*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2013.838527

53 (2015) 515–523
January

Taylor & Francis
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# Adsorption of methylene blue on strongly basic anion exchange resin (Zerolit DMF): kinetic, isotherm, and thermodynamic studies

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Received 9 July 2013; Accepted 17 August 2013

ABSTRACT

This work explored the adsorption potential of Zerolit DM-F (ZDMF) resin for methylene blue (MB) removal form aqueous system in batch mode. Both linear and non-linear models have been applied to kinetic and isotherm data. Practical feasibility of ZDMF was testified by performing breakthrough, desorption, and regeneration studies. Results showed optimum adsorption (24.75 mg/g) at pH 10. Contact time studies showed equilibration time ranged between 30 and 90 min for various MB concentrations ($C_o$—25–200 mg/L). Kinetic modeling studies showed applicability of pseudo-first-order model at various MB concentrations while, isotherm studies showed applicability of Freundlich model at various temperatures. Thermodynamics studies showed endothermic and spontaneous process. The breakthrough studies showed that 550 mL of MB solution ($C_o$—50 mg/L) which was prepared separately in deionized water and tap water matrix could be passed through the columns without detecting MB traces. The breakthrough and exhaustive capacities in deionized water and tap water matrix were found to be 27.5 and 45 mg/g, respectively. Desorption studies showed optimum MB recovery (86%) with 5 M HCl solution while, regeneration studies revealed 10.20 and 16.28% loss in adsorption and desorption after five consecutive cycles, respectively.

*Keywords:* Anion exchange resin; Adsorption–desorption; Methylene blue; Regeneration; Breakthrough

## 1. Introduction

Dyes are the coloring agents widely used in textiles, paper and pulp, pharmaceutical, cosmetic, and leather industries [1]. Incomplete fixation during dying process leads to significant dye loss, in turn enhancing their concentration in effluent discharges causing adverse effects to both flora and fauna. Though, methylene blue (MB) is not considered to be a very toxic dye but it can cause some harmful effects such as increased heart rate, vomiting, shock, cyanosis, jaundice, diarrhea, and tissue necrosis on human beings [2]. Therefore, it is imperative to treat effluents containing dye before being discharged to diminish their toxic effects. Various treatment techniques such as membrane filtration [3], flocculation [4], photocatalytic degradation [5], chemical oxidation [6], and ozonation [7] have been widely utilized for decontaminating dye effluents. The techniques involving dyes

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degradation might generate certain byproducts that could be more toxic and carcinogenic even in traces than a dye itself, making degradation technique unfit for its intended use [8]. Among these physicochemical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [9]. Effectiveness even at lower concentration, lower operative cost, simplicity of the design, and no by-product generation are some of the merits of adsorption process [9]. Moreover, the ability of adsorption to remove toxic chemicals without producing any toxic byproducts, thereby keeping quality of water undisturbed, has also popularized the adsorption technique in comparison to electrochemical, biochemical, or photochemical degradation processes [10–14]. MB, a cationic dye widely used for dying applications [15]. If ingested, MB may cause nausea, vomiting, profuse sweating, and mental confusion [16]. Concerning the hazardous effects, it is essential to treat effluents containing MB before being discharged to the water bodies.

Various synthetic and natural adsorbents such as coalesced chitosan activated carbon composite [17], spinel magnesium aluminate nanoparticles [18], $Fe_3O_4$/maize cob composites [19], $Mn_3O_4$/silica composite [20], *Saccharomyces cerevisiae* [21], and *Citrus sinensis* Bagasse [22] have been utilized for the adsorption of MB from aqueous phase. Carbonaceous adsorbents derived from different precursors have also been reported for MB removal [23,24]. However, high pressure drop in fixed bed columns and potential channeling are the major demerits specifically when using carbon-based adsorbents [25]. The use of resins as adsorbent for dyes removal has an upper hand over conventional and non-conventional adsorbents. Structurally, resins are granular resulting less pressure drop in column operations and they could be regenerated economically [26].

Considering aforementioned merits in this study, we have tested the adsorption potential of commercially available Zerolit DM-F (ZDMF) resin by taking MB as a model adsorbate by batch process. Kinetic and thermodynamic parameters were studied. Linear and non-linear modeling studies were carried out. To check the economic feasibility and industrial applicability of ZDMF resin; desorption, regeneration, and breakthrough studies were also carried out.

## 2. Experimental

### 2.1. Chemicals and materials

ZDMF (a mixed-bed ion exchange resin) was purchased from the Permutit Company Limited London, England. MB (chemical formula: $C_{16}H_{18}N_3OS$; formula mass: 333.6 g/mol; $\lambda_{max}$: 670 nm) was supplied by Merck, Germany. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased by BDH Laboratory Supplies Poole, England. All reagents and chemicals used were of analytical reagent (AR) grade or as specified. The MB stock solution (1,000 mg/L) was prepared in deionized (D.I) water (Millipore Corporation, Bedford, MA, USA).

### 2.2. Preconditioning of adsorbent

The ZDMF resin was kept overnight in 0.1 M NaOH solution. It was washed with D.I. water until it attains neutral pH. It was further dried at 40°C for 10 h. To avoid dirt and moisture, dried resin was stored in a desiccator for further studies.

### 2.3. Adsorption studies

Batch adsorption studies were carried out in 50 mL capped Erlenmeyer flasks. The adsorbate solution of known concentration was equilibrated with ZDMF resin under ambient temperature conditions over a shaker at 100 rpm. At equilibrium, the adsorbate was filtered off by using Whatman filter No. 41 and residual concentration was measured by using UV–visible spectrophotometer at $\lambda_{max}$: 670 nm. The adsorption capacity ($q_e$, mg/g) was calculated as:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where $C_o$ and $C_e$ (mg/L) are the initial and equilibrium adsorbate concentrations, $V$ (L) is the volume of adsorbate, and $m$ (g) is the mass of adsorbent.

Kinetics studies were carried out by varying initial adsorbate concentrations ($C_o$, 25–200 mg/L). The samples were collected at specified time intervals until equilibrium was established. The pH studies were carried out in pH range 2–10. The solution pH was adjusted by adding 0.1 M NaOH and 0.1 M HCl solutions and was measured by Orion two star pH meter (Thermo Scientific, USA). Isotherm studies were carried out by varying reaction temperature (20–50°C) and initial adsorbate concentration (25–500 mg/L).

### 2.4. Breakthrough studies

The ZDMF resin (1.0 g) was taken in glass column (0.6 cm internal diameter) with glass wool support. One liter of MB solution of initial concentration 50 mg/L was passed through a column at 1 mL/min flow rate. The effluent was collected in 50 mL fractions

and the amount of MB (C) was determined in each fraction by UV–visible spectrophotometer. The breakthrough curve was obtained by plotting $C/C_o$ vs. volume of the effluent. Domestic and industrial effluent discharges usually contains carbonates and bicarbonates salts of calcium, magnesium, and sodium. Therefore, the breakthrough studies were performed by preparing MB solution in tap water matrix following aforementioned procedure.

### 2.5. Desorption and regeneration studies

Desorption and regeneration studies were also carried out by batch process. Acids (HCl; $H_2SO_4$; carboxylic acid; and oxalic acid) of various concentrations, base (0.1 M NaOH), and solvents (acetone; ethanol; and methanol) were used as eluents. The ZDMF resin (0.5 g) was initially saturated with 50 mL MB solution of initial concentration 50 mg/L on shaker at 100 rpm for an hour. After equilibration, the resin was washed several times with D.I. water to remove MB traces. Then, ZDMF resin was treated for an hour with 50 mL of 0.1 M HCl solution (eluent) over a shaker at 100 rpm (to desorb MB). Similar procedure was repeated with other eluents and concentration of MB eluted was determined using UV–visible spectrophotometer.

To make adsorption process economically feasible, it is essential to testify regeneration potential of ZDMF resin. ZDMF resin (0.5 g) was saturated for an hour with MB solution (50 mL) of initial concentration 50 mg/L. The spent ZDMF resin was washed several times with D.I. water to remove unadsorbed MB traces. To regenerate spent ZDMF resin, it was treated with 50 mL of 1.0 M HCl solution. Similar procedure was repeated for five consecutive cycles.

## 3. Results and discussion

The adsorption potential of untreated ZDMF resin was tested for MB. The observed MB adsorption was 53% ($C_o$, 50 mg/L). Further, ZDMF resin was treated with 0.1 M NaOH solution to enhance anionic charge over ZDMF resin surface which in turn enhanced cationic MB adsorption up to 98% for the same concentration.

### 3.1. Effect of pH

The solution pH plays a significant role during adsorption process as it influences solute solubility and uptake capacity over the adsorbent surface. For dyes, changes in the structural and color stabilities as well as degree of ionization are also solution pH dependent [27]. The effect of pH for MB adsorption on ZDMF resin was testified for pH range 1–10. The adsorption gradually increased with increase in pH attaining optimum value (24.75 mg/g) at pH 10 (Fig. 1). At lower pH (acidic), adsorbent surface would be surrounded by hydronium ions, which could hinder the cationic adsorbate interaction with binding sites over adsorbent surface. As the pH increased (basicity increased) deprotonation of surface sites occur which facilitates MB adsorption over resin surface. The observed point of zero charge ($pH_{PZC}$) of ZDMF resin was 6.9. Above $pH_{PZC}$, adsorbent surface was positively charged and below $pH_{PZC}$, adsorbent surface was negatively charged. The $pH_{PZC}$ value was also in good agreement with aforementioned results (i.e. optimum adsorption at $pH > pH_{PZC}$). The pH study results revealed that electrostatic interactions between negatively charged adsorbent surface (at $pH > pH_{PZC}$) and positively charged MB ions might be the possible adsorption mechanism.

### 3.2. Effect of contact time and adsorption kinetics

Contact time studies were conducted by varying MB initial concentration from 25 to 200 mg/L. The equilibration time at various concentrations ranged between 30 and 90 min. The initial adsorbate concentration provides an essential driving force to overcome the mass transfer resistance between the aqueous phase and solid adsorbent. The increase in initial adsorbate concentration from 25 to 200 mg/g increased driving force and reducing mass transfer resistance between the aqueous phase and solid adsorbent which in turn increased MB equilibrium adsorption capacity

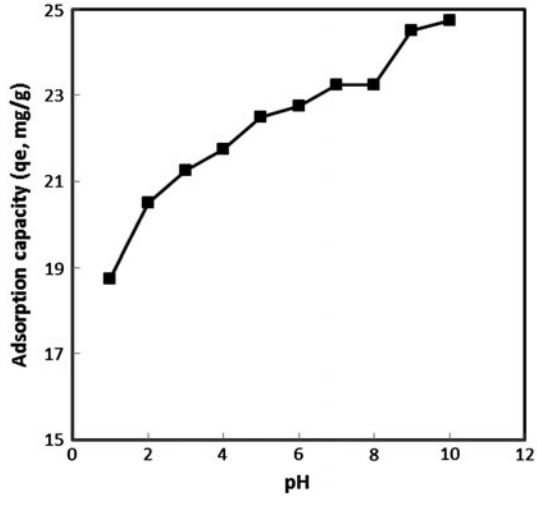


Fig. 1. Effect of pH on MB adsorption onto ZDMF resin.

from 3.1 to 24.7 mg/g, respectively. Initially at various MB concentrations, the adsorption was appreciable fast as observed by steep slope indicated the availability of readily accessible adsorption sites on adsorbent surface. The process gradually became slow down as it reached to equilibrium which was due to the saturation of adsorption sites (Fig. 2).

In order to configure out appropriate model to fit both linear and non-linear forms of pseudo-first-order kinetic, pseudo-second-order kinetic and Elovich model have been applied to kinetic data. Pseudo-first-order kinetic equations in non-linearized and linearized forms are given as [28]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{3}$$

where $q_e$ and $q_t$ (mg/g) are adsorption capacities at equilibrium and time, $t$, respectively.

$k_1$ (1/min) is pseudo-first-order rate constant.

Pseudo-second-order kinetic equations in non-linearized and linearized forms are given as [29]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} \times t \tag{5}$$

where $k_2$ (g/mg min) is a pseudo-second-order rate constant.

Elovich model is given as:

$$q_t = \frac{1}{B} \ln(AB) + \frac{1}{B} \ln(t) \tag{6}$$

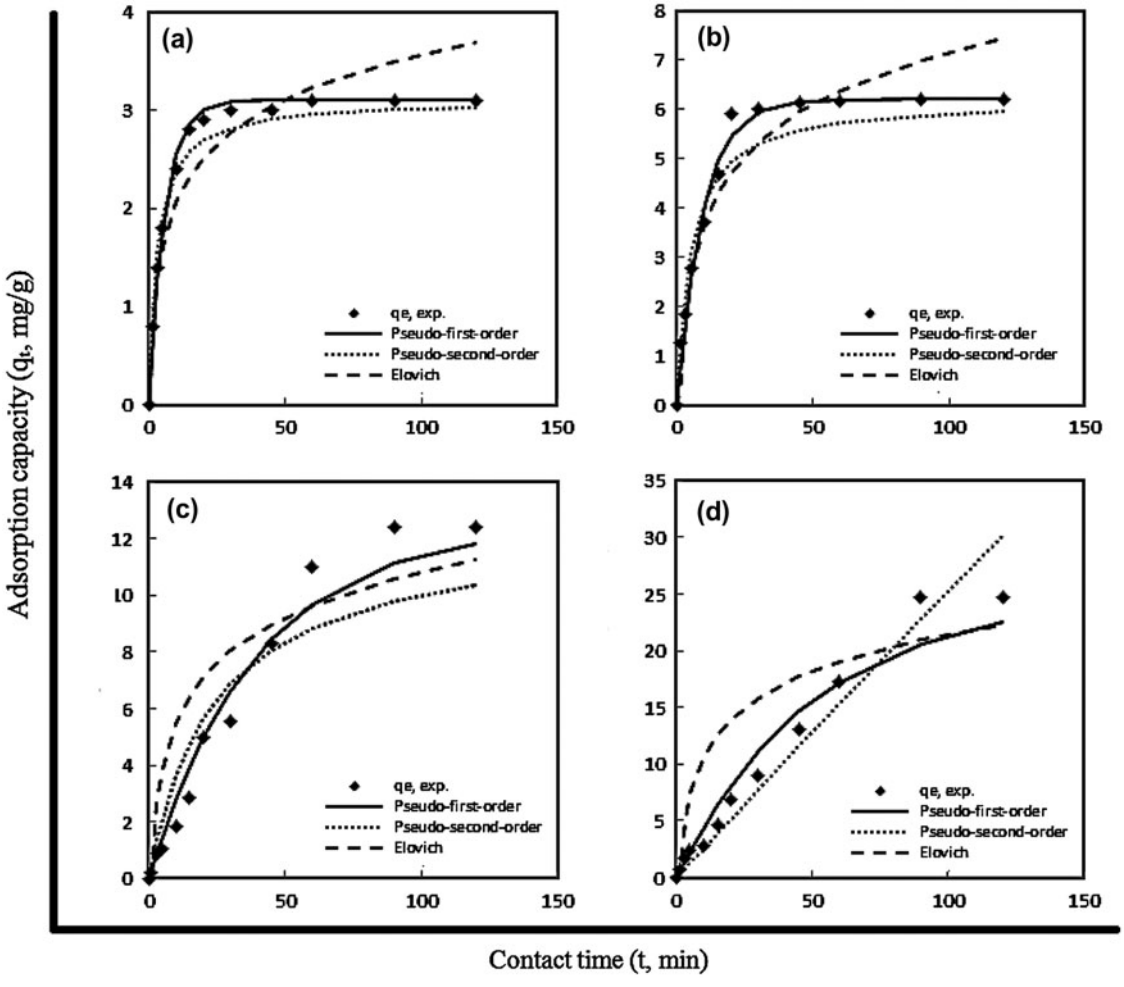


Fig. 2. Non-linear kinetic models for MB adsorption onto ZDMF at different concentrations: (a) 25 mg/L, (b) 50 mg/L, (c) 100 mg/L, and (d) 200 mg/L.

where $A$ (mg/g min) is the initial sorption rate and $B$ (g/mg) is related to the extent of surface coverage and activation energy for chemisorption.

To measure the fitness of non-linear model to experimental kinetic data residual or sum of squares error (SSE) was applied as an error function. It can be defined as:

$$\mathrm{SSE} = \sum_{i=1}^{n} (q_{e,\mathrm{cal}} - q_{e,\mathrm{exp}})^2 \quad (7)$$

where $q_{e,\mathrm{cal}}$ and $q_{e,\mathrm{exp}}$ are the calculated and experimental adsorption capacities at equilibrium, $n$ is the number of observations.

Data fitted well to pseudo-first-order kinetics model as evident by higher regression coefficient ($R^2$) values and agreement between theoretical and experimental adsorption capacity values at various MB concentrations obtained by linear and non-linear models (Tables 1(a) and (b)). The applicability of pseudo-first-order model was also confirmed by non-linear kinetic model plots (Fig. 2). Pseudo-first-order model applicability confirmed that MB adsorption onto ZMDF resin was physical in nature. These results agreed well with previously reported results for brilliant blue FCF and malachite green adsorption on hen feathers, respectively [30,31].

### 3.3. Effect of concentration and adsorption isotherms

The concentration studies were carried out by varying MB concentration from 25 to 500 mg/L and temperature from 20 to 50°C. The adsorption increased with the increase in MB concentration and temperature. The increase in adsorption with increase in temperature revealed endothermic nature of adsorption process.

Linearized and non-linearized forms of Langmuir and Freundlich isotherm models were applied to data

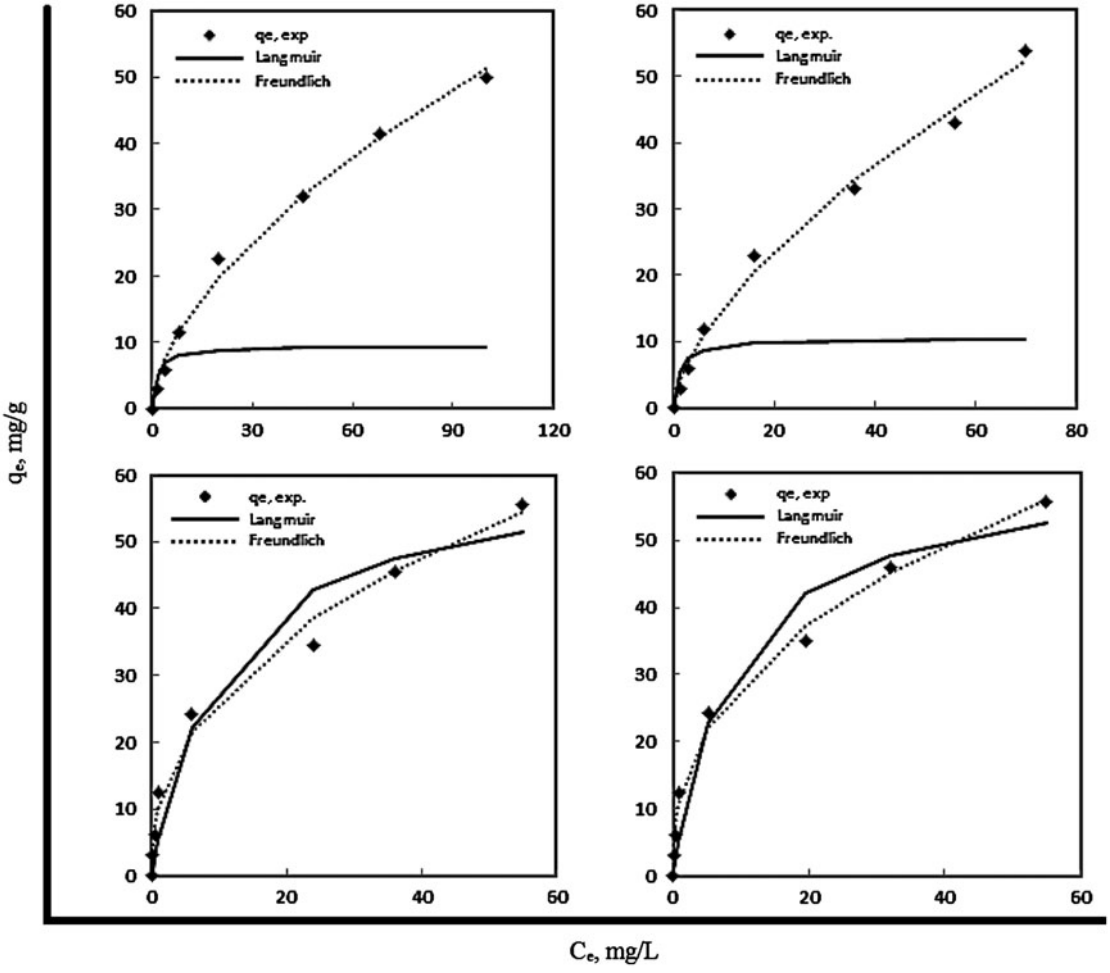


Fig. 3. Non-linear adsorption isotherms for MB adsorption onto ZDMF at (a) 20°C, (b) 30°C, (c) 40°C, and (d) 50°C.

(Fig. 3). Langmuir model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface and each molecule adsorbed onto the surface requires equal adsorption activation energy, while Freundlich model describes reversible adsorption and is not restricted to the formation of a monolayer.

Langmuir model in linearized and non-linearized form are given as [32]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{8}$$

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} \times C_e \tag{9}$$

where $k_L$ (L/mg) and $q_m$ (mg/g) are Langmuir constants related to the binding energy with a pH-dependent equilibrium constant and the maximum adsorption capacity determined by the number of reactive surface sites in an ideal monolayer system, respectively.

Freundlich model in linearized and non-linearized form are given as [33]:

$$q_e = k_F C_e^{1/n} \tag{10}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{11}$$

Table 1(a)
Non-linear kinetics for MB adsorption on ZDMF resin

| Models | Concentrations ($C_o$, mg/L) | | | |
|---|---|---|---|---|
| | 25 | 50 | 100 | 200 |
| *Pseudo-first-order* | | | | |
| $q_{e,exp}$, mg/g | 3.10 | 6.21 | 12.42 | 24.74 |
| $q_{e,\ theo}$, mg/g | 3.10 | 6.21 | 12.42 | 24.74 |
| $K_1$, 1/min | 0.1734 | 0.1079 | 0.0253 | 0.0199 |
| $R^2$ | 0.9798 | 0.9796 | 0.9608 | 0.9443 |
| SSE | 0.1698 | 0.8591 | 7.083 | 36.175 |
| *Pseudo-second-order* | | | | |
| $q_{e,exp}$, mg/g | 3.10 | 6.21 | 12.42 | 24.74 |
| $q_{e,theo}$, mg/g | 3.02 | 5.96 | 10.33 | 30.141 |
| $K_2$, g/mg min | 0.1076 | 0.0319 | 0.0033 | 0.0004 |
| $R^2$ | 0.9614 | 0.9120 | 0.8177 | 0.9541 |
| SSE | 0.2103 | 2.604 | 26.472 | 46.848 |
| *Elovich* | | | | |
| $A$, mg/g min | 1.769 | 4.086 | 6.5743 | 7.934 |
| $B$, g/mg | 1.536 | 0.665 | 0.4321 | 0.2154 |
| $R^2$ | 0.8922 | 0.9068 | 0.7080 | 0.6660 |
| SSE | 1.149 | 5.194 | 55.298 | 306.702 |

Table 1(b)
Linear kinetics for MB adsorption on ZDMF resin

| Model | Concentrations ($C_o$, mg/L) | | | |
|---|---|---|---|---|
| | 25 | 50 | 100 | 200 |
| *Pseudo-first-order* | | | | |
| $q_{e,exp}$, mg/g | 3.10 | 6.21 | 12.42 | 24.74 |
| $q_{e,\ theo}$, mg/g | 2.66 | 5.42 | 12.88 | 24.78 |
| $K_1$, 1/min | 0.1453 | 0.0827 | 0.0239 | 0.0166 |
| $R^2$ | 0.9999 | 0.9996 | 0.9739 | 0.9875 |
| *Pseudo-second-order* | | | | |
| $q_{e,exp}$, mg/g | 3.10 | 6.21 | 12.42 | 24.74 |
| $q_{e,theo}$, mg/g | 3.20 | 6.58 | 25.44 | 49.50 |
| $K_2$, g/mg min | 0.1091 | 0.0292 | 0.0004 | 0.0002 |
| $R^2$ | 0.9996 | 0.9974 | 0.8192 | 0.6626 |
| *Elovich* | | | | |
| $A$, mg/g min | 3.9381 | 3.1431 | 1.1486 | 1.953 |
| $B$, g/mg | 1.9635 | 0.8188 | 0.3416 | 0.1874 |
| $R^2$ | 0.9001 | 0.9099 | 0.8555 | 0.7939 |

where $k_F$ (mg/g) $(L/mg)^{1/n}$ and $n$ are the Freundlich constants indicating adsorption capacity of adsorbent and measure of deviation from linearity of the adsorption, respectively.

Data revealed applicability of Freundlich model at different temperatures as indicated by higher regression coefficient ($R^2$) values for both linear and non-linear models (Table 2). The values of $k_F$ for both linear and non-linear models increased with the increase in reaction temperature indicated the increase in adsorption efficiency with the increase in temperature.

### 3.4. Thermodynamics studies

Thermodynamics parameters were analyzed by varying MB concentration from 25 to 500 mg/L. The temperature range used during the study was 20–50°C. Various thermodynamics parameters such as standard enthalpy change ($\Delta H^\circ$), standard entropy change ($\Delta S^\circ$), and Gibb's free energy change ($\Delta G^\circ$) were evaluated.

Gibb's free energy change ($\Delta G^\circ$) was calculated as:

$$\Delta G^\circ = -RT \ln K_c \tag{12}$$

$$\ln K_c = \frac{C_{Ae}}{C_e} \tag{13}$$

where $R$ is a universal gas constant (8.314 J/mol K), $T$ is an absolute temperature (K), $K_c$ is the equilibrium constant, and $C_{Ae}$ and $C_e$ are the equilibrium concentration of MB on ZDMF resin and in the solution (mg/L), respectively.

Table 2
Adsorption isotherm models for MB adsorption on ZDMF resin

| Model | Parameters at various temperatures, ℃ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Linear | Non-linear | Linear | Non-linear | Linear | Non-linear | Linear | Non-linear |
| *Langmuir* | | | | | | | | |
| $q_m$, mg/g | 68.027 | 9.430 | 71.942 | 10.433 | 55.866 | 61.438 | 56.818 | 60.798 |
| $K_L$, L/mg | 0.2124 | 0.756 | 0.0306 | 0.854 | 0.1723 | 0.0950 | 0.1982 | 0.1146 |
| $R^2$ | 0.9840 | 0.3338 | 0.9536 | 0.3282 | 0.9507 | 0.9500 | 0.9663 | 0.9572 |
| *Freundlich* | | | | | | | | |
| $K_F$, $(mg/g)(L/mg)^{1/n}$ | 3.7058 | 3.4377 | 4.1862 | 3.5350 | 8.6408 | 10.1079 | 9.3231 | 11.5839 |
| $1/n$ | 1.7522 | 0.5866 | 1.6961 | 0.6337 | 2.1349 | 0.4206 | 2.1533 | 0.3931 |
| $R^2$ | 0.9904 | 0.9922 | 0.9917 | 0.9919 | 0.9926 | 0.9867 | 0.9898 | 0.9919 |

The values of $\Delta H^\circ$ and $\Delta S^\circ$ were obtained from Van't Hoff plot ($\ln K_c$ vs. $1/T$):

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \quad (14)$$

The positive values of $\Delta H^\circ$ indicated endothermic nature of adsorption process at various MB concentrations (Table 3). This showed that increase in heat energy exceeded the exothermicity of MB ions to attach to the solid resin surface. Endothemic adsorption process was also observed by Amido Black 10B adsorption on hen's feather [34]. The positive values of $\Delta S^\circ$ at various MB concentrations suggested the randomness at solid/solution interface. The negative values of $\Delta G^\circ$ depicted spontaneity of adsorption process and the spontaneity increased with increase in temperature [35]. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were decreased with increasing initial MB concentration which was due to the difference in the attractive forces between MB and binding sites over adsorbent surface. At lower MB concentration, there was a greater favor of MB adsorption due to cooperative and non-cooperative availability of MB ions at higher binding energy. This indicated that MB adsorption on the ZMDF resin decreased at higher aqueous phase MB concentrations as compared to lower concentrations.

### 3.5. Breakthrough studies

Breakthrough studies were conducted in D.I. and tap water matrix. The breakthrough curves (Fig. 4) showed that 550 mL MB solution of 50 mg/L intial concentration could be passed through the columns without detecting any traces of MB in both matrixes. The observed breakthrough and exhaustive capacities in both matrixes were same 27.5 and 45 mg/g, respectively. These results demonstrated that ZDMF resin could be effectively utilized for the treatment of dye industry effluents even though these effluents contain carbonates and bicarbonates of sodium, calcium, and magnesium.

Table 3
Thermodynamics parameters for MB adsorption on ZDMF resin (MB concentration from 25 to 500 mg/L; temperature range 20–50℃)

| $C_o$, mg/L | $\Delta H^\circ$, kJ/mol | $\Delta S^\circ$, J/mol K | $-\Delta G^\circ$, J/mol | | | |
|---|---|---|---|---|---|---|
| | | | 293 K | 303 K | 313 K | 323 K |
| 25 | 82.46 | 301.60 | 6301.94 | 7416.35 | 13773.9 | 14213.9 |
| 50 | 71.51 | 263.42 | 6119.24 | 7116.58 | 11957.5 | 13306.3 |
| 100 | 70.62 | 259.96 | 5948.72 | 6930.16 | 11957.5 | 12943.7 |
| 200 | 41.81 | 160.33 | 5351.90 | 6151.74 | 9045.53 | 9729.28 |
| 300 | 25.51 | 101.31 | 4226.46 | 5018.13 | 6354.77 | 7159.34 |
| 400 | 24.16 | 95.52 | 3863.50 | 4572.24 | 6021.68 | 6557.8 |
| 500 | 19.02 | 77.18 | 3376.30 | 4572.24 | 5441.37 | 5615.22 |

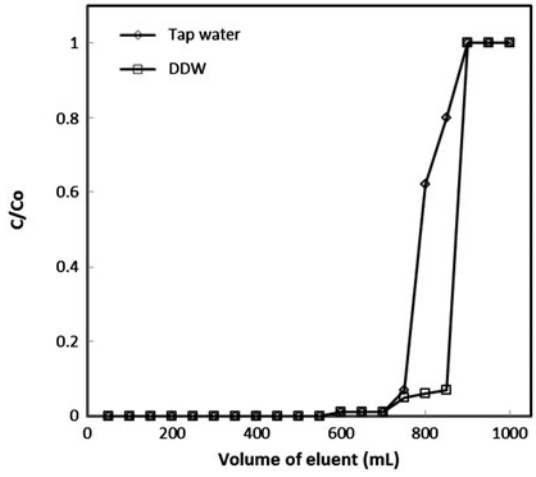


Fig. 4. Breakthrough curve for MB adsorption on ZDMF resin.

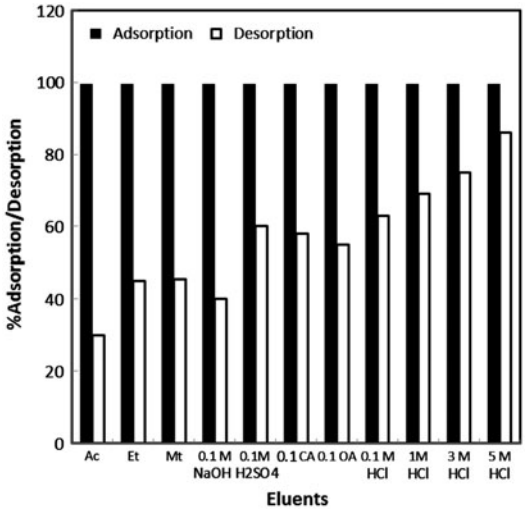


Fig. 5. Desorption studies of MB from ZDMF resin using various eluents.

### 3.6. Desorption and regeneration studies

Desorption and regeneration studies were carried out to check the recovery of adsorbed MB from ZDMF resin and to further reutilize it. Various acids, bases, and solvents were used as eluents. Optimum MB recovery was observed with HCl. It was also noted that MB recovery increased from 63 to 86% with the increase in HCl concentration from 0.1 to 5 M, respectively (Fig. 5). Desorption of MB by HCl suggested that the adsorption of MB on ZDMF resin was due to ion-exchange and electrostatic interaction.

Regeneration studies were conducted to check the reusability of spent ZDMF resin. The adsorption was reduced from 98 to 88% after five consecutive cycle while, desorption reduced from 86 to 72% (Fig. 6). The regeneration studies showed that ZDMF resin could be efficiently utilized for MB removal and recovery without any appreciable loss in the adsorptive performance.

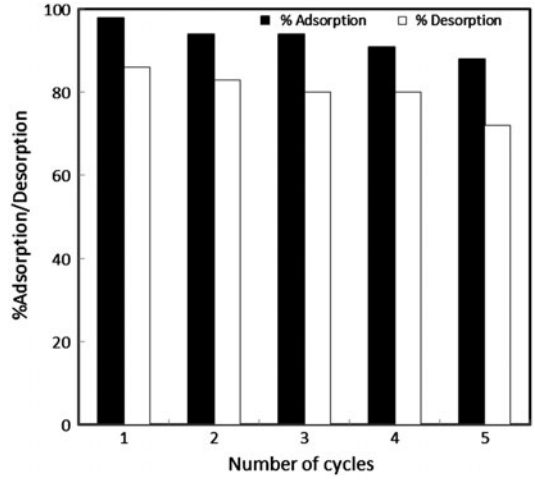


Fig. 6. Batch studies to regenerate the ZMDF resin.

## 4. Conclusions

The observed results showed that ZDMF resin is an excellent adsorbent for the removal of MB from aqueous solutions. The maximum adsorption of MB (24.75 mg/g) using ZDMF was observed at pH 10. The kinetics data were best fitted in pseudo-first-order rate equation as evident from the values of regression coefficients ($R^2$). The adsorption isotherm studies showed that Freundlich model was better fitted. The negative values of $\Delta G^{\circ}$ suggested that the adsorption was spontaneous in nature. The positive value of $\Delta H^{\circ}$ and $\Delta S^{\circ}$ indicated endothermic adsorption process randomness at solid/solution interface. Breakthrough studies revealed effectiveness of ZDMF resin for MB removal with no significant effect of solvent (D.I. and tap water) matrix. Regeneration studies showed that ZDMF resin could be efficiently utilized for MB removal and recovery without appreciable loss in the adsorptive performance confirming economic feasibility of ZDMF resin.

## Acknowledgment

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project no. RGP-VPP-043.

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