Preparation of Highly Stable DUT-52 Materials and Adsorption of Dichromate Ions in Aqueous Solution

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ABSTRACT: Highly stable DUT-52 materials were synthesized by the hydrothermal method and well-characterized by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and X-ray photoelectron spectroscopy (XPS). In order to systematically study the adsorption of dichromate ions in aqueous solution by the DUT-52 materials, a single factor experiment, kinetic experiment, thermodynamic experiment, competition ion experiment, and material regeneration experiment were designed. Based on the H-bond interaction between the dichromate ions and the H atoms of a NDC2 ligand, the DUT-52 materials showed a maximum removal rate of 96.4% and a maximum adsorption capacity of 120.68 mg·g⁻¹ with excellent selective adsorption and material regeneration. In addition, the process of adsorption of dichromate ions by the DUT-52 materials is in accordance with the pseudo second-order kinetics and Langmuir models, and the adsorption mechanism and the important role of the H-bond interaction were reasonably explained using the XPS pattern and theoretical calculation. Accordingly, DUT-52 can be regarded as a multifunctional material for efficiently removing dichromate ions from the wastewater.

INTRODUCTION

Chromium mainly exists with two valence states (+3 and +6) in nature, and hexavalent chromium ions have strong toxicity and mutational and carcinogenic properties. Hexavalent chromium ions can enter an organism via a variety of ways, lead to damaging of the body, and cause sound hoarse, nasal mucous atrophy, nasal perforation, emphysema and sclerosis diseases, etc.¹⁻⁵ At present, the removal methods of dichromate ions mainly include precipitation, membrane separation, adsorption, ion exchange, biotreatment, and chemical oxidation, as well as a combination of these methods.⁶⁻¹⁰ Some of the above methods endow with severe problems such as high engineering technical difficulty, high potential risk, high cost investment, low adsorption capacity, and weak selection ability. An adsorption method is widely used, due to its easy operation, high efficiency, large adsorption capacity, and recyclable regeneration. However, microporous adsorbent materials (such as activated carbon, large pore resin, natural zeolite, molecular sieve, and silica gel) in the nature have an irregular and relatively complex structure, lacking the functional groups or characteristic structures for capturing dichromate ions in wastewater, and there are no large enough pores and nanocages for capturing and storing dichromate ions.¹¹⁻¹⁵

In recent years, a class of metal–organic frameworks (MOFs) were built by inorganic metal ions and organic ligands, compared with the traditional frame structure, molecular sieve, and activated carbon, which show high porosity, large specific surface area, good stability, and simple synthesis process.¹⁶⁻²⁰ Structurally speaking, the heavy metal ions enter the nanopore or nanocages of MOF materials and interact with the active sites to realize the function of efficient capture and separation. However, they would have to face various harsh environments requiring high thermal stability of MOF materials and chemical stability in their practical application. To date, only a small number of microporous MOFs have both high thermal and chemical stability, such as zeolitic imidazolate frameworks, material ssofituate Lavoisier frameworks, porphyrin-class MOF and Zr-based MOF materials, and so forth.¹⁶⁻²⁰ Recently, highly stable MOF materials have obtained some progress in the capture and isolation of dichromate ions.²¹⁻²⁷ For example, a cationic porous MOF was prepared by using a neutral triazidazole ligand and AgClO₄⁻ which is available through anion exchange for high capacity and rapid capture and separation of dichromate ions (Cr₂O₇²⁻) in water.²⁶ An anionic zirconium-based MOF material (ZJU-101) with a specific surface of 561 m²·g⁻¹, which is much lower than 1862 m²·g⁻¹ of MOF-867, was obtained, but the material can selectively adsorb and separate Cr₂O₇²⁻ anions from the aqueous solution by the ion
exchange, whose highest adsorption amount is 245 mg·g⁻¹.²⁷ Although some progress has been achieved in the highly stable MOF materials with regard to the capture and separation of dichromate ions, the design and preparation of highly stable MOFs and their application in the efficient capture and separation of dichromate ions from wastewater remain a challenging work.

In this work, well-known and highly stable DUT-52 materials were first used for the adsorption of dichromate ions, and the single factor experiment, kinetic experiment, thermodynamic experiment, competition ion experiment, and material regeneration experiment were designed. In addition, the adsorption process of DUT-52 materials was explored, and the adsorption mechanism was reasonably explained by the X-ray photoelectron spectroscopy (XPS) pattern and theoretical calculation. These results provide an idea for the removal and separation of dichromate ions in wastewater.

**RESULTS AND DISCUSSION**

**Structural and Morphological Characterization.** The prepared DUT-52 materials were characterized by powder X-ray diffraction (XRD), and the characteristic peaks of the experimental and simulated peaks of DUT-52 materials are basically consistent, which proves the successful formation of porous DUT-52 materials. The characteristic peak position of the activated sample of DUT-52 materials was basically unchanged,²⁸,²⁹ indicating that the high-temperature activated
sample still maintains the crystal state (Figure 1a). DUT-52 materials were observed as a type of white powder with a regular morphology but uneven size by scanning electron microscopy (SEM) in Figure 1d. The thermal stabilities of the prepared DUT-52 material samples were characterized by thermogravimetric analysis (TGA). The results showed that the DUT-52 materials mainly lost the guest solvent molecules in the temperature range of 200–400 °C, while the frameworks began to decompose after 550 °C, indicating that DUT-52 materials exhibit a high thermal stability (Figure 1b). In addition, DUT-52 materials can exist stably in 0.1 mol·L⁻¹ sodium hydroxide aqueous solution, 0.1 mol·L⁻¹ hydrochloric acid solution, H₂S, H₂O, and various organic solvents, indicating that DUT-52 materials also have the exceptional chemical stability.³⁰⁻³² Therefore, DUT-52 materials have both exceptional chemical stability and high thermal stability.

The structure of DUT-52 materials is similar to that of UiO series, which is formed by connecting [Zr₆O₄(OH)₄] with 12 NDC²⁻ ligands. This shows that a three-dimensional periodic structure with each octahedral hole shares its triangular window with eight tetrahedral cages.³⁰⁻³² DUT-52 materials have two kinds of channels with the sizes of 14 and 11 Å, respectively (Figure 1c). The Brunauer–Emmett–Teller (BET) value and pore volume of the DUT-52 materials were characterized with an ASAP2020, and the results show that the N₂ adsorption and desorption curves of DUT-52 materials at 77 K conform to Type-I type with a maximum adsorption amount of 480.64 cm³·g⁻¹, and the calculated BET value is 1685 m²·g⁻¹, and the pore volume is 0.65 m³·g⁻¹ (Figure 1d). Compared with the same series of materials, DUT-52 materials have large specific surface area and pore volume and can be used to adsorb various gas molecules, heavy metal ions, and organic pollutant molecules with the potential application value and application prospects in the environmental field.³⁰⁻³²

**Adsorption Experiment.** In order to explore the optimal conditions for the adsorption of dichromate aqueous solution by DUT-52 materials, four single factor optimization experiments were designed, including the dosage of DUT-52 materials, the initial concentration of dichromate aqueous solution, temperature, and pH values of the dichromate aqueous solutions.

When the dosage of DUT-52 materials is less than 35 mg, the removal rate of dichromate increases with the dosage of DUT-52 materials, and when the dosage of DUT-52 materials is more than 35 mg, the removal rate exhibits a negative correlation (Figure 2a). It is possible that increasing the dosage of DUT-52 materials can increase the adsorption active sites of the material, while the limited concentration of dichromate will reduce the utilization of the adsorption sites of the material, resulting in a decrease in the removal rate of unit mass adsorbent.³³⁻⁴⁰ Therefore, the optimal dosage of DUT-52 materials is selected as 35 mg with a removal rate of 48.4%.

When the initial concentration of dichromate aqueous solution increases from 10 to 25 μg·mL⁻¹, the removal rate increased gradually. When the initial concentration of dichromate aqueous solution exceeds 25 μg·mL⁻¹, the removal rate decreased gradually with the increase of dichromate aqueous solution.
solution concentration (Figure 2b). When the initial concentration of dichromate aqueous solution increases, the removal rate of DUT-52 materials for dichromate reaches equilibrium, the adsorption amount no longer increases, and the removal rate gradually decreases. Thus, when the concentration of dichromate aqueous solution was 25 μg·mL⁻¹, the highest rate of dichromate removal was 74.4%. The optimum adsorption temperature of DUT-52 materials for dichromate is 35 °C, and the removal rate is 76.6% (Figure 2c). The most suitable adsorption temperature for dichromate adsorption by DUT-52 materials is 35 °C with a removal rate of 76.6%. When the temperature is in the range of 25–35 °C, the removal rate changes little, while when the temperature is higher than 35 °C, the removal rate decreases gradually with the temperature. Dichromate aqueous solution with a pH value of 3.02 had the highest removal rate of 96.4%. When the pH value is greater than 3.02, the removal rate of dichromate gradually decreases with the increasing solution pH (Figure 2d). When the pH value is between 2 and 5, the dichromate aqueous solution is dominated by HCrO₄⁻ and Cr₂O₇²⁻; when the pH value exceeds 7, the dichromate aqueous solution is dominated by CrO₄²⁻. Therefore, the removal of the dichromate ions in the aqueous solution is favored for the DUT-52 materials under acidic conditions.

Therefore, the results show that the optimal adsorption conditions are as follows: the dosage of DUT-52 materials is 35 mg, the initial concentration is 25 μg·mL⁻¹, the adsorption temperature is 35 °C, and the pH value of solution is 3.02, whose removal rate reaches the maximum value of 96.4%.

Since the industrial wastewater usually contains some co-existing anions such as NO₃⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻, Cl⁻, AC⁻, and so forth, it is necessary to explore the influence of these co-existing ions on the removal of dichromate ions. The concentrations of the different ions were set to be consistent with the dichromate ions, and the results show that most of the co-existing ions have only mild effects on the adsorption of dichromate ions (Figure 3a), which indicates that DUT-52 materials can maintain their commendable capture capacity for dichromate ions in the presence of interfering ions. The reusability of DUT-52 materials after the adsorption of dichromate ions was further investigated, and the methanol–acetic acid was selected as the effluent in the regeneration experiments. After five recycles, the removal rate of dichromate ions can still reach up to 80.3% and the framework stability of DUT-52 materials after five recycles still remains intact, which were confirmed by the XRD patterns and SEM (Figure 3b). The experimental results show that the aqueous solution of dichromate with different concentrations gradually reaches equilibrium with the passage of oscillated time, and its adsorption capacity does not increase. When the equilibrium concentration is 300 μg·mL⁻¹, its maximum adsorption capacity is 120.68 mg·g⁻¹, which has reached the adsorption equilibrium (Figure 3d). Compared with other materials, its maximum adsorption capacity belongs to the moderate level (Table S1).

The adsorption kinetics can reflect the adsorption rate of dichromate by DUT-52 materials. According to the data of adsorption time and adsorption capacity, the quasi-first-order
kinetics and quasi second-order kinetics are fitted by formulas 3 and 4 in which the pseudo first-order kinetic fitting curve is obtained using $\ln(q_e - q_t)$ and $t$, and the pseudo second-order kinetic fitting curve is obtained using $t/q_e$ and $t$, to obtain the kinetic process of adsorption of dichromate by the DUT-52 materials. The experimental results show that the $R^2$ value of the pseudo second-order kinetic model is 0.9999 (Figure 3c), indicating that the linear relationship is very good within the performed concentrations. It can be inferred that the adsorption process of dichromate ions by the porous DUT-52 materials, which conforms to the pseudo second-order kinetic model. The Langmuir and Freundlich models were fitted by eqs 5 and 6 in which $c_e/q_e$ is plotted with the $c_e/q_e$ to obtain the Langmuir isotherm, while the Freundlich isotherm is obtained by plotting $\ln c_e$ with $\ln q_e$. The experimental results show that the $R^2$ value of Langmuir isotherm is 0.9987 with a better linearity (Figure 3d). Therefore, the thermodynamic process of dichromate in the DUT-52 materials is more consistent with the Langmuir model.

Thermodynamic energy can determine whether the reaction can occur, according to eqs 7, 8, and 9, $1/T$ acts as the transverse coordinate and $\ln K$ acts as the ordinate, to obtain the thermodynamic linear fitting curve. At 308, 318, 328, 338, and 348 K, the Gibbs free energy ($\Delta G$) values are all negative (Table S2), which reveals that the adsorption process of DUT-52 materials on dichromate in aqueous solution is performed spontaneously, and the $\Delta G$ value gradually increases, indicating that the increased temperature is not conducive to the adsorption process. The enthalpy change ($\Delta H$) values in the adsorption process are negative, indicating that the adsorption process is an exothermic process, the entropy change ($\Delta S$) values in the adsorption process are positive, indicating that the adsorption process is an entropy increasing process, and its adsorption rate is greater than the desorption process.33–41

Figure 4. (a) and (b) SEM and elemental mapping of DUT-52 materials before and after adsorption of dichromate ions; (c) XPS spectra of DUT-52 materials before and after adsorption of dichromate ions; and (d) adsorption mechanism of dichromate and DUT-52 with hydrogen bonding interaction.
Therefore, the process of dichromate adsorption in aqueous solution by DUT-52 materials is a spontaneous and exothermic process.

**Adsorption Mechanism.** The sign for the Cr element can be found in the spectrum of elemental mapping and XPS spectra of DUT-52 materials after the adsorption of dichromate ions (Figure 4a–c), and the peaks at 588.07 and 579.22 eV can be assigned to Cr2p1/2 and Cr2p3/2, respectively (Figure 4c). From XPS spectra of DUT-52 materials before and after adsorption of dichromate ions, it can be observed that the peaks of Zr3d and O2s basically had no change, while the peak for Cls has subtle changes, indicating that these H atoms of the NDC2− ligand were involved in the adsorption process. The adsorption locator module of Materials Studios was performed to investigate the adsorption sites of dichromate in the pores of DUT-52 materials. During the simulation process, the structure of DUT-52 materials was kept as rigid with atoms frozen at their crystallographic positions. The force field parameters for the framework atoms and adsorbents were both taken from Universal force field, while the partial charges for the framework atoms of DUT-52 materials were estimated by the QEq method. The possible adsorption mechanism for dichromate ions adsorbed into the pores of DUT-52 materials mainly involves the H-bond interaction between the O atom of dichromate and the H atom of the NDC2− ligand (Figure 4d), which plays an important role in the capture of dichromate ions.

**CONCLUSIONS**

The highly stable and porous DUT-52 materials have been prepared by the hydrothermal method and were characterized by XRD, TGA, SEM, and XPS. The effect of DUT-52 on the adsorption process of dichromate ions in aqueous solution was explored through the experiments under different conditions. The research results show that DUT-52 materials show the maximum removal rate of 96.4% and the maximum adsorption capacity of 120.68 mg·g−1 with excellent selective adsorption and material regeneration. In addition, the analysis of the kinetic and thermodynamic data shows that the adsorption process of dichromate by DUT-52 conforms to the pseudo-second-order kinetic model and the Langmuir model, and the adsorption mechanism as well as the important role of H-bond interaction was reasonably explained by the XPS pattern and theoretical calculation. Therefore, DUT-52 can be regarded as a multifunctional material to efficiently remove dichromate ions from the wastewater, which can provide an idea for the wastewater treatment.

**MATERIALS**

**Materials and Methods.** All the chemical reagents were commercially purchased and used without further purification. An XRD-6000 X-ray powder diffractometer (Shimadzu, Japan); FEI Quanta 200F scanning electron microscope (FEI), thermogravimetric analyzer (Mettel-Toledo, Switzerland); ASAP 2020 (Mike Instruments); PHS-2E pH meter (Shanghai); and UV-2802PCs spectrophotometer (Shanghai Unico Instruments Co., Ltd.) were used; XPS data were collected on an ESCALAB 250 XPS, using Al Ka X-rays as the excitation source.

**Preparation of DUT-52.** ZrCl4 (1.03 mmol, 230 mg) was dissolved in 20 mL of N,N′-dimethyldiformamide (DMF) in a 50 mL polystyrene reactor, which was sonicated for 5 min. Then, 2,6-naphthaleinic acid (216 mg, 1 mmol) was added into the mixture solution and sonicated for 5 min, and then, 3 mL of acetic acid was added, and the mixture was sonicated for 15 min, which was heated in an oven (120 °C) for 24 h and cooled to room temperature. The prepared samples were centrifuged and washed three times with fresh DMF, the solvent was exchanged with ethanol 3 times, the samples were dried and activated under vacuum for 4 h, and the white powder of the activated DUT-52 materials was obtained.

**Adsorption Experiment.** A certain dosage of DUT-52 materials was added into 10 mL of dichromate aqueous solution with a certain concentration and pH, which were oscillated at different temperatures for 30 min and filtered using a 0.45 μm hydrophobic PTFE membrane, and the residual concentrations of dichromate ions were determined by UV spectrophotometry.

\[
R = \frac{[c_0 - c_e]}{c_0} \times 100
\]

\[
q_e = \frac{(c_0 - c_e)V}{m}
\]

where \(c_0\) is the initial concentration of the dichromate ions (μg/mL), \(c_e\) is the equilibrium concentration of dichromate ions (μg/mL), \(V\) is the volume of dichromate ions (mL), \(m\) is the dosage of adsorbent DUT-52 materials (mg), and \(q_e\) is the adsorption capacity (μg/mg).

The removal rate (R) and the adsorption capacity \((q_e)\) of the DUT-52 materials were calculated using eqs 1 and 2.

**Regeneration Experiment.** The DUT-52 materials after adsorption of dichromate ions (20 mg) were dispersed into the mixture (40 mL) of methanol and acetic acid (1:1, v/v). The resulting suspension was stirred for 12 h, and the solid was collected through the concentration. Finally, the collected solid was washed with ethanol and dried and activated under vacuum for 4 h.

**Competition Ion Experiment.** First, 35 mg of DUT-52 materials was added into 10 mL of dichromate aqueous solution (25 μg/mL) with different competition ions (NO3−, CO32−, SO42−, PO43−, Cl−, and AC−) and pH (3.02) under 35 °C, which were oscillated for 30 min and filtered using a 0.45 μm hydrophobic PTFE membrane, and then, the residual concentration of dichromate ions was determined.

**Adsorption Kinetics.** DUT-52 materials (35 mg) were added into 10 mL of dichromate aqueous solution with different initial concentrations (10−1000 μg/mL) and pH (3.02) under 35 °C, which were oscillated different times and filtered using a 0.45 μm hydrophobic PTFE membrane, and then, the residual concentration of dichromate ions was determined.

\[
\ln(q_e - q_i) = \ln q_e - k_1t
\]

\[
t/q_e = 1/k_2q_e^2 + t/q_e
\]

where \(q_i\) is the adsorption capacity corresponding to \(t\) (μg/mg), \(q_e\) is the adsorption capacity (μg/mg), \(k_1\) and \(k_2\) are the kinetic rate constants, and \(t\) is the adsorption time (m).

The kinetic relationship in the adsorption of dichromate aqueous solution by the DUT-52 materials was calculated based on the quasi-primary kinetic equation (eq 3) and the quasi-secondary kinetic equation (eq 4).

**Adsorption Thermodynamics.** First, 35 mg of DUT-52 materials was added into 10 mL of dichromate aqueous solution...
solution with different initial concentrations (10–1000 μg/mL) and pH (3.02) under different temperatures (35–75 °C), which were oscillated for 360 min and filtered using a 0.45 μm hydrophilic PTFE membrane, and then, the residual concentration of dichromate ions was determined.

\[
c_{e}/q_e = c_{e}/q_{\text{max}} + 1/q_{\text{max}} K_l
\]

(5)\[ \ln q_e = \ln K_F + 1/n \ln c_e \]

(6)

where \( q_{\text{max}} \) is the maximum saturated adsorption capacity (μg/mg), \( q_e \) is the adsorption capacity (μg/mg), \( K_l \) is the Langmuir adsorption constant related to the adsorption energy, \( K_F \) is the Freundlich adsorption constant related to the adsorption capacity, \( n \) is a temperature-dependent constant, and \( c_e \) is the equilibrium concentration of dichromate ions (μg/mL).

The thermodynamic relationship in the adsorption of the dichromate aqueous solution by the DUT-52 materials was calculated based on the Langmuir equation (eq 5) and the Freundlich equation (eq 6).

\[
K = q_e/c_e
\]

(7)

\[
\ln K = \Delta S/R - \Delta H/RT
\]

(8)

\[
\Delta G = -RT\ln K
\]

(9)

where \( K \) is the thermodynamic equilibrium constant, \( R \) is the gas adsorption constant (8.314 J/mol K), \( T \) is the absolute temperature (K), and \( \Delta G, \Delta S, \) and \( \Delta H \) are the Gibbs free energy, entropy, and enthalpy, respectively. The \( \Delta G, \Delta S, \) and \( \Delta H \) of the DUT-52 materials can be calculated according to eqs 7, 8, and 9.

### Associated Content

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00373.

Cr(VI) ion adsorption performance of some reported MOFs and thermodynamic equilibrium constants (PDF)

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**Notes**

The authors declare no competing financial interest.

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