Construction of MOF-shell porous materials and performance studies in the selective adsorption and separation of benzene pollutants†

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Metastable Cu₂O is an attractive material for the architectural design of integrated nanomaterials. In this context, Cu₂O was used as the sacrificial agent to form the core–shell structure of Cu₂O@HKUST-1 by in situ growth technology. The MOFs with BOPs adsorption property were gathered together by a Cu₂O etching method, and the hollow structure of the HKUST-1 shell material with fast BOP adsorption was successfully constructed. The adsorption experiments showed that the HKUST-1 shell has a good adsorption effect on nitrobenzene pollutants in wastewater. The investigation of various factors affecting the adsorption, thermodynamic and kinetic equations was carried out. The adsorption equilibrium was reached within 30 min, and the maximum adsorption capacity was 94.67 mg g⁻¹ at 298 K. The adsorption capacity of nitrobenzene by the HKUST-1 shell is in good agreement with the Freundlich model and the second-order kinetic model. The possible mechanism of adsorption of nitrobenzene by the HKUST-1 shell was discussed. The experimental results suggested that Cu-BTC materials have potential applications for wastewater treatment involving benzene pollutants.

Introduction

With the development of modern agriculture and industry, a large number of toxic and harmful pollutants have entered the environment and threatened the survival and development of human beings.¹–⁴ Benzene organic pollutants (BOPs) are the hardest to handle and potentially cause long-term harm, as a new type of pollutant.⁵–⁶ BOPs mainly come from industrial wastewater and domestic sewage from the chemical industry, the coking industry, the printing and dyeing industries, etc.⁷–⁹ Therefore, the research and development of effective BOP reduction technology has become an urgent problem to be solved in the field of environmental science.¹⁰–¹² Currently, there are a variety of treatment technologies for BOPs, among which the adsorption method is favored.¹³⁻¹⁴ This method mainly concentrates the pollutants in the environment onto the surface of a porous adsorbent, thus achieving a method of pollutant removal.¹⁵⁻¹⁷ This method has the advantages of low cost, a simple design, a wide application range, no secondary pollution and easy regeneration of the adsorbent. It is expected to become a new generation of a highly efficient and energy-saving environmental pollution control technology, and it is also a research hotspot in the field of environmental science and technology.¹⁸⁻¹⁹

As an emerging class of crystalline materials, HKUST-1 (Cu₃(BTC)₂(H₂O)₃, BTC = 1,3,5-benzenetricarboxylate, also known as MOF-199) is one of the most extensively studied metal–organic frameworks (MOFs), which have gained tremendous attention due to their great structural diversities and potential applications.²⁰⁻²¹ In recent years, great progress has been made in the synthesis of core–shell or yolk–shell materials.²⁴⁻²⁵ However, MOFs with a yolk–shell structure are the most typical representative of multifunctional composite materials. MOFs can be used as the core or as the shell, and a stable core–shell or yolk–shell structure can be formed by self-assembly. On the other hand, Cu₂O is an important and low-cost p-type semiconductor, which can be frequently employed as a hard template for synthesizing hollow nanomaterials, because it can be easily dissolved and removed by ammonia or acid. Moreover, Cu₂O can be used as a sacrificial template for the spontaneous deposition of various NPs (e.g., Au, Pt, or Pd) by galvanic replacement reactions, and no additional reducing agents are required.²⁶ Zhan et al. prepared...
Cu₂O@HKUST-1@Au, which showed high catalytic activities towards liquid phase alcohol oxidation reactions. The addition of a small amount of PVP greatly prevents the aggregation of Au NPs, in order to prepare hollow MOFs with different cavities.²⁷ Samal et al. reported the adsorption and degradation of CV and CR dyes in aqueous solution using Au@Cu₂O core–shell nanostructures.²⁸ The synergistic effect in the Au@Cu₂O core–shell nanostructure facilitates the catalytic activity compared to the monometallic Au NPs. We believe that the general synthetic strategy for a Cu-based MOF using Cu₂O in the solid state as a sacrificial template can also be extended to prepare other types of core–shell or yolk–shell structured adsorbents, and even the preparation of different shapes of hollow HKUST-1 for selective adsorption of environmental pollutants.²⁹

In existing work, although research into the use of MOFs to treat pollutants in the water phase has made some progress, there are still some limitations and shortcomings. For example, the adsorption rate of nitrobenzene is slow; the specific surface area is small; the adsorbent is unstable. Up until now, the etching of MOFs onto a hollow structure and the adsorption of nitrobenzene have not been reported.

In this work, we shall describe the synthesis of a MOFs shell (i.e., HKUST-1) porous material by in situ growth technology, and the characteristics of the HKUST-1 shell and its adsorption properties such as adsorption equilibrium, kinetics, thermodynamics and adsorption mechanism were investigated. Influencing parameters, such as pH, ionic strength and different initial concentrations, were evaluated to characterize the extent of nitrobenzene adsorption. Remarkably, the HKUST-1 shell was demonstrated to exhibit significantly fast adsorption for nitrobenzene. In addition, the material can realize a green adsorption process of adsorbent recovery and utilization.

Experimental section

In recent years, researchers have used a variety of “soft” and “hard” template methods to enable the in situ aggregation of MOF micro/nanocrystals during the synthesis process. By removing the template, cavity structures have been successfully introduced into the aggregate. In this paper, we used the Cu₂O sacrificial agent template method, which can spontaneously etch Cu₂O whilst producing protons in the MOF formation process, without an additional solvent etching step (Scheme 1).

Synthesis of the Cu₂O shell

In a typical synthesis, 1 g of poly-(vinylpyrrolidone) (PVP; MW ~55 000) was fully dissolved in 50 mL of a 0.5 M Cu(NO₃)₂·3H₂O aqueous solution under vigorous magnetic stirring. This was then followed by the immediate introduction of 60 μL of a N₂H₄·H₂O aqueous solution (35 wt%). Typically, the color changed to greenish-yellow within 5 s, indicating the formation of the Cu₂O shell. The reaction mixture was kept stirring for 2 min, and the product was collected by centrifugation at 8000 rpm for 10 min. Subsequently, the product was washed with ethanol and deionized water (volume ratio 1 : 1) three times to remove excess PVP, before being re-dispersed in 2.5 mL benzyl alcohol (BnOH), and stored in a refrigerator at 4 °C.

Synthesis of Cu₂O@HKUST-1

1,3,5-Tricarboxylic acid (H₃BTC, 0.055 mmol) was added into a mixture of BnOH (1.5 mL) and ethanol (0.1 mL) and then sonicated for 30 min to afford a homogeneous solution. Then, the Cu₂O shell dispensible solution that was prepared in the first step was added into the solution, and this was thoroughly mixed by hand, before being kept at room temperature for two hours, namely, until the Cu₂O@HKUST-1 product was obtained.

Synthesis of the HKUST-1 shell

The mixed solution of the above Cu₂O@HKUST-1 product was poured into a glass bottle and put into an oven. The product was heated and reacted at 80 °C for 12 h. The product was centrifuged at 5000 rpm for 5 min, and it was then washed repeatedly with methanol several times. The final product was dried.

Scheme 1  The synthetic strategy for the hollow structure of the HKUST-1 shell.
in a vacuum oven for 12 h to obtain the HKUST-1 shell material.

**Materials and methods**

Polyvinylpyrrolidone (PVP), Cu(NO₃)₂, trimesinic acid (H₃BTC), ethanol, and benzyl alcohol were analytical grade agents and were purchased from Aladdin (China). All of the phase compositions and crystal structures of the prepared samples were determined by powder X-ray diffraction (XRD) methods using Cu Kα radiation (\( \lambda = 1.54178 \) Å) (D/MAX-2500 diffractometer, Rigaku, Japan) with a Cu Kα radiation source (\( k = 1.54056 \)) over the 2θ range of 5°–90° at a scanning rate of 10° min⁻¹. The morphologies and structural details of the as-prepared samples were detected using scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, JEM-2100F). The X-ray photoelectron spectroscopy (XPS) data was obtained using a Thermo ESCALAB 250X (America) electron spectrometer with 150 W Al Kα X-ray sources. The IR spectra were acquired in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. TG measurements were carried out using a STA 449F3 thermal analyzer. The specific surface areas of the samples were characterized from the nitrogen adsorption–desorption data and Brunauer–Emmett–Teller (BET) measurements (ASAP2020, Micromeritics, USA). The mesopore size distribution was determined by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherm. UV–Vis diffused reflectance spectra (DRS) of the samples were obtained with a UV–vis spectrophotometer (UV-2450, Shimadzu, Japan), and BaSO₄ was used as the reflectance standard.

**Adsorption kinetics experiment**

The prepared samples were dried in a vacuum drying chamber for more than 24 h to remove guest molecules in the pores of the samples. Two nitrobenzene solutions with different initial concentrations of 50 mg L⁻¹ and 100 mg L⁻¹ were selected, 50.0 mg of the adsorbents were weighed and were added into 50 mL conical flasks with electromagnetic stirring. Samples were taken at the same time intervals. After adsorption, a 0.22 μm filter membrane was used to obtain the supernatant, and the maximum absorption wavelength of nitrobenzene was determined, in order to calculate the concentration of nitrobenzene pollutants after adsorption by MOFs. The adsorption equilibrium time and adsorption mechanism were discussed. According to the relationship between the adsorption time and the adsorption amount, an adsorption kinetic curve could be fitted.

**Adsorption isotherm experiment**

By optimizing the structure of MOFs, the effects of contact time, temperature, pH, ionic strength and initial NB concentration on the reaction were investigated. 50.0 mg of the sample powder was dispersed into 50 mL of the different mass concentration solutions of 10 mg L⁻¹, 20 mg L⁻¹, 50 mg L⁻¹, 80 mg L⁻¹ and 100 mg L⁻¹ of the nitrobenzene pollutant, at different temperatures of 298 K, 308 K and 318 K. This was carried out under the conditions of oscillating periods of time in an oscillator, until an adsorption equilibrium was reached, with a 0.22 μm filter membrane filtration process, in order to obtain a supernatant fluid and finally determine the nitrobenzene pollutant concentration after the absorption of MOFs materials. Then, the effect of the pH value was measured. It should be noted that the pH of the NB solution was adjusted with 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ NaOH solutions. The effect of ionic strength was investigated by separately added 5 mL 0.01 mol L⁻¹ NaCl, 5 mL 0.1 mol L⁻¹ NaCl, 5 mL 1 mol L⁻¹ NaCl solution and 5 mL deionized water.

The amount of NB adsorbed on the MOFs was calculated using the mass balance with eqn (1):

\[
q_e = \frac{(C_0 - C_e)V}{m},
\]

where \( q_e \) is the adsorption amount at equilibrium (mg g⁻¹), \( C_0 \) and \( C_e \) (mg L⁻¹) are the initial and final concentrations of NB, respectively, \( V \) is the volume of wastewater solution (L), and \( m \) is the mass of the adsorbent (g). The above relevant adsorption test experiments were repeated three times and the average value was taken as the overall result, to ensure the accuracy of the experimental data.

**Regeneration experiment**

Good adsorbents should have a good adsorption effect on pollutants after adsorption regeneration. In this experiment, the MOF material, after adsorption of nitrobenzene, was washed with distilled water and dried in a 100 °C oven, before being calcined in a 300 °C muffle furnace to remove the organic matter in the pores. The above steps were repeated at least three times to ensure that the nitrobenzene attached to the MOF material was completely removed. The MOF material treated above was used to carry out the experiment of four cycles of adsorption of nitrobenzene, and the adsorption performance after four cycles was compared, and the stability of the material was investigated.

**Results and discussion**

**Structure and morphology analysis**

Fig. 1 shows the XRD patterns of the HKUST-1 and HKUST-1 shells. It can be seen from the figure that the XRD pattern of the HKUST-1 experiment is highly consistent with the simulated single crystal structure, revealing that the phase purity of the crystal material is of pure phase. The results show that the diffraction peak positions and relative intensity of the synthesized HKUST-1 shell material are consistent with the crystal material, and this proves that the synthesized material is the HKUST-1 shell.

The morphologies and microstructures of the HKUST-1 shell were further investigated by TEM and SEM. As shown in Fig. 2(a), the sample morphology of the HKUST-1 shell is uniform, mostly irregular block shapes and aggregates, forming a hollow sphere, with a uniform particle size and par-
particle size distribution of about 100 nm. TEM images were used to further study the internal structure of the HKUST-1 shell adsorbent (Fig. 2(b)). It can be observed from the figure that the HKUST-1 shell is hollow and is surrounded by irregular HKUST-1 particles, and this further confirms that the HKUST-1 shell was successfully synthesized.

**Chemical states analysis**

XPS spectroscopy was employed to analyze the detailed chemical status of the samples. It was carried out to analyze the surface chemical compositions of the HKUST-1 shell. The XPS survey spectra of the HKUST-1 shell sample is shown in Fig. 3(a). This indicates that Cu, C and O elements are on the surface of the HKUST-1 shell. The Cu 2p XPS spectra for the HKUST-1 shell is also shown in Fig. 3(b), where the peaks of Cu 2p3/2 and Cu 2p1/2 are located at 934.6 eV and 954.8 eV, respectively. The peaks between 938 and 948 eV are satellite peaks, which are indicative of the paramagnetic chemical state of Cu²⁺. In Fig. 3(c), there are two peaks that correspond to the Cu–O bond (530.5 eV) and the O–H bond (531.5 eV). Fig. 3(d) shows two peaks at 283.03 eV and 287.03 eV, which can be derived from the C 1s of HKUST-1. The XPS results confirm the coexistence of Cu, C and O in the HKUST-1 shell.

**FT-IR and thermal stability analysis**

FT-IR spectra of the HKUST-1 shell before and after nitrobenzene adsorption were measured (Fig. S1†). By comparison, the infrared spectrum absorption peak shape is basically the same, and the absorption intensity changes accordingly. It can be seen from the figure that the characteristic absorption of the HKUST-1 shell at 730 cm⁻¹ before adsorption may be caused by Cu–O tensile vibration, in which oxygen atoms coordinate with Cu. A very wide peak was formed at 3100–3600 cm⁻¹, indicating the presence of loosely bound water molecules in Cu–BTC. The most important of these peaks are the C=O stretching vibration at 1639 cm⁻¹, the C–O stretching vibration (1447 cm⁻¹) belonging to the carboxyl group and the bending vibration of O–H at 1371 cm⁻¹, indicating the presence of the carboxylic acid group. After the adsorption of nitrobenzene, the absorption peak strengths at 730 cm⁻¹ and 1101 cm⁻¹ became stronger, and the absorption peak at 1038 cm⁻¹ disappeared, while the C=N stretching vibration peak appeared at 1176 cm⁻¹. This indicated that the adsorbent HKUST-1 shell had a certain interaction on the molecular structure after the adsorption of nitrobenzene, and this resulted in the pollutants being adsorbed into the pores of the material. The thermal stability of the HKUST-1 shell before and after adsorbing the pollutants was studied by TGA (Fig. S2†). The results show two steps of weight loss in the range of 30–800 °C. The first step is in the range of 30–180 °C, in which the loss of about 12.4% can be assigned to the guest molecules in the pores of the sample and a small number of guest molecules bound onto the metal in the sample skeleton. The second stage is in the range of 230–450 °C, and this is caused by decomposition into inorganic substances and gases at high temperatures, and the weight loss is about 31.4%. As the temperature continues to rise, the weight loss remains constant. By comparing the results, it can be seen that the TG curve after the adsorption of pollutants also has two steps of weight loss, but the temperature range is correspondingly lower.
larger. The above data show that the adsorbent has good thermal stability.

**Specific surface area and selective gas adsorption properties**

A high specific surface area is usually a prerequisite for good adsorption properties of MOFs materials. For this experiment, the adsorption–desorption isotherms obtained at 77 K and 1 atm are shown in Fig. 4a. The HKUST-1 sample shows a type I adsorption isotherm with an adsorption capacity of 447.8 cm$^3$ g$^{-1}$. The HKUST-1 shell belongs to the type IV isotherm, which has the characteristics of a hysteresis loop and a high pressure platform, reflecting the mesoporous characteristics of the material. The adsorption capacities of the HKUST-1 shell before and after adsorption of nitrobenzene were 534.9 cm$^3$ g$^{-1}$ and 208.5 cm$^3$ g$^{-1}$, respectively. In contrast, the adsorption capacity of the shell material was improved. The BET surface area of HKUST-1 was 514.6 m$^2$ g$^{-1}$, that of the HKUST-1 shell before adsorption was 731.37 m$^2$ g$^{-1}$, and the BET surface area after adsorption was 341.58 m$^2$ g$^{-1}$. The total pore volumes of the HKUST-1 shell before and after adsorption were 0.83 cm$^3$ g$^{-1}$ and 0.56 cm$^3$ g$^{-1}$, respectively. This is because, after the adsorption of organic compounds in the channel or shell has been dominated by organic molecules, the N$_2$ adsorption capacity and specific surface area decrease sharply. The pore size distributions of the as-prepared HKUST-1 shell samples were calculated from the adsorption branch of the N$_2$ isotherm using the Barrett–Joyner–Halenda (BJH) model, and this is shown in Fig. 4b. By comparing the red and black curves of the figure, the first peak appearing at 8 nm and 10 nm represents the pore channels with micropores. The wide peak at 18 nm is the hole accumulated by particles rather than the real hole of the material itself or that caused by the roughness of the material surface. The black curve and the red curve with more spikes represent the cavity size of the shell, which is about 25 nm. As each petalous structure consists of multiple MOF crystals, mesoporosity could be obtained, due to the inevitable defects at the intersection regions of adjacent crystals. In addition, the high surface area of the HKUST-1 shell provides huge capacity for the adsorption of organic molecules inside the pore structure.

Due to their large specific surface area, high pore occupancy rate and strong stability, MOFs have good prospects in the selective adsorption separation and storage of gas molecules. Therefore, we measured the adsorption of CO$_2$ and N$_2$ at 273 K and 298 K, respectively. Interestingly, the HKUST-1 shell has strong selective adsorption of CO$_2$ at different temperatures under 1 atm pressure. In addition, the adsorption isotherm of CO$_2$ also presents a typical IV curve, with the adsorption increasing gradually at the beginning, reaching a peak, and then suddenly desorption occurring, leading to obvious adsorption hysteresis. At 273 K, the adsorption capacities of CO$_2$ before and after nitrobenzene adsorption by the HKUST-1 shell were 123.67 cm$^3$ g$^{-1}$ and 33.44 cm$^3$ g$^{-1}$, while the adsorption capacities of N$_2$ were 14.39 cm$^3$ g$^{-1}$ and 9.13 cm$^3$ g$^{-1}$,
respectively (Fig. 5a). At 298 K, the adsorption capacities of CO₂ before and after nitrobenzene adsorption by the HKUST-1 shell were 91.98 cm⁢³ g⁻¹ and 28.40 cm⁢³ g⁻¹, while the adsorption capacities of N₂ were 12.44 cm⁢³ g⁻¹ and 4.46 cm⁢³ g⁻¹, respectively (Fig. 5b). By comparing the adsorption capacities of CO₂ and N₂ in the HKUST-1 shell, the adsorption capacities of N₂ and the MOFs skeleton were significantly lower than those of CO₂ under 273 K and 298 K, when the interaction between N₂ and the MOFs skeleton was weakened at a higher temperature. Therefore, we believe that this material has a potential application prospect in the separation of CO₂/N₂ mixed gas.³³ The adsorption capacity of the HKUST-1 shell for CO₂ was higher than for N₂, which could be attributed to the fact that the kinetic diameter of CO₂ is smaller than N₂ (CO₂, 3.3 Å; N₂, 3.6 Å). In addition, the good selective adsorption of CO₂ by the HKUST-1 shell can also be attributed to the higher quadrupole moment (−1.4 × 10⁻³⁹ cm²) of CO₂ compared to N₂ (−4.7 × 10⁻⁴⁰ cm²), and this leads to the specific interaction between CO₂ and the host framework to enhance the adsorption capacity.³⁴,³⁵

In order to understand the interactions between the HKUST-1 shell and CO₂, we calculated the adsorption isosteric heat Qˢᵗ of CO₂ by fitting the 273 and 298 K isotherms to the Clausius–Clapeyron equation.³⁶ At zero loading conditions, the adsorption enthalpy (Qₛₐ) is approximately 15 and 32 kJ mol⁻¹ before and after the adsorption of NB, respectively (Fig. S3†). These values are relatively lower than those of reported MOFs, such as MIL-101 (45 kJ mol⁻¹) and Zn-MOF-74 (38 kJ mol⁻¹), and are relatively higher than that of UMCM-1 (12 kJ mol⁻¹), and so on.³⁷–⁴⁰ This implies relatively strong interactions between CO₂ and the carboxyl groups, which is known to improve the binding affinity towards CO₂ molecules by promoting dipole-quadrupole interactions. In addition, after the adsorption of organic compounds in the channel or shell dominated, the value of Qₛₐ changed before and after adsorption of pollutants and increased with a decrease in CO₂ coverage. As mentioned above, host–guest interactions, adsorption mechanisms, and electrostatic interactions between polarizable CO₂ and the material structure are crucial for developing these novel selective CO₂ adsorption materials.

Selective adsorption of NB

Currently, there have been many reports on the adsorption/removal and separation of organic molecules using MOFs with a pore structure. When the MOF material has an appropriate size channel, organic molecules will diffuse into the channel. Through the difference in forces between the organic molecules and the skeleton of the MOF material, the retention time of organic molecules in the channel of the MOF material can

Fig. 4  (a) Nitrogen adsorption–desorption isotherms of the HKUST-1 shell at 77 K; (b) BJH pore size distribution plots of the HKUST-1 shell.

![Fig. 4](image)

Fig. 5  CO₂ and N₂ adsorption–desorption isotherms of the HKUST-1 shell before and after adsorption of nitrobenzene at 273 K (a) and at 298 K (b).

![Fig. 5](image)
be regulated, in order to achieve separation. Under normal circumstances, wastewater contains a variety of co-existing organic pollutants. In order to investigate the selective adsorption effect of NB by the HKUST-1 shell, phenol (BP) and p-nitrobenzene (PNP) were selected as comparative adsorbents. The results are shown in Fig. 6, and it can be seen from the figure that the adsorption effect of the HKUST-1 shell on NB is far greater than that on BP and PNP. The maximum adsorption capacity at 298 K is 94.67, 16.10 and 43.02 mg g⁻¹, respectively.

Effect of pH value

For most adsorption processes, the initial pH value of the solution is one of the main factors. In this work, we first studied the adsorption performance of the HKUST-1 shell in the pH range of pH = 3.0–12.0 at 298 K. The concentration of 50 mg L⁻¹ was selected as an example. As shown in Fig. 7, the adsorption capacity of the HKUST-1 shell with NB also increases with the increase of pH value in the process from acidic to neutral. Under neutral conditions, the adsorption capacity remained almost constant. When the pH value was increased to alkaline conditions, the adsorption capacity decreased significantly. This is due to the change in the surface structures and properties of adsorbate and the adsorbent depending on the pH of the solution. When the solution is at a lower pH, the skeleton of the HKUST-1 shell may be damaged, weakening the interaction between the shell and NB, leading to a significant reduction in the adsorption capacity. When the solution is at neutral conditions, the adsorption remains constant, and this is mainly due to weak ion competition, indicating that the solution has a mild acid-base environment, and NB is not capable of destroying the structure of the material. However, at a higher pH, the content of OH⁻ in the solution increases gradually, and the competition between it and NB increases gradually. At the same time, excess OH⁻ causes the crystallinity of the material to decline, and even the structure to collapse, leading to a gradual decrease in adsorption.

Effect of mixing time

About 50 mg of the sample was weighed and added into NB solution of 10 mg L⁻¹, 20 mg L⁻¹, 50 mg L⁻¹, 80 mg L⁻¹, 100 mg L⁻¹, 120 mg L⁻¹ and 150 mg L⁻¹, respectively. The effect of different mixing times on the adsorption of NB was investigated. The results are shown in Fig. 8 and show that within 15 min of the initial stage, the solutions with different mass concentrations showed a faster adsorption trend and the adsorption amount increased sharply. This was mainly due to certain hydrophobicity on the surface of the NB molecules, and this promoted the adsorption of NB on the MOF materials. With an increase in time, the adsorption capacity increased. When the time reached 30 min, the adsorption capacity essentially reached equilibrium, and this is when the adsorption process reached saturation state. At the same time, the equilibrium times of adsorption of NB by the HKUST-1
shell at different mass concentrations were compared, and it was found that different mass concentrations had almost no effect on the equilibrium time of adsorption. Moreover, the adsorption capacity reached saturation when the mass concentration was 100 mg L\(^{-1}\), indicating that the maximum adsorption concentration of nitrobenzene for the material was 100 mg L\(^{-1}\). Therefore, 30 min and 100 mg L\(^{-1}\) were selected as the best adsorption time and maximum concentration for NB adsorption by the HKUST-1 shell, providing good conditions for following research on the thermodynamics and kinetics performances of adsorption.

**Effect of temperature**

As shown in Fig. 9, the adsorption effects of the HKUST-1 shell with different mass concentrations at 298 K, 308 K and 318 K were tested. When the temperature of the adsorption increased from 298 K to 318 K, the adsorption quantity of the HKUST-1 shell decreased sharply, mainly due to the adsorption process being exothermic. This observation can be ascribed to the weaker interaction between the NB molecules and the HKUST-1 shell with an increase in temperature.\(^{45}\) In general, the effect of solution temperature on the adsorption capacity is small when the adsorption heat is small, and the greater the adsorption heat, the greater the effect of temperature on the adsorption capacity. If the temperature increases, the adsorption capacity decreases, indicating that a low temperature is beneficial to the adsorption process. If the temperature increases, the adsorption capacity increases, indicating that a high temperature is beneficial to the adsorption process. On the other hand, for the effect of temperature on adsorption, a low temperature is conducive to physical adsorption, and a high temperature is conducive to chemical adsorption.\(^{46}\) Through analysis of the above experimental results, it was found that a low temperature is more conducive to the adsorption of NB on the HKUST-1 shell.

**Effect of ionic strength**

The influence of ionic strength on adsorption mainly includes the influence on the morphology of the material and the adsorption point on the adsorbent surface. Since NaCl is a common substance used in the adsorption process of organic pollutants, in this study NaCl was selected to adjust the ionic strength of the NB solution. As shown in Fig. 10, with an increase in ionic strength, the adsorption amount of NB adsorbed by the HKUST-1 shell gradually decreased. This is mainly because NB is a weak polar hydrophobic pollutant. When the ionic strength of the solution increases from 0.01 to 1 mol L\(^{-1}\), the solubility of NB in the solution decreases, and this can promote the adsorption of NB in the hole of the HKUST-1 shell. However, the addition of NaCl will ionize Na\(^+\) and Cl\(^-\) in the aqueous solution. With the increase of ionic strength, the two kinds of ions will compete with the NB molecules for the adsorption point in the hole of the HKUST-1 shell, hindering the adsorption of NB.\(^{12}\) As a result, the increase of ionic strength reduced the adsorption amount of NB.

**Adsorption isotherms of NB in the HKUST-1 shell**

To explore the NB capture behaviors of the HKUST-1 shell, Fig. S4\(^\dagger\) shows the measured adsorption isotherms for NB at 298 K as a function of the equilibrium NB concentration in the ESI.\(^\dagger\) The advantage of the HKUST-1 shell on NB capture can be attributed to the large specific surface area (\(S_{\text{BET}} = 731.37 \text{ m}^2 \text{ g}^{-1}\)) and the suitable pore size. Therefore, the HKUST-1 shell exhibits good performance in the removal of NB from water, indicating that they are promising adsorbents for NB capture. Moreover, the Langmuir\(^{47}\) (eqn (2)) and Freundlich\(^{48}\) (eqn (3)) models were used to fit and examine the above adsorption isotherms obtained for NB. The Langmuir model was established based on several ideal conditions: (1) The surface of the adsorbent is uniform, and the energy of each adsorption center is the same. (2) The interaction

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**Fig. 9** The effect of adsorption temperature on the adsorption of NB by the HKUST-1 shell.

**Fig. 10** The effect of ionic strength on the adsorption of NB by the HKUST-1 shell.
between the adsorbed particles can be ignored. (3) Adsorption particles and an empty adsorption center can only be adsorbed through effective collision, and can only occupy one adsorption center, indicating that the adsorption is a monolayer and positioned. (4) Under certain conditions, adsorption and desorption rates are equal, in order to reach an adsorption equilibrium. However, the Freundlich model is an important type of surface adsorption with a pure empirical formula.

\[
\text{Langmuir isotherm: } \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{2}
\]

\[
\text{Freundlich isotherm: } \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}
\]

where \( q_e \) (mg g\(^{-1}\)) is the adsorbed amount at equilibrium; \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of the adsorbate; \( q \) (mg g\(^{-1}\)) is the maximum monolayer adsorption capacity; \( K_L \) (L g\(^{-1}\)) is the Langmuir constant related to the free energy of adsorption; \( K_F \) (L mg\(^{-1}\))\(^{1/2}\) mg g\(^{-1}\) is the Freundlich adsorption constant; \( 1/n \) (unitless) is a measure of adsorption intensity ranging between 0 and 1, which is also related to the magnitude of the adsorption driving force and the distribution of the energy sites on the adsorbent.

By substituting the fit parameters into the equation, the correlation coefficients of the Langmuir model and the Freundlich model are 0.8349 and 0.9773, respectively. From the linear correlation coefficient, \( R^2 \), it can be seen that the Freundlich isotherm of the HKUST-1 shell adsorption of NB can be better fitted than the Langmuir isotherm, indicating that the adsorption process of the HKUST-1 shell for NB is more consistent with the Freundlich isotherm, showing that the form of adsorption is heterogeneous adsorption in the HKUST-1 shell pore. Thus, it can be expected that by further increasing their surface areas, the number of adsorption sites will increase, and this will enhance their adsorption capacities for NB accordingly.

Adsorption kinetics of NB in the HKUST-1 shell

The process of adsorption kinetics is mainly based on the relationship curve between adsorption time and adsorption amount, and the data are fit through two classical models of kinetics, in order to discuss the adsorption mechanism. Presently, the most commonly used adsorption kinetic equations are the pseudo-first-order adsorption kinetic equations\(^5\) and the pseudo-second-order adsorption kinetic equations.\(^6\)

\[
\ln(q_e - q) = \ln q_e - K_1 t \tag{4}
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}
\]

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the adsorbed amount at equilibrium and at time \( t \), respectively; \( K_1 \) (min\(^{-1}\)) is the pseudo-first-order constant; \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order constant. By taking the adsorption time, \( t \), as the x-coordinate, \( \ln(q_e - q_t) \) and \( t/q_e \), as the y-coordinate can fit a linear line. According to the corresponding slope and intercept, we can calculate \( q_e \), \( K_1 \) and \( K_2 \). The previously mentioned two models include all steps of adsorption, such as external film diffusion, adsorption, and intraparticle diffusion.\(^7\)

Based on the two classical dynamics model to linear fitting of experimental data, the fit results and related parameters, shown in Fig. S5\(^\dagger\) and Table 1, by comparing the adsorption kinetics of the linear correlation coefficient under different concentrations, found that the second-order kinetic coefficient \( R^2 \) value of 0.9994 is far higher than the coefficient of the first-order kinetics, and that the adsorption capacity calculated by fitting was close to the actual adsorption capacity. Therefore, the adsorption process of the HKUST-1 shell on NB was in line with that of the pseudo-second-order kinetic model, indicating that the adsorption kinetics were mainly controlled by chemical action. It is clear that the value of \( K_2 \) decreases by increasing the initial NB concentrations, and this can be due to weaker competition of the adsorption surface sites at lower concentrations.\(^8\)

Regeneration of the HKUST-1 shell

The stability of the adsorbent is an important factor to be considered in its practical application. As shown in Fig. 11, we investigated the stability of the adsorbent of the HKUST-1 shell through a cyclic adsorption experiment. After four consecutive cycles of repeated use, the high adsorption performance of the HKUST-1 shell was still maintained. At the same time, Fig. S6\(^\dagger\) shows the PXRD pattern of the HKUST-1 shell before and after the adsorption reaction. It can clearly be seen that after four cycles of experiments, the characteristic diffraction peak position and ratio of the adsorbent are basically the same as before. The above results show that the HKUST-1 shell has high stability and good adsorption performance in the process of NB adsorption.

Adsorption mechanism

The factors affecting the adsorption, adsorption equilibrium isotherms, kinetics and thermodynamics were processed to understand the adsorption mechanism of the NB molecules onto the HKUST-1 shell. Since nitrobenzene is a non-ionicizable

<table>
<thead>
<tr>
<th>C_0 (mg L(^{-1}))</th>
<th>Q_{e,exp} (mg g(^{-1}))</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( q_e,\text{cal} ) (mg g(^{-1}))</td>
<td>( K_1 ) (min(^{-1}))</td>
</tr>
<tr>
<td>50</td>
<td>46.69</td>
<td>8.4469</td>
<td>1.039</td>
</tr>
<tr>
<td>100</td>
<td>94.91</td>
<td>6.7150</td>
<td>0.0441</td>
</tr>
</tbody>
</table>

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compound, the electrostatic interaction, ion-exchange mechanisms and ion-dipole interactions are negligible in this experiment. Therefore, hydrogen bonding and hydrophobic interactions can contribute to the adsorption mechanisms. The effect of pH value on the adsorption of nitrobenzene by the HKUST-1 shell can infer that there is a special interaction between nitrobenzene and the HKUST-1 shell, such as a hydrophobic interaction. The adsorption capacity of nitrobenzene decreased sharply with an increase in pH value. The reason for this may be that the HKUST-1 shell material is relatively stable and has high acidic resistance. However, it is easy to degrade in alkaline solution, which will reduce the hydrophobicity of the material and destroy its structure. Therefore, in future research, the stability of the non-ionizable compound adsorbent should be improved.

Conclusions

In this work, a HKUST-1 shell material with a hollow structure was successfully synthesized by an in situ growth technique, and this material can selectively adsorb NB during water separation. The adsorption experiment of NB showed that the adsorption amount demonstrated a linear growth trend with an increase of the mass concentration of the solution, where the maximum concentration can reach 100 mg L$^{-1}$ with a maximum equilibrium adsorption capacity of 94.67 mg g$^{-1}$. With an increase in temperature, pH value and ionic strength, the adsorption capacity of the HKUST-1 shell to NB decreased gradually. Using the experimental results obtained by fitting with the adsorption isotherm and kinetic equations, it can be determined that the adsorption of NB in the HKUST-1 shell is in line with that of the Freundlich model, indicating that the form of adsorption is heterogeneous adsorption in the hole of the HKUST-1 shell. The adsorption process agrees well with the second-order kinetic model, indicating that the adsorption kinetics are mainly controlled by chemical action. Regeneration experiments showed that the HKUST-1 shell has good stability and adsorption capacity in the process of adsorption of NB. Therefore, the HKUST-1 shell is promising for efficient capture of BOPs from water, and the results may be helpful for in-depth research of MOFs in the application of environmental fields.

Conflicts of interest

There are no conflicts to declare.

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