

RESEARCH PAPER

Influence of amine group on the adsorptive removal of basic dyes from water using two nanoporous isorecticular Zn(II)-based metal organic frameworks

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ABSTRACT

Dyes are the most abundant hazardous components existing in the environment because of their extensive use in industries. So, in the present study, two isorecticular Zn(II)-MOFs, TMU-16 and TMU-16-NH₂, were used for the adsorptive removal of harmful cationic dyes from aquatic medium. In order to improve the removal efficiency, optimization of the experimental conditions was carried out as a function of pH, MOF dosage, dye concentration and contact time. The maximum removal capacity was obtained at pH 12, 10 mg of MOF and 20 min as the contact time. The adsorption isotherms of each dye over both sorbents matched with the Langmuir model, and the adsorption kinetics followed the pseudo-second order kinetic model. The dye adsorption over TMU-16-NH₂ is higher than that over TMU-16, indicating that the addition of amine groups in MOF network played an important role in the adsorption process, because of electrostatic interactions and hydrogen bonding. Thermodynamic studies indicated that adsorption process is spontaneous and endothermic.

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INTRODUCTION

Recently, an important and vital global problem is the environmental pollution by hazardous organics because of their effects on the human health and ecological systems [1-3]. The most abundant hazardous components existing in the environment are dyes. Pigments and dyes are present in waste water and natural water, because of their extensive use in industries such as the textile, leather, paper, printing, dyestuff, and plastic [4-7]. Consequently, the development of methods for the removal of dyes in waste water is of particular significance. Therefore, a variety of the physical, chemical and biological methods have been used in the removal of dyes [8, 9]. Adsorption has been widely recognized as a powerful technique for removal of dyes [10-12]. The most attractive aspect

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of this technique is the comparatively low cost, wide range of applications, simplicity of design, easy operation, low harmful secondary products and facile regeneration of the sorbents [13-15].

During the last years, metal organic frameworks (MOFs), as organic-inorganic hybrid solids which can exhibit completely regular large cavities and open channels, have received much attention. These characteristics have made them the valuable organometals for frequent use in a variety of research areas, including adsorption/storage in gases [16, 17], separation of chemicals [18, 19], drug delivery [20] and catalysis [12, 22].

MOFs are among the materials widely used as the sorbents due to their unique multifunctional structure that can generate various interactions with functional groups such as electrostatic and

hydrogen bonds [13, 23].

In 2010, Haque *et al.* reported the first dyes removal application of MOFs [24]. Then, they studied kinetics and thermodynamics parameters of methyl orange and methylene blue adsorption from aqueous solution with MOF-235 [25]. MIL-101(Al) and MIL-101-NH₂(Al) have been used for adsorptive removal of methylene blue and methyl orange from aqueous solutions in order to observe the effect of the amine groups on the sorption behavior [26].

The aim of this work is to introduce the efficient sorbents for significant removal of hazardous dyes from aqueous media, and understand the influence of amine functionalization on the adsorption capacity of cationic dyes. Two isorecticular porous Zn(II)-MOFs (TMU-16 and TMU-16-NH₂) have been applied as sorbents. Chemical structures of dyes used in this work are displayed in the Table S1. Cationic dyes are dyes with basic role in the reaction and usually negative charged unites. These dyes can change the color of water and highly influence the water quality.

The effect of various parameters including pH, contact time, dye concentration and the amount of sorbent on the removal process are also investigated.

EXPERIMENTALS

Materials and methods

All materials were purchased from commercial suppliers (Sigma-Aldrich and Merck Company), and used without further purification. X-ray powder diffraction patterns were performed using a Philips X'pert diffractometer with an X-Ray tube anode Co ($\lambda=1.78897 \text{ \AA}$). An ECS 4010 CHNS made in Costech Italy was used to elemental analyses (carbon, hydrogen, and nitrogen). FT-IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) using KBr pellet were recorded by VERTEX 70 FT-IR spectrometer. Surface area analysis and textural parameters were measured by Belsorp MiniII Japan instrument. Thermogravimetric analyzer TGA-50 (Shimadzu Japan) was used to thermogravimetric analysis (TGA). A Shimadzu UV-1800 spectrophotometer was applied to determine the dye concentrations.

Synthesis of MOFs

Isorecticular porous TMU-16 and TMU-16-NH₂ were prepared according to the reported procedure [27]. TMU-16 and TMU-16-NH₂ were synthesized using a bipyridyl-type ligand (4-bpdh) mixed into two dicarboxylate homologous

ligands, 1,4-benzenedicarboxylic acid (H₂BDC) and 2-amino-1,4-benzenedicarboxylic acid (NH₂-BDC), respectively. Syntheses of TMU-16 or TMU-16-NH₂ were carried out in 2 steps: firstly, preparation of 4-bpdh and then preparation of TMU-16 and TMU-16-NH₂. 4-bpdh was synthesized according to the method reported earlier [28]. Briefly, preparation of TMU-16; Zn(NO₃)₂·6H₂O, 4-bpdh and H₂BDC were performed in a molar ratio of 1:0.5:1 and were dissolved in 15 mL of DMF as solvent. Then, the resulted solution was transferred into an autoclave and heated at 115 °C in oven for 3 days. TMU-16-NH₂ was also prepared using the same procedure using NH₂-BDC at a lower temperature (80 °C). Obtained crystals were washed by DMF and dried in a vacuum at 150 °C for 24 h.

Removal studies

Dye removal capacity of TMU-16 and TMU-16-NH₂ was evaluated by adsorption measurements. Initially, an aqueous stock solution of each cationic dye (1000 mg L^{-1}) was prepared in 100 mL of deionized water. By consecutive dilution with deionized water, 1-30 mg L^{-1} standard solutions of dyes were prepared. Calibration curves for each dye was obtained from the spectra of the standard solutions using the maximum absorbance at Optimization experiments were performed in order to fix the effective parameters of adsorptive removal, such as pH, mass of MOFs and sorption time. Before the addition of the MOFs (5-30 mg) into 10 mL of aqueous solutions of each dye at the concentration of 20-200 mg L^{-1} , the pH (1-12) was adjusted by dropwise addition of 0.1 M HCl or 0.1 M NaOH, respectively. Solutions were stirred for 5-60 min by magnetic stirrer at room temperature. Then, the sorbents were separated with centrifuging at 5000 rpm for 10 min. The final concentration of each dye in the solution phase was determined by UV-Vis spectrophotometer. The adsorptive amount of dyes was computed by equation 1:

$$q = \frac{C_i - C_f}{W} V \quad (1)$$

where q (mg g^{-1}) is the amount of dye adsorbed per gram of MOF, C_i (mg L^{-1}) and C_f (mg L^{-1}) are concentrations of dye before and after removal, respectively. W (mg) is the mass of MOF and V (mL) is the volume of work solution [29].

Adsorption capacity, as an important factor to show the efficiency of sorbents, was calculated from

Langmuir adsorption isotherm. Pseudo-second order kinetic model was employed to designate the kinetics of dyes adsorption. Thermodynamic functions like change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS), were determined from van't Hoff equation.

RESULT AND DISCUSSION

Characterization of MOFs

The synthetic MOFs were characterized by X-ray diffraction (XRD). XRD patterns of the synthesized MOFs are shown in Fig. S1. Comparing XRD patterns with previously reported results confirmed the formation of TMU-16 and TMU-16-NH₂.

Removal of dyes

Effect of the pH of solution

Generally, a number of different interactions between sorbent and adsorptive, such as electrostatic, acid-base, hydrogen bonding and π - π stacking interactions could be observed in adsorptive removal of dyes over MOFs [13]. It

is well-known that adsorption of dyes is highly dependent on the pH of solution. Thus, the UV-Vis spectra of solution with 20 mg L⁻¹ concentration of each dye at acidic and basic conditions at 300~800 nm were recorded (Fig. S2). Recorded UV-Vis spectra of dyes confirmed that the change of the initial pH of solution has a small effect on and the structure of dyes remains stable under changes of the pH of solution. At low pH, adsorption of cationic dyes over the sorbents decreases, but at high pH, the adsorption amount of dyes over the MOFs increases. These are attributed to the surface charges on MOFs. Table 1 shows the effect of pH on the removal of each dye. Due to the electrostatic interaction between negative surface of MOFs and positive charge of cationic dyes, the maximum adsorption of dyes was obtained at basic condition at pH=12.

The high adsorption of dyes over sorbents at basic conditions could be explained by Zeta potential measurements (Fig. 1). The decrease of Zeta potential suggested that the density of negative

Table 1. Influence of various experimental parameters including pH, amount of MOF, dye concentration and contact time on adsorptive removal by TMU-16 and TMU-16-NH₂.

Parameters	TMU-16				TMU-16-NH ₂			
	q (mg g ⁻¹)				q (mg g ⁻¹)			
	TBO	SO	JGB	BCB	TBO	SO	JGB	BCB
pH								
1	0.5	0.5	1.5	1.4	0.9	1.1	2.3	1.8
3	2.65	1.2	1.6	1.65	3.3	1.2	2.35	2.3
5	2.8	1.4	1.95	1.9	4.4	1.3	2.5	2.6
7	4	1.6	2	2.03	5.3	2.2	3.1	3.15
9	4.8	1.8	3	2.9	6	2.5	3.5	3.7
12	5.5	4	3.9	3.85	6.2	4.2	4.9	5
Amount of MOF (mg)								
5	3.5	3	2.2	3.3	4.25	3.3	2.4	3.5
10	4.3	4.2	3.7	4.15	5.6	4.7	4	4.5
15	5	5.1	5	4.4	6	6.2	6	5
20	5.6	5.8	5.4	5.7	6.2	6.4	6.2	6.2
25	5.8	6	5.5	5.85	6.2	6.4	6.2	6.2
30	6	6.15	5.7	6	6.2	6.4	6.2	6.2
Dye concentration (ppm)								
20	1.8	2	1.9	1.8	2.5	1.5	2.5	3.5
50	4	4	8	3.8	7	6	5	12
80	8	7.3	11.5	6	10.5	7.5	10.5	15
100	9	9	13	9	12	9	12	18
150	10	13	16	12.5	14	10	10.5	25
200	12	15	16.4	15.2	16	12	11	24
Contact time (min)								
10	1.5	0.8	2	2.8	2.5	1.5	2.2	3
20	4.2	3	4.3	5.2	5	4.2	4.7	5.5
30	4.4	3.3	4.4	5.3	5.2	4.3	4.75	5.5
40	4.5	3.3	4.5	5.3	5.2	4.3	4.75	5.5
50	4.6	3.3	4.5	5.3	5.3	4.4	4.75	5.5
60	4.8	3.5	4.8	5.3	5.4	4.4	4.8	5.6

TBO: Toluidine Blue O
 SO: Safranin O
 JGB: Janus Green B
 BCB: Brilliant cresyl Blue

charge over adsorbents increases with increasing the pH of solution. In the basic pH, the sorbents were covered by a layer of negative charge, therefore, capacity of removal is increased by decreasing the Zeta potential.

Effect of the MOF amount

The effect of the sorbent amount on adsorption capacity of dyes was studied in the range of 5-30 mg. Results are shown in Table 1. Initially, adsorption of each dye is proportional to the increase in the sorbent amount. As expected, availability to the surface area increases the adsorption of dyes. Gradually, removal of dyes varied with increasing the MOF dosage from 10 to 30 mg. This fact could be attributed to the overlapping or aggregation of sorption sites that decrease the available total sorption surface area for dyes molecules. Based on the results, 10 mg of sorbents was chosen as the optimum amount.

Effect of the dye concentration

Dye concentration showed a significant effect on the dye adsorption over MOFs. At first, due to increase in driving force of the concentration gradient, dye removal for both sorbents increased significantly with increasing the dye concentration, as indicated in Table 1. In high concentrations of dyes, adsorption of dyes did not significantly change, due to the aggregation of dyes around the adsorption sites.

Effect of the contact time

Contact time between dyes and MOFs is one of the important parameters affecting on the

performance of removal processes. Obtained results are shown in Table 1. The adsorption of the cationic dyes was firstly increased with contact time. Based on the results, increase of the contact time from 20 to 60 min did not change the adsorption of each dye significantly. These results ascribed to accumulation of the dye molecules around the active sites of MOFs. The UV-Vis absorption spectra of the dyes solution during the adsorption over MOFs at optimum conditions are shown in Fig. S3.

However, the dye adsorption over TMU-16-NH₂ is higher than that over TMU-16, indicating that the addition of amine groups into the MOF network played an important role in adsorption due to ability of NH₂ function to formation of hydrogen bonds.

Kinetic studies

Information about the rate and mechanism of adsorption was obtained from the adsorption kinetic studies. The kinetic parameters are required for better modeling and designing of an adsorption process. Pseudo-second order kinetic model (Eq. 2) was used for adsorption of dyes over TMU-16 and TMU-16-NH₂;

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

where q_e and q_t (mg g⁻¹) are the amounts of dyes adsorbed over sorbent at equilibrium and t time, k_2 (g mg⁻¹ min⁻¹) is the pseudo-second order rate constant [30]. Kinetic data were well fitted to the pseudo-second order kinetic model due to the good calculated correlation coefficients, as indicated

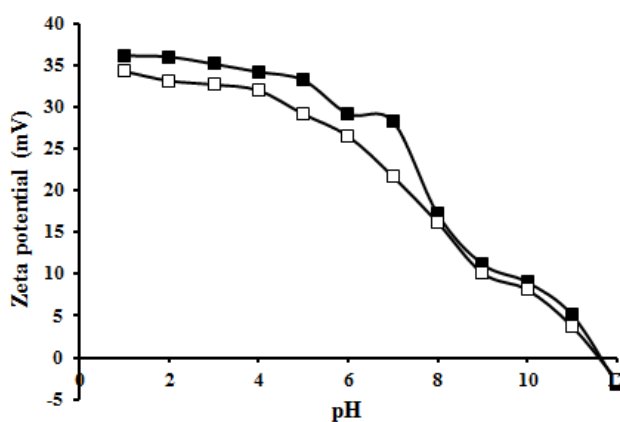


Fig. 1. Zeta potential curves of TMU-16 (□) and TMU-16-NH₂ (■) at various pHs.

in Fig. 2. The pseudo-second order rate constants were determined for each dye, and are summarized in Table 2.

Thermodynamic studies

Langmuir model was used to deduce the effect of the grafting amine groups on the adsorption behavior. The adsorption capacity was calculated using the linear form of Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \quad (3)$$

where q_e (mg g⁻¹) is the amount of dyes adsorbed at equilibrium, C_e (mg L⁻¹) is the concentration at equilibrium, q_0 (mg g⁻¹) is the maximum adsorption,

and b is the Langmuir constant (L mg⁻¹ or L mol⁻¹) [29].

After adsorption for 12 h, adsorption isotherms were obtained at 25 °C, and results are shown in Fig. 3 and Table 3.

When amine groups are added to the network of MOFs, hydrogen bonding plays an important role in increase of adsorption ability of MOFs [13]. Adsorption capacity of each dye over TMU-16-NH₂ is higher than that over TMU-16. These dyes contain sulfur, nitrogen or oxygen atoms participating in hydrogen bonding with grafted amine groups in TMU-16-NH₂.

Comparison maximum dye capacity over these MOFs with reported data in the adsorptive removal

Table 2 Pseudo-second order kinetics parameters for dyes adsorption over TMU-16 and TMU-16-NH₂. Table 3 Langmuir parameters for the adsorption of dyes over TMU-16 and TMU-16-NH₂.

Dyes	TMU-16-NH ₂		TMU-16	
	k ₂ [*]	R ²	k ₂ [*]	R ²
Toluidine Blue O	0.0073	0.989	0.00118	0.996
Safranin O	0.0081	0.978	0.0051	0.997
Janus Green B	0.0052	0.999	0.0111	0.998
Brilliant Cresyl Blue	0.0087	0.999	0.0085	0.989

* g mg⁻¹ min⁻¹

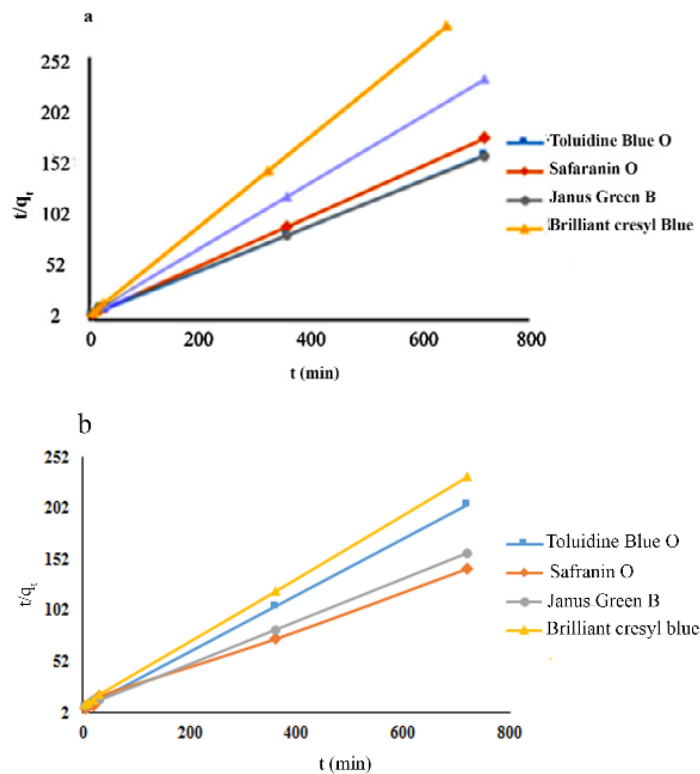


Fig. 2. Plots of pseudo-second order kinetics of dyes adsorption over (a) TMU-16-NH₂ and (b) TMU-16.

Table 3 Langmuir parameters for the adsorption of dyes over TMU-16 and TMU-16-NH₂.

Dyes	TMU-16-NH ₂						TMU-16					
	298		308		318		298		308		318	
	q ₀ ^a	b ^b	q ₀ ^a	b ^b	q ₀ ^a	b ^b	q ₀ ^a	b ^b	q ₀ ^a	b ^b	q ₀ ^a	b ^b
Toluidine Blue O	610	0.63	792	1.01	919.12	2.87	534.5	0.63	645.62	0.92	829.23	1.44
Safranin O	645	0.50	842.14	0.99	924.38	1.60	575.19	0.31	732.85	0.47	869.21	0.82
Janus Green B	700.72	0.34	822.11	0.68	944.73	1.10	632.6	0.34	759.12	0.40	887.24	0.86
Brilliant Cresyl Blue	639.72	0.50	905.12	0.50	1132.4	2.56	512.2	0.82	699.3	1.34	866.55	1.78

^a mg g⁻¹
^b L mg⁻¹

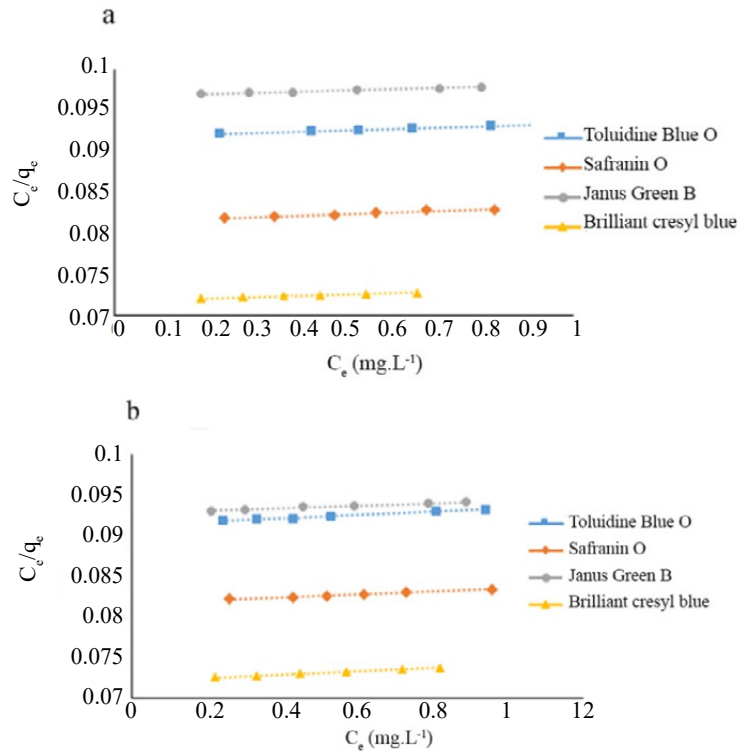


Fig. 3. Linear plot of the Langmuir equilibrium model of adsorption dyes over (a) TMU-16-NH₂ and (b) TMU-16.

of studied dyes (Table 4) demonstrated that TMU-16 and TMU-16-NH₂ are excellent sorbents for removal of basic dyes. For example, in the case of Janus Green B maximum reported adsorption capacity by other sorbents is 250 mg g⁻¹, while with TMU-16 and TMU-16-NH₂ are 632.6 and 700.72 mg g⁻¹, respectively.

To illustrate the relationship between adsorption process and temperature, thermodynamics functions such as G, H and S were calculated by the following equations:

$$\Delta G = -RT \ln b \quad (4)$$

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T

is the temperature (K) and b is Langmuir constant (L mg⁻¹) [43]. For each dye, the temperature of 10 mL of sample solutions containing 20 mg L⁻¹ of dye was adjusted at two different temperatures including 35 and 45 °C. Results are shown in Fig. 4. Plotting of $\ln b$ vs. $1/T$ makes possible determination of the enthalpy and entropy of adsorption process (Fig. 5). Obtained results from the thermodynamic studies are summarized in Table 5. The negative value of G indicated that the adsorption of the dyes over TMU-16 and TMU-16-NH₂ is feasible and spontaneous. Because of the positive ΔH value, removal processes over these sorbents are endothermic. The positive values of ΔS can be due to replacement of several solvent molecules by a dye molecule that is the driving force of the reaction.

Table 4 Comparison of maximum dyes adsorption capacity of MOFs with previously reported sorbents obtained from Langmuir adsorption isotherm model.

Dye	Sorbent	q (mg g ⁻¹)	Ref.
Janus Green B	ZnO/Zn(OH) ₂ -NPAC	81.3-98.03	[31]
	TLR-PA	51	[32]
	PAC	57	[32]
	MMMWCNTs	250	[33]
	CNTs	166.67	[33]
	OMWCNTs	56	[34]
	SDS-γ-Fe ₂ O ₃	172.4	[35]
	TMU-16	632.6	This Work
Brilliant Cresyl Blue	TMU-16-NH ₂	700.72	This Work
	CMC-Ac H	9.45	[36]
	HN	494.2	[37]
	Natural Clay	42	[38]
	SDS-γ-Fe ₂ O ₃	166.7	[35]
	TMU-16	512.2	This Work
	TMU-16-NH ₂	639.72	This Work
	Toluidine Blue	Gypsum	25
Pulp fibers		70	[40]
TMU-16		534.5	This Work
TMU-16-NH ₂		610	This Work
Safranin O	Nickel sulfide NPs	46	[41]
	Magnetic Mesoporous Clay	18.48	[42]
	TMU-16	575.19	This Work
	TMU-16-NH ₂	645	This Work

TLR-PA=Phosphoric-acid-treated tendu leaf refuse, PAC= Powdered activated carbon, MMMWCNTs= Magnetic-modified multi-walled carbon nanotubes, CNTs= Carbon nanotubes, OMWCNTs =Oxidized multiwalled carbon nanotubes, HN= AAm-AMPSNa-MMT hydrogel nanocomposite, CMC-Ac H= Carboxy methyl cellulose incorporated acrylic hydrogels, NPs=Nanoparticles, SDS= Sodium dodecyl sulphate.

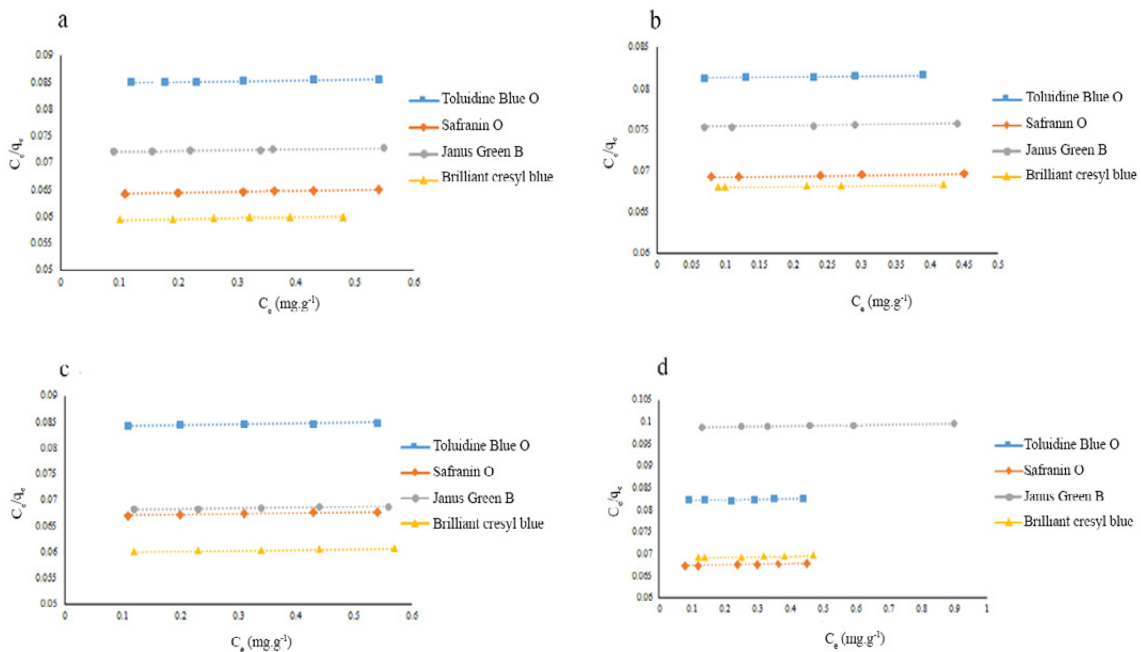
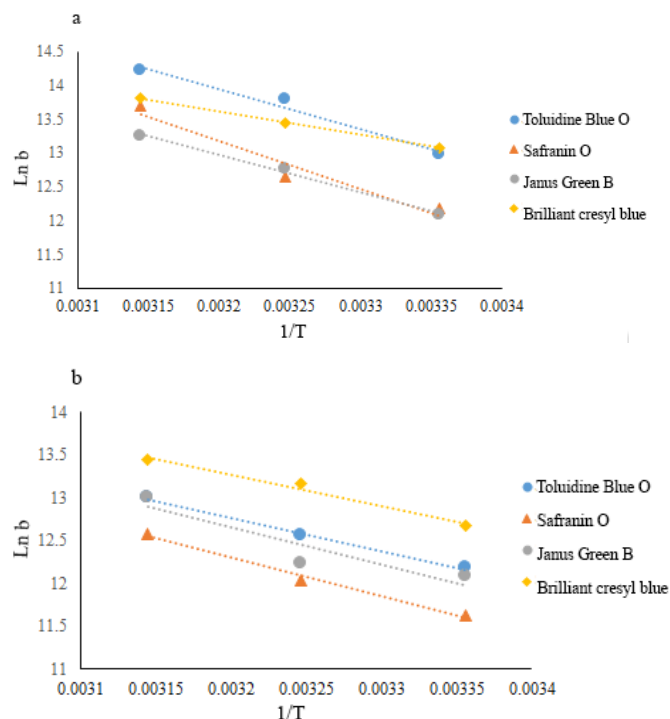


Fig. 4. Langmuir plots for the adsorption of dyes over sorbents at different temperatures: TMU-16-NH₂ ((a), (b) at 308 and 318 K, respectively) and TMU-16 ((c), (d) at 308 and 318 K, respectively).

Table 5: Adsorption thermodynamics functions of dyes over TMU-16 and TMU-16-NH₂.

Dyes	TMU-16-NH ₂				TMU-16					
	-ΔG (kJ mol ⁻¹)			ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	-ΔG (kJ mol ⁻¹)			ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
	Temperature (K)					Temperature (K)				
	298	308	318			298	308	318		
Toluidine Blue O	32.14	34.17	35.2	48.81	272.19	30.17	31.1	32.19	32.08	208.81
Safranin O	30.17	31.32	33.9	59.05	289.55	28.78	29.8	31.14	37.46	222.1
Janus Green B	29.91	31.62	32.8	46.03	255.11	29.92	30.3	32.2	35.98	220.3
Brilliant Cresyl Blue	32.4	33.31	34.2	28.62	204.76	31.4	32.6	33.3	30.29	207.26

Fig. 5. Van't Hoff equation plot of dyes adsorption over (a) TMU-16-NH₂ and (b) TMU-16.

CONCLUSION

In this study, two isorecticular nanoporous Zn(II)-MOFs, TMU-16 and TMU-16-NH₂, were found to exhibit the excellent adsorption capability for removal of cationic dyes from aqueous solutions. These MOFs showed a superior adsorption capacity and high adsorption rate for each dye. The adsorption isotherms fitted well to Langmuir model. Higher adsorption capacity was found for TMU-16-NH₂ compared to TMU-16 due to hydrogen bonding interaction between dyes and sorbent. Rate constants for each adsorption process of dye over MOFs were obtained with pseudo-second order kinetic model. Thermodynamic studies indicated that adsorption process is spontaneous and endothermic.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <http://nanochemres.org/>

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