Nanoporous Carbon Derived from MOF-5: A Superadsorbent for Copper Ions

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ABSTRACT: In this work, nanoporous carbon (NPC) was synthesized by direct carbonization of MOF-5 (a famous metal–organic framework). The structure and morphology of the prepared MOF-derived nanoporous carbon (MOF-NPC) were investigated by X-ray diffraction, N₂ adsorption/desorption isotherm, Raman spectroscopy, thermogravimetric analysis, and scanning electron microscopy methods. The MOF-NPC was then used to adsorb copper ions from aqueous solutions. To evaluate the performance of the prepared MOF-NPC to remove copper ions, both adsorption kinetics and adsorption equilibrium experiments were carried out and then the obtained data were modeled with various models. Also, the efficacy of temperature and the pH of the solution on the removal efficiency were checked. The results show that the prepared MOF-NPC is a superadsorbent for the removal of copper ions from aqueous solutions. Finally, the removal percentage of copper ions by the prepared MOF-NPC was compared with other activated carbon adsorbents to show its incredible efficiency.

1. INTRODUCTION

In recent years, the soil and water pollution by different contaminants is a serious threat to the environment. Among these pollutants, there are heavy metal ions, such as copper ions, which are released from various industries including mining, electroplating, extracting, and pigments. Heavy-metal ions are not biodegradable. Copper ions are an indispensable element for the health of the human body; however, it is toxic at high uptakes and may cause serious problems to humans, such as memory loss, kidney and liver damage, schizophrenia, and hypertension.

Up to now, different methods have been allocated to remove copper ions from aqueous solutions, including membrane processes, electrodeposition, reverse osmosis, ion exchange, nanofiltration, and adsorption. Among the above-mentioned methods, adsorption is preferred due to its high efficiency, cost-effectiveness, and convenience. So far, a great number of adsorbents have been reported to adsorb copper ions, such as Ag-doped ZnO, microstructured zinc oxides, γ-alumina, graphene oxide–chitosan aerogel, natural manganese dioxide, metal–organic framework (MOF)-derived nanoporous carbon (NPC), and nanoporous MOF-5.

New materials, such as nanoporous carbon, with features like high pore volume and specific surface area, good mechanical/thermal stability, and fast kinetics, exhibit a very high potential for use as catalyst supports, electrode, and gas storage and adsorbent materials. Recently, metal–organic frameworks (MOFs), which are ordered crystalline structure, have been used as a precursor to fabrication of nanoporous carbon. In our recent work, we have synthesized MOF-5, which shows excellent efficiency, and used it as an absorbent for copper ions.

In this research, we selected MOF-5 as a precursor. Then, it was directly carbonized to fabricate a nanoporous carbon (MOF-NPC) and employed to adsorb the copper ions from aqueous solutions. The adsorption of Cu ions was investigated by MOF-NPC under different conditions.

2. RESULTS AND DISCUSSION

2.1. Characterization. Morphology of the obtained MOF-5 and MOF-NPC were illuminated by scanning electron microscopy (SEM) images at different magnifications (Figure 1a–d). These images indicate that the morphology of MOF-NPC with cubic texture is similar to the parent MOF-5 structure. Thus, the carbonization process does not change the morphology of the precursor at 530 °C.

To determine the structural properties of MOF-NPC, N₂ adsorption–desorption experiment was carried out, and the results are shown in Figure 2a,b. The MOF-NPC displays a type IV isotherm with a hysteresis loop, which demonstrates the presence of mesopores. The obtained hysteresis loop for MOF-NPC is similar to the simulated hysteresis loop (isotherm 7 in ref 31), which corresponds to a porous solid with the following structural parameters: very low ratio of macropore surface area to the total surface area and also...
medium ratio of micropore volume to total pore volume. The structural properties of the MOF-NPC are listed in Table 1.

Table 1. Porosity Characteristics of the Prepared MOF-NPC

| sample  | BET surface area (m²/g) | pore volume (cm³/g) | average pore size (nm) |
|---------|------------------------|---------------------|------------------------|
| MOF-NPC | 473                    | 0.593               | 1.82                   |

The X-ray diffraction (XRD) schema of the MOF-NPC is shown in Figure S1. A board peak centered at 2θ = 21° approves the formation of graphitic carbon structures.

The structure of nanoporous carbon derived from MOF-5 was investigated using Raman spectroscopy. In Figure S2, the spectra shows two main peaks related to carbon; the D band at 1375 cm⁻¹ and G band at 1581 cm⁻¹ correspond to the structural imperfections and tangential vibrations, respectively. The relative ratio of the "D" to "G" peak intensity (I_D/I_G) is commensurate to the number of imperfections in nanoporous carbon; because this ratio is <1, it is clear that the graphitic structure is dominant in the prepared adsorbent.

Thermogravimetric analysis (TGA) for the investigation of decomposition behavior of MOF-5 was performed under argon atmosphere with a heating rate of 10 °C/min from ambient temperature to 600 °C. The observed TGA curve of MOF-5 (Figure S3) is similar to the previously reported curves. As the figure shows, the main mass loss due to carbonization occurs between 420 and 510 °C.

2.2. Adsorption Kinetics. Generally, the kinetics investigations can reveal important information about the adsorption process. So, the performance of the adsorbent for the elimination of copper ions was determined by the kinetics studies of adsorption. Figure 3 shows that the adsorption of copper ions is a function of time. In Figure 3, it is clear that the uptake of copper ions into the MOF-NPC is sharp in the early moments and reaches an equilibrium after few minutes. The reason for these observations is that the number of available sites for absorption in the initial stages is high.

To model the adsorption kinetics data, different kinetic models (Table 2) have been used. Table 3 demonstrates the results of modeling with various models. According to the values obtained for r² (correlation coefficient) and root-mean-square (RMS) error, it is obvious that the pseudo-n-order (PnO) model represents the best fitting to the experimental kinetics data. The fitting of this model to the adsorption kinetic data reveals that the surface of the MOF-NPC as an adsorbent is heterogeneous for the adsorption of copper ions.

2.3. Adsorption Isotherm. How to interact adsorbent with adsorbate when the process achieves an equilibrium condition is indicated by the adsorption isotherm. In Figure 4, the data related to the equilibrium adsorption of copper ions by the prepared MOF-NPC is shown. By increasing the initial concentration of copper ions, the qₑ value increases up to the saturation value.

To calculate the maximum adsorbent absorption capacity, the equilibrium adsorption data were fitted to the modified
Table 2. Kinetics Models of Adsorption

| kinetics model | abbreviation | nonlinear equation | refs |
|----------------|--------------|--------------------|------|
| mixed-order    | MOE          | \( q = q_0 \frac{1 - e^{-k_1t}}{1 + k_2t} \) | 33   |
| pseudo-first-order | PFO          | \( q = q_0(1 - e^{-k_1t}) \) | 34   |
| pseudo-second-order | PSO          | \( q = \frac{k_2q_0^2}{1 + k_2t} \) | 34   |
| pseudo-n-order | PnO          | \( q = q_0 - ((n - 1)k_1t + q_0^{n-1})^{1/n} \) | 35   |
| fractal-like pseudo-first order | FL-PFO        | \( q = q_0(1 - e^{-k_1t^n}) \) | 36, 37 |
| fractal-like pseudo-second order | FL-PSO        | \( q = q_0 \frac{1}{k_2^n} e^{-k_2^n q_0 t} \) | 36, 37 |
| mixed surface reaction and diffusion controlled | M-SR-DC | \( q = q_0 \frac{a}{a + (bt/2)^{1/2}} - 1 \) | 38   |

Figure 4. Adsorption isotherm of copper ions by MOF-NPC.

Langmuir (eq 1) and the modified Langmuir–Freundlich (eq 2) models, which have been recently presented for the adsorption from the liquid phase.\(^{39}\)

\[
q_e = \frac{q_m K_{ML} C_e}{C_e + (K_{ML} - 1)C_e} \quad (1)
\]

\[
q_e = \frac{q_m (K_{MLF} C_e)^n}{(C_e - C_s)^n + (K_{MLF} C_s)^n} \quad (2)
\]

where \( q_e \) is the amount of adsorbate per unit mass of the adsorbent at equilibrium time and \( q_m \) is the monolayer adsorption capacity. \( K_{ML} \) and \( K_{MLF} \) are the equilibrium constants of modified Langmuir and modified Langmuir–Freundlich, respectively. \( C_s \) is the equilibrium concentration and \( C_e \) is the saturation concentration of the solute (for the present system, the \( C_s \) value for CuSO\(_4\)-SH\(_2\)O is 184 g/L).\(^{40}\) and \( n \) is the surface heterogeneity constant. The results of the fitting are listed in Table 4.

Due to the obtained \( r^2 \) (correlation coefficient) and the RMS error values, the modified Langmuir–Freundlich model demonstrates better the adsorption of copper ions by adsorbent. The modeling of adsorption equilibrium data with modified Langmuir–Freundlich model demonstrates that the adsorbent surface is heterogeneous and provides various adsorption sites for adsorption. This result is consistent with the conclusion gained from kinetics modeling.

The maximum adsorption capacity (\( q_m \)) of the prepared MOF-NPC for copper ions based on modified Langmuir–Freundlich model is almost equal to 1071 mg/g. This amount is much higher than the maximum adsorption capacity of the other activated carbons that have been used for adsorption of copper ions. Very high adsorption capacity of the prepared MOF-NPC indicated that this is a superadsorbent for copper ions.

The percentage removal (Re% = 100 × (\( C_0 - C_e \))/\( C_0 \)) of copper ions by the prepared MOF-NPC was compared with several commercial activated carbons such as granular activated carbon, activated carbon cloth, powdered activated carbon, MOF-NC13, and MOF-5\(^{14}\) as adsorbents. Figure 5 shows the results of the removal percentage after 45 min and also 6 h. As can be seen, the efficiency of MOF-NPC to remove copper ions is much more than that of other absorbents used (about 10 times higher than commercial activated carbons). And, this suggests that the prepared absorbent (MOF-NPC) is an efficient superadsorbent.

Table 3. Obtained Constants of Different Kinetics Models for the Adsorption of Copper Ions by the Prepared MOF-NPC

| kinetics model | \( a \) (min\(^{-1}\)) | \( b \) (min\(^{-1/2}\)) | \( \alpha \) | \( k_1 \) (s\(^{-1}\)) | \( k_2 \) (g/mg) | \( k_s \) (g/mg) | \( n \) | \( q_e \) (mg/g) | \( r^2 \) | RMS |
|----------------|------------------------|------------------|--------|-----------------|----------------|----------------|------|---------------|-------|-----|
| MOE            | 9.74                   | 0.061            |        |                 |                |                |      | 381.1         | 0.9916 | 14.69 |
| PFO            | 0.059                  |                  |        |                 |                |                |      | 381.6         | 0.9909 | 14.29 |
| PSO            | 0.0002                 |                  |        |                 |                |                |      | 414.1         | 0.97   | 24.58 |
| PnO            | 0.071                  | 0.96             |        |                 |                |                |      | 381.2         | 0.9912 | 14.11 |
| FL-PFO         | 1.15                   | 0.04             |        |                 |                |                |      | 374.4         | 0.9906 | 14.76 |
| FL-PSO         | 1.70                   | 0.0004           |        |                 |                |                |      | 385.1         | 0.9963 | 9.76  |
| M-SR-DC        | −0.046                 | −0.00025         |        |                 |                |                |      | 383.1         | 0.9881 | 16.36 |

Table 4. Obtained Constants of Various Isotherms for the Adsorption of Cu Ion onto MOF-NPC

| isotherm         | \( q_m \) (mg/g) | \( K_{ML} \) | \( K_{MLF} \) | \( n \) | \( r^2 \) | RMS |
|------------------|-----------------|--------------|---------------|------|-------|-----|
| modified Langmuir| 824.58          | 17,215       | 17,215        | 0.52 | 0.9608 | 56.42|
| modified Langmuir–Freundlich | 1071.67 | 7781.83      | 7781.83       | 0.52 | 0.9915 | 28.03|
40% of copper ions adsorption capacity of MOF-NPC can be recovered after exposure to sulfuric acid.

3. CONCLUSIONS
In this work, heterogenic nanoporous carbons were prepared by carbonization of MOF-5, and the morphology of the prepared adsorbent did not change during carbonization. The obtained nanoporous carbon (MOF-NPC) indicated great adsorption efficiency for the removal of copper ions compared with commercial activated carbons. Both kinetic and equilibrium experimental data indicated that MOF-NPC provides heterogenic surface for the adsorption of copper ions with different adsorption active sites.

The adsorption investigation at different temperatures shows that with increasing temperature, the removal efficiency of MOF-NPC for copper ions increases. The maximum percentage of copper ions removed by MOF-NPC was obtained at pH 5.2.

4. EXPERIMENTAL METHODS

4.1. Preparation of MOF-5 and Nanoporous Carbon. MOF-5 was prepared according to our previous report. Briefly, 0.82 g of terephthalic acid (BDC) and 3.86 g of zinc nitrate tetrahydrate were added to 112.8 mL of dimethylformamide and then the resultant mixture was mildly stirred until whole of solids were dissolved at ambient conditions. The reaction mixture was heated under a reflux for 4 h at 130 °C. After about an hour, a white powder (MOF-5) appeared. The resultant sample was cooled to ambient temperature. The precipitate was detached and carefully washed. The obtained white powders were dried for 3 h at 60 °C in a vacuum oven.

For the fabrication of porous carbon, about 500 mg of MOF-5 was loaded in a ceramic crucible and then, to remove the solvent molecules, the sample was placed into the vacuum oven and degassed at 200 °C for 3 h. Afterward, the sample was heated at a constant heating rate of 5 °C min\(^{-1}\) in a tube furnace to 530 °C for 8 h under the protection of nitrogen flow. Finally, the sample was cooled to ambient temperature.

4.2. Adsorption Experiments. For the determination of the residual concentration of copper ions, the complexometric method was applied. In this method, Zincon \(^{41}\) (in a buffer solution, at pH = 7) and UV/visible spectrophotometer (at 600 nm) have been used. The performances of the MOF-NPC as an adsorbent to eliminate copper ions were evaluated from both equilibrium and kinetics viewpoint.

The kinetics experiments were performed using various samples of 2 mg of adsorbent and 10 mL of copper ions solution with a constant initial concentration (300 ppm). The samples were stirred in water bath shaker with 150 rpm at room temperature (25 °C). After centrifugation, they were sampled to measure the residual concentration of copper ions at different time intervals.

The equilibrium experiments were accomplished by adding 4 mg of MOF-NPC into 10 mL of several solutions with different concentrations of copper ions (10–1000 ppm). The samples were placed in a shaker at 150 rpm and 25 °C. After 24 h, the adsorbent was separated by centrifugation and the equilibrium concentration of copper ions measured.

The adsorption capacity (amount of copper ions adsorbed per unit mass of adsorbent) was obtained by using eq 3

\[
q_e = \frac{C_0 - C_e}{M} V \quad \text{or} \quad q_t = \frac{C_0 - C_t}{M} V
\]
where \( q_t \) and \( q_e \) are the amount of adsorbate per unit mass of the adsorbent at time \( t \) and equilibrium, respectively. \( C_0 \) and \( C_e \) are the concentrations of copper ions in the solution at initial, any time, and equilibrium, respectively. \( V \) is the volume of the solution and \( M \) is the mass of the adsorbent.

Using a method conducted by Faria et al., \(^{42}\) \( \text{pH}_{\text{pzc}} \) (pH of point of zero charge) of MOF-NPC has been obtained.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02278.

XRD and Raman spectra of MOF-NPC, TGA curve of MOF-5, effect of temperature on the removal percentage of \( \text{Cu}^{2+} \) by MOF-NPC, plot of point of zero charge pH, removal efficiency of recycled MOF-NPC (PDF)

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**Notes**

The authors declare no competing financial interest.

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