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U(VI) adsorption onto covalent organic frameworks-TpPa-1

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Graphical Abstract: with UO²⁺ UO²⁺ Cr³⁻, Sr²⁺, Cd³⁺ Cs⁺, Mg²⁺ Cr³⁺, Sr²⁺, Cd³⁺ Cs⁺, Mg²⁺ COF-TpPa-1 Water without UO²⁺ Radioactive waste water

1	
2	U(VI) Adsorption onto Covalent Organic
3	Frameworks-TpPa-1
4	
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13	Abstract: Covalent organic frameworks (COFs) represent an exciting new type of
14	porous organic materials, which are constructed with organic building units via strong
15	covalent bonds. Here in, the COF-2,4,6-Triformylphloroglucinol p-Phenylenediamine
16	(COF-TpPa-1) was synthesized by solvothermal method for the removal of U(VI)
17	from aqueous solution. Effects of pH, adsorption dose, contact time, uranium solution
18	concentration, temperature and adsorption and desorption cycle on the efficiency of
19	COF-TpPa-1 removal of U(VI) are investigated. SEM, XRD, TGA and FT-IR were
20	employed to characterize the samples and analyze adsorption mechanism. The results
21	manifested COF-TpPa-1 has the high adsorption capacity (q_m =152 mg/g), quick
22	adsorption kinetic, high selectivity, outstanding recycle performance and good
23	resistance to acids, bases and high temperature.
24	Keywords: Covalent organic framework; COF-TpPa-1; U(VI); Adsorption;

25 desorption;

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26 **1. Introduction**

27 With the development of economy, the problems of energy shortage and 28 environmental pollution bring challenge to sustainable development of human 29 economy. Nuclear power is more and more irreplaceable in energy system as a kind of 30 clean and efficient energy [1]. As usage of nuclear power reactors developing [2,3], 31 which had leaded to several safety accidents and produced lots of radioactive wastes, 32 especially the containing uranium, plutonium and other radionuclides waste water, 33 had caused very serious environmental problems. Thus, separation, enrichment and 34 recovery of uranium from nuclear industrial effluents or other liquid are not only 35 significant in effective utilization of resources or environmental security [4], but also 36 reduce the potential threat of radionuclides to environment and human health [5–7].

In the past few decades, several efficient separation technologies, such as chemical precipitation, solid-phase extraction, membrane separation, ion-exchange and adsorption, have been developed for the capture and recovery of U(VI) from the natural environment [8–10]. Among these technologies, the adsorption has been widely employed as the primary method of recovery of uranium aqueous solution due to its simplicity and continuity of operation, mature method, high efficiency, and environmental friendly [11–17].

In radiation-related ions researches, kinds of materials have been developed to 44 collect radioactive ions, for example, optode membrane [18], MOFs [19] and 45 46 mesoporous silica [20]. So far, various materials, such as carbon-based materials 47 [21,22], clay materials [23,24], graphene-based materials [24], nanoscale zero-valent 48 iron materials [25,26] and metal organic frameworks (MOFs) [27,28], have been used 49 as adsorbents to capture U(VI) from aqueous solutions. However, carbon-based 50 nanomaterials like graphene and carbon nanotubes were costly and the preparation 51 process was quite complicated. Clay minerals have chemical stability but low 52 adsorption capacities and removal rates. Zero-valent iron materials were unstable and 53 non-reusable, also harmful to the surrounding environment. And most of MOFs own

bad chemical stability. Therefore, developing a new type of materials with high
efficiency, low cost, high stability is of great significance to remove U(VI) in practical
applications.

57 As an emerging porous crystalline material, covalent organic frameworks (COFs) 58 [29] are prepared by various coupling reactions and have periodic two-dimensional or three-dimensional structures [30-32]. Since their discovery, COFs have received a lot 59 60 of attention as they are highly crystalline and light weight materials possessing 61 exceptionally high surface area with a definite pore size distribution pattern [33,34]. 62 Due to its unique structure and nature, COFs has been applied in gas storage [35,36], 63 catalysis [37,38], electricity [39], etc. Furthermore, COFs have great potential for the 64 adsorption and separation metal ions due to its sufficient functional points [40-42]. 65 Many COF materials have been reported in past few years. For example, a kind of graphene-synergized 2D covalent organic framework (GS-COF) obtained via an in-situ 66 67 loading of a covalent organic framework (TDCOF) on graphene sheets has been 68 reported with the maximum adsorption capacity of 220 mg/g [32]. Several other COFs 69 also have been reported by the same group. They showed the stability and functionality 70 of COFs in condition of high acidity and strong radiation existing in nuclear industry 71 [30–32,43].

In this work, COF-TpPa-1 was prepared to remove of uranium from aqueous solution, the effects of pH, adsorption dose, contact time, uranium solution concentration, temperature, adsorption and desorption cycle were investigated detailedly. The SEM, XRD, TGA and FT-IR were also employed to characterize the samples and analyze adsorption mechanism. The results show that COF-TpPa-1 has high adsorption capacity, good acid and base resistance It can be used for treating uranium-containing radioactive wastewater.

79 2. Experimental detail

80 2.1 Reagents and instruments

81 All common chemicals used in this study were purchased from Aladdin 82 (Shanghai, China) and are of analytical grade. The 721 spectrophotometer (Shanghai, 83 China) was used for the detection of the U(VI). SEM measurements was carried out 84 using a Nova Nano SEM 450 (Czech Republic), equipped with Oxford X-Max 85 spectrometer. X-ray diffraction were collected by a Bruker AXS D8 Discover powder 86 diffractometer (Germany). Thermal analysis was carried out by TGA Q500 thermal 87 analysis system (TA Instruments, USA). The FT-IR spectra were performed on a 88 Nicolet 380 (Thermo, USA). Nitrogen adsorption and desorption isotherms were 89 measured at 77 K using an BELSORP-max analyzer.

90 2.2 Synthesis of 2,4,6-Triformylphloroglucinol

91 Hexamethylenetetraamine (15.098 g, 108 mmol) and phloroglucinol (6.014 g, 49 92 mmol) was added into 90 mL trifluoroacetic acid under N2. The solution was heated at 93 100 for 2.5 h. Then 150 mL of 3 M HCl was added and the solution was heated at 94 $100\square$ for 1 h. After cooling to room temperature, the solution was filtered through 95 Celite, extracted with 350 mL dichloromethane, dried over magnesium sulfate, and 96 filtered. Rotary evaporation of the solution afforded 1.23g (5.87 mmol, 11%) of an 97 off-white powder. The pure sample was obtained by sublimation. 1H NMR (400 MHz, 98 CDCl3) data indicated near 99% purity, giving 14.12 (s, 3H, OH), 10.15 (s, 3H, CHO) 99 ppm.

100 2.3 Synthesis of COF-TpPa-1

101 0.3 mmol (63 mg) of 2,4,6-Triformylphloroglucinol (TP), 0.45 mmol (84.7 mg) 102 p-Phenylenediamine (Pa-1) was added into a Pyrex tube with 1.5 mL butyl alcohol 103 and 1.5mL 1,2-dichlorobenzene. The mixture was sonicated for 20 min, followed by 104 addition of 0.5 mL of 3 M aqueous acetic acid. After that, the tube was degassed by 105 freeze-pump-thaw cycles for three times, sealed under vacuum and heated at 120 °C 106 for 3 days. The reaction mixture was cooled to room temperature and washed with 107 deionized water, dimethylacetamide and acetone. The resulting dark red powder was

108 dried at 120 °C under vacuum for 12 hours.

109 2.4 Uranium adsorption experiments

110 Uranium adsorption experiments were performed in batches method. 111 COF-TpPa-1 was added into 50 mL plastic centrifuge tubes containing 20 mL of 112 U(VI) solution with specific initial U concentration(C_0) with stirring. The pH was 113 adjusted by HCl/Na₂CO₃. The adsorption experiments were carried out by putting the 114 plastic centrifuge tubes into a thermostatic shaker bath at 25 for 150 min, with 115 rotation speed of 250 rpm. Then, 1 mL solution withdrawn from centrifuge tubes was 116 centrifuged at 10000 rpm for 8 min. the concentration of U(VI) at time t (C_t) was 117 detected by arsenazo (III) spectrophotometric method at 650 nm. The desorption rate, distribution coefficient (K_d) and equilibrium adsorption capacity(q_e) were calculated by 118 119 the Eqs. (1), (2) and (3), respectively [44,45]:

120 Remove rate =
$$\frac{(C_0 - C_e)}{V} \cdot m$$
 (1)

121
$$q_e = \frac{(C_0 - C_e) \cdot V}{w}$$
 (2)

122
$$K_d = \frac{C_0 - C_e}{C_e} \cdot \frac{V}{w}$$
(3)

where C_0 (mg/L) is the initial concentration, C_e (mg/L) denotes the equilibrium concentration, V (L) is solution volume and w (g) is adsorbent weight. All data of batch experiments were obtained in triplicates.

126 2.5 Chemical stability studies

127 COF-TpPa-1 was added into four glass bottles of 15 mg each. 6 M HCL, 6M 128 NaOH, 1M HNO₃ and H₂O were added respectively to for samples. The first three 129 were placed at room temperature for 72 hours and the fourth was keep at $100\Box$ for 130 same 72 hours. Then, samples were washed several times with deionized water for 131 XRD.

133 After each adsorption study, the solid liquid separation by high-speed centrifuge to 134 recover the spent COF-TpPa-1, which was then washed several times with acidic 135 solution (HCL, 1 mol/L) to remove the U(VI). The recovered COF-TpPa-1 was 136 thoroughly washed with deionized water and methyl alcohol, dried at vacuum, and 137 used for further adsorption investigation. During the repeated adsorption studies, 138 U(VI) adsorption capacity (q_e) was calculated. The adsorption and desorption 139 processes were repeated up to 4 times, to further ascertain the recyclability of 140 COF-TpPa-1.

141 **3. Results and Discussion**

142 3.1 Characterizations of COF-TpPa-1

143 Chemical stability experiments were performed by soaking COF-TpPa-1 in 1 144 mol/L HNO₃, 6 mol/L NaOH and HCl, and 100 deionized water for there days. then 145 these samples was analyzed by XRD. The results were shown in Fig. 1. Compared 146 with the Fig. 2, it can be easily concluded that COF-TpPa-1 possesses good chemical 147 and temperature stability.

148 To confirm the chemical stability of the samples during adsorption of U(VI), powder X-ray diffraction (XRD) of pristine and U(VI)-loaded samples were tested. As 149 150 shown in Fig. 2, The diffraction peaks between the samples before and after 151 adsorption were no significantly different before adsorption. Major XRD patterns for 152 the U(VI)-loaded samples basically the same as the pristine samples, suggesting its high chemical stability even after loading of U(VI). Moreover, the XRD Spectrum of 153 154 COF-TpPa-1 before and after adsorption matched well with its simulated data. The 155 simulated data was obtained by theoretical calculation and MS software simulation. 156 There is no corresponding JCPDS card with this kind of COF material. But our 157 simulation data matches well with the eclipsed model in the paper of Suvendu Karak 158 et al. [46].





160 **Fig. 1** XRD patterns of the samples after HCL (6 M, soaked for 72 h), HNO₃ (1M,

161 soaked for 72 h), NaOH (6 M, soaked for 72 h) and H_2O (100 \Box , soaked for 72 h)







163 164

Fig. 2 XRD patterns of the samples before and after adsorption.

Scanning electron microscopy (SEM) an accelerating voltage of 10 kV was used to observe the microscopic morphology before and after adsorption. It is obvious that COF-TpPa-1 shows a radial cluster structure in the SEM images. There are no significant differences between the surface of U(VI)-loaded samples and pristine samples.



Fig. 3 SEM results of pristine and U(VI)-loaded samples. (a), (b) and (c) are
COF-TpPa-1 samples before adsorption; (d), (e) and (f) are COF-TpPa-1 samples
after adsorption.

174 N_2 adsorption and desorption experiments were carried out at 77 K to investigate 175 the surface area and porosity of COF-TpPa-1. The N₂ adsorption and desorption 176 isotherm of it is shown in Fig. 4. From the isotherm the Brunauer-Emmett-Teller 177 (BET) surface area was found to be 704 m²/g. According to the inset of Fig. 4, the 178 result suggests the average pore diameter was 1.86 nm.





179

183 To determine the thermal stabilities of COF-TpPa-1, thermogravimetric analysis (TGA) for COF-TpPa-1 was performed. The results are shown in Fig. 5. In the range 184 185 of $25-100\Box$, the rapid reducing of weight can be attributed to the volatilization of physically adsorbed water and residual solvent outside and inside its pores. After that, 186 187 the COF-TpPa-1 was stabile before $300\square$. In the range of $300-400\square$, the weight loss 188 sharply increases due to the pyrolysis of some functional groups on the surface of 189 COF-TpPa-1. The most significant weight loss occurs after 400□, which suggests the destruction and decomposition of the basic skeleton of COF-TpPa-1 [14]. 190



191

192 193

adsorption.

Fig. 5 Thermal gravimetric analysis (TGA) of the samples before and after

194 The samples were also analyzed by Fourier transform infrared spectroscopy (FT-IR) in the wavenumbers range between 4000 and 500 cm⁻¹, and the obtained 195 results had been illustrated in Fig. 6. The adsorption bands at 3355 cm⁻¹ is assigned to 196 the O-H stretching vibration. The band at 1256 cm⁻¹ is attributed to the C-N bending 197 198 vibration of COF-TpPa-1. The aromatic -C=C- stretching frequency of the benzene ring appears at 1450 cm⁻¹. The band at 1574 cm⁻¹ is assigned to the C=C bending 199 vibration. The strong peaks at 1256 cm⁻¹ (-C-N) and 1574 cm⁻¹ (-C=C) have clearly 200 shown the formation of the β -ketoenamine-linked framework structures [46]. 201

202 Comparing the spectrum of COF-TpPa-1 samples before and after adsorption, it can 203 be found that there is a very weak adsorption band at 916 cm⁻¹. This is because U=O 204 bonds were formed after adsorption. The adsorption band is not obvious for its low 205 ratio to others.



206 207

Fig. 6 FTIR spectra of COF-TpPa-1 before and after adsorption.

208 3.2 Effect of pH value on U(VI) adsorption

209 pH value is one of the most important parameters. It determines the speciation of 210 uranium ions [47]. The effect of pH value on adsorption capacity (q_e) of U(VI) are 211 described in Fig. 7. The adsorption capacity of U(VI) is strongly dependent on pH 212 values because of the morphological distribution of uranium at different pH values. 213 When pH value is lower than 4, uranium exists predominantly as uranyl ions. When the pH value increases to more than 4, there begins to form uranium hydrolyzate. such as 214 $UO_2(OH)^+$, $(UO_2)_3(OH)_5^{2+}$, $(UO_2)_2(OH)_2^{2+}$. When pH increases to more than 5, another 215 216 uranium hydrolyzate of UO₂(OH)₂·H₂O is formed. Then, more than pH=8, anionic 217 form becomes to be the major form. Thereby, COF-TpPa-1 primarily adsorbs the 218 uranium hydrolysate. The U(VI) adsorption capacity increases slowly from pH=1 to pH=4, then a sharply increase was observed in the pH range of 4-6, subsequently 219 220 rapidly decreases at pH=6-9 was observed. At pH=6, COF-TpPa-1 shows up strongest



ability to adsorb uranium. Thus, this pH value is chosen for the further study.



Fig. 7 E \square ect of pH on the U(VI) adsorption for the COF-TpPa-1 adsorbent. (C₀=100 mg/L, m=10 mg, t=12 hours, T=298 K).

225 3.3 Adsorption kinetics and adsorption mechanism analysis

226 To obtain the kinetic parameters of adsorption, the effect of contact time on U(VI) 227 adsorption on COF-TpPa-1 is studied. The results are shown in Fig. 8. The adsorption 228 capacity rapidly increased in the first 100 mins, then increased slowly from 100 min to 5 hours. There is no significant changing of adsorption capacity after 5 hours, 229 230 indicating the adsorption reaction reached equilibrium. The rapid growth of 231 adsorption capacity is attributed to the relatively higher concentration of U(VI) during 232 the initial time of adsorption reaction. In order to analyze the kinetic at length, 233 pseudo-first-order and pseudo-second-order were employed to fit the experimental 234 data [44,48]. The result is shown in Fig. 9. The resultant fitness represents the 235 corresponding adsorption mechanism [49]. The pseudo-first-order and 236 pseudo-second-order models can be described by following two equations:

237
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
 (4)

238
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
 (5)

where the k_1 (min⁻¹) and k_2 (g·mg⁻¹·min⁻¹) are the adsorption rate constants in the pseudo-first-order and pseudo-second-order adsorption kinetic models, respectively. q_t (mg·g⁻¹) and q_e (mg·g⁻¹) are the adsorption quantities at time t and at adsorption equilibrium, respectively. Kinetic parameters of two kinetic models are listed in Table 1.

The linear correlation coefficient (R^2) is used to check the validity of each model. 244 In Table 1, fitting result indicates that the correlation coefficient R^2 of 245 246 pseudo-second-order kinetic model was larger than pseudo-first-order kinetic model. And the adsorption capacity calculated by pseudo-second-order kinetic model 247 $(q_{e,cal}=97.2 \text{ mg/g})$ is closer to the experiment value $(q_{e,exp}=94.1 \text{ mg/g})$. Therefore, the 248 pseudo-second-order kinetic model could better describe the adsorption process of 249 COF-TpPa-1 on U(VI) and demonstrated that the adsorption process was chemical 250 251 adsorption.





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255

256

Fig. 9 The fitting by (a) pseudo-first-order and (b) pseudo-second-order models (the black points and red line present the experimental and simulated values, respectively).

Table 1 Kinetic parameters of pseudo-first-order and pseudo-second-order models.

Adaorhont	- (mg/g)	pseudo-first-order			pseudo-second-order		
Ausorbeni	$q_{\rm e,exp}$ (mg/g)	$q_{ m e,cal}(m mg/g)$	$k_1 (\min^{-1})$	R^2	$q_{ m e,cal}(m mg/g)$	k_2 (g·mg ⁻¹ ·min ⁻¹)	R^2
COF-TpPa-1	94.054	41.849	0.00177	0.9646	97.182	0.0005501	0.9995

260 3.4 Adsorption isotherm

In order to obtain its maximum adsorption capacity, the adsorption capacity of
 COF-TpPa-1 for U(VI) was performed by taking different the uranium concentration

from 0 to 300 mg/L at $25\Box$. As shown in Fig. 10, with the increasing of uranium concentration, the adsorption capacity increases. The adsorption gradually reaches saturation when the initial uranium concentration is more than 150 mg/L. the maximum adsorption capacity is up to 152 mg/g, which is comparable with the value observed in the most reported porous materials. The adsorption capacity and optimal pH value of some other porous materials are shown in Table. 2.



Fig. 10 Adsorption isothermal of COF-TpPa-1 for U(IV) (pH=6, V=20 mL, t= 480

271

269

Table 2 A comparison among some other porous materials for U(VI) removal.

Compounds	Adsorption capacity (mg/g)	Optimal pH value	Adsorption site	Reference
S _X -LDH	330	6	Polysulfide anions	[5]
MOF-76	298	3	Unclear	[28]
UiO-68-P(O)(OEt) ₂	217	2.5	Phosphorylurea	[50]
MIL-101-DETA	350	5.5	Amine	[51]
ED-MIL-101	200	4.5	Amine	[52]
Zn(HBTC)(L)	115	2	Carboxyl	[53]
Co-SLUG-35	118	5	Ion exchange	[54]
COF-HBI	211	4.5	Benzimidazole	[31]

273 To learn more about the adsorption, the common isothermal adsorption model of

274 Langmuir and Freundlich model are also utilized. Assuming that there is no interaction

275 between adsorbates, and all the adsorption sites of solid surface are same and distribute 276 uniformly, then it results uniform monolayer adsorption and conforms to the Langmuir 277 adsorption model. Supposing that the adsorbate arrives at the non-uniform surface of 278 the adsorbent from the liquid phase, and the adsorbent has di erent adsorption sites on 279 the surface, thus leading to di erent adsorption energies and unevenly distributed 280 surface adsorption heat, then the adsorption is uneven multilayer adsorption and in 281 accordance with the Freundlich model. In this system, Langmuir and Freundlich models were selected, and the fitting results were shown in Fig. 11. Its linear 282 expressions are as following [55]: 283

$$284 \quad \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

$$285 \quad \log q_e = \log K_F + \frac{1}{n} \log C_e$$

$$(6)$$

$$(7)$$

where $q_e \text{ (mg/g)}$ is the adsorption capacity when adsorption reaches equilibrium, q_m (mg/g) is the theoretical saturation adsorption capacity, $C_e \text{ (mg/L)}$ is the equilibrium concentration, b (L/mg) is the Langmuir adsorption-related constant, n and $K_F \text{ (L/mg)}$ are Freundlich equilibrium constants.



290



291

294

Fig. 11 Fitting the adsorption isotherm by (a) Langmuir and (b) Freundlich models(the black points and red line present the experimental and simulated values,

respectively).

In order to get the saturated adsorption capacity of the COF-TpPa-1 and determine the adsorption type, Langmuir and Freundlich model were used to fit the experimental data. The results are illustrated in Fig. 11 (a), (b) and Table 3.

298 The results of calculation and simulation indicated that the behavior of U(VI) 299 adsorption onto COF-TpPa-1 are fitted well by the Langmuir model, suggesting that 300 the adsorption behavior is monolayer-type. However, the Freundlich model is widely 301 used in describing multilayer adsorption process [56]. The fitting line of the 302 Freundlich model is not matching well with the behavior of U(VI) adsorption onto COF-TpPa-1, which is monolayer-type. And the correlation coefficient R^2 of 303 304 Langmuir adsorption isotherm model was greater than the Freundlich model. It means 305 the Langmuir model was more suitable than the Freundlich model for describing the 306 adsorption process of COF-TpPa-1 on U(VI), which demonstrated that the adsorption 307 of U(VI) onto this adsorbent was dependent on the completion of the chemisorption monolayer. 308

309

Table 3 Isotherm parameters of Langmuir and Freundlich models

	Langmuir model			Freundlich model		
Adsorbent	$q_{\rm m}({\rm mg/g})$	b (L/mg)	R^2	$K_{\mathrm{F}}(\mathrm{mg}^{1-\mathrm{n}}\cdot\mathrm{g}^{-1}\cdot\mathrm{L}^{\mathrm{n}})$	1/n	R^2
COF-TpPa-1	168.1	0.0672	0.9965	32.3288	0.3198	0.8405

310 3.5 Thermodynamics

The effect of the temperature which was studied at T=298, 308, 318, 328, 333 K on U(VI) adsorption by COF-TpPa-1 is shown in Fig. 12. As can be seen, the adsorption capacity of COF-TpPa-1 increasing rapidly with the temperature from 298 K to 333 K, denoting an endothermic process. The thermodynamic analysis is calculated according to Eqs. (8) and (9):

316
$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
 (8)
317 $\Delta G = \Delta H - T \Delta S$ (9)

318 where ΔS is entropy change (J/mol·K), ΔG is Gibbs free energy change (kJ/mol), *T* is 319 temperature (K), ΔH is enthalpy change (J/mol·K), *R* is gas constant of 8.314 320 J/(mol·K), and K_d is partition coe cient.

321 To acquire the thermodynamic data of the adsorption process, the plot of $\ln K_d$ 322 versus 1/T was used to calculate the enthalpy of the adsorption process according to 323 the slope and intercept of its linear equation. Calculation results were listed in Table 4. 324 ΔH is positive and greater than 40kJ/mol. It means that this reaction is mainly a 325 chemical endothermic process. Positive ΔS indicates that the adsorption reaction can 326 be proceed in the ambience. ΔG is negative, so the reaction can proceed spontaneously. 327 Gibbs free energy decreases with increasing temperature, indicating that an increase 328 in temperature promotes the reaction.





Adsorption and desorption experiments were performed for 4 times, the repeatedavailability of COF-TpPa-1 was shown in Fig.13. As can be seen, the remove rate of

338 U(VI) by COF-TpPa-1 have not reduced during cycles from 1 to 4 in sequence. The 339 remove rate of U(VI) by COF-TpPa-1 was about 70% during four cycles, it has not 340 reduced. This indicated that the chemical stability of COF-TpPa-1 was very well. The 341 desorption e□ciency was about 96% in four cycles. The elution process did not 342 damage the material and it was reused for four cycles with no observation of 343 extraction capacity loss.





Fig. 13 Recycling for the adsorption of U(VI) by COF-TpPa-1.

346 *3.7 Effect of competitive ions*

In practical applications, the system of uranium adsorption usually contains many other metal ions. Thus, the selective separation ability of COF-TpPa-1 towards uranium was confirmed using batch adsorption experiments in solution containing 6 coexisting ions (UO^{2+} , Cr^{3+} , Sr^{2+} , Cd^{3+} , Cs^+ , Mg^{2+}). As shown in Fig. 14, the q_e for U(VI) is up to about 150 mg/g, which is far more than others. The results demonstrated the high selectivity of COF-TpPa-1 for U(VI).

³⁴⁵



353



Fig. 14 The competitive sorption capacities and selectivity of COF-TpPa-1 for U(VI) over competing ions ($C_0 \approx 50 \text{ mg/L}$ for all cations, t=480 min, m=10 mg, T=25 °C).

357

358 **Conclusions**

For effective adsorption of U(VI) from aqueous solution, the COF-TpPa-1 was prepared through solvothermal method. The results show that such adsorbent can effectively adsorption U(VI), leading to high adsorption capacity up to 152 mg/g. The value is comparable with some COFs for such purpose. The adsorption process of COF-TpPa-1 strongly depended on pH value and temperature. Adsorption processes

364 corresponded to the Freundlich model and pseudo-second order kinetic model. The 365 calculation results of thermodynamic study show that the adsorption process was 366 endothermic, freedom increase, and spontaneous reaction. In adsorption and 367 desorption experiments, the adsorbent shows good chemical stability and recyclability. 368 The selectivity experiments results demonstrated the high selectivity of COF-TpPa-1 369 for U(VI). XRD patterns for the U(VI)-loaded samples matches well with the pristine 370 samples, suggesting its high chemical stability even after loading of U(VI). The SEM 371 images shows a radial cluster structure of COF-TpPa-1. FT-IR have clearly shown the 372 formation of the β-ketoenamine-linked framework structures. Overall, COF-TpPa-1 373 shows high adsorption capacity for U(VI), good chemical stability, high selectivity 374 and recycle performance. It can be used for treatment radioactive waste water 375 containing uranium.

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- 1. The covalent organic frameworks-2,4,6-Triformylphloroglucinol p-Phenylenediamine (COF-TpPa-1) was synthesized by solvothermal method, and applied in the removal of U(VI) from aqueous solution.
- 2. COF TpPa-1 owns dramatic chemical stability (in 6 M HCl, 6 M NaOH, 1 M HNO3 and 100 soaked for 3 days keeping intact structure).
- 3. This material owns high adsorption capacity ($q_m=152 \text{ mg/g}$) and excellent recycle performance (almost unchanged removal rate after four adsorption and desorption cycles).

Graphical Abstract Legend:

Covalent organic frameworks (COFs) represent an exciting new type of porous organic materials, which are constructed with organic building units via strong covalent bonds. In this study, the COF-2,4,6-Triformylphloroglucinol p-Phenylenediamine (COF-TpPa-1) was synthesized by solvothermal method for the removal of U(VI) from aqueous solution. The results manifested COF-TpPa-1 has the high adsorption capacity (q_m =152 mg/g), quick adsorption kinetic, high selectivity, outstanding recycle performance and good resistance to acids, bases and high temperature.