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Materials for energy and sustainability

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# Amidoxime-based materials for uranium recovery<sup>DOI: 10,1039/C9TA14082D</sup> removal

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### 10 Abstract

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Resource and environment are two eternal themes of social development. Nuclear 11 energy, a green source with high energy density, can greatly alleviate the pressure of 12 energy crisis in today's society. To guarantee the long-term sufficient supply of nuclear 13 fuel, mining seawater uranium is imperative. Meanwhile, the great threats of uranium 14 to ecological security and human health make it urgently needed to remove uranium 15 from environment. To achieve these ends, a large number of materials with the specific 16 functions have been born as a result. Among them, amidoxime-based materials serve 17 as one of the most promising candidate and main participant in uranium extraction from 18 aqueous systems due to their special affinity to uranium. However, there is still huge 19 room for improvement in amidoxime-based materials at economic efficiency and 20 21 performance. In this paper, we provide a comprehensive review on amidoxime-based materials for uranium recovery and removal, including the synthesis strategies, 22 characterizations and types of amidoxime-based materials, the influence factors during 23 24 uranium extraction, and the binding mechanisms between amidoxime ligands and uranyl ions as well as cost drivers in applications. Meanwhile, the shortcomings of 25 current research as well as future development directions and research hotshots were 26 also pointed out. Based on the in-depth analysis of the literatures currently available, 27 28 demand-oriented strategy to fabricate new generation of amidoxime-based adsorbents was proposed, and means to enhance the adsorbent performance were discussed from 29 30 four aspects including adsorption capacity, selectivity, kinetics and regenerability. This paper aims to provide guidance for the purposeful design of novel amidoxime-based 31

- View Article Online materials, and to provide advices on circumventing unfavorable factors and solving the 32
- technical problems for uranium recovery and removal. 33
- Keywords: amidoxime group; uranium; seawater; adsorbents; energy and 34
- environment. 35

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Population surge, environmental pollution, and energy shortage are the three major 63 global problems facing modern society. Energy and environmental issues, in particular, 64 pose a great obstacle to the development of human society.<sup>1, 2</sup> Fossil fuel represented 65 by coal and oil, as the traditional energy resources, will be eliminated within 100 years.<sup>3</sup> 66 not only because they are unclean and are the chief culprit of many environmental 67 problems comprising global warming and ozone depletion, but also because they are 68 non-renewable and will eventually be exhausted as the increasing needs.<sup>4</sup> Nuclear 69 70 power generation is considered as the best alternation to meet the needs of population growth.<sup>4, 5</sup> During 2000 to 2013, nuclear power accounted by approximately 20% 71 electricity generation in the U.S. and 13% in the globe.<sup>6</sup> 72

73 Uranium, the main nuclear element, is increasingly needed.<sup>7</sup> The main source of uranium fuel around the world is terrestrial uraninite by far.<sup>8</sup> However, the global 74 conventional uranium reserves (7.6 million tons) may be exhausted in a century.<sup>9, 10</sup> 75 76 Increasing attention thus has been paid to the ocean since mining uranium from seawater was first proposed 50 years ago.<sup>11</sup> The total uranium reserves in seawater are 77 nearly a thousand times the identified terrestrial supply.<sup>12</sup> reaching 4.5 billion metric 78 tons,<sup>13</sup> which provides the possibility of solving the current energy crisis and 79 guaranteeing future uranium resources.<sup>14</sup> Besides, less environmental impacts and 80 fewer processing steps make this strategy more exciting.<sup>12, 15</sup> Therefore, uranium 81 82 extraction from seawater is listed as one of the seven chemical separations that can change the world.<sup>16</sup> However, ultra-low concentration (ca. 3.3 ppb),<sup>13</sup> stable existence 83

84	form $(Ca_2UO_2(CO_3)_3(aq)^{17, 18}$ or $[UO_2(CO_3)_3]^{4-19}$ , extremely complex system
85	environment (with almost all naturally occurring elements, <sup>12</sup> as partly showed in Table
86	1), and immense seawater volume <sup><math>20</math></sup> make it strategically important to develop
87	adsorbents with high-performance to achieve in situ seawater uranium extraction. <sup>21</sup>
88	Consequently, a large number of research teams from different organizations
89	containing Japan Atomic Energy Agency (JAEA),22-26 Oak Ridge National Laboratory
90	(ORNL), <sup>27-29</sup> Pacific Northwest National Laboratory (PNNL), <sup>30-32</sup> Lawrence Berkeley
91	National Laboratory (LBNL) <sup>10, 18, 19</sup> as well as universities in America, <sup>30, 33-35</sup> Japan, <sup>33,</sup>
92	<sup>36-38</sup> South Korea, <sup>39</sup> Thailand <sup>40</sup> and China <sup>41-43</sup> and so on, have attempted to design and
93	develop advanced deployable adsorbents to this end since mid-1960s.44
94	Despite uranium species is a limited precious strategic source for nuclear energy

95 generation, their presence in undesirable places poses an enormous threat to ecological safety and human health due to their long-lived radionuclide and toxicity.<sup>34, 45</sup> As 96 reported, uranium and its compounds entering the body can be deposited in lungs and 97 98 may move to kidney through the blood flow, resulting in the progressive or irreversible damage and failure to organs, and even direct death.<sup>46-48</sup> It is considered one of the most 99 dangerous heavy metals in the environment.<sup>49, 50</sup> It thus is an urgent requirement to 100 disposal the uranium-contaminated water safely and effectively.<sup>51</sup> According to the 101 standard of the U.S. Environmental Protection Agency (EPA), the maximum 102 permissible concentration for uranium in drinking water is 30  $\mu$ g/L. <sup>52</sup> In the guidelines 103 of Australia, Canada and the World Health Organization (WHO), the values are 20, 20, 104 and 9µg/L, respectively.<sup>53, 54</sup> Based on Gilman's study, the maximum tolerable uranium 105

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106	View Article Online intake regulated by WHO is 0.6 µg/kg of body weight per day. <sup>55</sup> Uranium contaminants
107	in the environment are mainly derived from nuclear industrial effluent and mining
108	wastewater, <sup>56</sup> which also serve as the promising pool of uranium. <sup>57, 58</sup> In the other words,
109	uranium separation from wastewater can improve the aquatic environment, and
110	meantime, the gained uranium can once again be an important source of nuclear fuel. <sup>59</sup>
111	Adsorption is highly recognized as an efficient, inexpensive and easy-to-use
112	method for uranium capture. <sup>13, 22</sup> Commonly used adsorption materials can be roughly
113	divided into inorganic adsorbents (like metal oxides,60 clay minerals,61,62 Layered
114	Metal Sulfides, <sup>34, 63</sup> etc.), organic adsorbents (like chitosan, <sup>64</sup> bio-wastes, <sup>65, 66</sup> synthetic
115	polymers, <sup>67</sup> etc.). Inorganic adsorbents have the advantages of fast kinetics and simple
116	preparation but suffer from poor selectivity and low adsorption capacity. In contrast,
117	organic adsorbents are more promising, especially for adsorbents based on high affinity
118	ligands such as oxime, <sup>68</sup> amine/imine, <sup>67, 69, 70</sup> phosphonate, <sup>71</sup> phosphoramide, <sup>72</sup>
119	imidazole, <sup>73</sup> carboxyl or phenolic, <sup>74-76</sup> and amidoxime groups and so on. <sup>77</sup> Among them,
120	amidoxime has received the most attention. The oxime nitrogen, amino nitrogen and
121	oxime oxygen in amidoxime structure can all act as electron donors to coordinate with
122	uranyl ions and the amphoteric nature allows amidoxime-based adsorbents to chelate
123	uranium effectively under a wide pH range. <sup>78</sup> In fact, screening studies with more than
124	200 organo-functionalized materials have identified that poly(acrylamidoxime) derived
125	from polyacrylonitrile is the only adsorbent with ability to selectively extract uranium
126	at pH value close to seawater. <sup>79</sup> Since the 1980s, amidoxime-based materials have been
127	widely used to recover oceanic uranium. <sup>80</sup> After nearly 40 years of development, a

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variety of amidoxime-based materials have emerged one after another, and there are 128 also many successful cases. For instance, the researchers from Japan has obtained more 129 than 1 kg of uranium in the form of yellow cake using amidoxime-functionalized 130 nonwoven cloth by the stack system after 240 day of submersion.<sup>81</sup> Thus, the feasibility 131 of extracting uranium from seawater with amidoxime-group polymer is demonstrated.<sup>82</sup> 132 For another, motivated by the high affinity of amidoxime groups towards uranium, 133 extensive attempts have been made to prepare amidoxime-bearing scavengers for 134 removing U-contaminants from wastewater.83,84 135

Since the 21st century, the research on amidoxime and uranium has witnessed a 136 growth as Fig. 1. Although reviews on uranium extraction from seawater and uranium 137 removal form aqueous solution have been published,<sup>8, 85-87</sup> there are few reviews 138 focusing on amidoxime-based materials for uranium recovery and removal so far. As 139 the protagonist for capturing uranyl ions in seawater and contaminated water, all aspects 140 of amidoxime-based adsorbents are in urgent need of a comprehensive review. In this 141 142 paper, with amidoxime groups as a starting point, the synthesis, characterizations and types of amidoxime-based materials (Chapter 2 and 3), the influence factors during 143 extraction (Chapter 4), and the binding mechanisms between amidoxime ligands and 144 uranyl ions (Chapter 5) as well as cost estimation (Chapter 6) were reviewed in 145 146 detailed. It was proposed at the first time that the development of the new-generation of amidoxime-based adsorbents should be demand-oriented, and means to enhance the 147 adsorbent performance were discussed from four aspects namely adsorption capacity, 148 selectivity, kinetics and regenerability (Chapter 7). This article aims to provide 149

guidance for the purposeful design of novel amidoxime-functionalized materials and to 150 provide advices on solving the technical problems of uranium enrichment from 151 seawater and effluent. 152

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#### 2. **Preparation of amidoxime-based materials**

Amidoxime, as an effective functionality for uranium ions anchoring, possesses 155 superb chemical activity and excellent adsorption ability. This group can be structurally 156 regarded as the product in which oxygen atom on amide moiety is replaced by 157 isonitroso group, or the hydrogen atom of the imine on amidine moiety is exchanged 158 by hydroxyl group.<sup>88</sup> Thereby, the preparation and physiochemical properties of 159 amidoxime are closely related to its characteristic ligands, namely oxime moiety and 160 amino moiety. In this part, the common routes for amidoxime synthesis and its 161 characteristics are summarized in brief. 162

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2.1 164

The preparation

As early as the nineteen century, various amidoxime species have been prepared 165 despite they have not been employed to the fields of energy and environment. In an 166 incipient review, Eloy and co-workers have summarized ten different routes to 167 synthesize amidoxime as shown in Fig. 2.88 However, the Method II to X (M II-X) are 168 limited in operation or others, even can only be used in specific situation, leading to 169 that the mainstream strategy in the later development is achieved via Method I (MI), 170 i.e. treating nitriles with hydroxylamine under the basic condition. 171

172	View Article Online The nitrogen atom on hydroxylamine is expected to preferentially attack the carbon
173	atom on cyano group due to the higher nucleophilicity. Imino hydroxylamine or
174	amidoxime is thus formed, which is in dynamic equilibrium with each other (Fig. 3a,
175	there are two different possible routes since the hydrogen atom and hydroxyl moiety on
176	hydroxylamine molecule are not equivalent.) In general, the products mainly exist in
177	amidoxime form due to its more stable structure. However, according to the results of
178	quantum mechanical calculations (Fig. 3b), <sup>89</sup> the oxygen atom on hydroxylamine may
179	first attack the carbon atom on nitrile group due to that hydroxylamine oxygen atom
180	plays a stronger base role than the nitrogen atom does ( $Q_0$ = -0.563 vs. $Q_N$ = -0.331). So
181	that, the intermediate 3 was generated. Then, under the strong electrostatic attraction
182	between hydroxylamine nitrogen ( $Q_{\rm N}$ = -0.654) and imine carbon atom ( $Q_{\rm C}$ = 0.721), a
183	high energy of oxaziriding ring 4 was conformed. Due to the unstable three-membered
184	ring of intermediate 4, the C-O could cleavage to gain intermediate 5. After the
185	tautomerization, the acrylamidoxime6 was obtained (Fig. 3c). Besides, the formation
186	enthalpies of 5 and 6 provided a theoretical basis for the amidoxime structure to be
187	more stable (Fig. 3d).

Since the carbon-nitrogen double bond in amidoxime structure is defective in rotation, two different configurations of *Z*- and *E*- forms may exist in amidoxime structure as seen in **Fig. 4**. Only a few studies have reported the formation of *E*-type structure and all of them are N,N'-disubstituted amidoximes co-existing with *Z*-form.<sup>90</sup> There is a classic view that the resulting configuration dependents on the steric and electronic effects of the R-group.<sup>91</sup> Specifically, the substituted group, R, would result

194	in a steric hindrance preventing from the formation of Z-form amidoxime owing to its
195	relatively large size. But when the hydrogen atoms on amidoxime amino group are di-
196	substituted by other functionalities, the resistance to form E-form product also
197	remarkably increase, and thus, the coexistence of both are generated.
198	There are two pathways to introduce cyano-groups, i.e. in-situ generation and
199	functionality grafting/modifying. The former is relatively rare and the related instance
200	has only been reported by Yang et al.92 They pioneered a novel "one-pot" reaction, with
201	K <sub>4</sub> [Fe(CN) <sub>6</sub> ] as starting substances and Pd compounds as catalysts, for synthesizing
202	amidoxime compounds. By contrast, the latter is more widespread. Most of amidoxime-
203	based adsorbents deployed in marine environment are various polymeric materials
204	obtained from the polymerization of acrylonitrile followed by hydroxylamine
205	treatment.93 (This process cannot be reversed because the oxime moiety on the
206	amidoxime groups is capable of quenching radicals, inhibiting the polymerization of
207	olefins. <sup>94</sup> ). In addition, acrylonitrile can also be attached to various host materials by
208	cyanoethylation or surface graft polymerization. The as-fabricated adsorbents possess
209	the exceptional physiochemical properties of the matrix materials, which can be
210	employed in uranium or other metal ions adsorption from some specific situations, such
211	as uranium removal or recovery form nuclear industrial effluent.95 For instance,
212	acrylonitrile can be grafted onto chitosan matrix by cyanoethylation reaction with the
213	hydroxyl groups on chitosan backbone.96 Other than chitosan, various materials,
214	including silica gel, <sup>97</sup> zeolite, <sup>95</sup> multi-walled carbon nanotubes (MWCNTs), <sup>98</sup> reduced
215	graphene oxides (r-GO),99 potato starch,100 mesoporous silica,101 Metal Organic

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Frameworks (MOFs)<sup>102</sup> and so on, have been investigated as matrix to <sup>DOI: 10.1039/C9TA14082D</sup> 216 amidoxime groups as well. Besides acrylonitrile, other cyano-bearing compounds also 217 adopted prepare/modify adsorbing materials, which include 218 were to Diaminomaleonitrile (DAMN),<sup>103, 104</sup> 3,3-iminodipropionitrile,<sup>83, 105</sup> Malononitrile,<sup>106</sup> 219 Dicyandiamide,<sup>107</sup> 2-Butenenitrile,<sup>108</sup> (3-Cyanopropyl)triethoxysilane (CPTS)<sup>109</sup> and 3-220 hexenedinitrile <sup>110</sup> and so forth. The relevant content was reviewed in Chapter 3. It is 221 reasonable to believe that more and more nitrile-containing small molecules will be 222 explored and employed to optimize and upgrade adsorbents, especially after 223 224 amidoximation by hydroxylamine treatment.

Although the path to prepare the amidoxime-based material is single (MI in Fig. 225 2), the synthesis details are varied from person to person (Fig. 5). Approach 3 and 4 226 227 are more popular and widely adopted. The alkaline reagents used in the processes consist of not only inorganic base (e.g. sodium hydroxide, 95, 97 sodium carbonate, 111, 112 228 potassium hydroxide,<sup>9, 28</sup> potassium carbonate<sup>113, 114</sup>, etc.) but also organic matter (e.g. 229 triethylamine,<sup>115</sup> etc.), and the polar organic solvent also involves methanol,<sup>116</sup> 230 tetrahydrofuran<sup>117</sup> and ethanol.<sup>118, 119</sup> Kabay and colleagues have compared the different 231 detailed conditions for functionalization and found that acidic condition were not 232 beneficial to amidoximation process.<sup>120</sup> Zahri et al. made some trials to refine the 233 operational details in terms of energy conservation, resource and time saving.<sup>121</sup> 234 However, they still did not break through the framework of these four approaches. 235

The synthesis of di-amidoximes and poly-amidoximes are similar to that of mono-236 amidoximes, and thus, no detailed discussion is carried out in this paper. However, 237

238	there are two structures worth mentioning: glutaroimide-dioxime and and
239	glutardiamidoxime. Rao and coworkers have carried out a series of researches on these
240	two amidoxime derivatives. According to their works, when hydroxylamine reacts with
241	glutaronitrile at a ratio of 2 : 1, glutardiamidoxime can be formed at room temperature,
242	while at 80 - 90°C, the resulting product is glutaroimide-dioxime. <sup>122</sup> Besides, the open-
243	chain amidoxime can be converted into cyclic imide dioxime structure via heat
244	treatment in aprotic solvents. <sup>123</sup> It thus is reasonable to speculate that in the adsorbents
245	containing polyamidoxime moiety, two neighboring amidoxime units can strip off an
246	ammonia molecule and form the cyclic imide dioxime structure. However, the actual
247	situation and the conversion ratio are depended on the specific reaction conditions, and
248	in the future researches, it is expected to be studied in more detail.

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## 2.2 The structure and characterizations

The classical structure of amidoximes is that a carbon atom simultaneously bonded 251 252 to an amine group and oxime group connects with substitute R as exhibited in Fig. 2. The presence of both amino-moiety and oxime-moiety in such structure imparts 253 amphoteric properties to amidoximes <sup>78</sup> There are some debates in protonated structure 254 displayed as structure I and I' in Fig. 6a. In general, at acidic pH, the conversion of 255 amino-group in amidoxime structure from -NH2 to -NH3+(as depicted as structure I in 256 Fig. 6a) is widely recognized.<sup>124-126</sup> This result is supported by quantum mechanical 257 258 calculations. In penylamidoxime, amino nitrogen atom possesses a higher charge compared with the oxime nitrogen atom (-0.760 vs. -0.433),<sup>89</sup> which may imply that 259

260	View Article Online hydrogen ions tend to protonate amino-group under strong acidic environment to 101039/C9TA14082D
261	the structure I in Fig. 6a. However, another binding motif (structure I' in Fig. 6a) also
262	has its followers. <sup>127</sup> Since this difference does not affect the external performance of
263	amidoxime structures and their subsequent applications, few researches have focused
264	on the correct protonation modes. More in-depth work is needed to explore the various
265	situations and to propose a generally applicable mechanism. Inspired by atomic charges,
266	the reason for the facts that gem-Aminonitroso compound (Fig. 6b) has never been
267	identified anywhere and that amidoxime is more thermodynamically stable <sup>90</sup> can be
268	easily explained. As the pH increases, the amidoxime groups can be gradually
269	deprotonated into the uncharged form and negatively charged form (II and III in Fig.
270	6a). Therein, the point of zero charge (pHpzc) is pointed out because it plays a key role
271	in explaining the adsorption performance of amidoxime-based adsorbents to various
272	adsorbates under different pH conditions. In general, at pH > pHpzc, due to electrostatic
273	force, the negatively charged adsorbents are efficient to anchor cationic contaminants,
274	but do not work for anionic ones, and vice versa. It is noteworthy that the pHpzc is
275	generally an overall characteristic of strategic materials, which depends not only on the
276	acid-base properties of amidoxime groups but also on the nature of matrices themselves
277	and others functional group, if any. That is why the pHpzc values of various adsorbents
278	differ. For example, the value is 4.3 for amidoximated polyacrylonitrile/exfoliated Na-
279	montmorillonite composite, <sup>125</sup> 6.3 for poly(acrylonitrile)/amidoxime/bentonite
280	composite <sup>128</sup> and 10.5 for amidoximated MCM-41 silica decorated with
281	poly(acrylonitrile). <sup>129</sup> More pHpzc values of various amidoxime-based materials are

tabulated in Table 2. It can be found that most of these values fall between the first-282 order dissociation constant, pK<sub>a1</sub>, (i.e.5.78 for acetamidoxime, a sp<sup>3</sup>- hybridized form, 283 and 4.85 for benzamidoxime, a sp<sup>2</sup>- hybridized form, at 25°C) and the second-order 284 dissociation constant, pK<sub>a2</sub>, (i.e.13.21 for acetamidoxime and 12.36 for benzamidoxime 285 at 25°C) of amidoxime compounds.<sup>127</sup> As for the third-order dissociation of amidoxime 286 (IV in Fig. 6a), there has never been a related report regarding the determination of 287  $pK_{a3}$  yet, and the value is thus unknown.<sup>90</sup> 288

Some basic physical structural features of amidoximes including the average bond 289 290 lengths of N<sup>1</sup>-O, N<sup>2</sup>-C and N<sup>1</sup>-C can be obtained from Cambridge Crystallographic Data Center (CCDC). Functional group structures are mainly identified by infrared (IR) 291 spectroscopy, X-ray photoelectron spectroscopy (XPS), and Nuclear Magnetic 292 293 Resonance (NMR) spectroscopy. As discussed above, reduction of cyano compounds by hydroxylamine is the main method for the synthesis of amidoximes. The stretching 294 vibration of cyano-group corresponds to a strong peak of v(C=N) at ca. 2244 cm<sup>-1</sup> in IR 295 296 spectra. Therefore, the disappearance or weakening of the peak provides first-hand information for the conversion of cyano moiety. More importantly, the appearance of 297 some characteristic bands such as the stretching vibration peak of C=N (1500 - 1694 298 cm<sup>-1</sup>) and N-O (885 - 980 cm<sup>-1</sup>) bonds provide decisive evidences for the formation of 299 amidoximes.<sup>130</sup> Similar to pHpzc, the exact position of these characteristic adsorption 300 bands could be slightly affected by matrix materials and/or bulk circumstance (e.g. the 301 presence of hydrogen bonds). The adsorption bands ascribed to the stretching vibration 302 of O-H and N-H often cannot be characteristic because they are usually affected by the 303

304	view Article Online solvent used and the water in materials on the one hand. <sup>90</sup> On the other hand, they are
305	too common to be representative. More importantly, their bands are often overlapping
306	$(3000-3600 \text{ cm}^{-1} \text{ for } v(O-H)^{27} \text{ and } 3000-3600 \text{ cm}^{-1} \text{ for } v(N-H)^{20})$ and difficult to
307	distinguish them from each other. <sup>131</sup> The data of FT-IR spectra for various amidoximes
308	are tabulated in Table 3. The XPS presents the signals at 400.3 and 401.7 eV in N 1s
309	spectrum, corresponding to NH <sub>2</sub> -C=N-OH and NH <sub>2</sub> -C=N-OH, respectively, <sup>33</sup> and the
310	peaks at 286.18 eV in C 1s and 531.08 eV in O 1s spectrum are indicative of $NH_2$ -C=N-
311	OH and NH <sub>2</sub> -C=N-OH, respectively. <sup>132</sup> In the <sup>1</sup> H NMR spectra, two strong
312	characteristic peaks at 9.44 ppm and 5.81ppm are corresponded to the OH and $NH_2$
313	resonances, respectively. <sup>117</sup> Similarly, two singlets in the ranges of -85.30 to -98.30
314	ppm and of -317.40 to -319.40 ppm can be observed in <sup>15</sup> N NMR spectra, which are
315	attributed to NOH and $NH_2$ resonances, respectively. <sup>133, 134</sup> In <sup>13</sup> C NMR spectra, the
316	signal at approximately 149 ppm is ascribed to the carbon in the cyclic imide-dioxime,
317	while the peak at around 157 ppm is indicative of the carbon in amidoximes. <sup>135, 136</sup> As
318	a result, the low-field singlet of the $C(NH_2)$ =NOH has been found at 153.8 ppm. <sup>137</sup> The
319	basic physical and chemical properties of the amidoxime structure are shown in Fig. 7.
320	Besides, thermogravimetric analysis (TGA) has confirmed amidoxime structure
321	decomposes at the temperature range of 400 - 500°C (the peak locates at ~450°C). <sup>109</sup>
322	In Raman spectrum, the characteristic peaks of C=N, C=N, and N-O have been found
323	at 2254, 1662 and 943 cm <sup>-1,</sup> respectively. <sup>138</sup> Apart from these methods, some
324	technologies of amidoxime-bearing materials, such as X-ray Diffraction (XRD), <sup>106, 139</sup>
325	scanning electron microscope (SEM)98, 29Si MAS NMR spectra109 and transmission

326	view Article Online electron microscope (TEM) <sup>140</sup> and so on, are utilized to characterize the amidoxime-
327	based materials as well. However, none of these technologies are directed to amidoxime
328	structures, and their concerns are more on the matrix materials. Therefore, it is not
329	discussed in detail in this paper.
330	
331	3. Amidoxime-based materials and their uranium adsorption
332	performances

The development of high-performance adsorbents for marine uranium extraction is 333 an important response to deal with the depleting fossil energy and serious 334 environmental problems, to which great efforts have been devoted. Especially in recent 335 years, the involvement of the U.S Department of Energy (DOE) has greatly promoted 336 the development of this field.<sup>141</sup> Although some other adsorbents with different groups 337 such as carboxyl groups also exhibited excellent performance for uranium recovery,142 338 amidoxime-based materials are still the main force and are regarded as the most 339 340 promising candidates for uranium enrichment due to their high affinity to uranyl ions and safety for environment.<sup>143</sup> Since 1980s, a large number of amidoxime-based 341 materials have been designed and synthesized as presented in Fig. 8, which can be 342 roughly divided into polymeric materials, carbon-based materials, biosorbents, silica-343 based materials, new type of porous materials, and others. In this chapter, various types 344 of amidoxime-related adsorbents developed are summarized. 345

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# 3.1 Polymeric materials

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348	View Article Online Among a variety of amidoxime-based materials, polymeric adsorbents, as the most
349	important ones for seawater uranium extraction, are studied widely due to their
350	following merits: i) capable of deploying in seawater with high mechanical resistance
351	against attrition; ii) light weight; iii) high plasticity in shapes and lengths. <sup>144</sup> Common
352	means for obtaining them include treating the commercial polyacrylonitrile with
353	hydroxylamine <sup>130, 145, 146</sup> and amidoximating the grafting product of acrylonitrile and
354	comonomers. <sup>38, 147, 148</sup> Direct amidoximation of polyacrylonitrile is the simplest method
355	for obtaining amidoxime-based materials in early years. The degree of amidoximation
356	profoundly affects the density of amidoxime groups and mechanical properties of the
357	resultant materials. <sup>149</sup> Comparatively, the method of graft polymerization is more
358	advantageous. Radiation-induced graft polymerization (RIGP) <sup>150-152</sup> and atom transfer
359	radical polymerization (ATRP)93, 153 are widely used to achieve the grafting reaction
360	and their processes are illustrated as Fig. 9a and 9b. The advantages of RIGP lie in that
361	the amount of functional groups and the length of graft chains can be controlled by
362	irradiation conditions (dose, dose ratio) and grafting conditions (reaction time,
363	temperature). <sup>23</sup> Since most of the ligands are on the polymeric backbone, functional
364	groups possess better accessibility for uranium. <sup>29</sup> The common trunk materials includes
365	fabric polymers, <sup>23, 154, 155</sup> non-woven fiber, <sup>80, 156-159</sup> high-density polyethylene fibers
366	(HDPE), <sup>13, 160</sup> ultrahigh molecular weight polyethylene (UHMWPE) fibers, <sup>161-164</sup>
367	polyethylene-coated polypropylene skin-core (PE/PP) <sup>165, 166</sup> and some textiles like
368	nylon-66 <sup>167</sup> and so on. In contrast, much less host materials are selected for ATRP, and
369	PE fiber dominates. However, ATRP circumvents the drawbacks suffered by

370	View Article Online conventional radical polymerization such as high-cost radiation-induced DOI:10.039/C9TA14082D
570	conventional radical polymenzation, such as high-cost radiation-induced devices,
371	limited nitrile groups available for amidoximation caused by many undesirable
372	reactions <sup>44</sup> and incapacity in tuning the polymer structure including its composition,
373	conformation, and morphology. <sup>168, 169</sup> ATRP-derived adsorbents generally have
374	excellent adsorption properties because thier various parameters can be randomly
375	tailored by controlling the synthesis conditions (feed ratio, catalyst, time, temperature,
376	solvent, etc.). For instance, the adsorbent, p(2DVB-VBC)-2PAN, exhibited high
377	capacity (1.99 mg-U/g-ads) and fast kinetics (0.33 mg-U/g $\cdot$ d) after 27 d of contact
378	with 5 gallons of seawater. <sup>21</sup> Besides, the combination of RIGP and ATRP can further
379	optimize the structure of the synthesized amidoxime-based polymers. As reported, the
380	as-prepared PE-g-PVBC-g-(PAO-co-PAA)s has the unique polymer architectures of
381	brushes on brush, <sup>144</sup> and the incorporation of glycidyl methacrylate (GMA) by RIGP
382	has been proved to not only mitigate the hydrophobicity of the trunk material but also
383	provide more reaction sites for ATRP, yielding higher degree of grafting (d.g.).44 But
384	the hydrophilicity and grafting rate of adsorbents do not decide everything. Other
385	factors such as the conformational effect of the graft chain could also affect the
386	performance of adsorbents. In practical applications, the accessibility and availability
387	of the adsorption sites are more worthy of attention than the group density. In addition
388	to GIRP and ATRP, other approaches like reversible addition-fragmentation transfer
389	(RAFT) <sup>132, 170, 171</sup> and surface-initiated single electron transfer living radical
390	polymerization (SET-LRP) <sup>126</sup> have also proven to be feasible, which may show a
391	broader application prospect in the future.

392	View Article Online Most of monomers co-grafted with acrylonitrile are organic acids with vinyl molety
393	like acrylic acid (AA), <sup>24</sup> methacrylic acid (MAA), <sup>154</sup> 2-hydroxyethyl methacrylate
394	(HEMA), <sup>172</sup> acrylamide (AAm), <sup>157</sup> N,N-dimethylacrylamide (DMAAm), <sup>23</sup> vinyl
395	sulfonic acid (VSA),155 vinyl phosphonic acid (VPA),9 itaconic acid,28 etc. The
396	contribution of comonomers is mainly to improve the physicochemical properties of
397	adsorbents and to provide additional adsorption sites. <sup>173, 174</sup> On the one hand, their
398	introduction can improve the hydrophilicity of resultant adsorbents, promote the
399	diffusion of uranyl ions inside the fabric adsorbents <sup>154, 172</sup> and help the ions approach
400	the adsorption sites. <sup>124</sup> For this reason, the resins with amidoxime/carboxylic acid
401	groups had higher kinetics in artificial seawater than that with amidoxime group
402	alone.39 On the other hand, ionic groups can vary the local pH, affecting uranium
403	species present in seawater and the types of complex between amidoxime and uranyl
404	ions. <sup>24</sup> This may be why DAAm can make the adsorbent more hydrophilic but not
405	improve the performance as good as the carboxyl group. <sup>23</sup> In the other word, although
406	the synergistic effects of amidoxime and co-monomer groups together determine the
407	final performance of adsorbents, <sup>175</sup> the effect of different monomers is varied. For
408	example, the amidoxime-functionalized polyethylene nonwoven fabric co-grafted with
409	MAA displayed the most excellent adsorption performance for uranium, followed by
410	ITA and AA, AAm the worst. <sup>157</sup> The co-grafting of various acidic monomers endows
411	the PE fibers with the ability to adsorb uranium from simulated seawater in the
412	following order: VPS> ITA> MAA > VSA > AA. <sup>155</sup> VPA performs best, which may
413	be related to the lowest $pK_a$ of 1.3, <sup>155</sup> and its ability to bind uranyl ions. <sup>176, 177</sup> ITA with

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414 two carboxylic moieties in per molecule can make PE fiber more hydrophilic and HS<sup>COTAL4082D</sup> 415 co-grafting also affords a good result. AA plays the worst co-monomer due to 416 homopolymerization that can be suppressed by Mohr's salt.<sup>155</sup> In addition, different 417 order on uranium adsorption capacity occurred in PE fiber and PE nonwoven fabric 418 may imply that trunk materials also affect the ultimate adsorption behaviors. But the 419 impact of the interaction between co-monomers and matrix materials on uranium 420 adsorption remains unclear, which needs further investigation in the future.

Alkaline conditioning is an important process to be carried out before the use of 421 422 polyamidoxime-based materials. As reported, alkaline solutions can i) deprotonate the acidic groups and amidoxime groups,<sup>178</sup> ii) convert amidoxime groups into carboxylate 423 anions (Fig. 10a),<sup>31, 179, 180</sup> iii) convert unreacted cyano groups into carboxyl groups<sup>155,</sup> 424 <sup>181</sup> to increase the hydrophilicity,<sup>182-184</sup> and iv) convert two neighboring amidoximes 425 into cyclic imide-dioxime<sup>150, 185, 186</sup> to improve binding ability to uranium.<sup>187</sup> The 426 alkaline reagents widely used are KOH157, 179 and NaOH.124 NaOH is considered to be 427 428 better for AF1 adsorbent due to higher uranium adsorption capacity obtained and lower cost.<sup>188</sup> Besides, the increase in alkaline concentration, temperature and time can lead 429 to a higher uranium adsorption capacity in simulated seawater solution.<sup>143</sup> But in natural 430 seawater test, long conditioning time is not conducive to uranium uptake, not only 431 because of the conversion of amidoxime into less selective carboxylates, but also 432 because of the degradation of adsorbents.<sup>178</sup> Therefore, it was critical to select proper 433 conditioning temperature and time to minimize the physical damage. 434

Fiber-based amidoxime-based materials have long played a pivotal role in

recovering uranium from seawater.<sup>149, 189, 190</sup> However, so far, they still suffer from 436 some deficiencies, such as poor mechanical strength and corrosion resistance, 437 undeveloped pore structure, and low site utilization, making their use very limited and 438 costly. Moreover, the inevitable shrinkage of polymeric structure caused by post-439 amidoximation treatment further deteriorates the mechanical nature and surface area of 440 the grafted fibers,<sup>93, 160</sup> and melt-spinning fails to produce submicron or nanofibers.<sup>160</sup> 441 In order to get further development, we must break out the current inherent model and 442 find a new breakthrough. The work from Ning Wang's team seems to give us some 443 inspiration.<sup>191</sup> They developed the blow spinning PIDO NFs based on pre-444 amidoximation treatment (Fig. 10b). The obtained adsorbent prevails over all fibers 445 commercially available or investigated. More importantly, this method can achieve 446 mass production and has extremely high practical application value, which has opened 447 up the application field of amidoxime-based fibers to some extent and provides a new 448 idea for overcoming the common defects of amidoximated polymeric materials. 449

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# 3.2 Carbon-based materials

452 Carbon-based materials are characterized by large specific surface area, high 453 thermal/chemical stability, developed pore systems and wide range of sources,<sup>192, 193</sup> 454 but their adsorption capacities of uranium are generally low due to the hydrophobicity 455 and the lack of specific functional groups. As reported, the uranium uptakes are only 456 27.6 mg/g for graphene oxide (GO),<sup>194</sup> 26.7 mg/g for soluble starch-derived 457 hydrothermal carbon (HTCs)<sup>195</sup> and 24.9 to 39.1 mg/g for MWCNTs.<sup>196</sup> Even if the

458	View Article Online synthesis of the few-layer graphene oxide (FL-GO) weakened the self-aggregation
459	problem to some extent and increased the uranium adsorption capacity to 97.5 mg/g, <sup>30</sup>
460	the increment was not encouraging. After being modified with amidoxime groups (Fig.
461	11a), the situation becomes completely changed. Specifically, the incorporation of
462	amidoxime group increased the uranium adsorption amount to 398.41 mg/g for GO-
463	based adsorbent, <sup>140</sup> 455.6 mg/g for soluble starch-derived HTC <sup>195</sup> and 67.9 mg/g for
464	AO-MWCNTs, <sup>98</sup> at pH 5.0/6.0 and 298 K, respectively. The post-modification of DM-
465	AO doubled the uranium uptake of pristine GO and halved the equilibrium time. <sup>197</sup> In
466	addition, GO can be converted into reduced GO (rGO) during the hydroxylamine
467	treatment. The generated PAO/rGO achieved the maximum adsorption capacity of 872
468	mg/g at pH 4.0, much higher than that of rGO (29 mg/g) and PAO (161 mg/g). <sup>198</sup> Due
469	to the relatively low background sorption for U(VI), carbon-based materials can also
470	be uses as the platform to compare the affinity of various functional groups towards
471	uranium. <sup>199</sup> Taking AO-g-MWCNTs as an example, its theoretical maximum
472	adsorption amount for uranium reached 176 mg/g, which was 4.3 times higher than that
473	on oxidized MWCNTs, providing a strong evidence of the high affinity of amidoxime
474	group. <sup>146</sup> It can also be seen from above instances that, although various carbon-based
475	materials are functionalized by amidoxime groups, the uranium uptakes of the
476	MWCNTs-derived ones are apparently inferior to that of others, perhaps implying that
477	the matrix material largely determines the final adsorption properties of the adsorbents.
478	A concrete example that can prove this point is that AOGONRs, obtained by
479	amidoximating the graphene oxide nanoribbons (GONRs) converted from MWCNTs

based on longitudinal oxidation unzipping,<sup>200</sup> shows a relatively high uranium/<sup>COTA14082D</sup>
adsorption capacity (560 mg/g) and short equilibrium time (within 200 min).<sup>119</sup> In
general, GOs play the best solid matrix for amidoxime group followed by HTCs, carbon
nanofibers (CNFs), mesoporous carbon (MCs), activated carbon fibers (ACFs), and
MWCNTs.

Conventional surface functionalization processes generally result in pore blockage 485 and may damage the surface and pore structure of carbonaceous materials. Some 486 strategies such as the one proposed by Choi and Ryoo<sup>201</sup> have been adopted to solve 487 this problem. The synthesized AO-OMC series materials increased the uranium 488 adsorption capacity of the pristine CMK-3 by nearly 7 times, while retaining the 489 structural stability of the MC feedstock to a maximum extent.<sup>108</sup> The HTC-AO prepared 490 491 based on the chemical rationales of Morita-Baylis-Hillman and free-radical addition reactions is an almost prefect uranium adsorbents with following features: i) stable 492 physiochemical properties, and no significant change in its surface groups and the 493 494 adsorption performance for uranium after  $\gamma$ -irradiation treatment; ii) fast kinetics due to the absence of pores and voids; iii) amazing saturation sorption capacity of 1021.6 495 mg/g; iv) excellent selectivity towards uranium both in simulated nuclear industry 496 effluent at acidic condition.<sup>202</sup> Besides, sonication was proved to induce the cavitation 497 process, thereby circumventing potential pore blockage,<sup>33</sup> and the assistance of 498 ultrasound was reported to significantly increase the adsorption speed of the material 499 for uranium.<sup>203</sup> In a word, the excellent physicochemical properties of carbon-based 500 materials provide a good loading platform for amidoxime groups, while the high 501

affinity of amidoximes to uranium endows the specificity of carbon-based materials, 502

and their synergistic effect makes amidoximated carbon-based materials have 503 unparalleled uranium adsorption properties. 504

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3.3 **Biosorbents** 506

Compared with common polymer substrates such as PP and PE fibers, natural 507 biomass materials are more hydrophilic, biocompatible and non-toxic.<sup>204</sup> Not only is 508 biosorption cheap, it also largely reuses waste.<sup>205</sup> 509

510 Taking chitosan as an example, it is an aminopolysaccharide with abundant hydroxyl and amino groups, and it is widely regarded as environmentally friendly 511 adsorbent.<sup>100</sup> But it is poor in porosity<sup>106</sup> and mechanical properties.<sup>110</sup> Its solubility 512 under acidic conditions is also a headache,<sup>110</sup> which makes it diffcult to separate and 513 limits its application. Therefore, it is usually imparted with magnetic properties<sup>96, 106</sup> or 514 embedded in clay mineral like bentonite.<sup>110</sup> The cyano-containing reagents can be 515 introduced into chitosan backbone though substitution,<sup>106</sup> cyanoethylation reaction,<sup>96</sup> 516 and free-radical polymerization.<sup>110</sup> The introduction of amidoxime groups significantly 517 improves their reactivity to uranium with the theoretic maximum adsorbed amount 518 from 117.65 mg/g to 372 mg/g. Previous review believed that chitin/chitosan-bearing 519 materials may win a place in future uranium exploitation from seawater.<sup>206</sup> 520

In addition, the amidoximation of cell biomass, which is usually based on surface 521 functional groups on the cell wall like -NH<sub>3</sub>, -OH or -COOH,<sup>207</sup> has also achieved very 522 efficient performance in uranium uptake (621 mg/g for amidoxime-modified 523

524	Aspergillusniger), <sup>208</sup> kinetics (adsorption equilibrium can be established only in 45 min <sup>204,0,10,39/C9TA14082D</sup>
525	for amidoximated Trametestrogii pellets) <sup>209</sup> and selectivity. <sup>210</sup> The amidoxime-
526	modified Saccharomyces cerevisiae can still achieve high adsorption efficiency (75 -
527	100%) in salt lake samples with almost saturated metal ions (Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> ,
528	etc.) at pH 6. <sup>207</sup> Besides, the adsorption performance of the amidoxime-modified algal
529	biomass (366.8 mg/g) was significantly better than that of PEI-modified material
530	(279.5g) and native material (194.6mg/g), <sup>211</sup> once again providing a strong evidence
531	for the important role of amidoxime groups played on uranium adsorption. Wool fibers-
532	derived adsorbents overcome the drawbacks of most biomass adsorbents that are easily
533	degraded, <sup>212</sup> and the loading of nano-sized ZnO endows the amidoximated wool fiber
534	with a good anti-biofouling property. <sup>213</sup> In addition, cellulose and its derivatives have
535	also important research value for developing novel amidoxime-based adsorbent
536	materials, <sup>214, 215</sup> which is worthy of further research.

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#### 3.4 Silica-based materials

539 Silica-based materials have been active in the field of organic and inorganic 540 removal.<sup>216</sup> But pure silica is poor in selectivity toward specific target adsorbates. 541 Silica-based organic-inorganic hybrids have been considered as a breakthrough to 542 overcome this dilemma since they not only remain the stable 3-dimensional structure 543 of inorganic silica but also possess the specific chemical properties belonging to organic 544 functional groups.<sup>101, 217, 218</sup> The most attention has been drawn on mesoporous silica,<sup>129, 545 <sup>176, 219, 220</sup> especially for SBA-15. There are two approaches to fabricate amidoxime-</sup>

546	View Article Online functionalized SBA-15: co-condensation <sup>109</sup> and post-grafting. <sup>221</sup> The desired product
547	can be obtained by converting the cyano-groups on the precursor materials into
548	amidoxime groups (Fig. 11b). From the perspective of green chemistry and waste
549	utilization, the silica resource can also be provided by several byproducts, such as coal
550	fly ash <sup>138</sup> . The key processes in determining the structural properties of mesoporous
551	silica materials are template removal and pore formation, which are usually achieved
552	by calcination or solvent extraction. The former is most commonly used and the latter
553	may not remove the template completely. <sup>221</sup> But calcination always suffers from the
554	condensation of silanol groups, leading to less reactive sites for further grafting. Thus,
555	some subsequent operations such as treating with dilute $H_2O_2$ or alkali solution are
556	required to recover the reduced silanol groups. In this period, the alkali concentration
557	and operating temperature are particularly important. <sup>221</sup> Calcination does not apply for
558	the silica material prepared by co-condensation method because they carry organic
559	groups that cannot withstand high temperature. With regard to solvent extraction,
560	research has proved that both the structural features and uranium extraction
561	performance of the adsorbent treated by acidic ethanol are superior to those of the
562	adsorbent treated by pure ethanol. <sup>109</sup> Despite post-grafting process seems to undergo
563	more steps, its products exhibit higher uranium adsorption capacity than the
564	counterparts obtained by co-condensation. The reason could be due to that the organic
565	groups homogeneously distribute on the backbone of the co-condensation-derived
566	mesoporous silica, while the amidoxime groups on the SBA-15 obtained by post-
567	grafting method are concentrated on the outer surface and the pore entrance. <sup>222</sup>

568	View Article Online During the preparation of SBA-15, the morphology control is often achieved by
569	zirconium compounds (e.g. $ZrOCl_2 \cdot 8H_2O$ ). The addition of zirconium compounds
570	promotes the conversion of SBA-15 from long channels to short ones. <sup>223</sup> Since the short
571	axis of SBA-15 with short channels parallels to its channels, which is beneficial for
572	accelerating the diffusion of molecules and reducing the possibility of pore-blockage,
573	better adsorption performance and faster adsorption kinetics towards uranium ions are
574	expected to be accomplished. <sup>221, 224</sup> As reported, the addition of small amounts of Zr(IV)
575	ions can generate platelet SBA-15. <sup>223</sup> However, the lone pair electrons of cyano-groups
576	in CTES can form dative bonds with Zr(IV) ions. Therefore, during the co-condensation
577	in the presence of zirconium compounds, as the ratio of CTES/TEOS increase, the
578	morphology of resulting products gradually changes from platelet shapes to short rod
579	shapes and then to long shapes. But it is not true for post-grafting process. <sup>222</sup> Actually,
580	even though in the case without Zr(IV) ions, the ratio of CTES to TEOS can also have
581	a profound effect on the morphology and uranium adsorption performance of the
582	adsorbents.52 The same is true for the case where the cyano-containing reagent is
583	CPTS. <sup>109</sup> It is believed that the adsorption behavior of silica-based materials to uranium
584	is the overall results of the structural porosities and the density of amidoxime groups,
585	and that the best performance cannot be achieved unless they reached the ideal
586	balance.52 Therefore, the application of zirconium ions can only play a role in
587	controlling morphology, which does not mean that adding zirconium ions will
588	definitely obtain better adsorption effects.

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### 3.5 New type of porous materials

Porous materials have always played a pivotal role in adsorbents. Traditional ones like carbon-based materials and porous silica have been aforementioned. Over the past several decades, as rising stars of porous materials, MOFs and Covalent Organic Frameworks (COFs) have drawn a widely attention. Among them, MOFs have been developed earlier and received more research.

Similar to carbon-based materials, MOFs have outstanding physiochemical 596 attributes but poor selectivity to target ions.<sup>102, 115</sup> As expected, the synergistic effect of 597 MOFs and amidoxime makes the uranium adsorption applicable to a wider pH range, 598 broadens the application fields of the resultant adsorbents, and significantly increases 599 the loading capacity and affinity of MOFs to uranium.<sup>113</sup> The methods for synthesizing 600 601 amidoxime-functionalized MOFs involve chemical crosslinking the cyano-bearing agent (such as DAMN) with crosslinking agent (such as glutaraldehyde) prior to 602 amidoximation.<sup>102</sup> Moreover, they can also be obtained with the assistance of 603 microwave<sup>115</sup> or plasma technology.<sup>225</sup> Plasma-derived MOFs have more amidoxime 604 groups than chemical-derived one, but they have similar uranium uptake in real 605 seawater (2.74 mg/g vs. 2.68 mg/g). 606

607 COFs usually have highly ordered crystal and pore structure,<sup>226</sup> and various 608 functional units can be specifically incorporated in a pre-designable porous framework 609 through topological design.<sup>227</sup> In addition, the high thermal and chemical stability 610 endow them with the ability to cope with the extreme environments<sup>228</sup> that MOFs 611 cannot withstand.<sup>229</sup> The incorporation of amidoxime groups into COF structure can be

612	achieved thought modifying a versatile platform, diyne-based COF. The as-prepared
613	TCD-AO presented the best selectivity to uranium as compared to hydroxyl- and cyano-
614	functionalized ones. <sup>230</sup> Moreover, amidoxime functionalized COFs can be synthesized
615	by two steps: solvothermal reaction and hydroxylamine treatment (Fig. 12). Due to the
616	exceptional accessibility of the chelating groups and the cooperation of adjacent groups
617	in the specific channels, the resulting COFs exhibited much superior performance in
618	adsorption capacity, kinetics and affinity toward uranium than amorphous counterpart
619	did. It can reduce uranium concentration in various contaminated wastewater samples
620	from 1ppm to 0.01ppb in just a few seconds. <sup>231</sup> It shows the great potential of
621	amidoxime-functionalized COFs in uranium extraction. So far, the study on
622	amidoxime-functionalized COFs is strikingly absent and future research should focus
623	on simpler preparation, more effective functional groups exposure and lower prices for
624	large-scale applications.

Some other new type of porous organic polymers like porous aromatic framework 625 (PAF) and polymer of intrinsic microporosity (PIM) also serve as modification 626 platform to introduce amidoxime groups. Under the similar conditions, virgin PAF 627 performed a negligible uranium adsorption capacity, while the amidoxime 628 functionalized ones presented high adsorption amounts: 283 mg/g for PAF-1-629 CH<sub>2</sub>AO<sup>137</sup> and 385 mg/g for PAF-1-NH(CH<sub>2</sub>)<sub>2</sub>AO.<sup>232</sup> PIM is a porous organic polymer 630 with inherent microporosity. Studies have shown that amidoximation does not destroy 631 632 its inherent pores, and that the resulting adsorbent can be easily fabricated into a film for actual field application.<sup>117, 233</sup> Out of the consideration for the merits of the porous 633

organic polymers (POPs), including unique chemical stability, easy to molecular design 634 and controllable pore structure,<sup>234, 235</sup> and inspired by the fact that second-sphere 635 interaction in nature assists the chelation of proteins with well-folded scaffolds and 636 metal ions,<sup>35, 236</sup> three amidoxime-containing POPs as uranium nano-traps were 637 designed for uranyl binding. The incorporated amino-ligand has been observed to 638 enhance the overall uranophiles of the adsorbents because it can serve as hydrogen bond 639 acceptor and reduce the electron density of uranium in the complex, and ortho-640 substitution works better than para-substitution does.<sup>237</sup> Moreover, conjugated 641 microporous polymers (CMPs) bearing amidoxime groups have achieved simultaneous 642 adsorption and detection of uranyl ions.<sup>238</sup> The development of these new materials 643 offers potential possibilities for practical and efficient uranium recovery/removal, 644 deserving further attention. 645

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#### 647 **3.6 Others**

Natural clays,<sup>139</sup> synthetic mineral salts<sup>239</sup> and cyclic compounds<sup>240, 241</sup> and so on 648 have also been tried as solid matrix for amidoxime groups out of consideration for 649 economic effectiveness, ease of synthesis, biocompatibility or low toxicity. For 650 example, the amidoximated palygorskite shows several times higher uranium 651 adsorption capacity than bare one does (78.13 mg/g vs. 37.90 mg/g).<sup>111</sup> The surface 652 modification of montmorillonite by polyamidoxime not only enhances the mechanical 653 properties of the polymer, but also significantly improves the adsorption efficiency of 654 montmorillonite on uranium, which fully realizes the complementary advantages.<sup>242</sup> In 655

656	view Article Online particular, SMON-PAO fiber, a composite material of montmorillonite and
657	polyacrylamidoxime prepared by blow-spinning method, is characterized by rich
658	porosity, large surface area, high hydrophilicity and weak surface charge. Its adsorption
659	capacity has reached a surprising level of $9.59 \pm 0.64$ mg/g in filtered seawater at pH
660	8.0, <sup>243</sup> which is one of the highest value in closed-loop system to date. In addition, iron
661	oxide hydroxide (FeOOH) was used as supporting material for amidoximes to extract
662	theoretically 980.39 mg/g of uranium in 298 K, far higher than most of reported
663	uranium-extractants. <sup>244</sup> Also as an iron compounds, Fe <sub>3</sub> O <sub>4</sub> is often incorporated into
664	various materials, due to its magnetic properties, ease of preparation, and low toxicity,
665	to enhance their separation performance. In addition to the aforementioned chitosan,96,
666	<sup>106</sup> many materials like graphene oxide, <sup>104, 203, 245</sup> polymers, <sup>126, 132, 246</sup> and silicon, <sup>101</sup> have
667	been prepared into amidoximated magnetic materials. These magnetic materials often
668	have unique properties not found in other materials. For example, with the assistance
669	of a magnetic field, MNPs@PAO can be separated from the bulk solution within 12s. <sup>132</sup>
670	The magnetic nanoparticles in AO/mGO obtained by N2 plasma treatment has been
671	proved to not only improve the separation efficiency but also promote the reduction of
672	U(VI) to U(IV), which could be beneficial to the deposition of uranium on the material
673	surface and increase its uranium enrichment capacity. <sup>245</sup> But this phenomenon is not
674	limited to Fe <sub>3</sub> O <sub>4</sub> , ZVI/PAO adsorbent with zero valent iron as the magnetic core shows
675	similar separation and reduction performance. <sup>247</sup> More recently, melamine sponge and
676	halloysite nanotube were confirmed with high-efficiency to load amidoxime groups for
677	uranium extraction from seawater.248, 249 Black phosphorus nanosheets (BP), thanks to

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the photoinduced, photothermal, photoelectric and photocatalytic properties, endowed<sup>(COTAL4002D)</sup> the amidoxime-based adsorbent with strong coordination interactions to uranyl ions, increased electrostatic attraction to uranyl carbonate ion, and high antifouling activity.<sup>250</sup> It is conceivable that in the future, more and more matrix materials will appear for loading amidoxime to obtain better uranium adsorption properties. How to maximize the potential of materials and the reachability of amidoxime will be the main research direction.

Recently, electrochemical methods open another door for ion extraction, which can 685 overcome the drawbacks the traditional approaches have, such as low extraction 686 capacity and slow adsorption kinetics.<sup>251</sup> Cui and coworkers used half-wave rectified 687 alternating current electrochemical (HW-ACE) method with amidoximated electrode 688 (C-Ami electrode), implementing nearly 9 times higher adsorption capacity (1932 mg/g 689 vs. 200 - 220 mg/g) and 4 times faster extraction kinetics  $(2.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{ vs. } 5.0 \times 10^{-5} \text{ m}^{-1} \text{ s}^{-2} \text{$ 690 10<sup>-6</sup> M<sup>-1</sup> s<sup>-2</sup>) than physicochemical counterpart in uranium-spiked seawater. Even 691 692 through in real seawater, the extraction capacity of HW-ACE method also is 3 times superior to that of conventional method (1.62 µg vs. 0.56µg) after column-flow 693 experiment with 4 L seawater. The entire adsorption process consists of five steps and 694 can be efficiently regenerated by 0.1 M HCl with reverse bias (Fig. 13).<sup>252</sup> Due to the 695 presence of amidoxime groups, this system also shows a wonderful selectivity to uranyl 696 ions. The introduction of external electric fields may present some challenges and 697 additional investment for large-scale applications. Nevertheless, it cannot deny doubt 698 that the HW-ACE method is a promising alternation to extract uranium from seawater. 699

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Table 4 and Table 5 showed the adsorption amounts of various adsorbents in pure 701 water, brine water (simulated wastewater), simulated seawater, U-spiked seawater and 702 real seawater. It can be seen that the uranium adsorption capacities of various 703 adsorbents in pure water range from 6 to 1187.05 mg/L, which are significantly higher 704 than that of other types of water. Because of the developed pores and excellent 705 mechanical properties, carbon-based materials provide ideal loading platforms for 706 amidoxime group and generally exhibit superior uranium adsorption efficiency. In 707 708 brine solutions, carbon-based materials still maintain excellent adsorption performance. 2.0 PAO/rGO has afforded the highest uranium uptake of 872 mg/g.<sup>198</sup> Therefore, 709 amidoximated carbon-based materials have great potential in industrial wastewater 710 711 treatment. Significantly lower extracting efficiency and longer equilibrium time occurred in seawater and its simulants. Unlike pure water or brine water, polymer 712 adsorbents are the most important materials used in real/simulated/spiked seawater. The 713 714 uranyl uptakes of different amidoxime-based materials are in the range of 1.84 - 990.60 mg/g in simulated seawater and 0.10 - 1089.36 mg/g in U-spiked seawater, respectively. 715 Under the aid of electrochemical adsorption, this value can reach an astonishing 1932 716 mg/g.<sup>252</sup> In real seawater, the extraction capacities of the adsorbents for uranium are 717 0.124 - 28.1 mg/g. But the result of 28.1 mg/g reported by Kavakli and co-workers<sup>105</sup> 718 was questioned by Abney et al.<sup>8</sup> The values obtained from field experiments are 719 720 obviously lower than those obtained from laboratory-scale tests, and the adsorption capacity is highly correlated with the length of campaign. The property of the materials 721

used in filed application needs to be further strengthened for large-scale application. 722 Different from adsorption capacity with the theoretical maximum value, the selectivity 723 of various materials is hard to compare with each other. Although the selectivity of 724 materials to uranium can be characterized by related parameters, such as the selectivity 725 coefficient, <sup>132, 202, 220</sup> its value is greatly affected by experimental conditions and is 726 usually only used to compare the selectivity of the materials to different ions in a fixed 727 system, and the coefficient between various materials in different systems are not 728 strictly comparable. Therefore, it is strongly recommended to establish a uniform 729 standardized operating procedure or method to facilitate quantitative comparison of 730 uranium selectivity of various materials. 731

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# 733 4. Influence factors on uranium extraction over amidoxime-based 734 materials

The ultimate adsorption performance of amidoxime-based adsorbents on uranium 735 736 is the apparent behavior under the combined effect of many factors. In term of the adsorbents themselves, their physiochemical properties, including surface area, pore 737 size, grafting ratio, hydrophilicity, chain length, conformation, etc., may affect their 738 uranium adsorption behavior.<sup>144, 160, 253-255</sup> For example, the increased surface area can 739 theoretically provide higher grafting and more active sites,<sup>160</sup> but unless they are 740 available, uranium adsorption cannot be improved. Micropores are detrimental to 741 adsorption, mesopores may affect the amount of adsorption by changing the surface 742 area, while macropores are required for the active sites to contact the tricarbonatouranyl 743
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anion.<sup>253</sup> More importantly, the uranium recovery by various adsorbents is seriously<sup>View Article Online</sup> affected by water chemistry. Both the natural seawater and contaminated effluent are the complex systems that pose great challenges for the practical application of amidoxime-based adsorbents. In this chapter, four major influence factors namely pH, temperature, co-existing ions and biofouling were discussed with expectation of grasping the action rationales of each influencing factor and providing guidance for the

targeted design of the new generation amidoxime adsorbents.

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#### 4.1 pH

The effect of pH is often multifaceted. From the aspect of adsorbates, uranium 753 speciation is complex as a function of the solution pH no matter what kind of water 754 755 body (Fig. 14a and 14b).<sup>102, 256</sup> This means that uranium ions exist in diverse forms under different pH, which can alter the electrostatic interactions between uranium and 756 amidoxime groups. In addition, the different uranium species have inconsistent 757 758 hydration radius, and the accessibility of the functional ligands to uranium may change due to steric hindrance. However, the related researches are relative scarcity. It thus is 759 hard to acquire the contribution of the radius to the adsorption behavior. From the aspect 760 of adsorbents, the H<sup>+</sup> concentration in the system plays a crucial role on the 761 protonation/de-protonation process of amidoxime groups as discussed in Section 2.2. 762 This phenomenon could further affect the binding of amidoximated materials to 763 764 uranium species. As reported, the adsorbent hardly adsorbs the uranyl ions when pH less than 1.0. However, when the pH gradually increased and the amidoxime group was 765

766	View Article Online deprotonated, the adsorbent adsorption capacity correspondingly increased and Teached
767	the optimal value at pH 7.0 to 8.0.26 Besides, the swelling effect of polymeric
768	adsorbents at different pH conditions maybe another manifestation of the effect of
769	solution acidity. The conformational change and other potential interactions caused by
770	it could affect the availability of active sites on adsorbents and accelerate or decelerate
771	the uptake kinetics (especially in seawater system). <sup>144</sup> However, there are few studies
772	taking this onto account and enough attention should be paid to it in future researches.
773	In U-spiked systems and natural seawater, uranium species mainly exist in the form
774	of coordinated anions (Fig. 14a). It is reported that $H^+$ could convert the uranyl complex
775	from tricarbonate-type to bicarbonate-type, which facilitates the exchange reaction
776	between amidoxime groups and carbonate ligands and thus improves the adsorption
777	efficiency. <sup>24</sup> In addition, it is believed that the de-complexation of $[UO_2(CO_3)_3]^{4-}$ to
778	$\mathrm{UO}_2^{2^+}$ may be the rate-determining step for adsorption because the tricarbonate-type
779	anion is highly stable and hard to directly complex under the seawater conditions. <sup>175</sup>
780	The process could be catalyzed by proton in the bulk solution and the decreased pH
781	would accelerate the overall adsorption process, <sup>20</sup> which could be the reasons why the
782	acidic monomers such as AA and MAA often play the important role in polymeric
783	materials. In batch experiments, the pH verified in a wide range and the uranyl species
784	may vary dramatically with the change in pH (Fig. 14b), so does the surface charge on
785	the materials. As the pH gradually increases, the surface charge of the material changes
786	from positive to negative. This has a profound effect on the entire adsorption process.
787	Under the combined effect of various factors, many studies have found that the

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adsorption efficiency first increases and then decreases with the increase of pH, and the
optimal adsorption pH is usually 4 - 6 (Table 5).

Given all that, changing the uranyl species and the surface properties of the 790 materials are the main influence mechanism of the solution pH. Therefore, in the cases 791 of effluent, some pre-treatments like pH conditioning are beneficial to improve the 792 performance of amidoxime-based adsorbents. In the cases of seawater, although the pH 793 value is almost constant in marine environment, the maximum adsorption capacity of 794 deployed adsorbents can be achieved by the introduction of proper functional groups 795 (e.g. carboxyl group) into the matrix materials, which can change the local pH 796 conditions for enhancing the uranium uptake. 797

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4.2 Temperature

Temperature is one of the factors that must be considered for the location selection 800 of uranium recovery plant in the ocean and for the optimization of wastewater treatment 801 802 conditions. Thermodynamic studies usually show that the adsorptions of uranium by amidoxime-based adsorbents are spontaneous and endothermic processes with 803 increased randomness and that high temperature effectively promotes the adsorption 804 behaviors.<sup>198, 240</sup> Both the diffusion of uranyl ions from bulk solution to the active sites 805 and ligand exchange reactions between uranium and amidoxime group will be 806 accelerated at elevated temperature.<sup>186</sup> The macroscopic reflection is that a 10 K 807 increase in the seawater temperature (293 - 303 K) could lead to the higher uranium 808 adsorption kinetics of the AO hollow fiber by a factor of 3.<sup>36</sup> More recently, Kuo et al. 809

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810	found that the temperature rising from 8°C to 31°C not only increased the uranium
811	adsorption rate of AF1 and AI8 from seawater by near 7-fold, but also promoted
812	vanadium adsorption. Nevertheless, the mass ratio of vanadium to uranium adsorbed
813	on the adsorbents (V/U, w/w) diminished remarkably with increased temperature. <sup>257</sup>
814	That is to say, the amidoxime-containing adsorbents exhibited higher selectivity for
815	uranium over vanadium at elevated temperature. This may provide a strategy to
816	moderate vanadium inhibition of uranium recovery by amidoxime-based adsorbents
817	from seawater, which were described in Section 4.3. From that perspective, seawater
818	recovery plant should be built in a warmer ocean current that are conducive to improve
819	uranium capture performance. However, some important aspects such as the
820	temperature sensitivity of the adsorption process of competitive ions other than
821	vanadium and the effect of high temperature on the longevity of the adsorbent materials
822	have not received sufficient attention and research.

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**4.3 Co-existing ions** 

Seawater is an extremely complex system that contains almost all the natureoccurring elements. The average salt content in seawater accounts for about 3.5%, which is 10<sup>6</sup> - 10<sup>7</sup> times higher than uranium concentration,<sup>109</sup> posing a major challenge for extracting uranium from seawater. Among these co-existing ions, the Na content is the highest, followed by Mg, Ca and K (**Table 1**). The influences of alkali metals (Na and K) are generally neglected, since the extraction of uranium by amidoxime-group adsorbents is usually inner-sphere adsorption that is not affected by the ionic

832	strength. <sup>104, 111</sup> However, due to their overwhelmingly high concentration, their
833	influence on other ions (such as vanadium) may indirectly affect the adsorption of
834	uranium by amidoxime-based materials. <sup>258</sup> In contrast, Ca and Mg have much greater
835	interference because they can form Ca/Mg-UO <sub>2</sub> -CO <sub>3</sub> complexes with uranyl carbonate
836	anions in seawater. Their formation not only has impacts on the affinity between
837	uranium and amidoxime, but also reduces the favorable adsorption based on
838	electrostatic attraction or even changes the adsorption mechanism since they are charge
839	neutral.17 Although the complexing ability of Ca(II)/Mg(II) ions with amidoxime
840	groups is much smaller than U(VI), <sup>10</sup> they can still occupy some important sites on
841	adsorbents due to their high concentration. Fe is considered to be one of the main
842	competing species. Compared with uranium, it has 3-fold higher molar concentration
843	in seawater (Table 1) and stronger complexation stability with amidoxime group
844	because that it has greater charge density and that its d orbital electrons have greater
845	overlap with the donor atoms (such as N and O) on amidoxime group. <sup>259</sup> Consequently,
846	the adsorption amounts of iron by amidoxime-based materials are often 4 times or even
847	higher than that of uranium. <sup>13, 259</sup> Amidoxime groups also have moderately strong
848	complexation with other transition metals such as Pb(II), Cu(II), Ni(II) and Mn(II), but
849	neither of them can significantly affect the uranium adsorption. <sup>259, 260</sup>
850	Vanadium (V) is considered to be the biggest challenge. <sup>242, 261</sup> Although its mass

fraction is smaller than uranium, it has a higher molar content and affinity to amidoxime.<sup>262</sup> The complexes formed by amidoxime and vanadium, whether V(IV) or V(V), are documented to be more stable than the uranium counterparts.<sup>263</sup> As reported,

854	the adsorption capacity of AF1 to vanadium is about five times higher than that to
855	uranium, <sup>9</sup> and vanadium accounts for almost 20 times the adsorption site of uranium. <sup>264</sup>
856	The presence of vanadyl ions also brings trouble to materials elution. <sup>265</sup> Due to the
857	strong interaction between amidoxime group and vanadium, the elution process
858	requires harsh conditions such as strong acid and high temperature, which could result
859	in irreversible damage of the adsorbents. <sup>37, 266</sup> Regarding the high affinity of amidoxime
860	for vanadium, a series of publications have been carried out experimentally and
861	theoretically. <sup>37, 159, 264, 266-270</sup> Vanadium mainly exists in the form of $V(IV)$ and $V(V)$ in
862	seawater, of which the former accounts for only 10% to 15%. <sup>271</sup> Notwithstanding, the
863	interaction between V(IV) and amidoxime groups cannot be ignored because of the
864	irreversible damage of the adsorbents resulting from the oxidation of $V(IV)$ to $V(V)$ by
865	amidoxime-groups during extraction $^{267}$ and the much faster chelation kinetics V(IV)
866	possessed. <sup>268</sup> When the vanadium is bonded to the cyclic imide dioxime, the organic
867	group can even replace the oxygen in vanadyl ions. <sup>264</sup> The stability of the generated
868	non-oxido $V(V)$ complex is higher than that of the uranium counterparts, resulting in
869	the active sites occupied by vanadium no longer being accessible by uranyl ions.
870	Moreover, the complex remains stable over a wide pH range, which also rationalizes
871	the fact that it is difficult to elute vanadium from the adsorbents even under acidic
872	conditions. <sup>262</sup>

For anions, the main influence comes from carbonate and bicarbonate ions. Carbonate ions can form stable uranyl tricarbonate anions with uranyl cations, and the replacement of carbonate in uranyl tricarbonate is considered as the rate-determining

/iew Article Online step for uranium extraction.<sup>20, 175</sup> So does bicarbonate ion,<sup>24</sup> and it even can strongly 876 compete with the amidoxime to bond uranium, thus decelerating the uranium 877 adsorption kinetics.<sup>258</sup> The influence of other anions such as sulfate, nitrate, chloride 878 and perchlorate on the uranium extraction is rarely mentioned, but they need to be taken 879 into account when studying the strength of background ions, among which chloride 880 ions and perchlorate are often used in the preparation of simulated seawater (Table 4). 881 Inspired by the high affinity of phosphoryl groups to uranyl,<sup>199</sup> it is speculated that 882 phosphate ions, related to eutrophication,<sup>272</sup> also have strong binding to uranyl ions, 883 thus affecting the uranium extraction behavior of amidoxime-based adsorbents from 884 natural water to some extent, which should also be noticed. 885

886 Whether the adsorbents are employed into real seawater or industrial wastewater, 887 a large amount of cations and anions are inevitably co-existed. Compared with the 888 influence of cations, the role of anions is often neglected and studies are very scarce. 889 Therefore, systematic observation and exploration can be carried out in future studies.

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# 4.4 Biofouling

Biofouling is one of the most fundamental reasons for the discrepancies in adsorbents performance between laboratory tests and field experiments.<sup>273</sup> Biofouling is the accumulation of microorganisms, algae, plants or animals on the madid surfaces, which may even lead to the failure of uranium extraction form seawater.<sup>261, 274</sup> In general, biofouling involved four stages: i) marine microorganisms rapidly cover onto the surface once the adsorbent is deployed in seawater; ii) the individual bacterial cells

898	and diatoms start to adhere, settle and colonize; iii) microbial membrane gradually form
899	and the resulting rough surfaces can further capture more particles and organisms; iv)
900	organisms overgrow and form complex community structures on the surface of
901	materials. <sup>158</sup> The adverse impact of biofouling on uranium extraction is mainly reflected
902	in: i) prohibiting the contact between the ligands and seawater, making the reactive sites
903	on adsorbents inaccessible; ii) interfering the uranium extraction due to microbial
904	activity, and iii) restricting the reusability of the adsorbing materials. <sup>167</sup> Light is an
905	important factor influencing the degree of biofouling, <sup>275</sup> and deploying the adsorbents
906	below the photic zone can diminish the impact of biological contamination. <sup>276</sup> Within
907	a certain range, the biological activity will increase with increasing temperature, 190, 277
908	which exacerbates the biofouling, thereby deteriorating the uranium uptake of the
909	adsorbents. <sup>278</sup> However, this does not mean that implementing the uranium recovery at
910	a deeper position is a perfect solution for this issue. Regardless of the cost, both the low
911	temperature and high pressure in deep sea may have negative effects on the adsorption
912	behavior of uranium over amidoxime-based materials. The development of anti-fouling
913	adsorbents is an important strategy to deal with this dilemma. The antibacterial moiety
914	in this materials can be divided into two categories: inorganic nanoparticles (like nano-
915	TiO <sub>2</sub> , <sup>279</sup> AgNPs, <sup>280, 281</sup> nano-ZnO <sup>213</sup> etc.) and organic components (like guanidine
916	group, <sup>158</sup> quaternary ammonium salts, <sup>282</sup> chitosan, <sup>273</sup> and antibiotics, <sup>274</sup> etc.). The
917	mechanism of nanoparticle sterilization is mainly due to its cytotoxicity. Organic
918	compounds are more likely to adsorb bacteria, to change the permeability of their cell
919	membranes, and to affect their physiological functions, thereby inhibiting the their

View Article Online growth and eventually leading to their death.<sup>273</sup> In addition, the mechanism of 920 generating active oxygen radicals by photocatalytic properties to achieve sterilization 921 effects may provide new ideas for designing materials with high resistance to 922 biofouling.<sup>250, 283</sup> The researches on this anti-biofouling adsorbents has afforded 923 encouraging results in the laboratory.<sup>284</sup> However, the composition of microorganisms 924 that cause biofouling in the ocean is complex, including anaerobic bacteria, aerobic 925 bacteria, fungi and algae.<sup>213</sup> At present, the target species selected for laboratory-scale 926 antibacterial tests are usually relatively single, and research on amidoximated anti-927 928 fouling materials is insufficient. There remains challenge in on-site uranium extraction from the ocean. How to effectively shield or minimize the impact of biofouling on 929 uranium recovery from seawater while ensuring adsorption performance is still a hot 930 topic of future research. In addition, biofouling in industrial wastewater has not 931 received enough attention. Inspired by the research on the biofouling in seawater, the 932 negative effects of biological contamination in the process of removing uranium from 933 934 polluted water by amidoxime adsorbents must be taken seriously.

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In addition, the impacts of dissolved organic matter (DOM) and current velocity 936 on the uranium uptake behavior of amidoxime-based adsorbents have attracted 937 attention. The sea area with local oceanic current velocity greater than 8 cm/s is 938 recommended to deploy adsorbents to minimize mass transfer resistance and maximize 939 adsorption efficiency,<sup>285</sup> while the sea area with abundant DOM and dissolved iron 940 should be avoided.<sup>286</sup> It also indicates that the research on the interaction and cross-941

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effects of various influencing factors needs further improvement. Therefore, for 942 specific seawater and wastewater conditions, amidoxime-based adsorbents should be 943 purposefully synthesized according to the characteristics of different types of materials, 944 such as pH-sensitive, temperature-sensitive, antibacterial and corrosion-resistant 945 adsorbents. That is to say, demand-oriented new-generation adsorbents are supposed to 946 be taken into consideration, which can not only provide targeted uranium adsorption 947 with more excellent selectivity, but also can adapt to different environments due to 948 stronger durability. 949

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### 5. Binding mechanisms

Although amidoxime-based sorbents have been used to capture uranium from seawater for decades, the underlying mechanism is still not completely clear. Understanding the binding mechanism between amidoxime groups and uranyl ions can guide the rational design and field operation of adsorbents.<sup>287</sup> Therefore, it is extremely important for the development of new amidoxime-based adsorbents with higher adsorption capacity and better selectivity.

The investigations on the adsorption process of amidoxime-based materials towards uranyl ions are mainly accomplished though model fitting, technical characterizations and theoretic calculations. It is assumed the overall adsorption process contains four steps: (1) interparticle diffusion; (2) liquid film mass transfer; (3) intraparticle diffusion and (4) binding reaction.<sup>29</sup> Interparticle diffusion is often negligible for the fluidized adsorbents. But this may not be the case for fixed ones

/iew Article Online deployed in seawater. Nevertheless, researches at this stage rarely take it into account. 964 Liquid film diffusion is often very rapid due to the hydrophilic surface amidoxime-965 based materials generally have. Intraparticle diffusion directly determines the kinetic 966 properties of the adsorbents, which is related to the matrix materials. The uranium 967 adsorption by non-porous substrates like nano-diamond does not undergo the 968 intraparticle diffusion, affording an ultrafast kinetics.<sup>78</sup> While for the porous substrates 969 like carbon-based materials, the complex pore structure can significantly limit the 970 diffusion of target adsorbates and prolong the equilibrium time.<sup>288</sup> Owing to the high 971 972 uranium-affinity of amidoxime groups, binding reactions are often favorable. Many isotherm, kinetic and thermodynamic models have been widely used to describe the 973 adsorption processes. The fitting results indicate that the adsorptions of uranyl ion by 974 975 most of the amidoxime-based adsorbents are monolayer, spontaneous, endothermic and entropy increase processes, with obvious characteristics of chemisorption.<sup>212, 289</sup> 976 The specific chemical interactions between amidoxime and uranium are mainly 977 978 studied by means of adsorbents characterization before and after adsorption, in which the FT-IR spectra and XPS are the most widely used. The type and contribution of the 979 active groups can be determined based on the appearance/disappearance, 980 enhancement/attenuation and red/blue shift of the characteristic peaks in FT-IR spectra. 981 For example, the peak at 830 - 920 cm<sup>-1</sup> is usually used to identify uranyl ions on the 982 loaded materials.<sup>53, 138</sup> Some spectral results provide a strong evidence that the N-O 983 moiety could be the main active site,<sup>125, 239</sup> while others suggest amino group may also 984

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986	View Article Online uranium adsorption by amidoxime-based materials. XPS provides detailed information
987	on the binding reaction based on the peak position of the elemental bonding energy.
988	The N 1s spectrum of AO-g-MWCNTs composites demonstrates that both amino
989	nitrogen and oxime nitrogen could participate in binding uranium, <sup>146</sup> but that of 0.2AO-
990	OMC shows that the role in anchoring uranium is played by oxime groups rather than
991	amino ones. <sup>108</sup> The O 1s spectrum in AO-g-MWCNTs-U confirms the importance of
992	the oxygen-containing groups hanging on the composites surface, particularly oxime
993	moiety. <sup>157</sup> The XPS of AO-HTC provide the evidence that the uranium adsorption on
994	the functionalized HTC is relevant to both amino nitrogen and oxime oxygen. <sup>195</sup> The
995	FTIR and XPS information of the adsorbents are summarized in Table 3 and 6,
996	respectively.

997 By comparison, X-ray adsorption fine structure (XAFS)spectrum provides more detailed information involving the binding motif. The fits of extended XAFS (EXAFS) 998 on small molecules like benzamidoxime, acetamidoxime, and glutarimidedioxime 999 1000 proved that i) U=O bond remains after coordination; ii) the two oxygen atoms local in the axial direction of complex; iii) the coordination atoms (N or/and O) coordinate with 1001 the uranyl ion in the equatorial plane, and iv) the coordination number (CN) is mostly 1002 5 to 6.225, 290 Currently, the reported binding motifs mainly include (Fig. 15a): (I) 1003 monodentate coordination,<sup>291</sup> (II) bidentate chelation,<sup>292, 293</sup> (III)  $\eta^2$  motif,<sup>203, 294</sup> and 1004 (IV) tridentate fashion.<sup>187</sup> The formation of motif I is usually accompanied by the 1005 tautomerization from amidoxime to aminoitrone (Fig. 6b). Then the generated anionic 1006 oxygen can form a 1 : 4 coordination with uranyl center.<sup>291</sup> The motif II is widely 1007

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accepted as its theoretically stable five-membered ring configuration and is supported 1008 by FT-IR spectrum and XPS data.<sup>288, 295</sup> Generally, in this motif, two to three l 1009 bind to one uranyl center.<sup>22, 292</sup> After investigating the binding motif in a set 1010  $[UO_2(AO)_x(OH_2)_y]^{2-x}$  (x = 1 - 3) complexes using DFT calculation, it was found 1011 motif was the most thermodynamically stable form regardless of the CN, which 1012 confirmed by single-crystal X-ray diffraction (S-XRD) of UO2<sup>2+</sup> complexing with 1013 amidoxime molecular.<sup>294</sup> In addition, it has been suggested that the motif III re 1014 the most stable form no matter the pH level and the ratio of uranyl/amidox 1015 complexes,<sup>296</sup> even in the ionic liquid.<sup>297</sup> As reported, the bond lengths of U-O (2 1016 and U-N (2.44 Å) in acetamidoxime bonded via  $\eta^2$  motif (Fig. 15b)<sup>254</sup> are shorted 1017 that of U-O (2.46±0.02 Å) in coordinated water or methanol molecules, confirming 1018 high thermodynamic stability of  $\eta^2$ -type complexes.<sup>298</sup> The excellent binding be 1019 results from the fact that (N, O) 2p on oxime moiety has strong covalent interaction 1020 orbital hybridization with U 5f/6d,<sup>299</sup> and their interaction is more remarkable the 1021 between U 5f/6d and CO3<sup>2-</sup>/carboxyl group,<sup>300, 301</sup> which theoretically explain 1022 possibility of amidoxime-based materials for uranium extraction from sea 1023 Furthermore, it has been discovered the gradual addition of amidoximate anions 1024 into the uranyl equatorial plane of UO<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and  $[UO_2(CO_3)_3]^{4-}$  in  $\eta^2$  m 1025 shown in Fig. 16a and 16b, respectively.<sup>296, 300</sup> However, some different results 1026 that the  $UO_2(AO)_2(H_2O)$  complex with mixed motif for the two amidoximes is 1027 more stable than that with only  $\eta^2$  motif at the CCSD(T) level (Fig. 16c).<sup>290</sup> It is believed 1028 that the cyclic imide dioxime produced by the two adjacent amidoxime groups in 1029

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View Article Online polymeric adsorbents is primarily responsible for the high uranyl affinity and plays the

1031 actual role in uranium anchoring (motif **IV**),<sup>178</sup> which is supported by 1032 crystallographic,<sup>187</sup> thermodynamic<sup>302</sup> and computational<sup>303</sup> studies. It has been 1033 claimed that the cyclic imide dioxime has the ability to coordinate with uranyl in 1034 tridentate form with a higher binding constant<sup>304</sup> and that it can serve as a better electron 1035 donor thanks to its conjugated system, which endows the adsorbent with enhanced 1036 uranium uptake from seawater.<sup>123</sup>

Other than four binding motifs aforementioned, the  $\mu^2$ -oxo-bridged transition metal 1037 1038 was found though the EXAFS fitting of the fiber contacted with seawater, perhaps implying that the uranium extraction form the ocean occurs only after forming an 1039 advantageous binding pocket in situ by chelation of Ni<sup>290</sup> or Fe.<sup>305</sup> Recently, a novel 1040 bridging  $(\mu_2)$  zwitterionic amidoxime binding mode was put forward.<sup>306</sup> These seem to 1041 imply that the enigmatic binding mechanism between uranium species and amidoxime 1042 ligand is more complex than we have imagined, and the relentless pursuit of it will 1043 1044 remain one of the main research priorities. Besides, the environment in which the adsorbents are deployed, the nature of materials, the types of adsorbates, and the like 1045 may all cause a difference in the bonding motif between amidoxime and uranyl ion. 1046 However, most of the current research remains at the small molecule level, and the 1047 contribution of various factors and the synergy between the factors still lack relevant 1048 publications. 1049

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**Cost estimation** 

1052	View Article Online It is plausible to evaluate the quality and practicability of adsorbent based on the
1053	adsorption performances involving adsorption capacity and kinetics. But in actual
1054	large-scale applications, cost factor is an inescapable topic. Up to now, few publications
1055	can accurately calculate the cost of uranium extraction from seawater as it is a nontrivial
1056	task. The difficulty lies in the existence of too many uncertainties in this process, of
1057	which reduction will be one of the main directions for future research.82 With the
1058	continuous development of technology, the number of cost-driven design parameters
1059	will gradually increase. It is increasingly impractical to manually optimize system
1060	parameters to achieve maximum uranium production cost estimation, various cost
1061	budget models are thus developed. <sup>278</sup> The cost driving for seawater uranium extraction
1062	includes three major components: i) adsorbent preparation; ii) deployment and mooring;
1063	and iii) elution and purification (Fig. 17). <sup>307</sup> The former involves the expenses of matrix
1064	materials, the operations, amidoximation and possible base conditioning, of which the
1065	prices of matrix materials often dominates. For emerging materials ,such as MOFs and
1066	COFs, although they have excellent adsorption properties, their expensive production
1067	costs are often the chief restriction for their practical application, while the cost of
1068	polymeric adsorbents depends mainly on the monomers. Synthesis methods and
1069	conditioning conditions determine the expense of the operations and base conditioning.
1070	It has been reported that using NaOH in place of KOH can cut down by 21 - 30% of
1071	the cost for recovering uranium. <sup>188</sup> The capital consumption of the amidoximation
1072	process is relatively fixed, because of the similar hydroxylamine treatments (Fig. 5). In
1073	contrast, the field operation cost (including mooring and deployment) is more variable,

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which relates to the deployment mode (the amount of adsorbent use, etc.) and the 1074 ambient environment (temperature, pH, NOM, etc.) and so on. The proper amount of 1075 use and the selection of pH and temperature are critical to maximizing the adsorbent 1076 performance. Also, the impact of NOM is encouraged to be considered in economic 1077 assessment since it is ubiquitous.<sup>286</sup> The period of uranium extraction from seawater is 1078 very long (usually several months), and the length of campaign is directly related to the 1079 efficiency of uranium extraction from seawater. Study has shown that the overall costs 1080 associated with adsorbent preparation account for approximately 48% of the total 1081 uranium production cost.<sup>308</sup> But not always, when the adsorbent are stable enough to be 1082 reused many times, the mooring and recovery costs will dominate.85 1083

In addition, the cost derived from biofouling should be taken into consideration. On 1084 1085 the one hand, the two factors associated to biologic accumulation: length of campaign<sup>309</sup> and seawater temperature,<sup>310</sup> have an impact on the cost analysis. As mentioned above, 1086 biofouling is capable of restricting the reusability of adsorbents. Severe biofouling thus 1087 leads to a significant increase in uranium extraction cost.<sup>278</sup> Regenerability and 1088 reusability are very important for assessing the use value and economic performance of 1089 adsorbents.<sup>116, 311</sup> Meanwhile, the separation of the desired fuel elements from the 1090 loaded adsorbents is the ultimate goal and key step for uranium extraction from 1091 seawater. The eluting agents commonly used involve inorganic acids (HCl and HNO<sub>3</sub>, 1092 etc.),<sup>147</sup> organic acids (tartaric acid, malic acid and oxalic acid, etc.)<sup>150</sup> and Na<sub>2</sub>CO<sub>3</sub> 1093 solution.<sup>117, 233</sup> The acid solution can achieve relatively thorough elution, but they may 1094 hydrolyze the amidoxime group, thereby deteriorating the reusability of amidoxime-1095

1096	based materials and ultimately resulting in increased cost. <sup>125</sup> After their elution, the
1097	eluent usually needs to be further separated due to the lack of selectivity to the eluting
1098	elements, and the eluted material must undergo alkaline conditioning before each reuse.
1099	The situation of organic acids is similar to that of inorganic acids. As protic acids, they
1100	also have the potential to degrade the active ligands such as glutardiamidoxime. <sup>178</sup> The
1101	elution of the adsorbed material by the Na <sub>2</sub> CO <sub>3</sub> solution is more targeted, and the eluted
1102	material can be reused directly without the need for alkaline conditioning again. <sup>182</sup> On
1103	the basis of Na <sub>2</sub> CO <sub>3</sub> solution, the Na <sub>2</sub> CO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> system has been further developed in
1104	recent years <sup>180, 311</sup> This system allows for the selectivity based on Le Chatelier's
1105	principle and can even quantitatively elute uranium at room temperature during a
1106	certain period of time. <sup>311, 312</sup> In addition, the rate of elution of uranium can be
1107	accelerated by increasing $H_2O_2$ concentration. <sup>180</sup> However, higher concentration means
1108	higher cost. At the same time, as an oxidant, the damage of high concentration $H_2O_2$ to
1109	the adsorbent materials cannot be ignored. <sup>311</sup> Its concentration, thus, must be rationally
1110	controlled. In general, most adsorbents maintain good adsorption performance after
1111	desorption, with only a 3% to 5% decrease, but the difference may also result in
1112	significant changes in final cost. <sup>82</sup>
1113	Taking all these factors into account, the cost of uranium production from seawater

1113 Taking an diese factors into account, the cost of araman production from JAEA to be 1114 was estimated by Japanese researchers using a polymeric adsorbent from JAEA to be 1115 about 90,000 yen/kg-U under the assumption of uranium uptake of 2 mg-U/kg-ads after 1116 60 days of exposure.<sup>313</sup> An independent cost analysis in the U.S. estimates that the cost 1117 is \$ 1230/kg-U with a 95% confidence interval from \$ 1030/kg-U to \$ 1430/kg-U.<sup>314</sup> In

1118	View Article Online the total cost of \$ 1230/kg-U, adsorbent preparation and mooring each accounted for
1119	approximately 45% of the quota.85 The ORNL adsorbent has achieved nearly half of
1120	the cost cut-down to \$ 610/kg-U due to the updated material. <sup>160</sup> Optimization of
1121	operating parameters including length of campaign, amount of use and seawater
1122	temperature and so on can reduce 20% of cost. <sup>278</sup> However, this value is still much
1123	higher than the cost of land uranium mining of \$ 60-260/kg-U. <sup>315, 316</sup> Therefore, how to
1124	highlight the economic advantages of seawater uranium is a major issue facing people.
1125	There are two main ways to reduce the uranium production cost: i) developing high
1126	loading adsorbents and ii) preparing high tolerance adsorbents that allow the adsorbent
1127	to be reused multiple times efficiently.85 As estimated, only having uranium uptake of
1128	30 mg/g or uranium uptake of 6 mg/g and capable of repeated use for 10 times with
1129	adsorption capacity loss of no more than 3% per cycle (i.e., total adsorption capacity of
1130	51.9 mg/g), can the cost of adsorbents (\$ 290/kg-U) be comparable to the price of
1131	traditional terrestrial uranium supply and meet the economic requirements of seawater
1132	uranium extraction. <sup>166</sup> Therefore, the new generation of amidoxime-based adsorbents
1133	with high loading capacity, superior selectivity, fast adsorption rate, as well as excellent
1134	antibacterial and tolerance may attain this end, providing a possibility for the genuine
1135	realization of uranium extraction from seawater instead of land. <sup>317</sup> Recently, a dual-
1136	surface amidoximated halloysite nanotube, AO-HNTs, exhibited an acceptable cost of
1137	\$ 154/kg-U benefiting from low-cost raw materials and long service life. <sup>248</sup> In addition,
1138	a symbiotic system that combines an adsorbent with existing facilities, such as offshore
1139	wind turbines, has been appealed to reduce the mooring costs of uranium extraction

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from seawater.<sup>277, 318-321</sup> This strategy, with high operability and practical feasibility, is
 likely to have great potential in future marine uranium mining activities.

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# 7. Outlook and prospects

Adsorption of uranium in seawater and wastewater is an important issue in the fields 1144 of energy and environment. Polymeric fibers are the most mature materials in seawater 1145 uranium extraction.<sup>322</sup> There are significant differences in the water samples 1146 composition and operating environment in field experiments and laboratory tests, and 1147 these differences can even affect the chelating mechanism.<sup>305</sup> Therefore, field 1148 experiments with non-polymer adsorbents are urgently required. In wastewater, 1149 polymeric adsorbents may be degraded under the extreme conditions (like strong acid 1150 and radiation, high temperature, etc.) and experience swelling, shrinkage and/or 1151 cracking, resulting in reduced uranium extraction efficiency and even secondary 1152 pollution.<sup>323</sup> In contrast, non-polymer adsorbents, such as carbon-based materials, 1153 1154 appear to be more advantageous. Nevertheless, research on their removal behaviors in real industrial wastewater is still rare and should be drawn more attention. 1155

The high affinity of amidoxime to uranium is the basis for the wide application of amidoxime-based adsorbents as uranium extractants. Due to the abundant amidoxime groups, polymeric adsorbents will continue to be the backbone member for seawater uranium recovery in the future. However, the current polymeric materials still cannot meet the requirements of industrial applications in terms of economic benefits and performance. In order to obtain further upgrades in polymer properties, we must face

1162	up to their shortcomings and make more attempts at the material and technical reveis to
1163	seek breakthroughs. A series of groundbreaking work has set an example for us. <sup>166, 191,</sup>
1164	<sup>243, 324</sup> Relative to amount, the accessibility and availability of active groups are factors
1165	that should be paid more attention to.166 How to expose as many active groups as
1166	possible and make them effective contact with uranyl ions is a problem that needs to be
1167	focused in future research. For polymer adsorbents, it should be emphasized to increase
1168	the effective area during uranium adsorption as much as possible. Although designing
1169	microporous structures <sup>155</sup> and ultra-thin nanofibers <sup>191, 243</sup> are effective strategies, they
1170	may not meet the cost requirements of large-scale applications. Cationic cross-linking
1171	may be a means to break the bottleneck, which is worthy of further research. <sup>325</sup> For
1172	non-polymer adsorbents, the characteristics of the matrix material and the amidoxime
1173	group should be fully combined to achieve complementary advantages. In addition, it
1174	will be a major concern in the future to consciously designing the chemical structure of
1175	materials for enhancing their performance to capture uranyl ions. As reported, some
1176	microenvironments including hydrogen bonding, conjugated effect, and hydrophobic
1177	interaction may affect the stability of uranium complexes. Specifically, hydrogen
1178	bonding can lengthen the U-O bond length on the corresponding uranyl ion, while
1179	shortening the bond length between the coordination atom on the near equatorial plane
1180	and the central uranium ion.326 Therefore, the incorporation of functional groups
1181	capable of forming hydrogen bonds, such as amino groups, can improve the stability of
1182	the uranyl complexes obtained by interacting with the amidoxime group, thereby
1183	facilitating adsorption. <sup>237</sup> Conjugated systems, on the one hand, as electron donors can

View Article Online bond well with uranium, the electron acceptor.<sup>327</sup> On the other hand, their existence can 1184 make the coordination plane perpendicular to the uranyl ion, thereby reducing the steric 1185 hindrance during the complexation process.<sup>328, 329</sup> The hydrophobic interaction can 1186 separate the coordinated uranyl ion from the water system and make it stable.<sup>330</sup> As a 1187 result, the cyclic imide dioxime with the conjugated structure has higher reactivity to 1188 uranium than amidoxime,<sup>123</sup> and the amidoxime group connected with the aromatic 1189 moiety is expected to exert more excellent uranium coordination ability.<sup>331, 332</sup> Besides, 1190 the spatial distance between amidoxime groups and their amount in each unit also have 1191 impact on uranium adsorption.<sup>301</sup> The amidoxime having an additional di-ethylene 1192 spacer unit is reported to be more easily to anchor uranium than those without the 1193 units.<sup>333</sup> The adsorbents with bis-amidoximes were firmed to be more capable of 1194 trapping uranyl ions selectively<sup>334</sup> and efficiently<sup>335</sup> than ones with mono-amidoximes. 1195 The relationship between chemical structure and adsorption performance needs to be 1196 further explored in future research. Based on it and combined with arbitrarily designed 1197 1198 substrate platforms such as COFs, POPs, etc. we can design and synthesize adsorption materials with higher uranium affinity.<sup>336</sup> 1199 The selectivity of amidoxime-based materials to uranium can be regulated by their 1200

1201 chemical structure as well. As mentioned in **Section 4.3**, the presence of vanadium in 1202 seawater is the biggest obstacle to the uranium uptake over amidoxime-based 1203 adsorbents.<sup>242</sup> Two structures, namely the cyclic imide dioxime<sup>262</sup> and the imino 1204 hydroxylamine,<sup>269</sup> may be responsible for the high affinity of the vanadyl species. 1205 Cyclic imide dioxime can be formed during the synthesis and alkaline conditioning of

1206	View Article Online the polymeric materials. <sup>123</sup> As a strong electron donor, it plays an even more important
1207	role in the uranium adsorption process than the amidoxime group, <sup>191</sup> and the method of
1208	maximizing the cyclic form was thus proposed to enhance uranium adsorption
1209	efficiency. <sup>19, 185, 337</sup> Obviously, it may be feasible in systems without vanadium, but not
1210	for seawater. Recently, the concept, the random rotation of functional groups offers the
1211	equal opportunity to active sites and various competing ions to contact, <sup>338</sup> has provided
1212	new insights into the poor selectivity of materials. Since the complexation of
1213	glutaroimide-dioxime with uranium has faster kinetics than that with vanadium, even
1214	if its binding strength is weaker than that of the latter, uranium will preferentially
1215	occupy the adsorption sites. <sup>339</sup> Once bonded, the ligand in the 3D hierarchical porous
1216	amidoxime fiber can no longer rotate freely due to the pore confinement effect, thereby
1217	avoiding the easy replacement of anchored uranium by vanadium or others ions as the
1218	traditional adsorbents do. <sup>166</sup> This exhibits the great potential of 3D hierarchical porous
1219	structure for improving uranium selectivity. Imino hydroxylamine is formed by
1220	tautomeric rearrangement of amidoxime moiety. <sup>269</sup> Accordingly, the use of structural
1221	interventions to prevent the rearrangement can theoretically reduce the affinity of the
1222	material for vanadium and thereby increase its selectivity for uranium. One strategy is
1223	to remove the amino group from amidoxime. <sup>265</sup> This may be beneficial for the uranium
1224	selectivity of the material, but not for uranium affinity. Another way is to substitute the
1225	amino hydrogen atoms in the amidoxime structure with an alkyl group. This strategy
1226	indeed entails the adsorbents much more selective to uranium versus vanadium and
1227	ensures the non-compromised affinity of amidoxime for uranium (Fig. 18), <sup>270</sup> which

/iew Article Online appears to be worthy of widespread promotion. In addition to the regulation in structural 1228 level, methods such as ion imprinting<sup>340</sup> and bionic technology<sup>237</sup> can also be applied 1229 to improve the selectivity of materials. Selectivity studies on uranium versus other 1230 competitors by adsorbents under different conditions (such as temperature,<sup>257</sup> pH,<sup>341</sup> 1231 etc.) can guide us to conduct appropriate pretreatment before adsorption and help us to 1232 circumvent the undesirable reactions. At present, parameters that can be used for the 1233 comparison of selectivity between various adsorbents are lacking. It is recommended 1234 to establish a standardized operating system or method as soon as possible to 1235 1236 quantitatively characterize the selectivity of different materials.

Slow kinetics greatly hampered the practical use of the adsorbents.<sup>342</sup> There are 1237 many aspects that need to be considered for the improvement of the kinetics. For 1238 1239 polymeric adsorbents, the hydrophilic groups on the bifunctional adsorbents can promote the formation of the hydrogel layer on the surface of the material, which 1240 contributes to the diffusion of the target ions.<sup>342</sup> For non-polymer adsorbents, non-1241 porous matrix materials (such as nanodiamonds<sup>78</sup>) and materials with ordered pores 1242 structure (such as mesoporous silica,<sup>221, 224</sup> COFs,<sup>230</sup> etc.) can effectively avoid or 1243 accelerate the diffusion of ions in the pores, thereby reducing the equilibrium time. 1244 Considering that microorganisms can hinder the contact between uranium and reactive 1245 groups and affect the kinetic properties of materials, the adsorbents with biological 1246 resistance is encouraged to be developed. In addition, the combination of the high 1247 1248 affinity amidoxime group possesses with electrochemical adsorption can achieve rapid and massive uranyl uptake,<sup>252</sup> which opens up a new idea to simultaneously improve 1249

the uptake and kinetics. In the future, similar work needs to be carried out further, and
 more attempts are needed to determine various parameters so as to realize their
 industrial application as soon as possible.

The regeneration of adsorbents puts forward new requirements for the stability of 1253 adsorption materials and the selection of desorption reagents. On the one hand, the 1254 adsorbents are supposed to exhibit good mechanical strength and would better have 1255 separation properties like magnetism. Even if the application of magnetic materials in 1256 the field of uranium extraction from seawater is not promising,<sup>8</sup> they still have potential 1257 1258 in the field of uranium removal from contaminated water on the premise of ensuring magnetic nuclear stability and material properties. In general, more robust matrix 1259 materials and stronger functional group bonding have positive significance for 1260 1261 improving the reusability of adsorbent materials. The selection of eluting agents, on the other hand, is also crucial. As mentioned in Chapter 6, Na<sub>2</sub>CO<sub>3</sub> solution as eluent is 1262 better than that of acid solution in terms of selectivity and material protection. Na<sub>2</sub>CO<sub>3</sub>-1263 1264 H<sub>2</sub>O<sub>2</sub> system is regarded as promising eluting reagent for regenerating the amidoxime-1265 based materials on the premise of controlling the  $H_2O_2$  content. Moreover, considering that the solution pH is closer to 8.0 - 8.3 of seawater, bicarbonate solution is 1266 recommended to be a better alternative to elute seawater uranium.<sup>14, 116</sup> The 1267 development of emerging eluents and elution systems has profound practical 1268 significance for uranium extraction from seawater. More potential reagents need to be 1269 tried and developed, and the regeneration tests of materials also need to be refined and 1270 systematic. 1271

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Uranium extraction from seawater has developed rapidly in recent years. As the most important adsorbent, amidoxime-based materials have also made great progress in various aspects. However, there is still a certain distance to realize industrial application. Cost is the most fundamental cause of this situation. Therefore, the development of more advanced materials to cut down the cost of uranium extraction from seawater is a top priority for future research. To achieve this, the following four issues must be addressed: i) further improving the adsorption performances of the materials need to be further improved, including adsorption capacity, selectivity and kinetics; ii) further improving the regenerability of the materials and extending their longevity; iii) further strengthening the sturdy on binding mechanism and revealing the structure-properties relationship of amidoxime-based materials; iv) further improving the environmental adaptability of the materials, such as antifouling property. In these processes, more experiments should be performed in situ rather than in the laboratory and more advanced characterization techniques and theories such as EXAFS,<sup>245</sup> DFT,<sup>287</sup> de novo design,<sup>304</sup> and first-principles integrated modeling approach<sup>343</sup> are encouraged to be used. For materials used for uranium removal form contaminated water, the ideas above still hold true. However, the environment in which materials are exposed may be more variable, which imposes additional requirements on the acid resistance and the optimal adsorption conditions of the adsorbents used. The design, synthesis and application of adsorbents based on the physiochemical properties of the water body to be treated (i.e. "demand-oriented") may accomplish more targeted uranium enrichment and separation.

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## 1295 **8.** Conclusion

The fossil energy crisis and radionuclide pollution have attracted increasing 1296 attention to the utilization and management of uranium. The exploitation of uranyl 1297 resource from seawater is of strategic importance for the energy crisis that mankind is 1298 about to face or is facing. Meanwhile, the damage of uranium pollution to ecological 1299 environment also needs to be solved urgently. Amidoxime-based adsorbents as the most 1300 potential uranium extractors and scavengers have been studied over the past four 1301 1302 decades. The researchers coming from Japan, U.S. to the other countries have taken great efforts and made major breakthroughs in this field. In this paper, many aspects of 1303 amidoxime-based materials including synthesis, characterizations, types (polymers, 1304 1305 carbon-based materials, silica-based materials, biosorbents, new type of porous materials, and others), and influencing factors (pH, temperature, co-existing ions, and 1306 biofouling), binding mechanism as well as cost evaluation, were viewed in detail. From 1307 1308 the perspectives of adsorption capacity, selectivity, kinetics and regenerability, different strategies for improving the performance of adsorbents were comprehensively 1309 analyzed. In short, the essence of cost reduction lies in the improvement of material 1310 performance, and the key to the improvement of material performance lies in the 1311 realization of high dispersion and exposure of active sites (herein, amidoxime group) 1312 as much as possible. Moreover, the development of new-generation adsorbents needs 1313 to be demand-oriented to meet different needs. It is essential to use more advanced 1314 characterization methods and theories to thoroughly explore the binding mechanism 1315

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between uranium and amidoxime group and the the relationship between  $chemical^{View Article Online}_{POI: 10:1039/C9TA14082D}$ 

structure and material properties to guide the design and synthesis of next-generation materials. Amidoxime group is encouraged to be introduced into more new materials such as COFs. Perfectly integrating the merits of ligands and matrices enables excellent complement and synergy to each other. Amidoxime-based materials in the future must be characterized by high capacity and selectivity, fast kinetics, good reusability as well as strong antibacterial and acid resistance, which can cope with the complex marine environment and extreme wastewater conditions.

Based on the strong affinity and high selectivity of amidoxime group towards uranyl ions, the development of new-generation adsorbents with amidoxime will continue as before. This paper is expected to provide the guidance for rationally designing and synthesizing new-generation adsorbents with amidoxime group and to provide the suggestions for solving the technical problems of uranium extraction from seawater and uranium removal form effluent as soon as possible.

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## 1976 Figure captions

Fig. 1. Growth of the number of publications regarding the keywords "amidoxime" and "uranium" on indexed journals between 2000 and 2018. The insert pie graph presents that amidoximes are mainly used for seawater uranium extraction. The data are sorted from the research on "web of science".

Fig. 2. Ten synthesis pathway for amidoxime based on the work of Eloy and co-workers.plotted according to ref. 88.

Fig. 3. Schematic illustration of (a) two possible routes for hydroxylamine to attack cyano compounds under alkaline conditions; (b) the optimized results of quantum mechanical calculations for reactants (1 and 2), intermediates (3 and 4) and products (5 and 6); (c) the mechanism of formation of the amidoximes based on the results of quantum mechanical calculations; (d) enthalpy of formation of compounds 3, 4, 5, and 6 generated by the reagents 1 and 2. Reproduced with permission from ref. **89**. Copyright 2009, Springer.

1990 Fig. 4. *E* and *Z* forms of amidoximes. Reproduced with permission from ref. 90.1991 Copyright 2016, Elsevier B.V.

1992 Fig.5. Four approaches for converting cyano groups to amidoxime groups by1993 hydroxylamine treatment in the laboratory.

Fig. 6. (a) Protonation and deprotonation of amidoximes, and (d) Prototropic tautomeric
forms of amidoximes. Reproduced with permission from ref. 90. Copyright 2016,
Elsevier B.V.

1997 Fig. 7. The basic physical and chemical properties of the amidoxime structure, red

1998	numbers and arrows correspond to the data of <sup>1</sup> H, <sup>13</sup> C, <sup>15</sup> N NMR spectra, ppm; <sup>10</sup> dark
1999	blue numbers and arrows correspond to infrared data of various moieties, cm <sup>-1</sup> ; brown
2000	numbers correspond to bond length, Å, and green numbers and arrows correspond to
2001	XPS data of some atoms, eV.
2002	Fig. 8. Timeline for the development of various amidoxime-containing adsorbent
2003	materials for uranium recovery or removal from 1980s to 2019.
2004	Fig. 9. Schematic illustration of the entire process for preparing amidoxime-based
2005	polymeric adsorbentsvia (a) RIGP and (b) ATRP methods.
2006	Fig. 10. (a) The proposed conversion of poly(acrylamidoximes) to
2007	poly(acrylimidedioximes) and toeventually carboxylates in 1M NaOD at 80°C.
2008	Reproduced with permission from ref. 31. Copyright 2015, Royal Society of Chemistry.
2009	The insert graph exhibits proposed mechanism of conversion from amidoxime to
2010	carboxylate group in alkaline solution at 80°C. Reproduced with permission from ref.
2011	179. Copyright 2016, American Chemical Society. (b) The preamidoximation
2012	modification of PAN and the blow spinning process for mass fabrication of PIDO
2013	nanofibers. Reproduced with permission from ref. 191. Copyright 2018, Wiley-VCH
2014	Verlag GmbH & Co. KGaA, Weinheim.

Fig. 11. (a) Modification of amidoxime groups on the surface of carbon-based materials 2015 by radiation polymerization or chemical grafting. (b) Two approaches to prepare 2016 amidoximated SBA-15. 2017

Fig. 12. Schematic description of (a) the synthesis of COF-TpDb through the 2018 condensation of Tp (black) and Db (blue) and corresponding chemical transformation 2019

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from the cyano to amidoxime group, yielding COF-TpDb-AO and (b) the synthesis of 2020 COF-TpAab through the condensation of Tp (black) and Aab (green) and 2021

2022 corresponding chemical transformation from the cyano to amidoxime group, yielding

COF-TpAab and COF-TpAab-AO, respectively. Reproduced with permission from ref. 2023

231. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. 2024

Fig. 13. Physical processes in HW-ACE extraction. Reproduced with permission from 2025 ref. 252. Copyright 2017, Springer Nature. 2026

Fig. 14.(a) The relative proportion of U(VI) species,  $P_{CO2} = 3.8 \times 10.4$  atm,  $C_{IU(VI)}$  initial 2027 = 40.0 mg/L; T = 298  $\pm$  2 K, m/V = 0.10 g/L, I = 0.01 mol/L NaNO<sub>3</sub>. Reproduced 2028 with permission from ref. 256. Copyright 2018, Wiley-VCH Verlag GmbH & Co. 2029 KGaA, Weinheim; (b) Distribution of uranium (VI) species in aqueous solution with a 2030 2031 total concentration of 100 mg/L and pH values ranging from 1 to 10. Calculated by using a Medusa program. Reproduced with permission from ref. 83. Copyright 2016, 2032 Elsevier B.V. 2033

2034 Fig. 15.(a) The proposed coordination motifs for how amidoxime binds uranyl with corresponding crystal structures and CCDC identifiers when available. Reproduced 2035 with permission from ref. 290. Copyright 2016, Royal Society of Chemistry. (b) 2036 Structure models of oxygens used to fit the EXAFS data for uranylcontacted polymer 2037 samples. Reproduced with permission from ref. 254. Copyright 2019, Royal Society of 2038 Chemistry. 2039

Fig. 16. (a) Schematic diagram of the gradual replacement of coordination water in 2040 hydrated uranyl ions by amidoxime through  $\eta^2$  motif based on the result of ref. **296**. (b) 2041

View Article Online Proposed structural models of the  $[UO_2(CO_3)_{3-x}(AO)_x]^{(4-x)-}$  complexes when  $AO^{-104020/C9TA14082D}$ 2042 ligands gradually substitute carbonate ligands that bind to uranyl ions. Reproduced with 2043 permission from ref. 300. Copyright 2016, American Chemical Society. (c) Structures 2044 of uranyl complexes with formamidoxime obtained after geometry optimization at the 2045 B3LYP/SSC/6-311++G(d,p) level of theory. Reproduced with permission from ref. 290. 2046 Copyright 2016, Royal Society of Chemistry. 2047 Fig. 17. Cost drivers for seawater uranium extraction. 2048 Fig. 18. Ligand selectivity for  $UO_2^{2+}$  over (a)  $VO_2^{++}$  and (b)  $VO_2^{++}$  ions. Ligands: 2049 2050 acetamidoximate (Acetam); N,N-dimethylacetamidoximate (Dimeacetam); N,N-dimethylbenzamidoximate 2051 benzamidoximate (Bzam) (Dimebzam). and Reproduced with permission from ref. 270. Copyright 2016, Royal Society of 2052

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Fig. 7.



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Fig. 10.







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Fig. 12.

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Fig. 17



## 2114 Table legends

- 2115 Table 1. Concentrations of selected elements in seawater.
- 2116 Table 2. The pH<sub>pzc</sub> values of various amidoxime-based materials.
- 2117 Table 3. The FT-IR data of various amidoxime-based materials.
- 2118 Table 4. Adsorption performance of various amidoxime-based materials for uranium
- 2119 from real seawater, U-spiked seawater and simulated seawater.
- 2120 Table 5. Adsorption performance of various amidoxime-based materials for uranium
- 2121 from pure water and brine solution.
- Table 6. The XPS data of various amidoxime-based materials.

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alamant	Concentration in seawater		alamant	Concentration in seawater		
element	mg/kg (ppm) <sup>a</sup>	mol/L <sup>b</sup>	- element -	mg/kg (ppb) <sup>a</sup>	mol/L <sup>b</sup>	
Na	10800	0.468	Li	180	$25.9 \times 10^{-6}$	
Mg	1290	$53 \times 10^{-3}$	Rb	120	$1.4 \times 10^{-6}$	
Ca	413	$10.3 \times 10^{-3}$	Mo	10	$0.1  imes 10^{-6}$	
Κ	400	$10.2 \times 10^{-3}$	Ni	5	$85.2 \times 10^{-9}$	
Sr	8.1	$92.4 \times 10^{-6}$	Fe	3.4	$60.9 \times 10^{-9}$	
Anions			U	3.3	$13.9 \times 10^{-9}$	
Cl	19400	0.547	V	1.83	$35.9 \times 10^{-9}$	
$SO_4$	2701	$28.1 \times 10^{-3}$	Cu	0.9	$14.2 \times 10^{-9}$	
HCO <sub>3</sub>	145	$2.38 \times 10^{-3}$	Mn	0.2	$3.64 \times 10^{-9}$	
Br	65	$0.814 \times 10^{-3}$	Pb	0.03	$0.145 \times 10^{-9}$	

<sup>a</sup>: Data reported in ref. **8**, **10**, **38**, **258**, **259**, **322**.

<sup>b</sup>: Seawater density is calculated at 1g/mL.

2	1	2	8

2141 Table2.

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Adsorbents	The pH <sub>pzc</sub> values	Ref.
0.2AO-OMC <sup>b</sup>	2.80	108
AO-HTC <sup>b</sup>	4.69	195
P(AO)-g-CTS/BT °	6.7	110
AM-MG-CH °	8.13	106
Amidoxime-modified algal cells <sup>c</sup>	10.0	211
ABS °	4	214
ami-MSN <sup>d</sup>	2.5	138
AMD-MCM-41 <sup>d</sup>	10.5	129
PAO/Organo-B composite <sup>f</sup>	6.3	128
Na-Mont-APAN <sup>f</sup>	4.3	125
FeOOH-APAN <sup>f</sup>	8.4	244

<sup>b</sup>: carbon-based materials; <sup>c</sup>: Biosorbents; <sup>d</sup>: Silica-based materials; <sup>f</sup>: Others.

2154 Table 3.

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	Functional groups (cm <sup>-1</sup> )					Dſ
Adsorbents	О-Н	C-N	C=N	N-O	N-H	Ref.
Hydrogel containing PAO <sup>a</sup>	3000 - 3600	-	1650	920	3000 - 3600	20
AO-DETA <sup>a</sup>	-	-	1636	920	-	30
AI series adsorbents <sup>a</sup>	3230	-	1645	930	3390	9
AF series adsorbents <sup>a</sup>	-	1245	1670	950	3400, 3450	28
PE-GMA-AN-HEA <sup>a</sup>	-	1391	1642	931	-	44
MNPs@PAO <sup>a</sup>	3115		1659	916	3115	132
AO-IDAN <sup>a</sup>	-	-	1608	980	-	140
PP-g-PAO nonwoven fabric <sup>a</sup>	-	-	1656	938	-	156
PE-g-PAO nonwoven fabric <sup>a</sup>	3200 - 3500	-	1647	928	-	80
PE-g-P(AO-co-AA) <sup>a</sup>	-	-	1643	928	-	157
UHMWPE-g-P(GMA-co-MA)-EDA-AO a	3000 - 3500	-	1655	923	3000 - 3500	161
UHMWPE-g-(PAO-co-PAA) <sup>a</sup>	3000 - 3600	-	1650	920	3000 - 3600	162
AF160-2 <sup>a</sup>	-	1277	1644	935	3391, 3267	179
H-ABP fiber <sup>a</sup>	3100 - 3500	1381	1642	916	3100 - 3500	166
PAO/PVDA <sup>a</sup>	-	-	1647	945	-	84
AF1 <sup>a</sup>	-	1370	1670	950	1580 <sup>I</sup>	123
PIDO NF <sup>a</sup>	-	1381	1638	933	-	191
PAAC <sup>a</sup>	-	-	1650	940	3390	341
AOMGO <sup>b</sup>	-	-	1651	923	-	104
AGH <sup>b</sup>	3440	-	1610	971	3440	140
AO-MWCNTs <sup>b</sup>	-	-	-	926	1656 <sup>I</sup>	98
p-AO/CNF <sup>b</sup>	~ 3400	1290	1500	935	~ 3400	289
AO-HTC <sup>b</sup>	-	1274	1631	927	-	195
C-Ami electrode <sup>c</sup>	3100 - 3300	-	1635	912	1572 <sup>I</sup>	252
MAO-chitosan-U <sup>c</sup>	3443		1666	-	1574 <sup>I</sup>	96

P(AO)-g-CTS/BT °	-	1269	1694	920	Vi D <b>301944</b> .1039	ew Article Online 9/C9 <b>1/41/9</b> 082D
AM-MG-CH °	-	-	1614	932	-	106
AMAN <sup>c</sup>	3200 - 3500	-	1649	902	-	210
AMAN-U °	3300 - 3500	-	1629	885	-	210
PAO-B °	-	-	1649.3	935.4	-	207
S-CP20*-AO <sup>d</sup>	3400	-	1650	960	1580 <sup>I</sup>	109
ami-MSN <sup>d</sup>	3354		1655	949	-	138
DFNS/pDA/AOPNI d	-	1345	1650	947	-	342
SBA-AO-0.4 d	3346	-	1651	944	1598 <sup>I</sup>	52
PPN-6-PAO <sup>e</sup>	3200 - 3400	-	1653	933	-	27
COF-TpDb-AO °	-	-	1646	924	-	231
MIL-53(Al)-AO °	-	-	1652	951	-	102
UiO-66-AO <sup>e</sup>	-	-	1652	951	-	113
AO/MOF <sup>e</sup>	-	-	1650	936	-	225
UiO-66-AO <sup>e</sup>	-	-	1655	919	-	115
RAF-1-CH <sub>2</sub> AO <sup>e</sup>	-	1381	1638	933	-	137
Amidoxime-PIM-1 <sup>e</sup>	-	-	1656	915	-	117
TMP-g-AO <sup>e</sup>	3194	1269	1649	920	3194	239
TMP-g-AO-U <sup>e</sup>	3194	1269	1649	913	3194	239
C8A-AO <sup>f</sup>	3376	-	1668	928	3481	240
SMON-PAO <sup>f</sup>	-	1386	1650	939	-	243
Na-Mont-APAN <sup>f</sup>	-	1096	1652	924	-	125
Pal/PAO <sup>f</sup>	-	-	1653	910	3372	111

2155 <sup>a</sup>: Polymeric materials; <sup>b</sup>: carbon-based materials; <sup>c</sup>: Biosorbents; <sup>d</sup>: Silica-based materials; <sup>e</sup>: New

2156 type of porous materials; <sup>f</sup>: Others.

2157 <sup>I</sup>: Peak corresponding to bending vibration of N-H. Those without special explanation are stretching

vibrations. The upward and downward arrows respectively indicate that the adsorption peak isenhanced or weakened.

Table 4.

	Adsorption capacities				
Adsorbents –	mg/g conditions				
Real seawater					
HDPE-g-PAA-co-PAO <sup>a</sup>	0.13	Seawater desalination plant; $m = 4$ g; $FR = 80$ cm/s; $T = 21 \pm 2^{\circ}C$ ; $t = 15$ d. (SM)	13		
AO-UHMWPE <sup>a</sup>	0.25	East China Sea of Xiamen Island; $\sim$ 3 below the sea surface; t = 60 d; (BP)	164		
UHMWPE-g-P(AO-co-AA) <sup>a</sup>	0.77	Xiamen Island in the East China Sea; $FR = 0.2 - 0.6 \text{ m/s}$ ; $t = 60 \text{ d}$ . (BP)	163		
AO-phon-DETA-80 ª	0.789	MSL of PNNL; t = 20.8 d. (BE)	30		
MAA-cografted AO fiber <sup>a</sup>	0.90	15 m below the surface of the sea located about 6 km offshore at MutsuSekine-Hama in Aomori Prefecture in Japan; $m = 0.5$ g; $t = 20$ d. (SM)	172		
PE-g-P(AO-co-MAA) <sup>a</sup>	1.05	MSL of PNNL;FR = 250 - 300 mL/min; T = $20 \pm 2^{\circ}$ C; t = 56 d.(FTCS)	157		
AO-UHMWPE-7 <sup>a</sup>	1.41	East China Sea; pH 7.5 -7.9; FR = 0.2 - 0.6 m/s; S = 31 psu; pH 7.5 - 7.9; T = 21.4°C; t = 15 d. (BP)	261		
PE-g-PVBC-g-(PAO-co-PAA) -2 a	1.56	MSL of PNNL; $m = 60 \text{ mg}$ ; $FR = 250 - 300 \text{ mL/min}$ ; $T = 20 \pm 2^{\circ}\text{C}$ ; $t = 42 \text{ d.}(FTCS)$	144		
P(2DVB-VBC)-2PAN <sup>a</sup>	1.99	ORNL; $m = 10 \pm 3 \text{ mg}$ ; $V = 5 \text{ gallons}$ ; $t = 27 \text{ d.}(BE)$	21		
UHMWPE-g-(PAO-co-PAA) <sup>a</sup>	2.3	MSL of PNNL;T=20°C; t = 42 d. (FTCS)	162		
PE-g-PVBC-g-(PAO-co-PAA)-b- PAA -2.1 <sup>a</sup>	3.02	MSL of PNNL; m = 60 mg; FR = 250 - 300 mL/min; T = $20 \pm 2^{\circ}$ C; t = 56 d. (FTCS)	144		
AI 11(1 h conditioning) <sup>a</sup>	3.25	MSL of PNNL; $C_U = 2.9 \text{ ppb}$ ; $S = 30.8 \text{ psu}$ ; $FR = 250 \text{ mL/min}$ ; $T = 20 \pm 2^{\circ}\text{C}$ ; $t = 56 \text{ d}$ . (FTCS)	9		

PAO-PE <sup>a</sup>	3.3	Sequim Bay; $C_U = 3.3 \text{ ppb } T = 20 \pm 2^{\circ}C$ ; $t = 56 \text{ d.}$ (FTCS)	82
AI 11 (3 h conditioning) <sup>a</sup>	3.35	MSL of PNNL; $C_U = 2.9$ ppb; S= 30.8 psu; FR = 250 mL/min; T = 20 ± 2°C;t = 56 d.(FTCS)	9
AF 1 (3 h conditioning) <sup>a</sup>	3.41	MSL of PNNL; $C_U = 2.9$ ppb; S = 30.8 psu; FR= 250 mL/min; T = 20 ± 2°C;t = 56 d.(FTCS)	28
AF 1 (1 h conditioning) <sup>a</sup>	3.83	MSL of PNNL; $C_U = 2.9$ ppb; S = 30.8 psu; FR = 250 mL/min; T = 20 ± 2°C;t = 56 d. (FTCS)	28
DMSO-heat-treated AF8 <sup>a</sup>	4.48	MSL of PNNL; FR = 250 mL/min; T = $20 \pm 0.2^{\circ}$ C; t = 56d. (FTCS)	123
LCW fiber <sup>a</sup>	6.02	Sequim Bay; m = $\sim 10$ g; FR = 250 mL/min; T = 20 ± 1°C; t = 56 d. (FTCS)	189
PIDO NF <sup>a</sup>	8.7	South China Sea.; $V = 5$ T; r.t.; $t = 56$ d. (FTCS)	191
H-ABP fiber <sup>a</sup>	11.50	coastal marine areas of Guangdong, China; $C_U = 3.1$ ppb; S = 29.6 ± 0.4 psu; pH 8.0 ± 0.1; FR = 1.5 L/min; T = 26.3 ± 0.5°C; t = 90 d. (FTCS)	166
Amidoximated poly(DPAAm) <sup>a</sup>	13.08	the seashore of MutsuSekine-Hama in Japan; $m = 0.05$ g; FR = 6 mL/min at T = 25°C; t = 1 h. (FTCS)	105
Amidoximated poly(DPAAm) a	27.13	the seashore of MutsuSekine-Hama in Japan; $m = 0.05$ g; $FR = 6$ mL/min at $T = 25$ °C; $t = 7$ d. (FTCS)	105
Amidoximated poly(DPAAm) <sup>a</sup>	28.1	the seashore of MutsuSekine-Hama in Japan; $m = 0.05$ g; $FR = 6$ mL/min at $T = 25$ °C; $t = 1$ d. (FTCS)	105
UiO-66-AO <sup>e</sup>	2.68	Bohai in China; m = 1 mg; V = 1 L; r.t.; t = 3 d. (BE)	115
AO/MOF <sup>e</sup>	2.74	Huanghai in China; $m = 40 \text{ mg}$ ; $V = 40 \text{ mL}$ ; $t = 90 \text{ min}$ . (BE)	225
POP-oNH <sub>2</sub> -AO <sup>e</sup>	4.36	m = 5 mg; V = 5 gallons; 100 rpm; r.t.; t = 56 d. (BE)	237
MA@PIDO/Alg sponge <sup>f</sup>	1.87	South China Sea; $m \sim 60 \text{ mg}$ ; $V = 5,000 \text{ L}$ ; pH 6.5; r.t. $t = 24h$ . (FTCS)	249
AO-HNTs <sup>f</sup>	5.70	South China sea, near Haikou city; m = 10 mg; V = 100 L; pH 8.0; r.t.; t = 5 d. (FTCS)	248
AO-HNTs <sup>f</sup>	9.01	South China sea, near Haikou city; m = 10 mg; V = 100 L; pH 8.0; r.t.; t = 30 d. (FTCS)	248

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SMON-PAO <sup>f</sup>	$9.59 \pm 0.64$	South China sea, near the Boundary Island; FR = 1 L/h; pH 8.0; r.t.; t = 56 d. (FTCS)	243
BP-PAO <sup>f</sup>	$9.27 \pm 0.43$	South China sea, near Wanning city; m = 10 mg; V = 100 L; pH 8.0; T = 25°C.; t = 56 d. (BE, with natural light)	250
BP-PAO <sup>f</sup>	$11.76 \pm 0.43$	South China sea, near Wanning city; m = 10 mg; V = 100 L; pH 8.0; T = 25°C.; t = 56 d. (BE, with simulated light)	250
Spiked seawater			
PP-g-AO3 <sup>a</sup>	0.10	Bohai Sea; m = 125 mg; V = 500 mL; $C_U = 1.26 \times 10^{-7}$ M; pH 8.0; T = 298.15 K; t = 16 d. (BE)	158
polymer gel <sup>a</sup>	6.96	Andaman Ocean, Thailand; $C_U = 300$ ppb; $T = 25^{\circ}C$ ; $t = 28$ d.(FTCS)	147
polymer gel <sup>a</sup>	9.64	Andaman Ocean, Thailand; $C_U = 840$ ppb; $T = 25^{\circ}C$ ; $t = 28$ d. (FTCS)	147
polymer gel <sup>a</sup>	334	Andaman Ocean, Thailand; $C_U = 30$ ppm; $T = 25^{\circ}C$ ; $t = 7$ d. (FTCS)	147
polymer gel <sup>a</sup>	409	Andaman Ocean, Thailand; $C_U = 2140$ ppm; $T = 25^{\circ}C$ ; $t = 7$ d. (FTCS)	147
AO/MAA hydrogel <sup>a</sup>	432.41	Andaman Ocean, Thailand; $C_U = 2245$ ppm; $T = 25^{\circ}C$ ; $t = 7$ d. (FTCS)	38
PIDO NF <sup>a</sup>	951	South China Sea.; $m = 15 \text{ mg}$ ; $V = 5 \text{ L}$ ; pH 8.0; $C_U = 8 \text{ ppm}$ ; FR = 5 L/min; t = 24 h; (FTCS)	191
c-AO/CNFs <sup>b</sup>	199.20 <sup>1</sup>	m/V = 0.6 g/L; pH 8.1; T = 293 K; t = 24 h. (BE)	289
p-AO/CNFs <sup>b</sup>	248.14 <sup>I</sup>	m/V = 0.6 g/L; pH 8.1 ; T = 293 K; t = 24 h. (BE)	289
C-Ami electrode <sup>b</sup>	200 - 220	Half Moon Bay, USA; $C_U = 1000$ ppm; $t = 1$ d; by physiochemical adsorption (FTCS)	252
C-Ami electrode <sup>b</sup>	1932	Half Moon Bay, USA; V = 15 mL; $C_U$ = 1000 ppm; t = 1 d; by HW-ACE (EA)	252
PPN-6-PAO (3% KOH 80°C conditioning for 3h) <sup>e</sup>	4.81	Sequim Bay; m = 10 mg; V ~ 1 L; 100 rpm; $C_U \sim 80$ ppb; t = 42 d. (BE)	27

COF-TpAab-AO <sup>e</sup>	127	$m = 5 mg; V = 200 mL; C_U = 20 ppm; r.t.; t = 300 min. (BE)$	231
MA@PIDO/Alg sponge <sup>f</sup>	291.51	South China Sea; m ~ 60 mg; V = 5,000 L; $C_U$ = 5 -150 ppm; pH 6.5; r.t. t = 24 h. (FTCS)	249
SMON-PAO <sup>f</sup>	$1089.36 \pm 64.31$	South China sea; $m = 10 \text{ mg}$ ; $V = 5 \text{ L}$ ; $C_U = 8 \text{ ppm}$ ; pH 8.0; r.t.; $t = 36 \text{ h}$ . (FTCS)	243
Simulated seawater			
AAm/AO hydrogel <sup>a</sup>	~ 0.2	m ~1 mg; V = 100 mL; Various elements with a concentration 100 times higher than seawater; $C_U$ =4 ppb; pH 8.3; t =3 d. (BE)	38
PP-g-AO3 <sup>a</sup>	1.84	m = 25 mg; V = 100 mL; $C_U$ = 4.2 × 10 <sup>-6</sup> M; 0.438 M NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 8.0; T = 298.15 K; t = 4 d. (BE)	158
UHMWPE-g-P(GMA-co-MA)-EDA- AO <sup>a</sup>	1.97	$C_U$ = 3.6 ppb; S = 35 psu; FR = 25 ±2 ,L/min; pH 8.1 ± 0.3, T=25 ± 1°C; t = 42 d. (FTCS)	161
PE/PP-g-(PAAc-co-PAO) <sup>a</sup>	2.27	100 mg; V = 5 L;C <sub>U</sub> = 330 $\mu$ g/L; 100 rpm; Various elements with a concentration 100 times higher than seawater; pH 8.0; T = 25°C; t =1 d. (BE)	165
HDPE-g-PAA-co-PAO <sup>a</sup>	2.51	m = 0.2 g; $C_U$ = 3.6 ppb; S = 35 psu; FR = 35 ± 2 mL/min; T = 25 ± 2°C; t = 42 d. (FTCS)	13
AO-UHMWPE-1 a	2.93	$C_U = 331$ ppb; S = 35 psu; FR = 20 ± 2 mL/min; pH 8.1; T = 25 ± 2°C; t = 42 d. (FTCS)	261
AO-UHMWPE <sup>a</sup>	2.97	m = 0.2 g; $C_U$ = 3.6 ppb; S = 35 psu; FR = 20 ± 2 mL/min; pH 8.0 ± 0.3; T = 25 ± 2°C. (FTCS)	164
AO-UHMWPE <sup>a</sup>	4.54	m = 0.2 g; V = 5 L; C <sub>U</sub> = 330 ppb; S = 35 psu; 100 rpm; pH 8.1; T = 25°C; t = 1 d. (BE)	164
UHMWPE-g-P(AO-co-AA) <sup>a</sup>	7.01	m = 0.2 g; V = 5 L; C <sub>U</sub> = 331 ppb; S = 35 psu; pH 8.1; 100 rpm; T = 25°C; t = 24 h. (BE)	163
P(2DVB-VBC)-2PAN <sup>a</sup>	80	$C_U \sim 6$ ppm; pH 8; r.t.; t = 24 h. (BE)	21
PE-g-PVBC-g-(PAO-co-PAA)-b- PAA -2.1 <sup>a</sup>	79.4	m ~15 mg; V = 250 mL; C <sub>U</sub> = 6 ppm; 10123 ppm Na <sup>+</sup> ; 15529 ppm Cl <sup>-</sup> ; 140 ppm HCO <sub>3</sub> <sup>-</sup> ; pH 8; T = 20 - 25°C; t = 24 h. (BE)	144

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PE-g-PVBC-g-(PAO-co-PAA)-2 <sup>a</sup>	80.0	m ~15 mg; V = 250 mL; C <sub>U</sub> = 6 ppm; 10123 ppm Na <sup>+</sup> ; 15529 ppm Cl <sup>-</sup> ; 140 ppm HCO <sub>3</sub> <sup>-</sup> ; pH 8; T = 20 - $25^{\circ}$ C; t = 24 h. (BE)	144
PE-g-PVBC-g-(PAO-co-PAA)-2 <sup>a</sup>	174.1	m ~15 mg; V = 750 mL; C <sub>U</sub> = 6 ppm; 10123 ppm Na <sup>+</sup> ; 15529 ppm Cl <sup>-</sup> ; 140 ppm HCO <sub>3</sub> <sup>-</sup> ; pH 8; T = 20 - 25°C; t = 24 h. (BE)	144
PP-g-Vim <sup>+</sup> Br <sup>-</sup> AO <sup>a</sup>	119.76 <sup>II</sup>	m = 20.0 mg; V = 500 mL; 0.438 M NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 8.0; T = 298.15 K; t = 50 h. (BE)	156
PE-GMA-AO-HEA (400% of d.g.) <sup>a</sup>	123	$m \sim 15 \text{ mg}; V = 750 \text{ mL}; C_U = 8 \text{ ppm}; 193 \text{ ppm NaHCO}_3; 25600 \text{ ppm NaCl}; \text{pH} \sim 8; \text{r.t.}; t = 24 \text{ h.} (BE)$	44
PE-GMA-AO-HEA (1900% of d.g.) <sup>a</sup>	165	$m \sim 15 \text{ mg}; V = 750 \text{ mL}; C_U = 8 \text{ ppm}; 193 \text{ ppm NaHCO}_3; 25600 \text{ ppm NaCl}; \text{pH} \sim 8; \text{r.t.}; t = 24 \text{ h.} (BE)$	44
AI series adsorbents <sup>a</sup>	171-187	$C_U = 8 \text{ ppm}$ ; 193 ppm NaHCO <sub>3</sub> ; 25600 ppm NaCl; pH ~ 8; V = 750 mL; 400 rpm; r.t. ; t = 24 h. (BE)	9
AF series adsorbents <sup>a</sup>	170-200	C <sub>U</sub> = 8 ppm; 193 ppm NaHCO <sub>3</sub> ; 25600 ppm NaCl; pH ~ 8; V = 750 mL; 400 rpm; r.t.; t = 24 h. (BE)	28
MC-Ph-AO <sup>b</sup>	2.0 ±2.0	m/V = 0.1 g/L; C <sub>U</sub> = 5 ppm ; 300 rpm; pH 8.2; r.t.; t = 1 h. (BE)	199
MC-CA <sup>b</sup>	$13.1 \pm 1.5$	m/V = 0.1 g/L; C <sub>U</sub> = 5 ppm ; 300 rpm; pH 8.2; r.t.; t = 1 h. (BE)	199
ZS-CP40*-AO <sup>d</sup>	30.4	m = 50 mg; V = 50 mL; $C_U$ = 17 mg/L ; 25.6 g/L of NaCl; 193 mg/L of NaHCO <sub>3</sub> ; t = 24 h. (BE)	109
S-CP40*-AO <sup>d</sup>	51.1	m = 50 mg; V = 50 mL; $C_U$ = 17 mg/L; 25.6 g/L of NaCl; 193 mg/L of NaHCO <sub>3</sub> ; t = 24 h. (BE)	109
S-CP40 <sup>*E</sup> -AO <sup>d</sup>	57.3	m = 50 mg; V = 50 mL; $C_U$ = 17 mg/L; 25.6 g/L of NaCl; 193 mg/L of NaHCO <sub>3</sub> ; t = 24 h. (BE)	109
MSA-III <sup>d</sup>	31.1 <sup>I</sup>	m = 4 mg; V = 40 mL; $C_U$ = 5 ppm; 300 rpm; pH 8.3 ± 0.1; r.t.; t = 1 h. (BE)	176
MSCA-I <sup>d</sup>	58.1 <sup> I</sup>	m = 4 mg; V = 40 mL; $C_U$ = 5 ppm; 300 rpm; pH 8.3 ± 0.1; r.t.; t = 1 h. (BE)	176
RAF-1-CH <sub>2</sub> AO <sup>e</sup>	40	m = 5 mg; V = 200 mL; C <sub>U</sub> = 7.05 ppm; 438 mM NaCl; 2.3 mM NaHCO <sub>3</sub> ; r.t.; t = 25 h. (BE)	137
PPN-6-PAO (3% KOH r.t. conditioning for 3h) <sup>e</sup>	64.1	m = $13.0 \pm 1.0$ mg; V = $250$ mL; C <sub>U</sub> = $0.034$ mM; 438.607 mM NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 7.97; r.t.; t = $24$ h. (BE)	27

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PPN-6-PAO (3% KOH 80°C conditioning for 3h) <sup>e</sup>	65.2	m = $13.0 \pm 1.0$ mg; V = $250$ mL; C <sub>U</sub> = $0.034$ mM; 438.607 mM NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 7.97; r.t.; t = $24$ h. (BE)	27
AO-HNTs <sup>f</sup>	456.24	m = 10 mg; V = 1L; C <sub>U</sub> = 32 ppm; 438.607 mM NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 8.0; T = 25°C.; t =13 d. (FTCS)	248
POP-oNH <sub>2</sub> -AO <sup>e</sup>	290	m = 3 mg; V = 400 mL; $C_U \sim 10.3$ ppm; 25.6 g/L NaCl; 0.198 g/L NaClO <sub>3</sub> ; r.t.; t = 300 min. (BE)	237
BP-PAO <sup>f</sup>	$760.97 \pm 32.17$	m = 10 mg; V = 5 L; $C_U$ =8 ppm; 438.607 mM NaCl; 2.297 mM NaHCO <sub>3</sub> ; pH 5.0; r.t.; t = 40 h. (BE, without simulated sunlight)	250
BP-PAO <sup>f</sup>	990.60 ± 37.39	$m = 10 \text{ mg}; V = 5 \text{ L}; C_U = 8 \text{ ppm}; 438.607 \text{ mM NaCl}; 2.297 \text{ mM NaHCO}_3; \text{ pH 5.0}; \text{ r.t.}; t = 32 \text{ h}. (BE, with simulated sunlight)}$	250

m is the mass of the adsorbents; S is salinity; V is the volume of the solution;  $C_U$  is the concentration of uranium species; FR is flow rate; t is the time; T is the temperature; SM is submerged mode; FTCS is flow-through column system; BE is batch experiments; BP is buoy platform; EA is electrochemical adsorption.

<sup>a</sup>: Polymeric materials; <sup>b</sup>: carbon-based materials; <sup>c</sup>: Biosorbents; <sup>d</sup>: Silica-based materials; <sup>e</sup>: New type of porous materials; <sup>f</sup>: Others.

<sup>1</sup>: the value converted from adsorption efficiency (%); <sup>II</sup>: theoretical value calculated by Langmuir isotherm model.

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A. J	Adsorption capacities			
Adsorbents	mg/g	conditions		
Pure water				
PA66-g-PGMA-IDPAO <sup>a</sup>	21.09	m = 15mg; V = 50 mL; $C_U$ = 1 - 25 mg/L; pH 5.0; T = 25°C; t = 36 h. (BE)	167	
PA66-g-PGMA-IDPAO <sup>a</sup>	41.98	m = 15mg; V = 50 mL; $C_U$ = 1 - 25 mg/L; pH 5.0; T = 55°C; t = 36 h. (BE)	167	
PP-g-AO3 <sup>a</sup>	112.0 <sup>I</sup>	m = 25 mg; V = 100 mL; $C_U$ = 10 - 100 ppm; pH 8.0; T = 298.15 K; t = 15 h. (BE)	158	
PAOBI <sub>82</sub> <sup>a</sup>	169.49 <sup>1</sup>	m = 17.6 mg; V= 200 mL; $C_U$ = 10 <sup>-3</sup> - 5 × 10 <sup>-5</sup> M; pH 7; T = 298.15 K; t = 12 h. (BE)	171	
UHMWPEF-AO <sup>a</sup>	176.99 <sup>I</sup>	$m = 5 mg; V = 5 mL; C_U = 50 - 350 mg/L; pH 4.0; T = 298 K; t = 24 h. (BE)$	53	
MNPs@PAO <sup>a</sup>	216.45	M = 10 mg; V = 20 mL; pH 6.0; T = 298.15 K; t = 20 h. (BE)	132	
PIDO NF <sup>a</sup>	860.58 ± 13.56	$m = 15 mg; V = 5 L; pH 8.0; C_U = 8 ppm; FR = 5 L/min; t = 24 h. (FTCS)$	191	
PIDO NF <sup>a</sup>	$1187.05 \pm 28.45$	m = 15 mg; V = 5 L; pH 7.0; $C_U$ = 8 ppm; FR = 5 L/min; t = 24 h. (FTCS)	191	
MC-Ph-AO <sup>b</sup>	6.0±3.0	m/V = 1 g/L; pH 4.0; C <sub>U</sub> = 100 ppm; r.t.; t = 1h. (BE)	199	
MC-CA <sup>b</sup>	$13.0 \pm 6.0$	m/V = 1 g/L; pH 4.0; C <sub>U</sub> = 100 ppm; r.t.; t = 1h (BE)	199	
AO-MWCNTs <sup>b</sup>	67.9	m = 10 mg; V = 10 mL; $C_U$ = 10 - 100 mg/L; pH 5.0; T = 298 K; t = 240 min. (BE)	98	
AO-MWCNTs <sup>b</sup>	79.8	m = 10 mg; V = 10 mL; $C_U$ = 10 - 100 mg/L; pH 5.0; T = 308 K; t = 240 min. (BE)	98	

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AO-MWCNTs <sup>b</sup>	93.3	$m = 10 \text{ mg}; V = 10 \text{ mL}; C_U = 10 - 100 \text{ mg/L}; \text{ pH 5.0}; T = 318 \text{ K}; t = 240 \text{ min.}$ (BE)	
mGO-PAO <sup>b</sup>	89.9 <sup>I</sup>	m = 20 mg; V = 50 mL; pH 6.0; T = 298 K; t = 24 h. (BE)	203
AO-g-MWCNTs <sup>b</sup>	176 <sup>I</sup>	m = 20 mg; V = 20 mL; pH 4.5; T = 298.15 K; t = 240 min. (BE)	146
ACFs-AO <sup>b</sup>	191.6 <sup>1</sup>	m = 10 mg; V = 30 mL; pH 5.0; T = $298 \pm 0.5$ K; t = 48 h. (BE)	288
0.2AO-OMC <sup>b</sup>	245	m = 10 mg; V = 50 mL; $C_U$ = 50 mg; pH 5.0; T = 298.15 K; t = 90 min. (BE)	108
0.2AO-OMC <sup>b</sup>	322.6 <sup>I</sup>	m = 10 mg; V = 50 mL; pH 5.0; T = 298.15 K; t = 90 min. (BE s)	108
AGH <sup>b</sup>	398.41 <sup>I</sup>	m = 10 mg; V = 20 mL; pH 6.0; r.t.; t = 6 h. (BE)	140
AO-HTC-DAMN <sup>b</sup>	493 <sup>I</sup>	m = 10 mg; V = 25 mL; $C_U$ = 20 - 300 mg/L; pH 4.3; T = 293 K; t = 120 min. (BE)	118
AO-HTC <sup>b</sup>	724.6	m = 10 mg; V = 10 mL; pH 5.0; T = 308.15 K; t = 240 min. (BE)	195
GO-DM-AO <sup>b</sup>	935	m = 10 mg; V = 20 mL; $C_U$ = 500 mg/L; pH 8.04 ± 0.01; T = 25°C; t = 6 h. (BE)	197
HTC-AO <sup>b</sup>	1021.6	m = 10 mg; V = 150 mL; $C_U$ = 300 mg/L; pH 4.5; T = 298.15 K; t = 120 min. (BE)	202
P(AO)-g-CTS/BT °	49.09 <sup>I</sup>	m = 0.025g; V = 12.5 mL; pH 8.0; C <sub>U</sub> = 100 mg/L; T = 298 K; t = 60 min. (BE)	110
P(AO)-g-CTS/BT °	143.59 <sup>III</sup>	m = 0.025g; V = 12.5 mL; $C_U$ = 25 - 300 mg/L; pH 8.0; T = 30°C; t = 60 min. (BE)	110
P(AO)-g-CTS/BT °	165.09 <sup>III</sup>	m = 0.025g; V = 12.5 mL; $C_U$ = 25 - 300 mg/L; pH 8.0; T = 40°C; t = 60 min. (BE)	110
P(AO)-g-CTS/BT °	208.96 <sup>III</sup>	m = 0.025g; V = 12.5 mL; $C_U$ = 25 - 300 mg/L; pH 8.0; T = 50°C; t = 60 min. (BE)	110
Wool-g-AO °	59.35	m = 100 mg; V = 100 mL; $C_U$ = 15 - 220 mg/L; pH 5.0; T = 30°C; t = 60 min. (BE)	212
MAO-chitosan <sup>c</sup>	117.65 <sup>I</sup>	m = 20 mg; V = 20 mL; $C_U$ = 10 - 600 mg/L; 150 rpm; pH 6; T = 298 K; t = 5h. (BE)	96

	PAO-B °	126.9 <sup>I</sup>	m = 5 mg; V = 5 mL; $C_U$ = 5 - 120 mg/L; pH 5 ± 0.3; T = 25 ± 1°C; t = 2 h. (BE)	207
	AM-MG-CH °	357 <sup>II</sup>	m/V = 0.2 g/L; $C_U$ = 15 - 300 mg/L; pH 4.0; 150 rpm; T = 20 ± 1°C; t = 48 h. (BE)	106
	AM-MG-CH °	372.95 <sup>I, II</sup>	m/V = 0.2 g/L; $C_U$ = 15 - 300 mg/L; pH 4.0; 150 rpm; T = 20 ± 1°C; t = 48 h. (BE)	106
Amidox	ime-modified algal cells <sup>c</sup>	366.8	m = 50 mg; V = 25 mL; $C_U$ = ca. 1000 mg/L; pH 5.0; T = 25 ± 1°C; t = 2.0 h. (BE)	211
	ZGEA °	584.60	m/V = 0.05 g/L; C <sub>U</sub> =40 mg/L; pH 5.5; t = 120 min. (BE)	344
	AMAN °	621	m = 20 mg; V = 100 mL; $C_U$ = 0.2 - 0.8 mg/L; pH 5.0; 300 rpm; T = 298 K; t = 3 h. (BE)	208
	AMCM-0.4 <sup>d</sup>	$105 \pm 3$ <sup>I</sup>	m = 5 mg; V = 5 mL; $C_U$ = 50 - 200 mg/L; pH 4.5; T = 25°C; t = 2 h. (BE)	220
	AMD-MCM-41 <sup>d</sup>	493.6	m = 10 mg; V = 5.0 mL; 150 rpm; pH 5.0; T = 323 K; t = 2.0 h. (BE)	129
	c-AO@SBA-15 <sup>d</sup>	516	$m/V = 0.1 \text{ g/L}; C_U = 100 \text{ mg/L}; \text{ pH 6.0}; T = 25^{\circ}\text{C}; t = 240 \text{ min.} (BE)$	222
:	g-AO@SBA-15 d	625	$m/V = 0.1 \text{ g/L}; C_U = 100 \text{ mg/L}; \text{ pH 6.0}; T = 25^{\circ}\text{C}; t = 240 \text{ min.} (BE)$	222
	AO-SBA-15 <sup>d</sup>	601	$m/V = 0.1 \text{ g/L}; \text{ pH 6.0}; C_U = 100 \text{ mg/L}; T = 25^{\circ}\text{C}; t = 3 \text{ h.} (BE)$	221
	AO-H-SBA-15 <sup>d</sup>	709	$m/V = 0.1 \text{ g/L}; \text{ pH 6.0}; C_U = 100 \text{ mg/L}; T = 25^{\circ}\text{C}; t = 3 \text{ h.} (BE)$	221
D	FNS/pDA/AOPNI <sup>d</sup>	626	m = 10 mg; V = 20 mL; $C_U$ = 500 mg/L; pH 8.00; T = 25°C; t = 12 h. (BE)	342
DFN	S/pDA/AOPNI-NH2 <sup>d</sup>	678	m = 10 mg; V = 20 mL; $C_U$ = 500 mg/L; pH 8.00; T = 25°C; t = 12 h. (BE)	342
	TMP-g-AO <sup>e</sup>	35.37 <sup>I</sup>	$m = 50 mg; V = 50 mL; pH 8.2 \pm 0.1; T = 298.15 K; t = 3 d. (BE)$	239
P	AF-1-CH <sub>2</sub> NHAO <sup>e</sup>	102 <sup>I</sup>	m = 5 mg; V = 10 mL; $C_U$ = 1 - 400 ppm; pH ~ 6; r.t.; t = 24 h. (BE)	232
RA	AF-1-NH(CH <sub>2</sub> ) <sub>2</sub> AO <sup>e</sup>	385 <sup>I</sup>	m = 5 mg; V = 10 mL; $C_U$ = 1 - 400 ppm; pH ~ 6; r.t.; t = 24 h. (BE)	232

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113	m = 20 mg; V = 50 mL; $C_U$ = 160 mg/L pH 5.5 ± 0.1; T = 25°C; t = 24 h. (BE)	184.1 <sup>I</sup>	UiO-66-AO <sup>e</sup>
113	m = 20 mg; V = 50 mL; $C_U$ = 160 mg/L pH 5.5 ± 0.1; T = 25°C; t = 24 h. (BE)	194.8	UiO-66-AO <sup>e</sup>
238	m/V = 0.25 g/L; $C_U$ = 5 × 10 <sup>-5</sup> mol/L; pH 6.0 ± 0.1; T = 298.15 K. (BE)	251.9 <sup> I</sup>	CMPAO-4 °
231	m = 4.5 mg; V = 400 mL; $C_U$ = 9.25 ppm; pH ~ 6. (BE)	256	POP-TpAab-AO <sup>e</sup>
231	m = 4.5 mg; V = 400 mL; $C_U$ = 9.25 ppm; pH ~ 6. (BE)	305	COF-TpAab-AO °
231	m = 4.5 mg; V = 400 mL; $C_U$ = 9.25 ppm; pH ~ 6. (BE)	322	POP-TpDb-AO <sup>e</sup>
231	m = 4.5 mg; V = 400 mL; $C_U$ = 9.25 ppm; pH ~ 6. (BE)	394	COF-TpDb-AO <sup>e</sup>
231	$m/V = 045 mg/mL$ ; $C_U = 23.1 - 265.2 ppm$ ; $pH \sim 6$ ; overnight. (BE)	355 <sup>I</sup>	POP-TpDb-AO <sup>e</sup>
231	m/V = 045 mg/mL; $C_U$ = 23.1 - 265.2 ppm; pH ~ 6; overnight. (BE)	408 <sup>I</sup>	COF-TpDb-AO °
137	m = 5 mg; V = 20 mL; $C_U$ = 8.6 - 165.7 ppm; pH ~ 6; r.t.; overnight. (BE)	304 <sup>I</sup>	RAF-1-CH <sub>2</sub> AO <sup>e</sup>
345	m = 5 mg; V = 25 mL; pH 4.0; r.t.; overnight. (BE)	427 <sup>I</sup>	TFPT-BTAN-AO °
237	m = 5 mg; V = 10 mL; $C_U$ = 36 - 356 ppm; pH 6; r.t.; t = 12 h. (BE)	440 <sup>I</sup>	POP-AO <sup>e</sup>
102	m = 20 mg; V = 50 mL; $C_U$ = 50 - 225 mg/L; pH 5.5; T = 15°C; t = 500 min. (BE)	454.54 <sup>I</sup>	MIL-53(Al)-AO e
237	m = 5 mg; V = 10 mL; $C_U$ = 36 - 356 ppm; pH 6; r.t.; t = 12 h. (BE)	530 <sup>I</sup>	POP-oNH <sub>2</sub> -AO <sup>e</sup>
237	m = 5 mg; V = 10 mL; C <sub>U</sub> = 36 - 356 ppm; pH 6; r.t.; t = 12 h (BE)	580 <sup>I</sup>	POP-pNH <sub>2</sub> -AO <sup>e</sup>
346	m = 5 mg; V = 50 mL; $C_U$ = 1 - 300 mg/L; pH 7; T = 298 K; t = 6 h (BE)	586	MIL-101-AO <sup>e</sup>

m = 50 mg; V = 100 mL; 100 rpm; pH 5.0; T = 30°C; t = 24 h. (BE)	111
m = 10 mg; V = 25 mL; pH 4.5; T = 25°C; t = 2 h. (BE)	78
m = 20 mg; V = 50 mL; $C_U$ = 25.98 - 654.1 ppm; 160 rpm; pH 8; T = 298 K; t = 4 h. (BE)	244
m/V = 0.05  g/L; pH 4.0 ± 0.1; IS = 0.1 M NaCl; T = 20 ± 1°C; t = 48 h. (BE)	198
m/V = 0.05  g/L; pH 4.0 ± 0.1; IS = 0.1 M NaCl; T = 20 ± 1°C; t = 48 h. (BE)	198
m/V = 0.05  g/L; pH 4.0 ± 0.1; IS = 0.1 M NaCl; T = 20 ± 1°C; t = 48 h. (BE)	198
$m/V = 0.05 \text{ g/L}; \text{ pH } 4.0 \pm 0.1; \text{ IS} = 0.1 \text{ M NaCl}; \text{ T} = 20 \pm 1^{\circ}\text{C}; \text{ t} = 48 \text{ h.} (\text{BE})$	198
m/V = 0.05  g/L; IS = 0.1 M NaCl; pH 4.0 ± 0.1; T = 20 ± 1°C; t = 48 h. (BE)	198
m/V = 0.05  g/L; IS = 0.1 M NaCl; pH 4.0 ± 0.1; T = 20 ± 1°C; t = 48 h. (BE)	198
m/V = 0.6 g/L; IS = 0.01 M NaCl; pH 3.5; T = 293 K; t = 24 h. (BE)	289
m/V = 0.6 g/L; IS = 0.01 M NaCl; pH 3.5; T = 293 K; t = 24 h. (BE)	289
$m/V = 0.2 \text{ g/L}; I = 0.01 \text{ M NaClO}_4; \text{ pH } 5.0 \pm .01; T = 298 \text{ K}; t = 24 \text{ h.} (BE)$	104
m = 10 mg; V = 50 mL; IS = 0.01 M NaClO <sub>4</sub> ; pH 4.5; T = 298 K; t = 240 min. (BE)	119
$m/V = 0.1 \text{ g/L}$ ; IS = 0.01 M NaNO <sub>3</sub> ; $C_U = 10 - 80 \text{ mg/L}$ ; pH 5.0; T = 298 K; t = 24 h. (BE)	219
m/V = 0.2  g/L; IS = 0.01 M NaClO <sub>4</sub> ; pH 5.0 ± 0.1; T = 298 K; t = 24 h. (BE)	52
m/V = 0.2  g/L; IS = 0.01 M NaClO <sub>4</sub> ; pH 5.0 ± 0.1; T = 318 K; t = 24 h. (BE)	52

Pal/PAO <sup>f</sup>

ND-AO<sup>f</sup>

FeOOH-APAN  $^{\rm f}$ 

78.13 <sup>I</sup>

285.8<sup>I</sup>

980.39<sup>I</sup>

PAO <sup>a</sup>	161	m/V = 0.05 g/L; pH 4.0 $\pm$ 0.1; IS = 0.1 M NaCl; T = 20 $\pm$ 1°C; t = 48 h. (BE)
0.25 PAO/rGO <sup>b</sup>	206	m/V = 0.05 g/L; pH 4.0 $\pm$ 0.1; IS = 0.1 M NaCl; T = 20 $\pm$ 1°C; t = 48 h. (BE)
0.5 PAO/rGO <sup>b</sup>	227	m/V = 0.05 g/L; pH 4.0 $\pm$ 0.1; IS = 0.1 M NaCl; T = 20 $\pm$ 1°C; t = 48 h. (BE)
1.0 PAO/rGO <sup>b</sup>	253	m/V = 0.05 g/L; pH 4.0 $\pm$ 0.1; IS = 0.1 M NaCl; T = 20 $\pm$ 1°C; t = 48 h. (BE)
4.0 PAO/rGO <sup>b</sup>	439	m/V = 0.05 g/L; IS = 0.1 M NaCl; pH 4.0 $\pm$ 0.1; T = 20 $\pm$ 1°C; t = 48 h. (BE)
2.0 PAO/rGO <sup>b</sup>	872	m/V = 0.05 g/L; IS = 0.1 M NaCl; pH 4.0 $\pm$ 0.1; T = 20 $\pm$ 1°C; t = 48 h. (BE)
c-AO/CNFs <sup>b</sup>	263.18 <sup>I</sup>	m/V = 0.6 g/L; IS = 0.01 M NaCl; pH 3.5; T = 293 K; t = 24 h. (BE)
p-AO/CNFs <sup>b</sup>	588.24 <sup>I</sup>	m/V = 0.6 g/L; IS = 0.01 M NaCl; pH 3.5; T = 293 K; t = 24 h. (BE)
AOMGO <sup>b</sup>	284.89 <sup>I, II</sup>	m/V = 0.2  g/L; I = 0.01 M NaClO <sub>4</sub> ; pH 5.0 ± .01; T = 298 K; t = 24 h. (BE)
AOGONRs <sup>b</sup>	502.6	m = 10 mg; V = 50 mL; IS = 0.01 M NaClO <sub>4</sub> ; pH 4.5; T = 298 K; t = 240 min. (BE)
KIT-6-AO-20% <sup>d</sup>	323.94 <sup>I</sup>	m/V = 0.1  g/L; IS = 0.01 M NaNO <sub>3</sub> ; C <sub>U</sub> = 10 - 80 mg/L; pH 5.0; T = 298 K; t = 24 h. (BE)
SBA-AO-0.4 <sup>d</sup>	386.75 <sup>I, II</sup>	m/V = 0.2 g/L; IS = 0.01 M NaClO <sub>4</sub> ; pH 5.0 ± 0.1; T = 298 K; t = 24 h. (BE)
SBA-AO-0.4 d	414.36 <sup>I, II</sup>	m/V = 0.2 g/L; IS = 0.01 M NaClO <sub>4</sub> ; pH 5.0 ± 0.1; T = 318 K; t = 24 h. (BE)

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SBA-AO-0.4 <sup>d</sup>	465.05 <sup>I, II</sup>	$m/V = 0.2 g/L$ ; $IS = 0.01 M NaClO_4$ ; $pH 5.0 \pm 0.1$ ; $T = 338 K$ ; $t = 24 h$ . (BE)	52
HCMP-AO <sup>e</sup>	450	m = 4 mg; V = 20 mL; IS = 0.01 M NaClO <sub>4</sub> ; $C_U$ = 10 - 200 ppm; pH 6; r.t.; overnight. (BE)	336
AO/MOF <sup>e</sup>	454.55 <sup>I</sup>	m/V = 0.5 g/L; C <sub>U</sub> = 10 - 50 mg/L; IS = 0.01 M NaClO <sub>4</sub> ; pH 5.0; T = 293 K; t = 24 h. (BE)	225
$PAO/MoS_2{}^{\rm f}$	47.4 <sup>I</sup>	m/V = 0.20  g/L; IS = 0.1 M NaCl; pH 5.0 ± 0.1; T = 298 ± 1 K; t = 24 h. (BE)	139
Fe <sub>3</sub> O <sub>4</sub> @PDA@PAO <sup>f</sup>	162.5	$C_U = 100 \text{ mg/L}$ ; IS = 0.01 M NaClO <sub>4</sub> ; T = 298 K; t = 26 h. (BE)	126
ZVI/PAO <sup>f</sup>	206 <sup>I</sup>	m/V = 0.20  g/L; IS = 0.1 M NaCl; pH 5.0 ± 0.1; T = 298 ± 1 K; t = 24 h. (BE)	247

2172 m is the mass of the adsorbents, V is the volume of the solution; FR is the flow rate; C<sub>U</sub> is the initial concentration of uranium species; t is the time; T is the temperature;

2173 IS represents ionic strength; FTCS is flow-through column system; BE is batch experiments.

<sup>a</sup>: Polymeric materials; <sup>b</sup>: Carbon-based materials; <sup>c</sup>: Biosorbents; <sup>d</sup>: Silica-based materials; <sup>e</sup>: New type of porous materials; <sup>f</sup>: Others.

<sup>1</sup>: the theoretical value calculated by Langmuir isotherm model; <sup>II</sup>: the value converted from the molar mass of uranium of 238 g/mol; <sup>III</sup>: the value converted from adsorption efficiency (%).

Table 6. 2177

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	Binding energy (eV)						
Adsorbents	$C_{1s}$	Ν	1s	$O_{1s}$	$U4f_{7/2}$	$U4f_{5/2}$	Ref. 🕇
	NH <sub>2</sub> - <u>C</u> =N-OH	$\underline{\mathbf{N}}$ H <sub>2</sub> -C=N-OH	NH₂-C= <b>№</b> -OH	NH₂-C=N- <b>O</b> H	<u>U</u> -AO	U- <u>U</u>	
PIDO NFs <sup>a</sup>	286.4	400.90	399.05	532.50	-	-	191 🔮
PIDO-U <sup>a</sup>	-	-	-	531.44	381.60	392.65	191 🦉
PAO/rGO b	-	$400.2\pm0.2$	$399.4 \pm 0.2$	-			140 ≓
AO-MWCNTs <sup>b</sup>	-	399.5	400.2	532.2	-	-	98 🗮
AO-g-MWCNTs <sup>b</sup>		399.7	400.4	533.3			146
0.2AO-OMC <sup>b</sup>		399.35	399.75	532.2	-	-	108
0.2AO-OMC-U <sup>b</sup>		399.35	401.1	533.1	381.48	392.39	108 💆
p-AO/CNFs <sup>b</sup>		402.9	401.3				289 💾
AO-HTC <sup>b</sup>	286.8	399.19	400.21	-	-	-	195 🖸
AO-HTC-U <sup>b</sup>	-	399.19	400.21	531.5	381.48	392.39	195 🕛
AOGONRs <sup>b</sup>	-	39	9.6	531.5	382.3	393.0	119 🎗
HTC-AO <sup>b</sup>	286.4	399.7		530.8	-	-	202
ACFs-AO <sup>b</sup>		399.2	400.0	533.1	-	-	288
mGO-PAO <sup>b</sup>	-	399.72	400.18	531.62	-	-	203 <
mGO-PAO-U <sup>b</sup>	-	399.72	400.54	531.78	-	-	203
P(AO)-g-CTS/BT c	285.89	399.7	400.5	532.1			288
U- P(AO)-g-CTS/BT <sup>c</sup>	286.08	399.41	401.29	533.1	381.39	392.24	110 7
ami-MSN <sup>d</sup>		399.27	399.89	531.07	-	-	138
ami-MSN <sup>d</sup>		399.40	400.29	532.45	-	-	146 🗖
SBA-AO-0.4 d	287.1	399.3	400.8	530.9	-	-	52 🔮
SBA-AO-U <sup>d</sup>	-	399.7	401.0	531.1	381.7	391.8	52 두
TMP-h-AO-U <sup>e</sup>	285.89	401.29	399.41	-	-	-	239
Na-Mont-APAN <sup>f</sup>	-	399.7	400.5	-	-	-	125 🕠
FeOOH-APAN <sup>f</sup>	-	399.4	400.3	532.3	-	-	244
FeOOH-APAN-U <sup>f</sup>	-	399.4	401.8	533.2	-	-	244
Pal/PAO <sup>f</sup>	286.37	399.72	400.58	-	-	-	111 😈
$PAO/MoS_2{}^{\rm f}$	287.62	400.40	399.20	531.08	-	-	139 📩

a: Polymeric materials; b: carbon-based materials; c: Biosorbents; d: Silica-based materials; e: New 2178

2179 type of porous materials; f: Others.

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