder X-ray diffraction (PXRD), on a Rigaku smartlab diffractometer with Cu Kα radiation (λ = 1.5406 Å). A scan speed of 8° min^{-1} was applied to record the pattern in the 2θ range of 5–90°. UV–vis spectra were recorded on a Shimadzu UV 1800 spectrophotometer using 10 mm path length quartz cuvette. FT-IR spectrum of MOF powder was recorded using IR Affinity FTIR analyser. For SEM imaging of the MOF before and after adsorption, the Merlin VP Compact (Carl ZEISS Germany make) with air lock chamber was used. To determine the crystal morphology transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2100F microscope at 200 kV operational mode. TEM samples were prepared by drop-casting a dilute solution in DMSO (0.5 mg/mL) on a carbon coated Cu-grid and by drying this at 50 °C for 12 h in vacuum oven. Surface area and pore volume of the adsorbent Fe-BDC MOF were determined using BET method (Sorptomatic 1990) after degassing at 110 °C under vacuum, using nitrogen adsorption at −196 °C and desorption while allowing the temperature to rise to ambient.

2.2. Synthesis of Fe-BDC

The MOF Fe-BDC was prepared by mixing Ferric nitrate nonahydrate (Merk, 4 mmol) and Terephthalic acid (BDC) (Lobachem, 2 mmol) in 40 mL DMF (Lobachem). To this solution 2 ml TEA (triethyl amine) (Lobachem) was added and the solution was stirred for 18 h in ambient condition. The obtained product was centrifuged, washed several times with pure DMF and dried under air atmosphere.

2.3. Dye removal study

Studies on removal of dye were carried out spectrophotometrically. All the experiments of MB dye removal by Fe-BDC MOF were carried out in batch conditions. Effect of various parameters such as contact time, temperature, adsorbent dose and initial concentration of dye was studied. Initially, the stock solution of methylene blue dye (100 mg/L or 100 ppm) was prepared by dissolving 10 mg of MB dye (AR grade, Merk) in distilled water and then making the volume upto 100 mL. All other subsequent solutions were prepared by diluting the stock solution. Absorption spectra of the solutions having different concentrations of MB dye were recorded. A linear relationship was observed between concentration of dye solution and absorbance. 5 mg of MOF (adsorbent dose) was added to a 10 mL solution of methylene blue dye and after adsorption the remaining dye concentrations were estimated by measuring absorbance at the λ_{max} = 663 nm. The removal efficiency (%) of MOF and dye uptake capacity, i.e. amount of dye (in mg) adsorbed on the surface per gram of MOF (Q_e) of adsorbent were calculated according to the following equations.

$$\text{Removal efficiency}(\%) = (C_0 - C_e) \times \frac{100}{C_0} \quad (1)$$

$$\text{Uptake capacity } Q_e(\text{mg/g}) = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

Here, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of dye solution, V (L) is the volume of dye solution and m (g) is the weight of MOF.

Effect of contact time, initial dye concentration, adsorbent dose, temperature and pH was studied by varying these parameters. In order to evaluate the effect of contact time, 5 mg of Fe-BDC MOF was added to per 10 mL methylene blue dye solution having concentration 1 ppm to 5 ppm. Concentration and absorbance of remaining dye was recorded at different time intervals. The equilibrium time, time required to achieve adsorption equilibrium, was found to be about 24 h. Percent dye adsorbed was estimated with time keeping other parameters fixed.

The effect of initial dye concentration was studied by using solutions of MB dye with different concentrations (1 ppm to 5 ppm). 5 mg of Fe-BDC MOF is added in each of these solutions.

To study the effect of sorbent dose on adsorption 5–25 mg of Fe-MOF were added to 5 ppm solution of methylene blue dye.

Effect of temperature on dye removal was studied at various temperatures viz. 30 °C, 35 °C, 40 °C, 45 °C and 50 °C for contact time of 6 h. For these studies, 5 mg of adsorbent was added to each 10 mL of dye solutions having varying concentration in the range of 1 ppm to 5 ppm.

2.4. Column study

A glass column having 18 cm length and 1 cm internal diameter was packed with 0.25 g of Fe-BDC MOF over a support of cotton wool, to perform the column operation. The length and cross section area of column bed was 0.3 cm and 0.8 cm^2, respectively. The MB dye solution of known concentration was filled in the column and allowed to pass downwards under the gravity at a flow rate of 1.3 mL/min. Aliquots of 6.5 mL effluent solutions were collected at regular time interval of 5 min and analysed spectrophotometrically for dye content. The column operations were stopped after about 80% exhaustion as the column was choked.

The breakthrough curve [21] is plotted in terms of C_t/C_0 versus time, where C_t is the concentration of effluent at time t and C_0 is the initial concentration influent dye solution. The volume of effluent, V_{ef} can be calculated by using the following formula.

$$V_{ef} = vt \quad (3)$$

where t (min) is the flow time and v (mL/min) is the flow rate.

Amount of dye adsorbed at time t, Q_{total} (mg) can be represented by area under the breakthrough curve, which can be determined by the integration (calculated using software OriginPro 8).

$$Q_{total} = v \int_{t=0}^{t=t} (C_0 - C_t)dt \quad (4)$$

The total amount of dye (m_{total}) sent to the column at time t can be calculated by:

$$m_{total} = C_0 vt \quad (5)$$

The dye removal R (%) can be calculated as:

$$R = \frac{Q_{total}}{m_{total}} \text{ X } 100 \quad (6)$$

The adsorption capacity of the adsorbent q_t (mg/g) at time t can be obtained by the use of following equation (calculated using software OriginPro 8).

$$q_t = \frac{v \int_{t=0}^{t=t} (C_0 - C_t)dt}{m} \quad (7)$$

where m is the amount of adsorbent used in column.

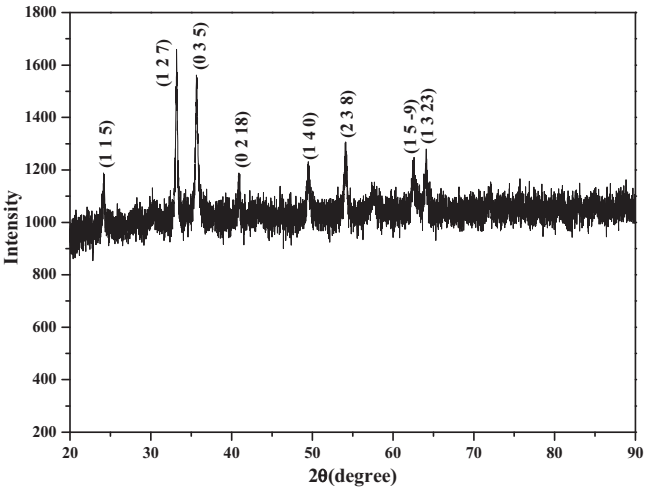

Fig. 1. PXRD of Fe-BDC.

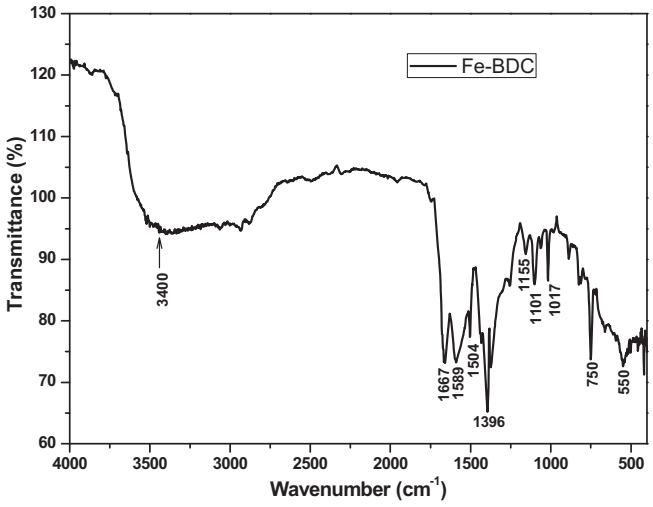

Fig. 3. IR spectrum of Fe-BDC.

3. Results and discussion

3.1. Characterization of Fe-BDC MOF

Fig. 1 shows the PXRD pattern, after annealing at 120 °C for 4 h of as-synthesised Fe-BDC MOF at room temperature. The observed PXRD pattern matches with ICDD file number (PDF-4+2014RDB) DB card number 00-055-1809. Rietveld refinement technique using PDXL software, performed with pseudo-voigt band profile after back ground correction, was carefully implemented. After rietveld refinement of the pattern it reveals monoclinic phase with space group P_12_1/C_1 and cell parameters a = 5.929 Å, b = 7.802 Å, c = 51.30 Å and β = 110.84° having refinement parameters R_{wp} = 3.65, R_p = 2.84, R_e = 3.18, S = 1.1485 chi^2 = 1.3191. Reliability of data is checked by goodness of fitting. The refinement results are shown in Fig. 2.

The FT-IR spectrum of MOF is shown in Fig. 3. The observed bands in IR spectrum were used to characterize the material. IR band at 750 cm^{-1} could be assigned due to benzene ring deformation mode. The broad absorption at ≈3400 cm^{-1} and ≈1300 cm^{-1} indicated that water and/or other gases have been adsorbed in the frameworks. Similar observations for some other metal organic frameworks have been reported by Tan et al. [22]. Red shift of C—H bending frequency from 1017 cm^{-1} indicates occurrence of hydrolysis reaction with Fe-C-O due to exposure of moisture present in the atmosphere. IR signal at 1398 cm^{-1} and 1101 cm^{-1} are assigned to C—O stretching and in plane O—H deformation. Broad peak at ~3400 cm^{-1} was due to surface-sorbed water. Peak at 1589 cm^{-1} could be assigned for C = C bond stretching vibrations of aromatic ring present in BDC [23]. Further, peak at around 550 cm^{-1} indicates the presence of strong Fe—O vibration band [24]. The observed

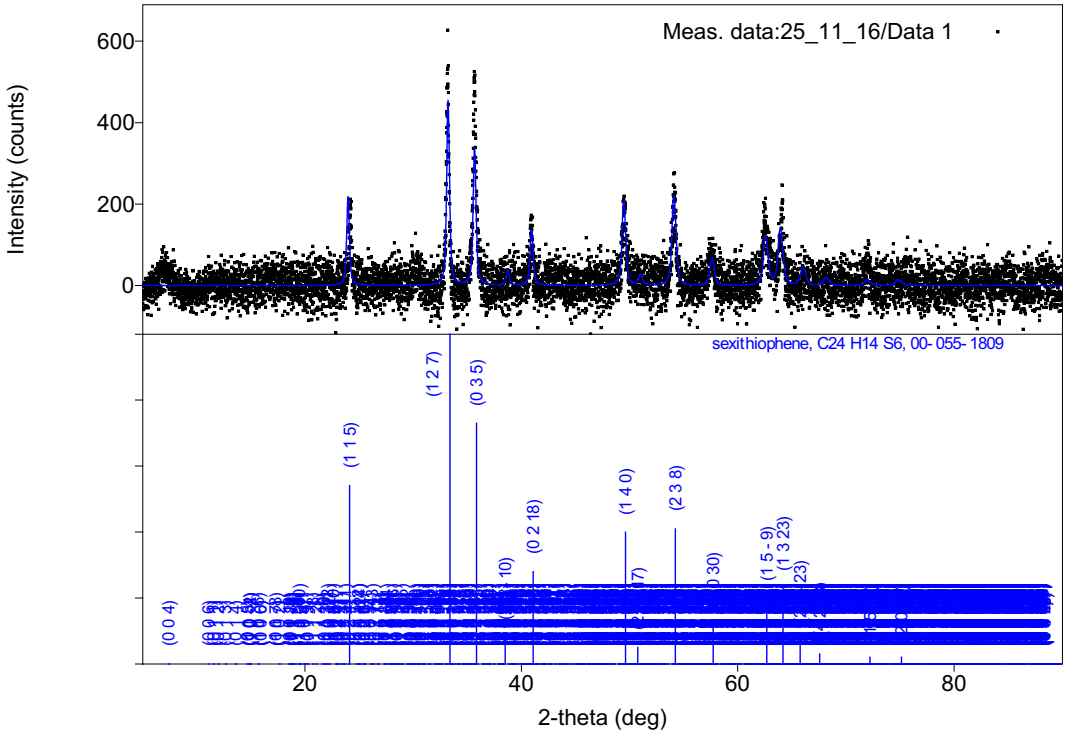

Fig. 2. Rietveld refinement fitting of PXRD of Fe-BDC.

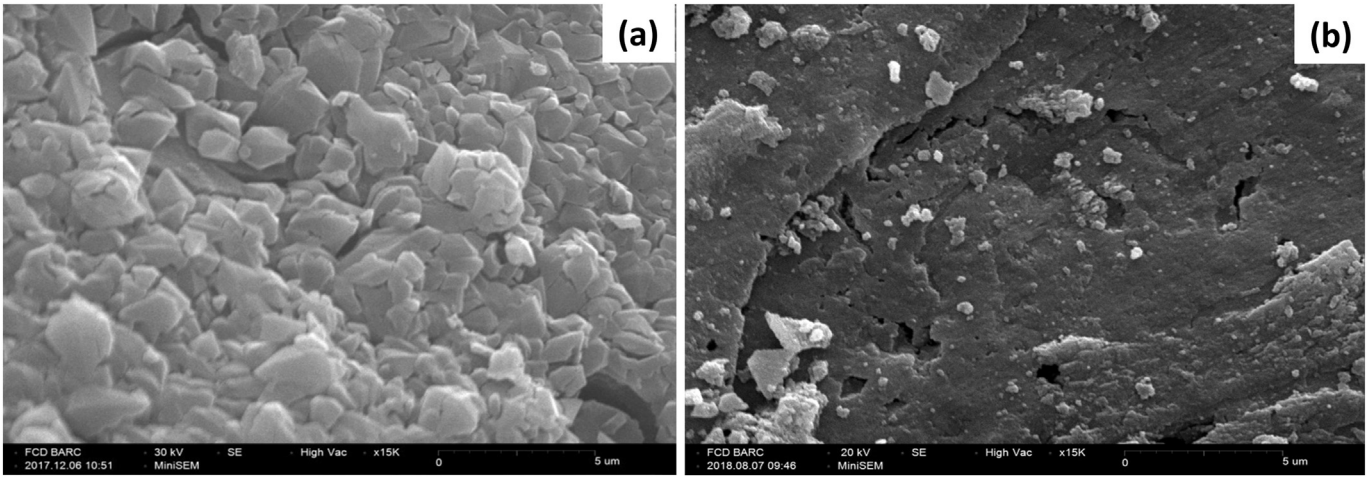

Fig. 4. SEM images of Fe-BDC MOF (a) before adsorption and (b) after adsorption.

vibrational bands suggest the formation of phase pure MOF without impurity within the detection limit of spectroscopy.

Fig. 4(a) and Fig. 4(b) show the surface micrographs of synthesised Fe MOF before and after dye adsorption respectively. SEM micrographs of Fe-BDC MOF depicted in Fig. 4(a) reveals the rough surface and pores which provide suitable binding sites for methylene blue dye molecules. SEM image of MOF after adsorption of methylene blue dye molecules at the surface is depicted in Fig. 4(b).

TEM image of synthesised Fe-BDC MOF is shown in Fig. 5. The particle size of synthesised MOF is found to be 10 nm.

Some other important physical properties of the material, such as pore volume and surface area were determined by use of standard procedures to be 0.076 cm^3/g and 46.02 m^2/g respectively.

3.2. Adsorption of methylene blue onto Fe-BDC MOF

3.2.1. Effect of contact time

Result of the dye removal (%) estimated using Eq. (1) from adsorption studies of methylene blue on MOF synthesised are shown in Fig. 6. It was observed that the extent of removal of methylene blue dye increases with increasing contact time. 24 h is considered as equilibrium time for this study. Initially methylene blue dye is adsorbed rapidly and with time its adsorption process slows down. This is due to the presence of large number of vacant sites initially, at the surface for dye adsorption and over a period of time, as more and more sites are occupied by dye molecules, it become difficult to occupy vacant sites due to repulsive forces between methylene blue adsorbed on the surface of Fe-BDC MOF and the MB present in solution phase [25].

3.2.2. Effect of initial dye concentration on adsorption of methylene blue onto Fe-BDC MOF

Fig. 7 shows the effect of initial dye concentration on adsorption by Fe-MOF. From the figure, it is clear that as the initial dye concentration increases from 1 ppm to 5 ppm, the percentage of dye removal increased from 79.4% to 86.5% after 24 h of adsorption process. It is also revealed that the amount of dye adsorbed per unit mass of adsorbent increases from 1.588 mg/g to 8.65 mg/g for Fe-BDC MOF. The increase in the adsorption capacity is probably due to increase in the mass gradient between the dye solution and Fe-BDC MOF as the initial dye concentration increases [26]. Further increasing the dye concentration initially does not result in any significant improvement in dye removal %.

3.2.3. Effect of adsorbent dose on adsorption of methylene blue onto Fe-BDC MOF

To study the effect of sorbent dose on adsorption, 5–25 mg of Fe-MOF were added in 5 ppm solution of methylene blue dye. It was

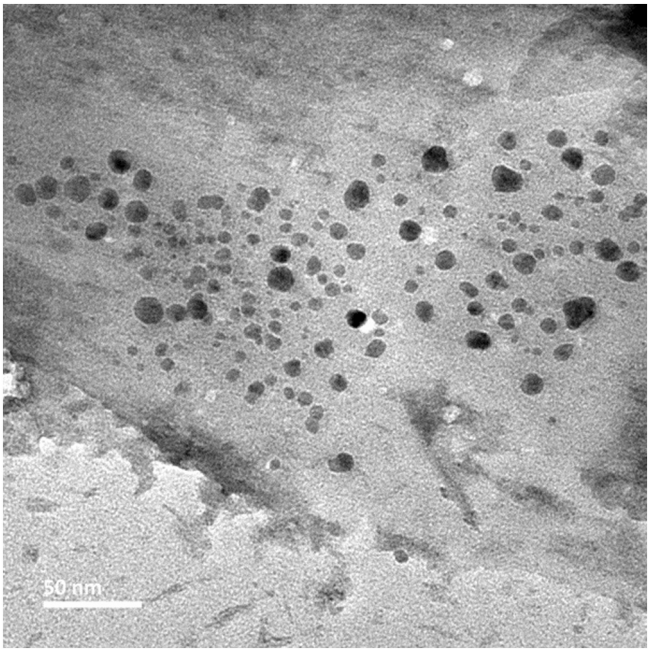

Fig. 5. TEM image of Fe-BDC MOF.

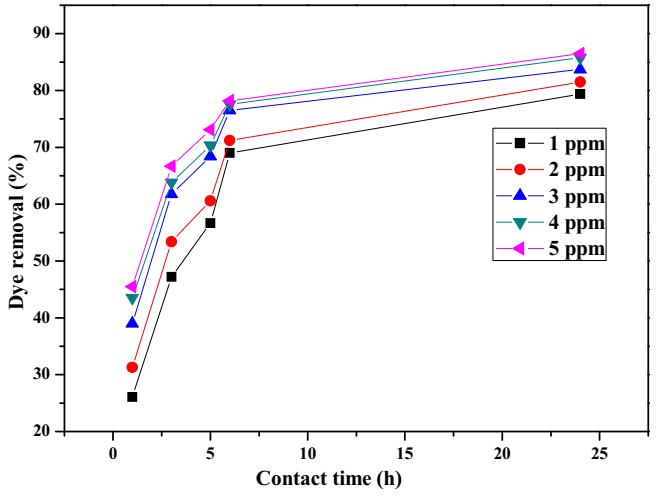

Fig. 6. Effect of contact time on removal of methylene blue dye.

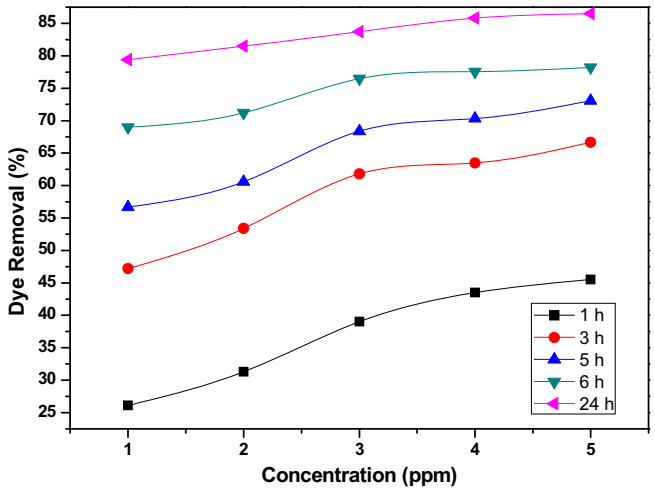

Fig. 7. Effect of initial concentration of dye.

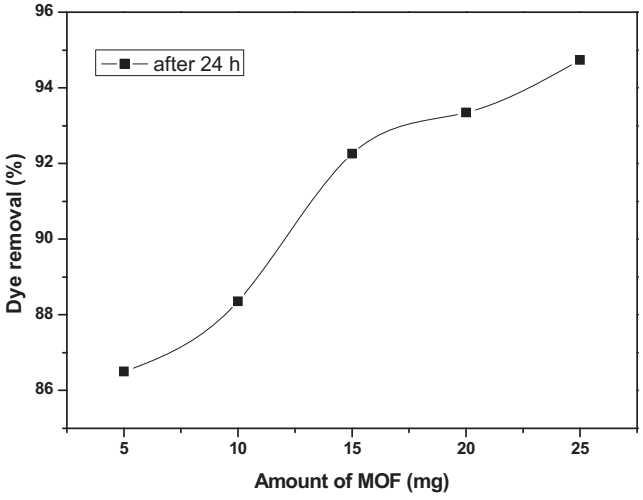

Fig. 8. Effect of variation of amount of MOF on removal of dye.

observed that removal of methylene blue dye increased with the increase in amount of Fe-MOF. The removal of dye increased from 86.5% to 94.74% with increase in amount of MOF (Fig. 8) due to increased surface area and adsorption sites [27].

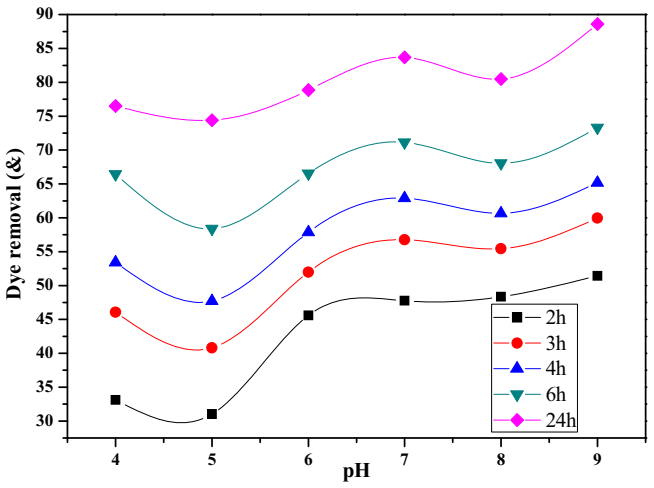

Fig. 10. Effect of initial pH of dye solution.

3.2.4. Effect of temperature on adsorption of methylene blue onto Fe-BDC MOF

Effect of temperature on dye removal was studied at various temperatures viz. 303 K, 308 K, 313 K, 318 K and 323 K for contact time 6 h. For these studies, 5 mg of adsorbent was added to each 10 ml of dye solutions having varying concentrations from 1 ppm to 5 ppm. Fig. 9(a) shows that dye adsorption increases with increasing temperature. Depending on initial dye concentration, approx. 89% to 92% of the dye is removed after 6 h at 323 K as shown in Fig. 9(a). This clearly indicates that the adsorption is an endothermic process [26,28]. From Fig. 9(b) it is clear that there is a linear increase in adsorption capacity with temperature which indicates that the adsorption of MB dye on Fe-BDC MOF is favourable at higher temperature [29].

3.2.5. Effect of solution pH on adsorption of methylene blue dye onto Fe-BDC MOF

pH of the solution is one of the very important factors in the adsorption process. We have, therefore investigated the effect of varying pH value of dye solution on adsorptive behaviour in the pH range 4–9. The dye removal behaviour with pH variation clearly reflects the higher removal percentage in basic condition in comparison to acidic conditions (Fig. 10). Methylene blue is a basic dye. In water it produces cations (C^+) and reduced ions (CH^+). If the solution pH is above the zero point of charge, the negative charge density on the surface of the MOF

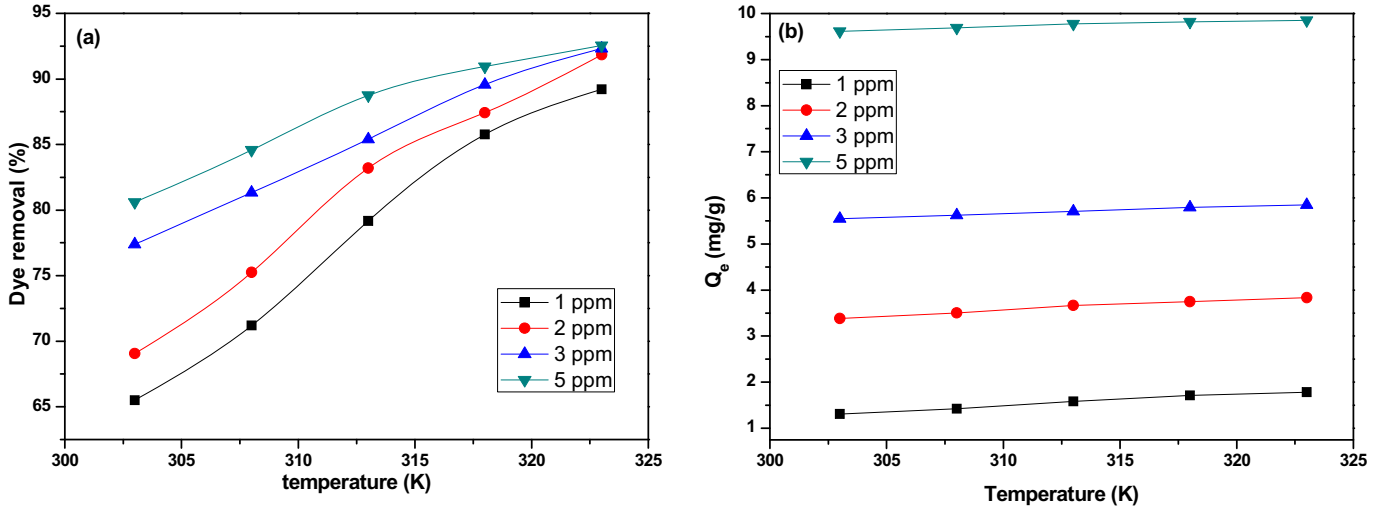

Fig. 9. Effect of temperature on (a) dye removal and (b) adsorption capacity.

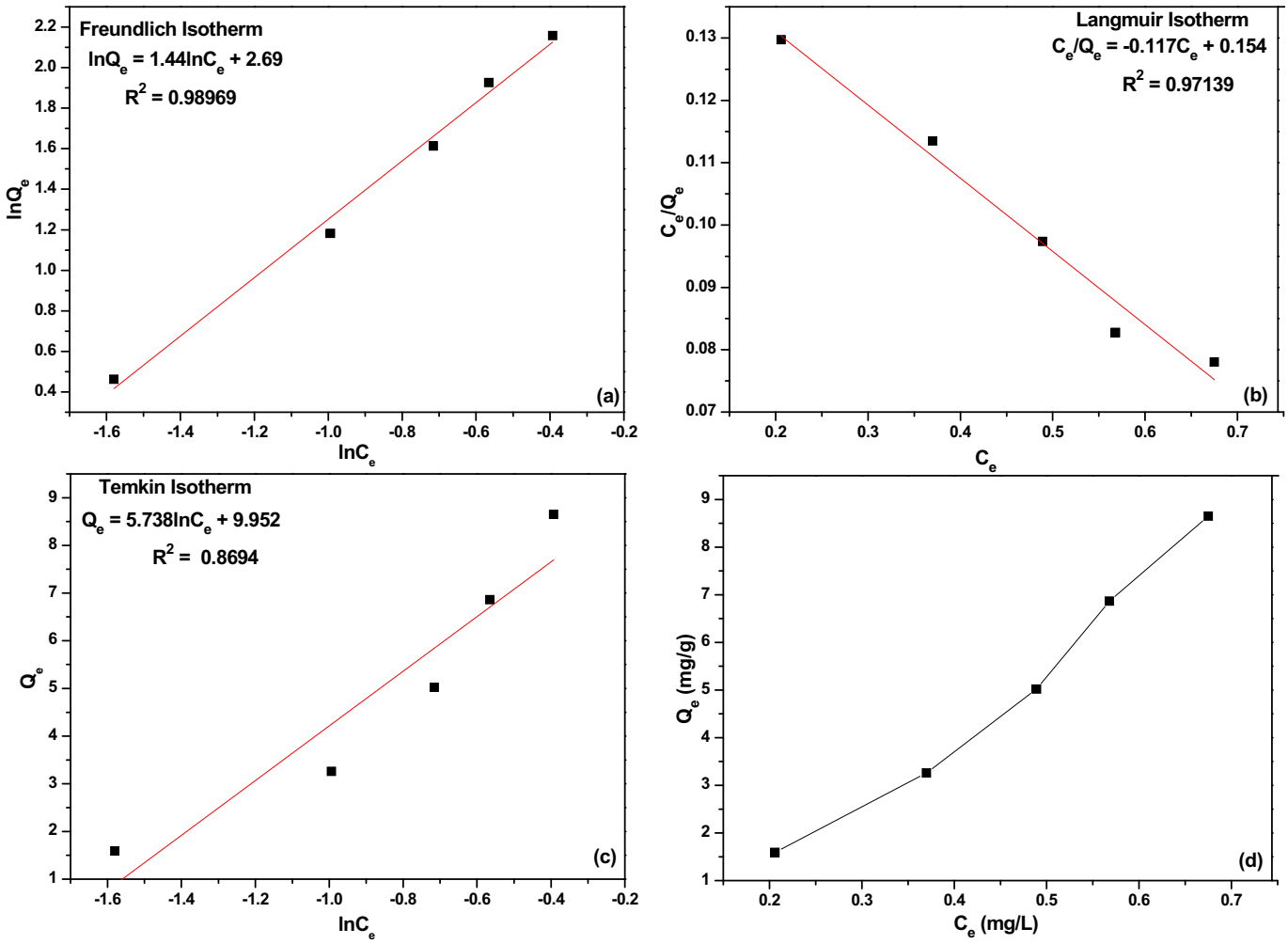

Fig. 11. Linear plot for (a) freundlich, (b) Langmuir, (c) Temkin adsorption isotherms and (d) plot between C_e and Q_e.

increases, which favours the sorption of basic (cationic) dyes. In addition, the basic dye will become protonated in the acidic medium and the positive charge density would be located more on the dye molecules, at low pH, resulting in the lower uptake. [30].

3.3. Adsorption isotherm study

Freundlich, Langmuir and Temkin isotherm models, are used to analyze the interaction of methylene blue with Fe-BDC MOF. Freundlich isotherm is based upon the non-uniform multilayer adsorption of dye molecule onto the heterogeneous surface of adsorbent. On the other hand, Langmuir isotherm takes into account the monolayer adsorption of dye molecules onto homogeneous surface of adsorbent without any interaction between the adsorbed dye molecules. In Temkin isotherm model there is a linear decrease in the heat of adsorption of all the molecules with coverage. The linear forms of Freundlich, Langmuir and Temkin isotherms are given as [11,29,31,32]:

$$\text{Freundlich isotherm}: \quad \ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

$$\text{Langmuir isotherm}: \frac{C_e}{Q_e} = \frac{1}{K_L Q_L} + \frac{C_e}{Q_L} \tag{9}$$

$$\text{Temkin isotherm}: Q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{10}$$

where Q_e (mg/g) is the amount of adsorbate adsorbed by adsorbent at equilibrium, C_e (mg/L) is the equilibrium concentration of dye solution,

Table 1
Isotherm parameters for methylene blue adsorption on Fe-BDC MOF.

Concentration of dye (mg/L)		Q_e (mg/g)	Freundlich isotherm			Langmuir isotherm			Temkin isotherm		
Initial	C_e		n	K_f	R^2	Q_L	K_L	R^2	b_T	K_T	R^2
1	0.206	1.588	0.694	147.761	0.98969	−8.547	−0.76	0.97139	431.783	5.665	0.8694
2	0.37	3.260									
3	0.489	5.022									
4	0.568	6.864									
5	0.675	8.650									

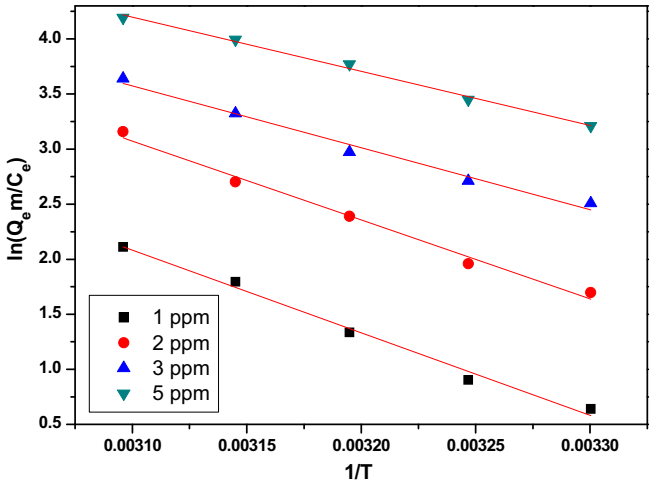

Fig. 12. Plot of ln(Qem/Ce) versus 1/T to give thermodynamic parameters.

K_f and n, K_L and Q_L, b_T and K_T are empirical constants incorporating all parameters affecting adsorption process for Freundlich, Langmuir and Temkin adsorption isotherms respectively. R is gas constant (8.314 J/molK) and T is temperature (K). In Freundlich isotherm, value of K_f and 1/n denotes adsorption capacity and adsorption intensity (surface heterogeneity) respectively. Similarly, in Langmuir adsorption isotherm Q_L is the Langmuir monolayer adsorption capacity [33]. Temkin adsorption isotherm suggests that the presence of energetically non-equivalent adsorption sites on the surface of adsorbent and the adsorption of adsorbate dye occurs on the more energetic adsorption sites at first [31].

Three linear fits are shown in Fig. 11(a–c) and the parameters for all isotherms are listed in Table 1. The relationship between amount of dye adsorbed (Q_e) and the remaining dye concentration in solution (C_e) is shown in Fig. 11(d). For present study, the best isotherm model [34] was determined by using Coefficient of determination (R^2). R^2 is a number indicating the proportion of the variance in the dependent variable which is predictable from the independent variable. Values of R^2 for various isotherm models are reported in Table 1. The results show that the Freundlich adsorption isotherm is best fitted with $R^2 = 0.98969$ revealing that the Freundlich isotherm is perfectly applicable to study the adsorption process. The linear plot for Freundlich isotherm gives K_f (= 14.76) as intercept and 1/n (= 1.44) as slope. The value of 1/n is found to be greater than 1 which clearly indicates that the adsorbent used for the adsorption is useful only for the adsorption of higher dye concentration [20].

3.4. Thermodynamic studies

Thermodynamic parameters viz. Free energy (G), enthalpy (H) and entropy (S) for the adsorption of dye on Fe-BDC MOF have been calculated using the following equations [29,35]

$$\ln\left(\frac{Q_e m}{C_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

where, ΔS, ΔH and ΔG are the change in entropy (kJ/mol/K), enthalpy (kJ/mol) and Gibb's free energy (kJ/mol) respectively. m is the adsorbent dose (g/L), C_e is the equilibrium concentration (mg/L) of dye solution, Q_e is the amount of dye adsorbed at equilibrium (mg/g), R is the gas constant (8.314 J/mol/K) and T is temperature (K).

The plot of $\ln(Q_e m/C_e)$ versus 1/T (Fig. 12) provides the values of ΔH and ΔS from its slope (ΔH/R) and intercept (ΔS/R). Values of ΔG were calculated by Eq. (12). The values of thermodynamic parameters are shown in Table 2. The feasibility of the adsorption process and its spontaneous nature is confirmed by the negative values of free energy [36]. Further, on increasing temperature, the increase of absolute values of ΔG suggests the adsorption is favourable at higher temperatures. Positive values of ΔH and ΔS describes that the adsorption process is endothermic and random at the adsorbent-solution interface. Since the value of ΔH is higher than 40 kJ/mol the adsorption proceeds via chemisorption [23].

3.5. Kinetic study

In order to interpret the experimental data, it is required to identify the steps that control the overall removal rate in the adsorption process. In order to understand the rapid initial phase of adsorption, chemisorptions and intra- particle diffusion, three kinetic models namely- Pseudo first order, Pseudo second order and intrapacticle diffusion model were applied for the investigation of mechanism of methylene blue dye adsorption on Fe-BDC MOF. Linear form of these models are expressed as [20,29]:

$$\text{Pseudo first order kinetics}: \ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{13}$$

$$\text{Pseudo second order kinetics}: \frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 {Q_e}^2} \tag{14}$$

$$\text{Intraparticle diffusion}: Q_t = k_i t^{1/2} + C \tag{15}$$

where, Q_e (mg/g) and Q_t (mg/g) are the amount of dye adsorbed at equilibrium and at time t (min) respectively and k_1 (min^{-1}), k_2 (g/mg·min), k_i ($mg/g \cdot min^{1/2}$) are rate constant of adsorption for pseudo first order, pseudo second order and intraparticle diffusion respectively. In intraparticle diffusion constant C reflects the boundary layer effect [20].

Three linear fits for the kinetic models are shown in Fig. 13(a–c) and their parameters are listed in Table 3. The result shows that pseudo second order kinetic model having rate constant (k_2) 4.89 × 10^{-2} g/mg·min is best followed by the adsorption of methylene blue on Fe-BDC MOF and the calculated uptake capacity (Q_e^{cal} = 9.009 mg/g) is in accordance with the experimental uptake capacity (Q_e^{exp} = 8.65 mg/g). From this we can conclude that by using Fe-BDC MOF, methylene blue dye is removed from its aqueous solution dominantly through chemisorptions process.

Table 2
Thermodynamic parameters for adsorption of MB on Fe-BDC MOF.

Dye concentration	ΔH (kJ/mol)	ΔS (kJ/mol/K)	ΔG (kJ/mol) at temperatures				
			303 K	308 K	313 K	318 K	323 K
1	62.331	0.211	−1.462	−2.514	−3.567	−4.620	−5.672
2	59.609	0.210	−4.125	−5.177	−6.229	−7.280	−8.332
3	46.763	0.175	−6.167	−7.040	−7.913	−8.787	−9.660
5	40.932	0.162	−8.093	−8.902	−9.711	−10.520	−11.329

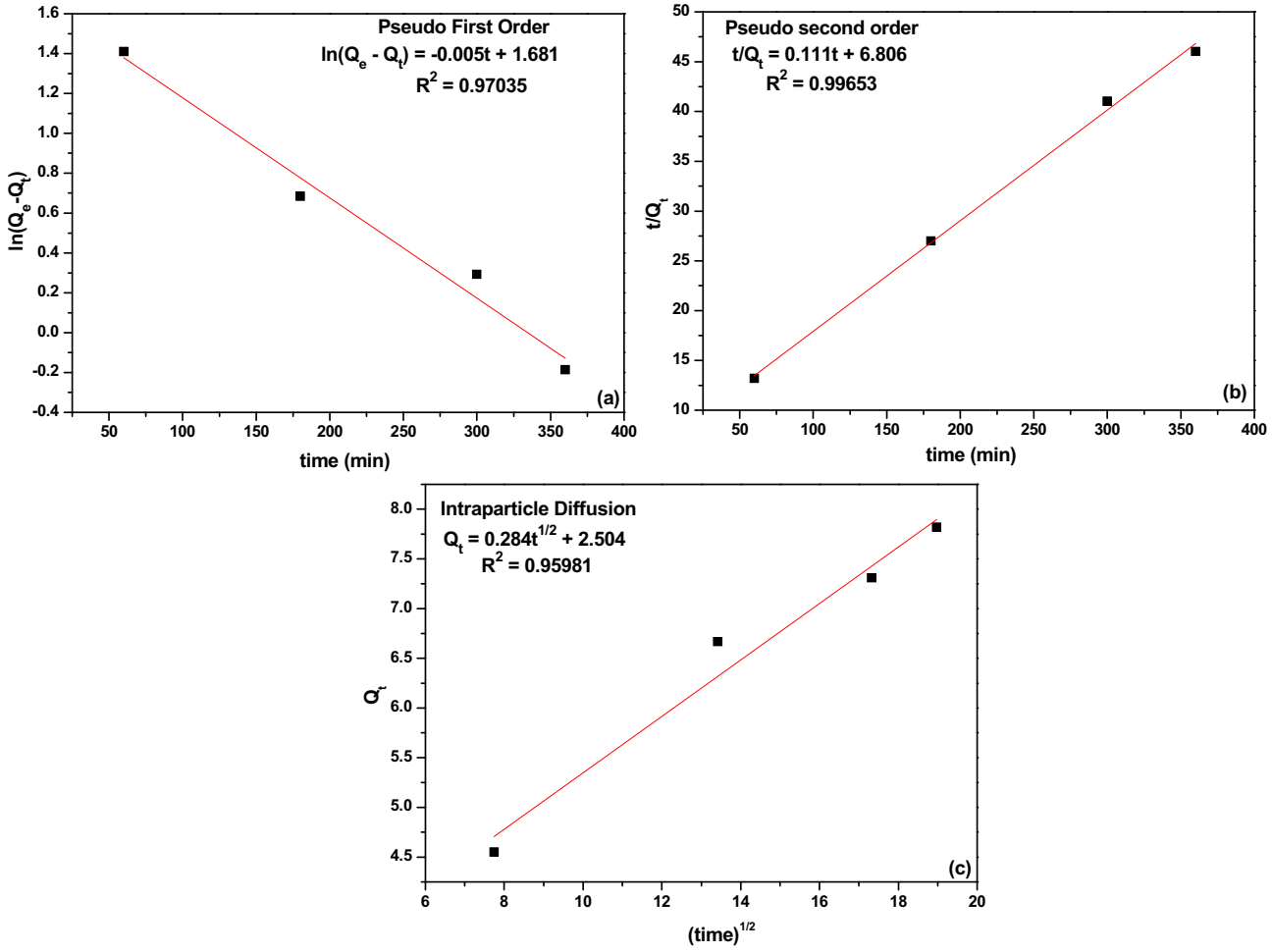

Fig. 13. Linear plot for (a) Pseudo first order, (b) Pseudo Second order and (c) Intraprticle diffusion.

4. Column operation for removal of MB dye

Column operation was done to test the practical utility of prepared adsorbent. The breakthrough curve (plotted between C_t/C_0 and time) and integral area (drawn by software OriginPro 8) are shown in Fig. 14. The breakthrough point was taken at $C_t / C_0 = 0.01$. According to the integral area, the calculated adsorption capacity of Fe-BDC MOF for MB was 5.52 mg/g. It is seen from Table 3 and Table 4 that column adsorption capacity is relatively lower than the batch adsorption capacity.

5. Comparison of adsorption of MB by Fe-BDC MOF with other adsorbents

The percentage dye removal of MB dye and removal capacity of Fe-BDC MOF has been compared with various other adsorbents reported in literature (Table 5) [37–42]. The result reveals that Fe-BDC MOF can be used as a promising adsorbent for MB dye removal from its aqueous solution.

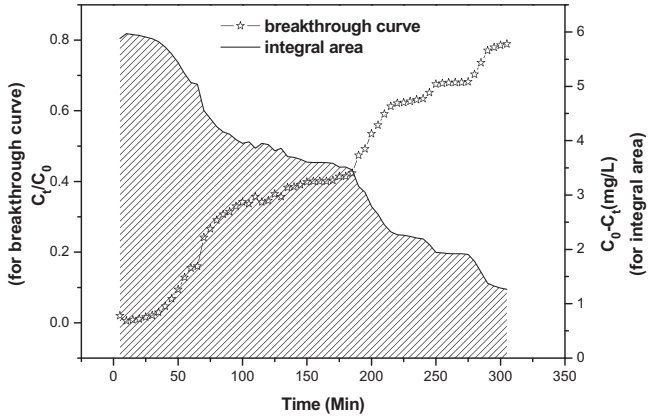

Fig. 14. Breakthrough curve (line, left vertical axis) and integral area (oblique line, right vertical axis) of methylene blue on Fe-BDC MOF fixed bed column.

Table 3
Kinetic parameters for adsorption of methylene blue on Fe-BDC MOF.

Q_e (mg/g)	Pseudo first order			Pseudo second order			Intraparticle		
	Q_e	K_1	R^2	Q_e	K_2	R^2	K_i	C	R^2
8.65 (5 ppm)	5.371	0.005	0.9704	9.009	0.049	0.9965	0.284	2.50	0.9598

Table 4
Parameters of breakthrough curve MB on Fe-BDC MOF fixed bed column.

Flow rate (mL/min)	t (min)	Peak area (mg·min/L)	q_e (mg/g)	m_{total} (mg/g)	Q_{total} (mg/g)	R (%)
1.3	305	1060.55	5.52	2.38	1.38	57.98

Table 5
Comparison with other adsorbents for the removal of MB dye.

Adsorbent	m (g/L)	C_0 (MB) (mg/L)	Dye removal (%)	Q_e (mg/g)	Ref.
Fe-BDC MOF	2.5	5	94.74	8.65	This work
Raw Mango Seed	10	50	99.136	25.36	37
Surface Modified Mango Seed	4	50	99.912	58.08	37
Persian Caolin	2	10	90	29.85	38
Fe_3O_4@C nanocomposite	0.4	30	99.9	52.5	39
Pine leaves	0.3	10	96.5	126.58	40
Citric Acid Modified Sawdust	2	25	91.2	111.46	41
CuO loaded Activated Carbon	1.1	50	99.2	10.54	42

6. Conclusion

Methylene blue dye has been efficiently removed from its aqueous solution by an iron based metal organic framework Fe-BDC MOF using batch and column techniques. Investigations on influence of various parameters such as contact time, adsorbent dose, pH, temperature and initial dye concentration on removal of MB have been carried out. At 50 °C temperature 92% MB dye was removed from 5 ppm dye solution within 6 h. In acidic medium, excess H^+ ions present in dye solution inhibit the adsorption. The equilibrium adsorption data showed significant correlation to Freundlich adsorption isotherm. The results indicate that the Fe-BDC MOF can be used for the removal of entire range of concentration of methylene blue dye. Thermodynamic parameters reveal that the adsorption process is spontaneous and endothermic in nature and proceeds through chemisorptions. Three kinetic models viz. pseudo first order, pseudo second order and intra-particle diffusion model were used to interpret interaction behaviour of the MOF surface with the MB dye and pseudo second order model was found to be most suitable to interpret the interaction between MB dye and Fe MOF.

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