Well-design and synthesis of a water- and heat-resistant UiO-67@CNTs composite for Congo red efficient capture

Yuning Jin<sup>a</sup>, Danping Wu<sup>a</sup>, Na Ma<sup>b</sup> and Wei Dai<sup>a</sup>,*

<sup>a</sup>Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, People’s Republic of China

<sup>b</sup>College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua 321004, PR China

*Corresponding author. E-mail: daiwei@zjnu.edu.cn

ABSTRACT

MOFs (metal-organic frameworks) significantly suffer from water- and heat instable issues, restricting their practical application, such as the capture of hazardous anionic dyes (e.g. Congo red, CR) from water. In present contribution, a series of novel composites (UiO-67@CNTs) composed of microporous UiO-67 (Zr6O4(OH)4(CO2)12) and mesoporous CNTs (carbon nanotubes) have been innovatively synthesized by an in-situ hydrothermal reaction strategy. This UiO-67@CNT impressively retains structural integrity whether contacted with strong acid, distilled water, and strong alkali conditions even for 20 days. Due to existence of CNT, its heat stability can reach up to 480 °C, which is superior to that of UiO-67. Open Zr(IV) sites, mesoporous, and high surface area in the structure of UiO-67@CNTs play associative effects for CR capture ability. CR uptakes over (5.0) UiO-67@CNTs can reach 1,024 mg/g, exceeding some other previous adsorbents in literature. Importantly, UiO-67@CNTs could retain a remarkable CR capture ability even after the fifth cycle. This work expands views for water-heat resistant MOF-based composite with excellent ability of CR capture.

Key words: adsorption, carbon nanotubes, Congo red, UiO-67, water-heat-resistant

HIGHLIGHTS

- UiO-67@CNTs exhibited outstanding hydrolytic stability, retaining intactness for 20 days even in strong acid and alkali.
- UiO-67@CNTs performed more excellent thermal stability until 480 °C.
- Novel UiO-67@CNTs have potential applications for CR capture.
1. INTRODUCTION

CR (Scheme S1) is one of the typical anionic dye, which is usually considered as highly toxic and persistent to cause serious hazards for ecological environment and public health (Yagub et al. 2014; Liu et al. 2019). Thus, elimination of CR pollutant becomes more and more urgent and necessary. It is well known that the MOF consists of organic linkers and metal ions or clusters (Gao et al. 2021; Uflyand et al. 2021). Owing to their superiorities of uniform pore sizes, high specific surface areas, and flexible tailor-ability etc., MOF is often considered as an inspiring candidate for CR capture from wastewater (Sarker et al. 2018; Wu et al. 2021). For examples, our group has investigated CR capture abilities by Cu-BTC or Zn/Cu-BTC@MC (Hu et al. 2014; Sarker et al. 2018). Compared with common sorbents (e.g. active carbon, and zeolite), Cu-BTC and Zn/Cu-BTC@MC with cationic open sites exhibited excellent adsorptive abilities towards anionic CR.

According to literature evaluations (Hu et al. 2014; Yagub et al. 2014; Sarker et al. 2018), as a matter of fact, there are three serious issues for CR capture through MOFs. Firstly, most of MOFs have water sensitivity and instability (Zhang et al. 2014; Huang et al. 2016). As stronger nucleophiles than organic ligands, coordination bonds between metal ions and organic ligand are very likely destroyed by contacted H$_2$O molecules, attributing to partial or total collapse of MOF structure. It is well known that Zr(IV) owns more strong coordination ability than common metals (e.g. such as Cu(II), Zn(II), and Ni(II)) (Zhou et al. 2013; Liu et al. 2015). Therefore, Zr-MOFs (e.g. UiO-67, Zr$_6$O$_4$(OH)$_4$(CO$_2$)$_{12}$, consist of Zr(IV),) have excellent stabilities of heat, water, and chemistry. However, coordination bonds constructed by Zr(IV) could also be destroyed by enduring contact with strong acid and strong alkali aqueous solutions (Morris et al. 2012; Liu et al. 2015). Zr-MOFs structure would also irreversible collapse after it contacted with water for a long time, which could definitely suffer from applications (Liu et al. 2015). Secondly, according to acknowledge of adsorption kinetics, microporous MOFs (e.g. UiO-67) could decrease diffusion coefficient of CR, which is disadvantageous for CR capture during the porous structure (Liu et al. 2019). For instance, MOF-5@AC composite was developed and applied for thiophenic compounds capture (Zhu et al. 2018). Larger pore channel of AC (activated carbon) was advantageous for the adsorbate molecules easily diffused and reached the metal active sites (Zhu et al. 2018). Therefore, uptakes of thiophenic compounds could enhance owing to the doping of AC components in MOF-5. Thirdly, good hydrothermal stability is also important for the application of MOFs under higher temperature conditions. For example, gas phase organic contaminants capture with MOFs industrial column is usually conducted more than 100–200 °C (Fukushima et al. 2010). Therefore, excellent thermal behavior of the MOFs would exhibit...
more suitable potential industry application. AC is a more suitable choice for improving the heat stability of composite adsorbent, and the cost is also related lower than that of MOF ones. Zn/Cu-BTC coated with mesoporous activated carbon to prepare the Zn/Cu-BTC@MC was also developed in our group (Liu et al. 2019). Our interesting results demonstrated that the Zn/Cu-BTC@MC can improve the stability of MOF, inhibiting the agglomeration of adsorbent particles, causing adsorbent uniform combination and enhancing the material’s heat stability and CR uptakes. In addition, CNTs consisting of sp2 carbon exhibit a cylindrical nano-objects (Zhang et al. 2022). Owing to some interesting properties, such as large specific surface area without pore diffusion restrictions, good water stability, as well as ease of functionalization, CNT has gained considerable attention in water purification. However, adsorption saturation is still the pivotal factor that restricts CNT for further application. Thus, development of various CNT composites were necessary to treat organic pollutants.

To improve and solve the mentioned weakness above, a novel composite, UiO-67@CNTs, was ingeniously designed and synthesized by a rapid one-pot hydrothermal strategy. CNTs could improve UiO-67 formation by increasing the dispersive forces within the UiO-67, suppressing their aggregation, and controlling UiO-67’s physicochemical properties such as structure, morphology, and size. It aims to open up a new and inspiring field of anion dye wastewater purification, we prove the CNTs modulation on the UiO-66 through experimental evidences, expecting to obtain a remarkable adsorption affinity toward CR molecules. The excellent CR capture ability was owing to the associative relations of Zr(IV) and CNTs. Importantly, UiO-67@CNTs achieved the purpose of pore expansion and improving the water resistant and hydrothermal stability, which was conducive to the adsorption of large size dye molecules such as CR, and we have also investigated the CR adsorbed rate and controlling steps, and the kinetic and equilibrium parameters were presented and compared to support the results. The schematic illustration of the highlights in this work was also displayed in Figure 1.

2. MATERIALS AND METHODS

2.1. Reagents and apparatus
Zirconium tetrachloride (≥98%, Shanghai Myrell Chemical Technology Co., LTD), Carbon nanotubes (J&K Scientific Co., LTD), Polyvinylpyrrolidone (≥99%, J&K Scientific Co., LTD), Congo red (≥96%, Shanghai Aladdin Co., LTD). Cobaltous nitrate hexahydrate (≥98%), N,N-dimethylformamide (≥99%), 4,4’-diphthalic acid (≥99%, Sigma-Aldrich), ethanol absolute (AR, ≥99%), concentrated hydrochloric acid (AR), triethylamine (AR), and acetone (AR) were all purchased from Sinopharm Chemical Reagent Co., LTD.

Figure 1 | Schematic illustration of UiO-67@CNTs composite.
A physical adsorption equipment (Micromeritics, ASAP 2020) was explored to investigate pore features. The morphologies of the samples were detected by Hitachi S4800 emission SEM (Scanning Electron Microscope). The crystal phases were recorded using Cu Kα radiation on a powder XRD (X-ray diffraction) equipment. FT-IR (Fourier Transform Infrared) spectra were tested at 25 °C on a Nicolet Nexus 470 spectrometer. Thermal stabilities were evaluated by a STA 449 F5 TGA (Thermogravimetric Analysis, Netzsch) under nitrogen atmosphere.

2.2. Synthesis of UiO-67
UiO-67 was synthesized using a similar hydrothermal technique based on the previously reported (Katz et al. 2013; Audu et al. 2016). Typically, 2.7 mmol ZrCl4 was dissolved totally in 50 mL DMF and 5 mL concentrated HCl and ultrasonic treated for 20 min. Then 3.8 mmol 4,4′-diphthalic acid and 100 mL DMF were added into above mixture solution. After that, the mixture was stirred at 800 rpm for 20 min, and sonicated until forming a homogeneous solution. Next, the mixture solution was putted to a 250 mL beaker and reacted at 80 °C for 12 h. The gotten white powders were washed with DMF and ethanol until the washing solution turn to clear, and dried overnight at 90 °C in a vacuum oven. Finally, the UiO-67 with a ~70% yield was achieved and collected in a vacuum desiccator.

2.3. Synthesis of UiO-67@CNTs
UiO-67@CNTs was synthesized using a similar hydrothermal technique of UiO-67 and relative reports (Jabbari et al. 2016; Ahsan et al. 2019), while mixing with CNTs according to the MOF/CNTs weight ratios of 3:10, 5:10, and 7:10, which were denoted as (3.0)UiO-67@CNTs, (5.0)UiO-67@CNTs and (7.0)UiO-67@CNTs, respectively. In detail, the CNTs of a certain quality were added to PVP (polyvinylpyrrolidone) aqueous solution (2 mg·mL–1, 30 mL). After ultrasonic for 1 h, the supernatant was removed after centrifugation, and the precipitate was dispersed in 30 mL deionized water. The CNTs solution was mixed with the precursor solution of UiO-67, and stirred at a speed of 800 rpm for 30 min. After natural cooling, the crystals were soaked and cleaned with ethanol solutions to eliminate any unreacted precursors, which was repeated three times every 12 h.

2.4. Batch tests
Adsorption isotherms of CR were obtained by batch tests in a series of 100 mL Erlenmeyer flasks with different initial CR concentrations (200–2,000 mg/L). Typically, 0.02 g adsorbents were mixed with CR model dye solution, and placed in an oscillating shaker (oscillation speed was 150 rpm·min–1) at 25 °C for 4 h to realize adsorption equilibrium. The sample solutions were filtered with filter paper to remove the sorbents, and CR content in the filtrate was tested by a UV-visible spectrophotometer at a maximum wavelength of 497 nm. CR uptakes, \(q_e\) (mg/g) was calculated by next equation:

\[
q_e = \frac{(C_o - C_e) \cdot V}{W}
\]

where \(C_o\) and \(C_e\) (mg/L) were the original and equilibrium contents of CR; \(V\) (L) was the solution volume, and \(W\) (g) was the sorbents weight.

3. RESULTS AND DISCUSSION
3.1. Characterizations
N₂ adsorption-desorption isotherms and textural data are accordingly presented and compared in Figure 2 and Table S1. On the basis of IUPAC (International Union of Pure and Applied Chemistry) classification (Jabbari et al. 2016; Ahsan et al. 2019), the UiO-67 exhibits microporous feature with a type I isotherms. The BET (Brunauer-Emmett-Teller) surface areas and average pore sizes of UiO-67, CNTs, and (5.0)UiO-67@CNTs are (1,289 m²/g and 1.92 nm), (185 m²/g and 14.58 nm), and (985 m²/g and 8.22 nm). Compared with UiO-67, the CNTs exhibit lower surface area and higher average pore size. While for (5.0)UiO-67@CNTs, there are a decrease of the surface area and an increase of the average pore size, attributing to existence of CNTs in its structure. Importantly, there is an obvious hysteresis loop at a relative pressure (P/P₀ = 0.80–0.90), indicating existence of a mesoporous feature in the (5.0)UiO-67@CNTs structure. The UiO-67 particles might be introduced into the tubular structure of CNTs, which could cause an increase of the surface area due to more porous contributions from UiO-67 structure. Accompanied by an increasing UiO-67 particles doping amount, the BET surface area of as-prepared UiO-67@CNTs significantly increase in comparison with CNTs, with 822 m²/g in (3.0)UiO-67@CNTs, and 985 m²/g in (5.0)
UiO-67@CNTs, respectively. While more UiO-67 is doped in the CNTs support, the pore might be restricted, resulting in the fact that the surface areas of (7.0)UiO-67@CNTs reduce to 903 m²/g. This structure indicates that the CNTs play a decisive contribution of pore expansion, which would be advantage for accepting the larger-size dye-molecules in the pore capacity.

We have employed FT-IR spectroscopy to investigate the functional group changes of the surface. FT-IR spectrums of UiO-67, CNTs, and UiO-67@CNTs are presented in Figure 3. Four similar characteristic sharp bands of UiO-67 and UiO-67@CNTs samples are clearly observed at 1,580, 1,390, 750, and 475 cm⁻¹, which are consistent with the results of previously report (Zhang et al. 2019). While the band intensities are different, attributing to the existence of CNTs in the composite. In detail, the characteristic sharp bands at 1,580 and 1,390 cm⁻¹ are attributed to O-C-O stretching vibrations of the terephthalic acid ligand (Kandiah et al. 2010; Yuan et al. 2015). The band position of 750 cm⁻¹ is induced by the Zr-O-Zr stretching vibration of tetragonal ZrO₂. Band position at ∼475 cm⁻¹ is the vibration band of Zr-O bond of ZrO₂. For CNTs sample, bands at 2,965 and 2,920 cm⁻¹ are asymmetric and symmetric C-H tensile vibration, the band at 1,630 cm⁻¹ can be ascribed to stretching vibration of carbonyl C = O (He et al. 2018).

Figure 2 | N₂ adsorption-desorption isotherms curves of CNTs, UiO-67, and UiO-67@CNTs.

Figure 3 | FT-IR spectra of CNTs, UiO-67, and UiO-67@CNTs samples.
To analyze and compare the crystal phase structure, XRD patterns of UiO-67, CNTs, and UiO-67@CNTs are accordingly presented in Figure 4. Diffraction peaks of UiO-67 at $2\theta = 5.6^\circ$, 6.8$^\circ$, and 17.1$^\circ$ are attributing to the main characteristic peaks of (222), (400), and (422) crystal planes, corresponding to the literature (Audu et al. 2016). Diffraction peaks of CNTs at 26.2$^\circ$ and 44.6$^\circ$ are accordingly corresponded to plane (002) and (100). It is clear that characteristic peaks of UiO-67 and CNTs in the UiO-67@CNTs samples can be simultaneously observed with a slightly decrease of the peak intensity, indicating that the composite still maintains good crystal structure. The crystal cell structures of the (3.0)UiO-67@CNTs, (5.0)UiO-67@CNTs, and (7.0) UiO-67@CNTs samples have similar and consistent characteristic peaks.

SEM images of UiO-67, CNTs, and (5.0)UiO-67@CNTs are displayed in Figure 5. The UiO-67 exhibited irregular crystal polygons, and the CNTs sample show uniform tubular structure with a smooth surface. Importantly, the (5.0)UiO-67@CNTs sample is still uniform tubular structure, while there are some obvious concave-convex shapes on the surface of the carbon tubulars. This is also an indirect evidence to prove the UiO-67 could be combined with CNTs to form UiO-67@CNTs composite.

TG results of the UiO-67 and (5.0)UiO-67@CNTs samples are presented in Figure 6. Mass losses of all the samples could be mainly segmented for three phases. First stage (25–200 °C) was attributed to the releasing of small volatile molecules with low boiling points (e.g. residual ethanol and water) (Katz et al. 2015; Gao et al. 2020a, 2020b). For UiO-67, a mass loss of ~20% is gradually observed at around 200 °C, which may be due to the release of adsorbed water from the material surface. In contrast, mass loss of (5.0)UiO-67@CNTs is only ~5% because of the existence of CNTs. Secondly, the mass loss appeared at ~430 °C for UiO-67 and 480 °C for (5.0)UiO-67@CNTs, and the mass loss is accelerated with the collapse of the samples. The second stage is due to the decomposition of organic linkers (Ko et al. 2015; Abazari et al. 2021; Goodenough et al. 2021). At 500 °C, the weight loss of UiO-67 is ~60%, whereas that for (5.0)UiO-67@CNTs is only ~15%. At 580 °C, weight loss of (5.0)UiO-67@CNTs is ~40% compared to 60% for UiO-67. These interesting results demonstrate that the heat stability of UiO-67@CNTs is much superior to that of UiO-67. Due to excellent thermal stability of carbon material, the CNTs in UiO-67@CNTs could significantly improve the heat resistant and decrease the decomposition efficiency.

3.2. Performances evaluation of CR capture

Adsorption isotherms of UiO-67, CNTs, and UiO-67@CNTs at pH 7 at 25 °C are displayed in Figure 7. Due to sensitivity of anionic CR towards the acids and bases, the color of CR solution changes from red to dark blue at low pH, and it becomes reddish in basic pH of up to 10 (Purkait et al. 2007; Sahara et al. 2019; Dat et al. 2022). Therefore, pH = 7 is selected in this study because anionic CR solution remains stable and no change in the color is observed at this pH value. Langmuir (1918), Freundlich (1906), Temkin (Chu 2021), and D-R (Dubinin and Radushkevich 1947) equations are employed to fit the isotherms data (Table S2). The line related constants ($R^2$ values) are calculated and collected in Table S3. For all the adsorbents, excellent fittings ($R^2 > 0.99$) to the Langmuir model (Figure S1) indicates CR capture over the homogeneous...
surface of the adsorbents is a monolayer adsorbed process. Fitting data is correspond with the Temkin model, verifying the heterogeneity of the adsorbent surface, and the adsorption process is definitely related to active sites of the surface. CR adsorbed onto the adsorbents increase rapidly at low equilibrium concentration region, and the uptake amounts increase gradually with the increase of equilibrium concentration. Anyway, our test data demonstrate that CR uptakes follow the

**Figure 5** | SEM images of (a) UiO-67, (b) CNTs, (c) (5.0)UiO-67@CNTs.

**Figure 6** | TG traces curves of UiO-67 (black line) and (5.0)UiO-67@CNTs (red line) sample.
order: (5.0)UiO-67@CNTs (1,400 mg/g) > (7.0)UiO-67@CNTs (1,024 mg/g) > (3.0)UiO-67@CNTs (711 mg/g) > UiO-67 (560 mg/g) > CNTs (438 mg/g). It is found that CR uptakes of (5.0)UiO-67@CNTs significantly increase in comparison with CNTs, attributing to acid-base interaction between open active Zr(IV) sites and CR molecules. Zr(IV) active sites increase with the increase of UiO-67 doping amount, attributing to higher CR uptakes of (5.0)UiO-67@CNTs than (3.0)UiO-67@CNTs. However, if more UiO-67 introduce into composite might block the pores of CNTs and cause an increase of CR diffusion resistance, undoubtedly decreasing the opportunity of accessible active Zr(IV) sites with CR. Thus, the sorbent with higher UiO-67 doping amount ((7.0)UiO-67@CNTs) exhibits a lower CR uptakes than that with UiO-67 less adding ((5.0)UiO-67@CNTs). Therefore, among all the samples, (5.0)UiO-67@CNTs exhibit highest CR adsorption capacity. CR uptakes of CNTs, (5.0)UiO-67@CNTs, and some other reported adsorbents are compared in Table S4. Clearly, CR uptakes of (5.0)UiO-67@CNTs exhibit an excellent CR capture ability, which is superior to the other adsorbents. Both UiO-67 and CNTs play decisive contributions to CR uptakes over the (5.0)UiO-67@CNTs. Existence of Zr(IV) sites in the UiO-67 structure might enhance CR uptakes, attributing to the effect of acid-base interaction. For CNTs, larger pore channel and surface area (Table S1) could be advantages for the diffuse rate and CR uptakes.

Effects of adsorbed time on CR uptakes over UiO-67, CNTs, and UiO-67@CNTs are exhibited in Figure 8, revealing CR uptakes increase with the increase of contacting time, and the adsorption reached equilibrium within ~200 min. It also indicates a rapid increase for CR uptakes is achieved before 30 min. Fast adsorption (initial stage) might be attributed to the
availability of the uncovered surface area and the empty active sites. CR kinetic parameters (Table S5) are calculated on basis of pseudo-first order, pseudo-second order, and intra-particle diffusion models. According to correlation coefficient ($R^2$), the pseudo-second order kinetics ($R^2 > 0.99$) exhibit better description for CR adsorbed process (Figure S2 and Table S6). Importantly, a plot of CR uptakes ($q_t$) versus the square root of time ($t^{1/2}$) is not linear throughout time range of adsorption (Figure S3), indicating intra-particle transport is not the only one rate-limiting stage. There are three stages during CR adsorption process. The first, sharper portion is attributed to diffusion of CR molecules through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intra-particle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage. Additionally, coefficients of kinetic diffusion ($D_{iq}$) are also calculated based on the Dunwald-Wagnen equation (Liu et al. 2019):

$$\ln \left[ 1 - \left( \frac{q_t}{q_e} \right)^2 \right] = \frac{\pi^2}{R_p} D_{iq} \cdot t$$

(2)

where $q_t$ (mg/g) is CR uptakes per unit mass sorbent at $t$ min, mg/g; $q_e$ is the equilibrium uptakes, mg/g; $R_p$ is the pore size of sorbent; $D_{iq}$ is diffusion coefficient.

Dunwald-Wagnen model is explored to fit the adsorption data by Equation (2), and the results are displayed in Figure S4. The calculated results provided in Table S7 indicate that $D_{iq}$ values of CR adsorbed onto CNTs (0.0021) and (5.0)UiO-67@CNTs (0.0017) are more than 5 times compared with that of UiO-67 (0.00033), which might be attributed to a relative larger space existence in mesoporous CNTs. Therefore, more CR molecules can be adsorbed onto CNTs compared to UiO-67 before 30 min. For UiO-67, electrostatic forces of positive charged Zr(IV) sites and negative charged CR are advantage for CR adsorption. Thus, anionic CR uptakes over the UiO-67@CNTs could be significantly enhanced by open Zr(IV) sites.

3.3. Performances of water-resistant and regeneration

Water stability is evaluated through the comparisons of CR uptakes and crystal phases by soaking as-prepared materials in strong acid (pH = 2), distilled water (pH = 7), and strong alkali (pH = 10) solutions for 20 days, respectively. XRD patterns for the UiO-67 and (5.0)UiO-67@CNTs before and after soaking in pH = 2, 7, and 10 water solutions are displayed in Figure 9. Whether in strong acid (pH = 2), strong base (pH = 10) or neutral aqueous (pH = 7) solution, crystal diffraction characteristics of (5.0)UiO-67@CNTs sample remain intact, ascribing to strong and sharp XRD peaks. In contrast, crystal diffraction characteristics peaks of UiO-67 remain intact after it contacted with neutral aqueous (pH = 7) solution for 20 days, while the peaks are completely different from that of UiO-67 and almost completely disappear after it contacted with strong acid (pH = 2), strong base (pH = 10) for 20 days, indicating a significant change occurred in the crystal structure of UiO-67. In addition, CR uptake capacities over the UiO-67 and (5.0)UiO-67@CNTs before and after soaking in pH = 2, 7, and

![Figure 9](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2022.062/1004472/wst2022062.pdf)

**Figure 9** | XRD patterns of UiO-67 and (5.0)UiO-67@CNTs before and after soaking in pH = 2, 7, and 10 water solutions.
10 water solutions are also investigated and compared in Figure 10. Obviously, UiO-67 exhibits strong water resistant in neutral water environment, while there are dramatically decreases for CR uptakes in strong acid (reduced by 71%) and alkali environment (reduced by 86%). On the contrary, the CR uptakes onto (5.0)UiO-67@CNTs still remain more than 80% after soaking in strong acid or alkali environment. These direct evidences prove that the water resistant ability of UiO-67@CNTs is superior to that of UiO-67.

On the other side, one of the most important requirements of an adsorbent is its long-life reusability over multiple cycles under the same adsorption conditions. This promotes the reduction of operating cost in real applications as well as reaches to a greener remediates. Dissolvent elution is considered as an effective method for adsorbent recyclability (Tian et al. 2019; Gao et al. 2020a, 2020b). After adsorption equilibrium, saturated (5.0)UiO-67@CNTs are added to the glass bottles containing 100 mL anhydrous ethanol with magnetic stirring for 4 h at 25 °C. Adsorption-regeneration tests are carried out five times, and the CR uptakes over the (5.0)UiO-67@CNTs are evaluated again. In comparison with fresh (5.0)UiO-67@CNTs sample, CR uptakes by less than 5% at the fifth recycle and remain CR capture ability (Figure 11). These results demonstrate that the (5.0)UiO-67@CNTs exhibit excellent recyclability with a negligible loss capacity of CR.

4. CONCLUSIONS

In summary, a novel water- and heat-resistant composite, UiO-67@CNTs, has been firstly developed as an effective adsorbent for CR capture. Even after contacting with strong acid, distilled water, and strong alkali for 20 days, UiO-67@CNTs sample continue to remain intact, as indicating by strong and sharp XRD peaks. More importantly, UiO-67@CNTs exhibit an

**Figure 10** | CR uptake capacities over the UiO-67 and (5.0)UiO-67@CNTs before and after soaking in pH = 2, 7, and 10 water solutions.

**Figure 11** | Effect of recycle times on (5.0)UiO-67@CNTs.
outstanding CR uptakes of 1,024 mg/g, attributing associative effects of mesoporous, and high surface area. Until the fifth cycle, CR uptakes reduce by ~5%, but still remain at a high value, indicating a potential application for CR capture from aqueous solutions. This study provides a new idea for the development of novel high-stability MOF composite materials for the application of real sewage purification.

**ACKNOWLEDGEMENTS**

We are thankful for financial support from the National Natural Science Foundation of China (No. 22178325).

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


First received 21 November 2021; accepted in revised form 7 February 2022. Available online 16 February 2022.