Facile Ultrasonic Synthesis of Zirconium Based Porphyrinic MOFs for Enhanced Adsorption Performance Towards Anionic and Mixed Dye Solutions

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Abstract

A porphyrinic mesoporous metal–organic framework (PCN-222(M) (M = Mn, Fe, Cu)) has been synthesized by a simple sonochemical preparation method without high temperature in a short period of time. The ultrasonic method for the preparation of PCN-222(M) was found to be an efficient procedure with a good quantitative yield (PCN-222(M)-U). Harmful cationic and anionic dyes have been removed from wastewater using PCN-222(M). The comparative study of the influences of metalloporphyrin and non-metal porphyrin frameworks (PCN-222) on the adsorption process has been performed. Remarkably high adsorption capacity over PCN-222(M) for the anionic dyes is reported. The porphyrinic metal center of frameworks and pH values affected dye adsorption capacity, indicating the effective role of electrostatic interactions on dye adsorption. Due to the aggregation of MB and MO, a significant increase in the adsorption capacity was observed in a mixture of MB-MO solution at pH 7. High adsorption capacity over PCN-222(M) has been estimated using Langmuir and Freundlich equations. The adsorption kinetics, thermodynamic parameters, stability and reusability of adsorbents have also been reported. The stability of PCN-222(M) in water over three months was investigated (PCN-222(M)-3).

Electronic supplementary material

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1 Introduction

During the last decade, the world has witnessed a severe rise in environmental pollution [1, 2]. One of the major types of environmental pollutions is water pollution, which is caused by a wide range of chemicals [3]. The toxicity of dyes and inappropriate discharge of such wastes play major roles in water pollution and the spread of diseases [4, 5]. Dye adsorption is a popular process to remove toxic dyes from water [6–8]. It is essential to develop high capacity adsorbents in order to remove organic pollutants [9]. Different adsorbents such as activated carbon, carbon nanotubes, zeolites, graphene, and metal–organic frameworks (MOFs) have been used to treat industrial wastewaters [10, 11]. Among the conventional adsorbents, MOFs are well-known due to their high surface area, porosity and stability [12], which make them good candidates for prospective applications such as gas separations [13], catalysis [14], sensors [15], photocatalysis and adsorption [16–27]. MOFs have been recently developed for the removal of pollutants, including chemical substances [28, 29].

In this work, PCN-222(M) (M = Mn, Fe, Cu) has been synthesized by a simple and fast sonochemical irradiation technique. Methylene blue (MB) and methyl orange (MO) have been elected as cationic and anionic dyes, respectively, to examine the adsorption behavior of the synthesized MOFs [30]. The adsorption capacity of metal free porphyrin framework (PCN-222) was reported [31]. Herein, metalloporphyrin framework (PCN-222(M)) has been studied to examine the influence of the metal center of porphyrins on dye adsorption. Dye adsorption capacity over PCN-222(M) increased in comparison to PCN-222. The results of the adsorption capacity of MB and MO over PCN-222(M) are reported using Langmuir and Freundlich models. The adsorption kinetics and thermodynamic parameters have also been examined [32]. The synthesized MOFs can be recovered and recycled for eight cycles, which reduces the cost of production. Overall, a simple method for the synthesis of PCN-222(M), high adsorption capacity and 100% recyclability in the first cycle are the advantages of the method developed in this work.
2 Experimental Section

2.1 Synthesis Procedure

The synthesis procedure of [5,10,15,20-Tetrakis(4-carboxyphenyl) porphyrinato]-M (MTCPP (M = Mn(III), Fe(III) and Cu(II)) and PCN-222(M) has been explained in the supporting information.

2.1.1 Synthesis of PCN-222(M) Under Ultrasound Irradiation (PCN-222(M)-U)

ZrCl₄ (0.32 mmol, 75 mg), MTCPP (50 mg, M = Mn(III), Fe(III) and Cu(II)) and benzoic acid (22 mmol, 2700 mg) in DEF (8 mL) were dissolved by ultrasound irradiation. The vial containing the mixture was set in the probe of an ultrasonic generator at 40–100 °C with power of 600 and 1200 W for 120 min. The solution was checked every 30 min. The unreacted starting materials and impurities were removed by ultrasound irradiation of PCN-222(M) (100 mg) in DMF (40 mL) for 1 h at 60 °C. The powder obtained was washed with DMF and pure acetone. Fresh acetone was added and the sample was maintained for 24 h. Finally, PCN-222(M)-U was decanted and placed in vacuum for 6 h (Scheme 1).

2.2 Adsorption Method Study

To examine the adsorption capacity, aqueous solutions of MB or MO (1000 ppm) were prepared by dissolving MB or MO in deionized water (stock solution). Aqueous solutions of MB or MO (20–250 ppm) were prepared by dilution of the stock solutions with water. The MB or MO concentrations were determined by UV–Vis spectroscopy. The synthesized adsorbents (5 mg) were added into MB or MO solutions (25 mL) and mixed in the dye solution by ultrasonication for 5 min. The pH of the solution may influence the extent of adsorption. pH values in the ranges of 3–9 were used to study the effect of pH on MB and MO adsorption. A mixture of MB and MO with an initial dye concentration of 20–100 ppm was tested. Dye solutions were stirred and retained for a fixed period of time (3 to 120 min) at different temperatures. The effect of temperature on MB or MO adsorption was studied at 298, 303, 308 and 318 K. At the determined time, a sample of the solutions was filtered by centrifugation at 12,000 rpm for 5 min and the absorbance was then measured by UV–Vis spectroscopy.

3 Results and Discussion

3.1 Characterization of Adsorbents

The mixture of ZrCl₄ and MTCPP with benzoic acid in DMF was subjected to ultrasound irradiation. The sonochemical process is known for the rapid synthesis of MOFs under mild process conditions. Finally, the optimum conditions for the synthesis of PCN-222(M)-U were determined as 60 °C for 90 min, with a power of 1200 W (Tables S1, S2, and S3). Needle shaped PCN-222(Mn)-U, PCN-222(Fe)-U and PCN-222(Cu)-U were obtained in yields of 49, 52 and 50%, respectively. The Mn, Fe, and Cu content in PCN-222(M)-U is determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) to be 3.74, 4.11, and 4.23 wt%, respectively (Table S4). Short reaction time and low temperature synthesis of MOFs are the benefits of this method. The powder X-ray diffraction (PXRD) patterns of PCN-222(M) and PCN-222(M)-U indicate similar peaks for PCN-222(Mn), PCN-222(Fe), PCN-222(Cu), suggesting that no extra phase formation or framework collapse happens during ultrasound irradiation (Figs. 1a, S1, and S2) [33].

The FTIR spectra of PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) prepared by ultrasonic irradiation and solvothermal methods are shown in Figs. 1b, S3 and S4 and [34]. The spectra of PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) show two peaks at \( \nu = 1708(1703)(1695) \) and \( 1415(1419)(1417) \) cm\(^{-1}\), corresponding to the COO (asymmetric) and COO (symmetric) stretching vibrations, respectively. The peaks corresponding to the C-H bond of the benzeno and pyrrole ring, C=C (phenyl and pyrrole) stretching functional groups, and pyrrole deformation are located at \( \nu = 2856–3068 \) (2889–3066), 1554–1604 (1523–1602), and 1324(1346)(1384–1346) cm\(^{-1}\), respectively. The peak due to C–H (out of plane bending of the phenyl rings) is observed at \( \nu = 719(719)(713) \) and 779(800)(806) cm\(^{-1}\). The M–N peaks are located at \( \nu = 1012(999)(1022) \) cm\(^{-1}\).
The absorption spectra of TPPCOOMe, [TPP-COOMe]MnIII, [TPP-COOMe]FeIIICl and [TPP-COOMe]CuIIICl are shown in Fig. S5. The UV–Vis spectrum of TPP-COOMe shows the Soret band (transition from π to LUMO) at λ = 419 nm and Q bands (HOMO → LUMO) at λ = 519, 549, 593, and 650 nm (Fig. S5a). The spectrum of [TPP-COOMe]MnIII shows the Soret band at λ = 420 nm and Q bands at λ = 572 and 687 nm (Fig. S5b). The absorption spectrum of [TPP-COOMe]FeIIICl shows the Soret band at λ = 428 nm and Q bands at λ = 548 and 692 nm (Fig. S5c).

In the spectrum of [TPP-COOMe]CuII, Soret and Q bands appear at λ = 421 and 542 nm, respectively (Fig. S5d).

PCN-222(Mn, Fe, and Cu) has fine needle shaped crystals (Fig. 1c, S6a, and S6b). The SEM images of PCN-222(M) and PCN-222(M)-U are shown in Fig. S7. A comparison of the SEM of both PCN-222(M) and PCN-222(M)-U show crystals in the same morphology, no essential difference has not appeared.

The thermal stability of PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) prepared by reflux and ultrasonic preparation methods was investigated (Figs. 1d, S8, and S9).
Generally, weight loss for all compounds occurs in two steps. First, the solvent molecules entrapped into the pores are removed below 160 °C. A negligible weight loss occurs up to 300 °C, followed by a gradual weight loss in the range of 300–600 °C. Furthermore, the proportions of the residue for the PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) were 26.5, 27 and 23%, respectively. The amounts of remnant and weight loss temperatures for PCN-222(M)-U are acceptably similar to those of PCN-222(M).

N₂ adsorption and desorption were measured at 77 K (Fig. 1e). The typical type IV isotherm of PCN-222(Mn)-U is suggested. For the material with pores in mesopore range, the isotherm indicates the pattern of type IV and also higher relative pressure (P/P₀ = 0.27) a step increase in N₂ uptake, suggesting mesoporosity [35, 36]. An N₂ uptake of 989.8 cm³ g⁻¹ (STP) and Brunauer-Emmet-Teller (BET) surface area of 2013.3 m² g⁻¹ have been observed. For PCN-222(Mn), the N₂ adsorption and desorption were measured at 77 K, which was acceptably similar to PCN-222(Mn)-U (Fig. S10). PCN-222(Mn)-U was used as an adsorbent. After dye adsorption, N₂ adsorption and desorption were measured at 77 K (Fig. 1f). An N₂ uptake of 1.7 cm³ g⁻¹ (STP) and Brunauer–Emmet–Teller (BET) surface area of 7.5 m² g⁻¹ have been observed. The typical type II isotherm of adsorbent is in good agreement with the penetration of the dye in the cavities.

Water-stable synthesized MOFs (PCN-222(M)-3) were characterized by PXRD patterns (Fig. 1a, S1, and S2), FTIR (Fig. S11), and SEM (Fig. S12), no loss of structural integrity of the framework has been caused.

We have described a new sonochemical synthesis of PCN-222(M). By optimizing different synthetic parameters such as reaction time and reaction temperature, we were able to obtain PCN-222(M) as a pure crystalline phase in excellent yields and in very short reaction times. FT-IR, PXRD, SEM, TGA analysis are in good agreement with the facile synthesis of PCN-222(M). The adsorption performance of PCN-222(M)-U was determined in this work.

### 3.2 Effect of pH

According to Eq. S1, the adsorption capacity of PCN-222(M) over the pH range of 3–9 was examined and the results are represented in Fig. S13. It was observed that maximum adsorption of MB occurred at pH 8. Indeed, in this pH range, the adsorbent surface is likely to have a net negative charge, which favors cationic dye adsorption. The maximum adsorption capacity of MO occurs at pH 4, at which MO becomes anionic, while PCN-222(M) has a positive potential and the porphyrinic metal center has a great role in the absorption of anionic dyes. The results indicate that electrostatic interactions between MOFs and dye molecules play a key role in the adsorptive removal of dyes from aqueous solutions.

### 3.3 Adsorption Kinetics

The effect of contact time on the MB and MO adsorption over PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) is shown in Figs. 2, S14 (a and, b), and S14 (c and, d), respectively. The parameters, equations and computations are reported in the supporting information. The kinetic models and the correlation coefficients over PCN-222(Mn), PCN-222(Fe), and PCN -222(Cu) are given in Tables 1, S5, and S6, respectively. The fitting curves of the adsorption kinetics of MB and MO over PCN-222(Mn), PCN-222(Fe) and PCN -222(Cu) are shown in Figs. 3, S15, and S16, respectively.

An appropriate correlation was found between the kinetic data and the pseudo-second-order equation, which indicates chemical adsorption [37, 38].

![Fig. 2 Adsorption capacity of PCN-222(Mn) over a MB, and b MO](image-url)
3.4 Adsorption Isotherms

Adsorption isotherms were used to describe the adsorption of methylene blue or methyl orange and mechanisms of their adsorption on PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu). The adsorption of dyes over the adsorbents (5 mg) was examined with 6 concentrations (20, 30, 40, 80, 100 and 250 mg L\(^{-1}\)), various contact times (3–120 min), three different temperatures (298, 308 and 318 K) and stirring at 200 rpm. Several mathematical models have been utilized for studying the adsorption of dyes over solid surfaces [30, 39]. The study of the adsorption equilibrium data of the adsorbents was carried out using the Langmuir (Eq. S5) and Freundlich (Eq. S6) models in this research. Isotherm parameters of MB and MO adsorption on PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) are calculated (Table 2, S7, and S8). The isotherms, which predict the adsorption behavior, can be utilized to outline the sorption system [40]. Generally, for the evaluation of the best fit, the values of the correlation coefficients \(r^2\) of linear plots of different models are considered. Values of \(r^2\) of a linear plot of the Langmuir model were better than those of the Freundlich model for all three adsorbents.

### Table 1 Adsorption kinetic parameters of MB and MO on PCN-222(Mn)

| Dye | \(C_0\) (mg L\(^{-1}\)) | Pseudo-first-order kinetics | Pseudo-second-order kinetics |
|-----|-------------------------|----------------------------|----------------------------|
|     | \(K_1\) (min\(^{-1}\)) | \(q_e\) (mg g\(^{-1}\)) | \(R^2\) | \(K_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(q_e\) (mg g\(^{-1}\)) | \(R^2\) |
| MB  | 200                     | 0.0347                     | 269.07                  | 0.9226 | 1.4 × 10\(^{-3}\) | 588.23                  | 0.9990 |
|     | 100                     | 0.116                      | 121.52                  | 0.7194 | 3.2 × 10\(^{-3}\) | 169.49                  | 0.9998 |
|     | 40                      | 0.137                      | 163.77                  | 0.8841 | 3.5 × 10\(^{-3}\) | 232.55                  | 0.9996 |
| MO  | 200                     | 0.031                      | 887.01                  | 0.9022 | 1.6 × 10\(^{-3}\) | 454.54                  | 0.9977 |
|     | 100                     | 0.118                      | 299.33                  | 0.9575 | 1.13 × 10\(^{-3}\) | 416.66                  | 0.9999 |
|     | 40                      | 0.119                      | 189.20                  | 0.9989 | 3.1 × 10\(^{-3}\) | 178.57                  | 0.9992 |

According to Table 1, \(C_0\): Dye concentration in wastewater at initial time (mg L\(^{-1}\)), \(k_1\): pseudo-first order rate constant (min\(^{-1}\)), \(k_2\): pseudo-second order rate constant (g mg\(^{-1}\) min\(^{-1}\)) Dye adsorption capacity increases according to \(k_2\), \(R^2\): Correlation coefficient, 5 mg of adsorbent.

![Plots of pseudo-first-order kinetics over PCN-222(Mn) of a MB, b MO. Plots of pseudo-second-order kinetics over PCN-222(Mn) of c MB, d MO](image-url)
The Langmuir isotherm can also be expressed in terms of a dimensionless separation factor, $R_L$, presented as Eq. S7. The computational expressions are reported in the supporting information.

All the adsorption systems studied indicate the favorable adsorption of the cationic and anionic dyes, as shown by the low value of $R_L$ ($0 < R_L < 1$). As shown in Figs. 4 and S17, and S18 and Tables 2, S7 and S8, the adsorption of MB and MO over PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu) fit the Langmuir model. The adsorption behavior of PCN-222(M)-3 was also determined. High adsorption performance was obtained. It is obvious that PCN-222(M) is a highly stable MOF, which makes it a good candidate for dye removal from aqueous solutions.

Table 2 Isotherm parameters of MB and MO adsorption on PCN-222(Mn)

| Dye | T (K) | $Q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R_L$ | $R^2$ | $n_F$ | $K_F$ | $R^2$ |
|-----|-------|---------------------|---------------------|-------|-------|-------|-------|-------|
| MB  | 298   | 925.92              | 0.026               | 0.562 | 0.974 | 2.20  | 53.75 | 0.879 |
|     | 308   | 833.32              | 0.037               | 0.037 | 0.951 | 2.294 | 76.53 | 0.915 |
|     | 318   | 714.21              | 0.012               | 0.210 | 0.997 | 2.265 | 73.23 | 0.870 |
| MO  | 298   | 1250                | 0.0509              | 0.354 | 0.9836| 2.266 | 133.23| 0.9478|
|     | 308   | 1111.1              | 0.0289              | 0.364 | 0.988 | 2.043 | 132.59| 0.907 |
|     | 318   | 1052.63             | 0.0204              | 0.0463| 0.966 | 2.20  | 131.008| 0.8383 |

According to Table 2, $C_e$: equilibrium concentration of adsorbent (mg g$^{-1}$); $Q_e$: quantity of dye adsorbed at equilibrium (mg g$^{-1}$); $Q_m$: Langmuir constant (maximum adsorbed capacity) (mg g$^{-1}$); $K_L$: Langmuir constant (L g$^{-1}$).

Fig. 4 Freundlich isotherm over PCN-222(Mn) of a MB, b MO at 298, 308, 318 K. Langmuir isotherm over PCN-222(Mn) of c MB, and d MO at 298, 308, 318 K.
3.5 Adsorption Thermodynamics

The thermodynamic parameters of adsorption of MB and MO over PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu), shown in Tables 3, S9 and S10, including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were computed by Eqs. S8, S9 and S10, respectively. The plots of lnK₀ vs. 1/T are presented in Fig. 5. Adsorption enthalpy (ΔH°) is negative, indicating that the adsorption process is exothermic and favorable for adsorption of MB and MO over MOFs. The ΔG° values of MB and MO are all negative, which indicates the spontaneity of the adsorption process [41]. The negative values of ΔS° show that randomness has decreased during the adsorption procedure. The equations are expressed in the supporting information.

It can be concluded from the thermodynamic parameters that with increasing temperature, the amount of Gibbs free energy |ΔG°| in the aforementioned MOFs has decreased. Furthermore, the adsorption capacity has increased with |ΔG°| increment, which can be due to the spontaneous process of the interaction. The adsorption performance of anionic and cationic dyes is related to metal center of porphyrin, so that PCN-222-(Mn) removes MO and PCN-222-(Cu) removes MB with more efficiency (Fig. 6).

3.6 Investigation of Adsorption Behavior in a Mixed Dye Solution

The adsorption capacity of MB and MO over PCN-222(M) remarkably increased in a mixed dye solution. Interestingly, the aggregation of cationic MB could be promoted in the presence of anionic dyes (MO) and vice versa [31, 42]. The effect of pH on the adsorption capacity in a mixed solution of MB-MO has been examined (Fig. 7). pH was selected at the preferred value of 7 for mixed dye solutions. The adsorption capacity of PCN-222(Mn), PCN-222(Fe), and PCN-222(Cu) greatly increased to 1321, 1420, and 1620 for MB, and 1760, 1630, and 1480 for MO, respectively, in the mixture. Indeed, one end of the MB dimer is linked with the adsorbent while the other end could pull MO. As shown in Fig. 8, the mixture of MB-MO has been removed in a short period of time (20 min) at pH 7.

3.7 Comparison of the Adsorbents with Those Reported in the Literature

Herein, the influence of the porphyrinic metal center on dye adsorption was studied. The comparison of the adsorption capacity of PCN-222(M) toward MB and MO with the previously reported MOFs is shown in Table 4. Although the MOFs in the top of the list (1–7) can adsorb either MB or MO and those in the middle of the list (8–11) are capable of removing both MB and MO, our synthesized MOFs have a strong affinity to both MB and MO. Adsorption capacity is improved by PCN-222(M), which can adsorb MO remarkably better than metal free PCN-222. The quick removal of

Table 3 Thermodynamic parameters of MB and MO adsorption onto PCN-222(Mn)

| Dye | T (K) | LnK₀ | ΔG° (kJ mol⁻¹) | ΔH° (kJ mol⁻¹) | ΔS° (J mol⁻¹ K⁻¹) |
|-----|------|------|---------------|---------------|------------------|
| MB  | 298  | 3.213| 8.289         | -46.119       | -126.94          |
|     | 303  | 3.198| 8.036         | -46.119       | -126.94          |
|     | 308  | 3.137| 7.962         | -46.119       | -126.94          |
|     | 318  | 2.020| 5.364         | -46.119       | -126.94          |
| MO  | 298  | 3.680| 9.129         | -40.452       | -105.92          |
|     | 303  | 3.552| 8.566         | -40.452       | -105.92          |
|     | 308  | 3.213| 7.184         | -40.452       | -105.92          |
|     | 318  | 2.711| 7.074         | -40.452       | -105.92          |

According to Table 3, K₀ is thermodynamic equilibrium constant, T is the temperature (K)
dyes is another advantage. MB and MO have been removed in 20 min.

### 3.8 The Reusability of Adsorbents

One of the most important issues in the adsorption process is the recyclability of the used adsorbent, which is very significant for industrial applications. In this work, the adsorbents were treated using 0.1 M HCl/methanol (1:9, v/v). After washing with DMF and acetone, the sample was maintained in fresh acetone for 24 h, after which it was dried in an oven at 100 °C for 6 h. The synthesized compounds were retained through eight consecutive cycles, the structural integrity of the synthesized compounds was confirmed by PXRD patterns (Fig. 1a, S1, and S2) and N2 adsorption–desorption isotherms (Fig. S19). The adsorption capacity in the first cycle was 100%, but it decreased after eight runs, as shown in Fig. 9. After the eighth cycle, the removal efficiency decreased to approximately 94.7 and 92.3% for MB and MO, respectively.

### 4 Possible Adsorption Mechanism

The adsorption capacity of PCN-222 (no metal) was reported for MB (906 mg g⁻¹, pH 9) and MO (589 mg g⁻¹, pH 5) [31]. In this work, the influence of the porphyrinic metal center of PCN-222(M) on dye adsorption has been investigated. The adsorption capacity of MB over PCN-222 (Mn, Fe, Cu) increased, (925, 909, 1111 mg g⁻¹, respectively, pH 8) compared to to PCN-222 (no metal). In addition, the adsorption capacity, of MO significantly increased (1250, 919, 1000 mg g⁻¹, pH 4) compared to PCN-222 (no metal). The hydroxyl groups of zirconium clusters decrease...
Therefore, acidic pH is beneficial to reach the maximum adsorption of the anionic dye. At high pH values, in the presence of hydroxyl groups of zirconium clusters, the positive charge of MOF decreased, which favors the adsorption of the cationic dyes. In addition, both cationic and anionic dyes can be adsorbed over PCN-222(Mn, Fe, Cu) by hydrogen bonding and π–π interaction between MOF and dye molecules (Scheme 2) [28, 31]. In a mixed dye solution, MB and MO are proposed to influence each other to adsorb on PCN-222(M), which greatly increases the dye adsorption capacity at pH 7 and 298 k. Moreover, the presence of the metal center of porphyrin in PCN-222(M) remarkably increases the adsorption capacity of anionic dyes due to the positive charge of porphyrinic metal center. The ΔG° values of MB and MO are all negative, which indicates the spontaneity of the adsorption process. The more negative ΔG° is in PCN-222(Mn), PCN-222(Fe), and PCN-222(Cu), the more dye adsorption takes place.

### 5 Conclusion

In this research, PCN-222(M) was synthesized by a fast and simple sonochemical method at considerably reduced reaction time with a good yield, similar to that of the solvothermal method. High adsorption capacity was observed for MB and MO. In comparison to the metal free PCN-222, the presence of metal center of porphyrinic framework significantly increased anionic dye adsorption due to the electrostatic interaction between dye molecules and PCN-222(M). The adsorption capacity of MB and MO over PCN-222(M) remarkably increased in a mixed dye solution. The high performance of PCN-222(M) in acidic pH confirms the claim. Furthermore, hydrogen bonding and π–π interaction occur

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**Table 4** The adsorption capacity of selected MOFs and PCN-222(Mn), PCN-222(Fe) and PCN-222(Cu)

| Entry | Adsorption capacity (mg g⁻¹) |
|-------|-----------------------------|
|       | Adsorbents | MB | MO | Organic linker | References |
| 1     | Fe₃O₄/Cu₃(BTC)₂ | 769 | NA | BTC | [43] |
| 2     | NH₂-MIL-125(Ti) | 400 | NA | BTC | [44] |
| 3     | ZJU-24 | 902 | NA | TPTC/TPHC | [45] |
| 4     | DUT-23(Cu) nanoparticle | 814 | NA | BTP/BPY | [46] |
| 5     | TMU-16-NH₂ | NA | 393.7 | NH₂-BDC/4-bpdh | [11] |
| 6     | MIL-53(Cr) | NA | 58 | 1,4-BDC | [47] |
| 7     | PED-MIL101 | NA | 194 | 1,4-BDC | [47] |
| 8     | NH₂-MIL-101(Al) | 762 | 188 | NH₂-BDC | [48] |
| 9     | MOF-235 | 252 | 477 | 1,4-BDC/DMF | [10] |
| 10    | MIL-100(Cr) | 643.3 | 211.8 | 1,3,5-BTC | [31] |
| 11    | PCN-222 | 906 | 589 | TCPP | [31] |
| 12    | PCN-222(Mn) | 925 | 1250 | MTCP | Present work |
| 13    | PCN-222(Fe) | 909 | 919 | MTCP | Present work |
| 14    | PCN-222(Cu) | 1111 | 1000 | MTCP | Present work |
| 15    | PCN-222(Mn) | 1321 | 1760 | MTCP | Present work |
|       | (MB-MO) | (MB-MO) | 1480 | (MB-MO) | Present work |
| 16    | PCN-222(Fe) | 1420 | 1630 | MTCP | Present work |
|       | (MB-MO) | (MB-MO) | 1480 | (MB-MO) | Present work |
| 17    | PCN-222(Cu) | 1620 | 1480 | MTCP | Present work |

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**Fig. 9** Reusability of adsorbents for the removal of MB and MO at pH 6
between MOF and dye molecules. The Langmuir model agreed with the equilibrium isotherm investigated in the present work, which demonstrated monolayer process for dye adsorption. The possible adsorption mechanism of the MB or MO over the PCN-222(M) showed that mesoporous cavities, electrostatic adsorption, hydrogen bonding, and π–π interactions played key roles in high adsorption capacity. The thermodynamic parameters, including ∆G°, ∆H°, and ∆S° indicate a spontaneous and exothermic adsorption process. We were able to obtain PCN-222(M)-U in good yields and in very short reaction times, high adsorption performance and desirable recyclability of the synthesized MOFs make them good candidates for wastewater treatment.

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