Original Article

Cesium separation from radioactive waste by extraction and adsorption based on crown ethers and calixarenes

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A B S T R A C T

Cesium is a major product of uranium fission, which is the most commonly existed radionuclide in radioactive wastes. Various technologies have been applied to separate radioactive cesium from radioactive wastes, such as chemical precipitation, solvent extraction, membrane separation and adsorption. Crown ethers and calixarenes derivatives can selectively coordinate with cesium ions by ion-dipole interaction or cation-π interaction, which are promising extractants for cesium ions due to their promising coordinating structure. This review systematically summarized and analyzed the recent advances in the crown ethers and calixarenes derivatives for cesium separation, especially focusing on the adsorbents based on extractants for cesium removal from aqueous solution, such as the grafting coordinating groups (e.g. crown ether and calixarenes) and coordinating polymers (e.g. MOFs) due to their unique coordination ability and selectivity for cesium ions. These adsorbents combined the advantages of extraction and adsorption methods and showed high adsorption capacity for cesium ions, which are promising for cesium separation The key restraints for cesium separation, as well as the newest progress of the adsorbents for cesium separation were also discussed. Finally, some concluding remarks and suggestions for future researches were proposed.

1. Introduction

Radiocesium ions have attracted much attention, especially in the field of radioactive wastewater treatment, for their radioactivity and other potential risks, as well as the difficulty with which they separate [1,2].

There are more than 30 isotopes of cesium. Among them, ^{133}Cs is the most stable one, whilst ^{134}Cs and ^{137}Cs are the most commonly observed fission products of uranium. The two types of radiocesium are the largest release of radioactivity after the Fukushima Daiichi nuclear power disaster of 2011 [3]. Compared with ^{134}Cs ($t_{1/2} = 2$ a; beta and gamma emission), ^{137}Cs ($t_{1/2} = 30$ a; beta and gamma emission) possesses a much longer half-life and a higher energy emission [4]. Additionally, with a half-life of 2.0×10^6 years, ^{135}Cs has an impact on long-term storage.

The radioactivity and chemical toxicity of radiocesium makes it highly concerned. The uptake of radiocesium by organisms will lead to the internal exposure of radiation, which is quite dangerous. Besides the radioactivity, cesium ions are water soluble, and are known to be incorporated into clay via migration and to be present in the range of several tens of centimeters on the ground. Meanwhile, as a non-essential element, cesium with a similarity of K^+ can be assimilated by all organisms, resulting in various kinds of diseases. Various exposure pathways (e.g. inhalation, external and internal exposure) of radioactive cesium increase the risk of public health [5,6]. Therefore, the treatment of radioactive wastewater is vital, especially taking into account the security concerns for human beings and sustainable development.

So far, various methods have been developed and applied for practical use for cesium removal from aqueous solutions, such as precipitation [7,8], solvent extraction [9], membrane separation [10–13], and adsorption [14–22]. Generally, radionuclides can only reduce their radioactivity through decay. The treatment of radioactive wastewater by a variety of physicochemical methods is essentially to concentrate the radionuclides and reduce the volume of the radioactive wastewater, so that it can be solidified for long-time storage or final disposition [23].

The separation of cesium ions from aqueous solutions is

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challenging, owing to its physical and chemical characteristics. The alkali metal group that includes Na^+, K^+ and Cs^+ is known for its homologous behavior. Although their crystal ionic radii have different values, ordered by Na^+ (116 pm) < K^+ (152 pm) < Cs^+ (181 pm) [24], they have comparable sizes in the order of Na^+ (228 pm) > Cs^+ (219 pm) > K^+ (212 pm) in completely hydrated states [25]. Considering the wide existence of Na^+ and K^+ in aqueous solutions, as well as their chemical similarities, the selective separation of cesium ion, which is usually below ppm or even ppb level, from aqueous solutions is extremely difficult. Furthermore, unlike heavy metal ions, monovalent cesium ions do not precipitate at various pH values or form insoluble complexes with most chemicals, such as sulfate and halides [26]. Above all, unexpected grafting and chain scissoring aroused by its radiation may change the structure of the applied materials during these operations [27]. This may result in the loss of adsorption capacity or decontamination factor.

Crown ethers and calixarenes derivatives have great potential for cesium separation. With unique guest-host structures, they can selectively coordinate with cesium ions via cation-π [28], ion-dipole [29] or other interactions, which is rather useful in solvent extraction and adsorption, and has been used in large scale application. For example, the Cesium Solvent Extraction Process (CSSX), which is also known as Caustic-Side Solvent Extraction Process (CSSX) [30], is specifically developed to separate cesium from alkaline waste. Previously, the extracting agents (e.g. dicarbollides, crown ethers and functionalized calixarenes) for the separation of Sr^{2+} and Cs^+ were summarized [31,32]. The radiation chemistry of these extracting agents was also introduced by [33]. Besides these, crown ethers-based adsorbents for strontium separation was recently reported [34]. An overview on adsorbents based on crown ethers or calixarenes for cesium removal will be meaningful, but it is still not yet comprehensive if without the consideration of their application as adsorbents for cesium ions.

This review mainly focused on the extraction and adsorption of cesium ions based on crown ethers and calixarene derivatives. Special attention was paid to the coordinating agents (e.g. crown ether and calixarenes) and the coordinating polymers (e.g. MOFs) due to their unique coordination ability and selectivity for cesium ions.

2. Crown ethers and calixarenes derivative

Since the first report of crown ethers in 1967, their unique coordinating properties have attracted great attention for alkali and alkaline earth cations [29]. Crown ethers are cyclic compounds consisting of several ether groups and can be functionalized by dibenzo, dicyclohexano, etc. Besides the simple crown ether, more sophisticated compounds with varying degrees of substitution have been developed.

Fig. 1 shows the simple crown ethers with varying degrees of substitution. These materials could be applied for cesium extraction with proper size match between targeted ions and the crown ethers' cavity.

Calixarenes are derived from the word 'calix' and 'arene' referring to its structural feature (resembling a vase) and aromatic building block, respectively. Specially, calix[4]arenes, which is constituted by four phenol units bridged with methylene groups, have attracted great attention for cesium removal [31]. Unsubstituted calix[4]arenes owe four kinds of conformations, including cone, partial cone, 1,3-alternate, and 1,2-alternate, as shown in Fig. 2(a). The introduction of crown ethers with n oxygen atoms on the polyethylene glycol chain, known as calix[4]arenes-crowns-n, can limited the variation of calix[4]arenes conformations, making them more rigid and showing higher coordination ability for
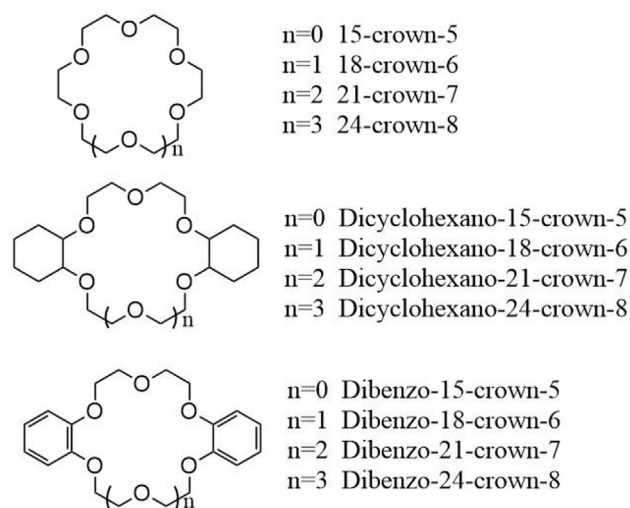

	n=0 15-crown-5
	n=1 18-crown-6
	n=2 21-crown-7
	n=3 24-crown-8
	n=0 Dicyclohexano-15-crown-5
	n=1 Dicyclohexano-18-crown-6
	n=2 Dicyclohexano-21-crown-7
	n=3 Dicyclohexano-24-crown-8
	n=0 Dibenzo-15-crown-5
	n=1 Dibenzo-18-crown-6
	n=2 Dibenzo-21-crown-7
	n=3 Dibenzo-24-crown-8

Fig. 1. Chemical structure of crown ethers.

specific metal ions [29]. The structural modification of calix[4]arenes and the appended crown ethers has a great effect on its selectivity of metal ions and solubility in alkane solvent [36,37]. For example, the polyethylene glycol chain of six oxygen atoms was more efficient and selective for cesium than other calix[4]arene derivatives containing five or seven oxygen atoms [38]. Fig. 2 also presents the chemical structure of several calix[4]arenes-crowns ethers [39–41]. Compared with simple crown ethers, it shows higher selectivity of cesium ions, although it is still relatively expensive for large scale application [42,43].

Calix[4]pyrrole is a macrocyclic compound composing of four pyrrole units with four fully substituted carbon atoms linking through their 2 and 5 positions [44]. It also has four possible conformations similar to unsubstituted calix[4]arenes, as shown in Fig. 3(**1a-1d**). It has been extensively studied as an attractive framework for the construction of multi-topic ion pair receptors that can concurrently bind Lewis basis anion by pyrrole NH-anion hydrogen bonds in organic media and target cations by functionalized pre-organized binding motifs (e.g. crown ethers and calixarenes). Fig. 3(**2–4**) presents some examples of its derivatives [44–46].

3. Solvent extraction for Cs separation

Solvent extraction is a conventional separation method based on the relative solubility of the target material in two different immiscible liquids. Despite the disadvantage of generating second waste, solvent extraction method has attracted much attention for cesium separation owing to its high selectivity, high efficiency, and convenience of operation. Additionally, there are situations where both carbonate and hydroxide anions can be extracted from the highly basic solution at the same time by the extractants, resulting in the reduction in pH without adding a proton source [47]. Herein, cesium extraction using crown ether, calix[4]arenes, and calix[4]pyrrole derivatives as extractants has been mainly discussed. Meanwhile, these extractants are the most extensively studies ones.

With cage structures, crown ethers can selectively extract Cs^+ by ion-dipole interaction between the cations and the negatively charged oxygen atoms of the polyether ring [29]. Although there have been substantial reports on the extraction of cesium ions by crown ethers, feasible process based on solely simple crown ethers extractants has not yet been successfully proved [43]. Table 1
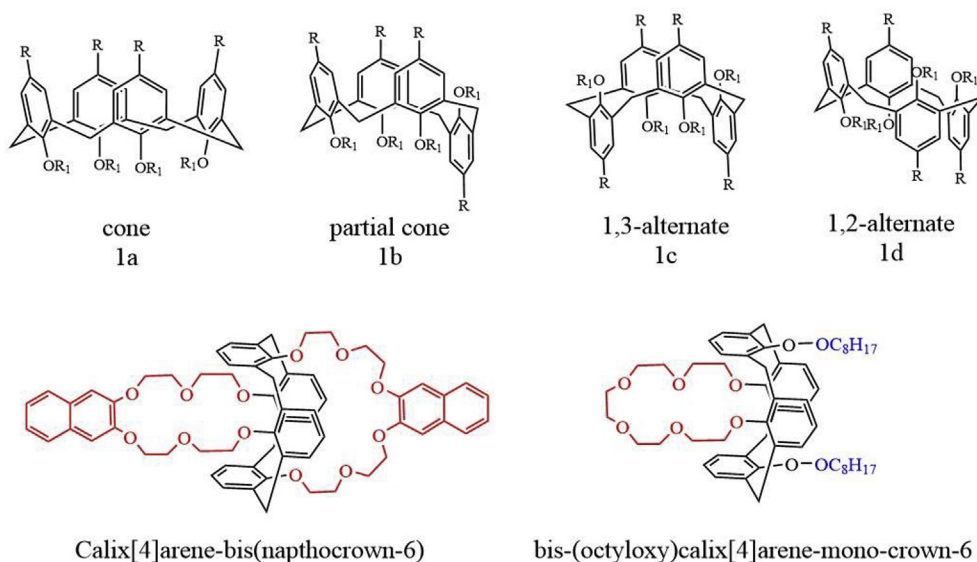
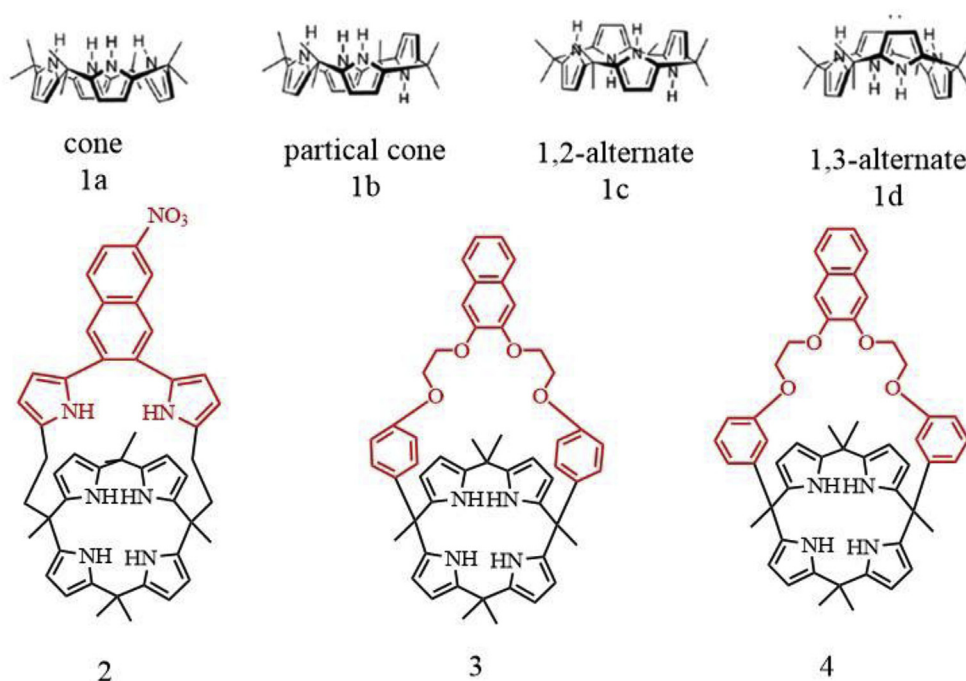**Fig. 2.** Chemical structures of various calix[4]arenes.

Fig. 3. Chemical structures of various calix[4]pyrrole.

presents the solvent extraction performance of some reported extractants towards cesium ions.

Crown ethers are chemically and radiolytically stable, which have been robust in chemically harsh, high-radioactivity environments. Therefore, they could be applied for separation of Cs^+ from radioactive wastes [43]. Russians separated a large quantity of radiocesium (about 10 MCi) from high-level waste in 1990s.

Recently, calixarenes with appended crown ethers have been developed for cesium extraction. Compared with simple crown ethers, they showed higher selectivity of cesium ions. Besides this, it is stable in acidic media [55] and can be easily stripped from the solvent by using water or dilute nitric acid solutions. However, it is relatively expensive. Therefore, it is of great importance to improve

the synthetic methods to make the price of calix[4]arenes more acceptable [39].

So far, calix[4]arenes-crowns-6 derivatives have been attracted great attention for cesium extraction due to its the presence of suitable pre-organized cavities in their frame work. According to the NMR and XRD analysis, cesium ions not only coordinated with the O of methylene groups, but also had a π-interaction with two opposite aromatic rings [56]. Furthermore, the selectivity of the complexation also depends on the modification of the calix[4] arenes. It has proved that additional aromatic groups, such as benzo and naphtho, and electron-donating groups, such as amino groups, could strength the cation-π interaction [57]. Besides the classical CH_2-bridged carlixarenes, Liu, et al. (2016) synthesized a new

Table 1
Extraction performance of some reported crown ethers and calixarenes derivatives.

Extractants	Chemical conditions for separation	Distribution ratio (D) for Cs^+	Separation factor (SF)	Refs
p-*tert*-butylsulfonylcalix[4]arene (SC4A)	Organic phase: 10^{-3} M SC4A in $CHCl_3$; aqueous phase: $[Cs^+] = [Sr^{2+}] = 10^{-4}$ M, pH = 6, T = 298 K; phase ratio = 1	Log D = 1.4	$SF_{Cs/Na} = 58.94$ $SF_{Cs/K} = 115.4$	[48]
18C6 DTBuB18C6 CC-A CC-B CC-C	Organic phase: 4.8×10^{-3} M ligand in nitrobenzene; Aqueous phase: 3 M HNO_3, simulated high level waste for pressurized heavy water reactor	5.20 (CC-A) < 37.48 (CC−B) < 51.16 (CC−C)		[49]
CalixBBC	Organic phase: 8.0×10^{-3} M CalixBBC in nitroanisole or chloroform Aqueous phase: $[Cs^+] = 5.0 \times 10^{-4}$ M; $[HNO_3] = 3.0/5.0$ M T = 298 K; phase ratio = 1	74.26 (CalixBBC/o-nitroanisole)	D values of other metals (e.g. Na, K, Rb, Sr, Ba, Ru, and Fe) are lower than 10.	[50]
DEHC[4]C6 DOC[4]DBC6 DOC[4]C6 DOC[4]BC6	Organic phase: 0.05 M ligand in chloroform Aqueous phase: 3 M HNO_3, $[CsCl] = 1 \times 10^{-5}$ T = 298 K; phase ratio = 1:3 (O:A)	3.6 (DEHC[4]C6) 3.8 (DOC[4]DBC6) 6.5 (DOC[4]C6) 8.6 (DOC[4]BC6)		[51]
PMMA-b-PSC4Py	Organic phase: 2 mM ligands in dichloromethane (5 mL) Aqueous phase: 5 mM solutions of CsF, CsCl, CsBr, KF, and NaF (5 mL each) phase ratio = 1		CsF > CsCl > CsBr CsF > KF > NaF	[52]
D(tBB)21C7	Organic phase: D(tBB)2lC7 and the organophilic sulfonic acid (HDDNS) in toluene Aqueous phase: 0.1 M nitric acid; 0.01	100	Cs > Rb > K > Na $SF_{Cs/Rb} = 1.2$ $SF_{Cs/K} = 5.6$ $SF_{Cs/Na} = 294$	[53]
Dibenzo-21-crown-7 derivatives	Organic phase: [crown ether] = 0.2 M in TBP Aqueous phase: 4 M nitric acid;	0.71−3.78	Maximum: $SF_{Cs/Na}$: 30	[54]

extractant, p-*tert*-Butylsulfonylcalix[4]arene (SC4A), which showed a high selectivity for both Cs^+ and Sr^{2+} simultaneously, as well as good radiation stability under the irradiation dose about 10^4−10^6 Gy. The coordination feature of SC4A: Sr and SC4A: Cs were 2:1 and 1:1, respectively [48]. More work should be done to further identify the mechanisms between cesium ions and calix[4]arenes.

The solvent has significant influence on Cs extraction by calix[4]arenes [49]. found that organic diluents were of great importance for Cs^+ extraction, and they followed the order of nitrobenzene > dichloroethane > chloroform > decanol ≫ carbon tetrachloride ~ n-hexane ~ toluene with calix[4]arene-bis(crown-6) as extractants. The interaction between H_3O^+ and nitrobenzene in the water-nitrobenzene extraction system was studied [58]. With the application of theoretical DFT calculation, as well as experimental study, the stability constant of extractant (E) with hydroxonium cation (H_3O) in nitrobenzene (nb) was calculated to be $log\beta_{nb}(E - H_3O^+, 25°C) = 5.9\pm0.2$, whilst $log\beta_{nb}(E - Cs^+, 25°C) = 9.0\pm0.1$. The optimal nitric acid concentration for the maximum cesium extraction efficiency was affected by extractants and diluents [50,51]. Additionally, ionic liquids were also used as solvents for cesium extraction, and some of them showed higher extraction efficiency than conventional systems [59]. Furthermore, synchrotron techniques combined with computer simulations were utilized to study the role of toluene solvent in the coordination of cesium ions by calix[4]pyrrole [28]. The results illustrated the cation−pi interactions in solvation of receptor-bound cations.

Previously, great efforts have been devoted to develop ion receptor for cesium ions. Nowadays, attention has also been paid into the ion-pair receptor (e.g. calix[4]pyrroles derivatives) that can concurrently bind both cation and anion [55], such as CsF [56], CsCl [37], $CsNO_3$ [57], Cs_2CO_3 and CsOH [47].

Besides cesium ions, the extraction of anionic ions at the same time has many benefits. The selective extraction of particular anionic ions could meet some specific requirements. For example, the extraction of OH^- and CO_3^{2-} as their cesium salts could decrease the pH value of the solutions without introducing ions [47]. In addition, the selective extraction of CsF by a calix[4]pyrrole-calix[4]arene pseudodimer was reported [60]. Especially, the extraction of

F^- or Cs^+ rarely occur if both ions did not existent in the same solution at the same time [61]. [52] also reported a diblock copolymer containing a calix[4]pyrrole anion binding subunit and a crown ether-like cation recognition motif for the simultaneously selective extraction of CsF. Reverse micelles were formed in the organic media owing to the copolymer self-assembles upon ion pair complexation, as shown in Fig. 4 [52].

The role of dilute solvents in cesium extraction by calix[4]pyrrole has been uncovered [28]. An interesting discovery was found by EXAFS analysis and molecular simulation that the aromatic solvents, toluene molecules, were bonded onto the open face of the cation-receptor complex by π-donor interactions and "capping the calix".

4. Adsorption for Cs separation

The adsorption capacity of adsorbents mainly relies on the coordinating structure [62,63]. Due to the extraordinary selectivity for cesium ions, sophisticated moieties (e.g. crown ethers and calixarene derivatives) were loaded into supporters by physical impregnation and chemical grafting methods [64]. Compared to chemical method, physical impregnation of coordinating agents into porous materials via intermolecular forces is simpler, but may suffer from the loss of effective active ingredients over operation time because of the weak interaction. Whilst, chemical grafting via covalent attachment could minimize the loss of extractants, but the subtle changes in ligand steric hindrance may greatly affect its reactivity [2].

So far, adsorbents bearing crown ethers/calixarenes derivatives and calixarenes-based metal-organic-frameworks [65] have been reported. With extractants of high affinity for cesium ions, this kind of adsorbents can not only efficiently adsorb cesium ions, but also avoid the secondary waste. This process is also known as solid-phase extraction or extraction chromatography [9,66]. Furthermore, as some of the calixarene derivatives have been applied as fluorescent optical chemosensors for cesium ions, their functionalized counterparts is likely to offer micromolar sensitivity and easily readable outputs (e.g. color/fluorescence change) of cesium detection results [67].
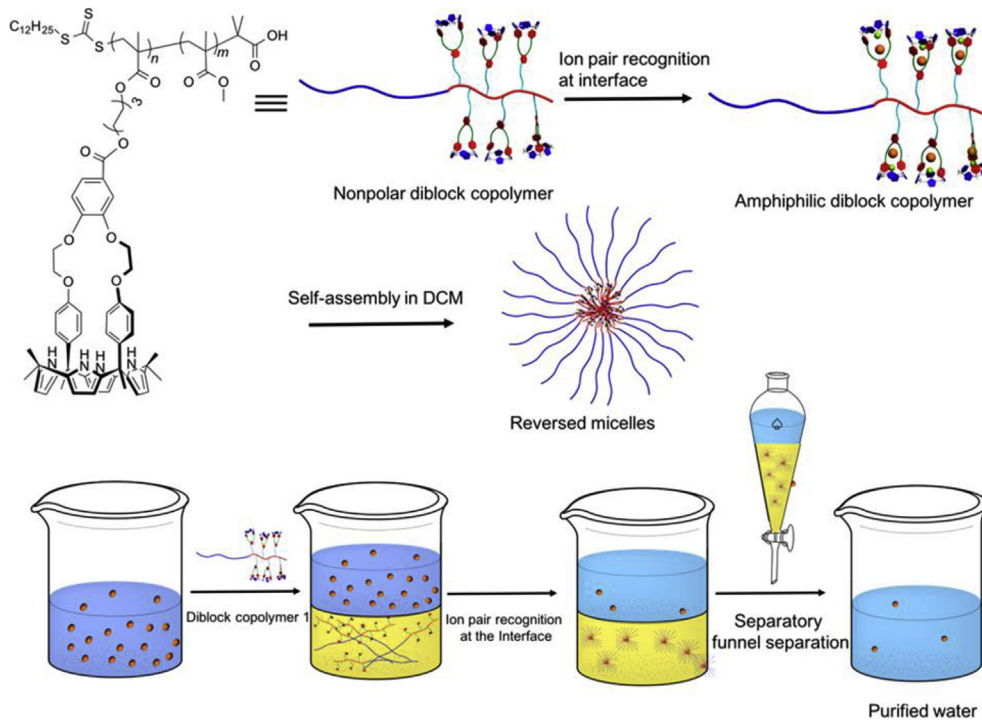
Fig. 4. Diblock copolymer and its self-assembly process for cesium extraction.

4.1. Adsorbents bearing crown ethers

Substantial crown ethers/calixarene derivatives have been tentatively grafted into various kinds of solids. Generally speaking, solid materials with or without adsorption capacity can be applied as the support of the synthetic adsorbents, as long as it is stable and modifiable. With high specific surface area, some inorganic materials have been applied as the support, such as SiO_2 [35,64,68]. As more artificial polymer become commercial available and economy acceptable, the modification and application of these artificial materials (e.g. fibers) for versatile purposes has become popular [66]. In addition, the application of magnetic particles as the supports can enrich the adsorbents with magnetic separation ability [69]. Table 2 shows the adsorption performance of some reported adsorbents bearing crown ether and calixarene derivatives.

Several methods can induce ligand grafting, such as conventional chemical reaction, irradiation, and plasma induced methods.

Compared to conventional chemical routines, radiation grafting induced by plasma and alpha rays needs neither chemical initiators nor other additives, which is more economy and easier control. However, it may arouse chain scissor or other kinds of structure damage. Additionally, physical methods, such as densely direct immobilization, has also been reported, yet it may suffer from elution [35].

Substantial crown ethers/calixarene derivatives have been reported being grafted into adsorbents, yet not always satisfying in terms of cesium adsorption from aqueous solutions. On the one hand, the structural modification may disturb the electronic cloud distribution resulting in the failure of the supramolecular complexation [73] One the other hand, these extractants show more affinity for cesium ions in organic solvents than rather than aqueous solutions [57].

The immobilization of macrocyclic ligand, dibenzo-24-crown-8 ether(DB24C8) onto inorganic mesoporous silica for cesium

Table 2
The adsorption performances of some reported adsorbents towards cesium ions.

Adsorbents	Supporters	Activate agents	Immobilization method	Adsorption conditions	Capacity (mg/g)	Selectivity	Refs
Conjugate adsorbent	Inorganic silica	Dibenzo-24-crown-8 ether	Physical method	$[Cs^+]$ = 0.038−0.75 mM; pH = 7.0; dosage = 10 mg/10 mL	77.70	$Cs^+>Na^+$ and K^+ (competitive sorption)	[35]
Calix[4] BNaphC@SiO$_2$−P.	SiO_2−P	1,3-calix[4]arene-bis(naph-crown-6)	Covalent connection	[Metal] = 5 mM; dosage = 0.25 g/5 mL; 3.0 M HNO$_3$; 298 K.	Removal percentage: >99.1%	$Cs^+> Rb^+ \gg Na^+, K^+, Ba^{2+}, Sr^{2+}, Rd^{2+}, Fe^{3+}$	[9]
Poly(AAc-co-B18C6Am) hydrogels	Polymers	benzo-18-crown-6-acrylamide	Covalent connection	$[Cs^+]$ = 2 mM; dosage = 9 g/L; pH = 6.0; 298 K	74.6	$Cs^+>K^+>Na^+>Li^+$	[70]
Fe$_3$O$_4$@18-Crown-6	Fe$_3$O$_4$@R −COOH particles	4′-formamidobenzo-18-crown-6	Covalent connection	Dosage = 0.1 g/50 L, 298 K	26.98	$Cs^+>NH_4^+>Rb^+>K^+>Na^+>Li^+$	[71]
C7C6CalixSi	Silica	C7C6Calix	Physical method	Dosage = 0.25 g/5 mL; 1.0 M HNO$_3$, 298 K, and a contact time of 120 min	0.1233 mM/g	Cs(I) over the other 9 metals, except for Rb(I). $SF_{Cs/Sr}$ = 116.3; $Sr_{Cs/Rb}$ = 0.131	[72]

removal has been developed by [35]. Besides high adsorption capacity (77.70 mg g^{-1}), it remained high selectivity for cesium ion even in the presence of high concentration of Na$^+$ and K$^+$. Although DB24C8 was immobilized onto silica by physical method, which avoided the destruction of the coordination structures, the as-prepared conjugate adsorbent could be regeneration several time without significant deterioration and adsorption capacity loss.

A new silica-calix[4]biscrown material was synthesized, and the effect of contact time and HNO$_3$ concentration on cesium removal was studied [9]. The results showed that CalixBNaphC6@SiO$_2$—P exhibited an excellent uptake capacity and selectivity for cesium ions than other metal ions, except for Rb$^+$ [74]. separated cesium ions from aqueous solutions using hollow fiber supported liquid membranes containing bis-(octyloxy)calix[4]arene-mono-crown-6.

18-Crown-6 ether functional groups were covalently connected into magnetic Fe$_3$O$_4$ particles via amidation reaction for the adsorption of cesium ions into its holes [71]. The as-prepared adsorbents showed a high adsorption selectivity for cesium ions in the presence of other co-existing ions. According to the DFT calculation, compared with other cations (K$^+$, Rb$^+$ and NH$_4^+$), Cs$^+$ binding with crown ethers was stronger with a binding energy of −70.02 kcal/mol.

Ion-recognizable hydrogels (poly(AAc-co-B18C6Am)) were synthesized for cesium removal [70]. The crown ether (B18C6Am) enriched the adsorbents with a good adsorption selectivity for cesium ions by forming stable "sandwich" Cs$^+$(B18C6Am)$_2$ complexes. Additionally, cesium ions could also be attracted by the positive charged Amm units by electrostatic attraction.

A ternary solid-state supramolecular adsorbent, composing of polymeric carrier (XAD-7), 25,27-bis(1-n-propoxy)-calix[4]26,28-crown-6 (for cesium selective adsorption), and 4,4′(5′)-di-*tert*-butyldicyclohexano-18-crown-6 (for Sr^{2+} selective adsorption), was synthesized for the simultaneous adsorption of Cs and Sr [75]. The adsorption capacity of 0.1396 mM/g and 0.1289 mM/g was achieved for Cs and Sr, respectively.

Azo-based probes for radioisotopes were synthesized by grafting basic orange 2 into alginate [75]. Besides the ability to removal cesium, cobalt, and strontium ions, the synthetic adsorbents could quantitatively detect cobalt and strontium ions with the help of RGB coordinates, yet not for cesium ions [75], providing an important direction for the development of cesium probe adsorbents.

Scintillator, Hf^{4+}, was introduced into the zeolite for the adsorption and announcement of radionuclides, such as ^{201}Tl and ^{137}Cs [76]. Their luminescence spectra recorded by UV- and X-irradiation and range from 300 nm to 720 nm, peaking about 400 nm. The luminescence structures were well studied and four possible luminescence mechanisms were proposed.

An interesting discovery of gallium—antimony—sulfide anion's selective incarceration for cesium ions has been found. Besides wide pH endurance, this adsorbent would prevent the leaching out of cesium ions through dynamically closing its holes, which is composed of 16-atom rings, as shown in Fig. 5 [77].

4.2. Metal-organic frameworks based on calixarene derivatives

Metal-organic frameworks (MOFs), which are prepared by reaction between organic linkers and metal ions by coordinative bonding, are an emerging class of porous materials that have attracted great attention in the fields of catalysis, sensing, adsorption, etc. due to its high specific surface areas (500—4500 m^2/g), facile functionalization and tunable pore size [78]. Its chemical tunability and structural diversity make it a viable candidate for cesium adsorbents [79].

The physicochemical structure of MOFs depends on the metal nodes and organic ligands. Its modification strategies were presented in Fig. 6, including metal node/linker modification and hybridization. The functionalization of ligands is mainly responsible for metal adsorption. The application of calix[4]arenes for the design of MOFs is favored owing to (a) their different conformations as shown in Fig. 3; (b) many coordinating sites by functionalization
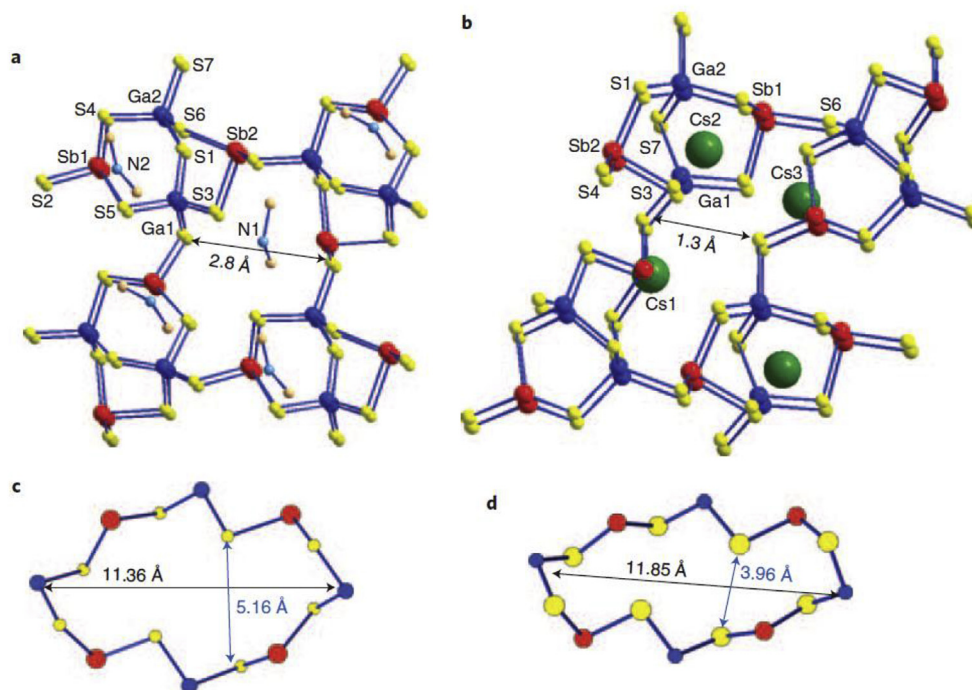

Fig. 5. (a) Pristine compound I; (b) Cs$^+$-exchanged product II; 16-membered ring of I and II in its (c) 'open' window state before cesium capture and (d) 'closed' state in response to Cs$^+$ insertion.
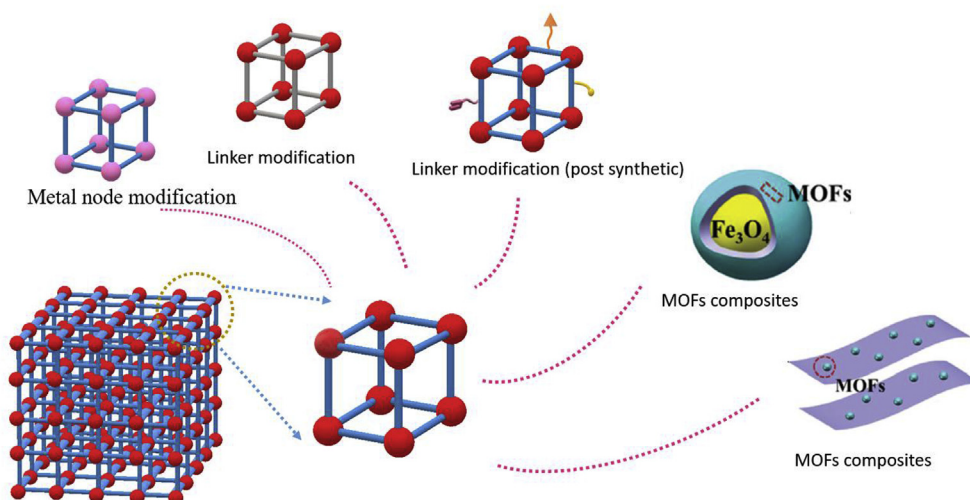
Fig. 6. Modification of MOFs by various strategies.

of the rims; and (c) facile functionalization. Recently, a review focusing on structure and properties of calixarene derivatives-based coordination polymers was published [65]. This kind of MOF is a potential and promising adsorbent for selective extraction of cesium ions [79].

So far, only several reports were related to the cesium adsorption by MOFs, whilst none calixarene derivatives-based coordination polymers for cesium adsorption was found [65,80,81]. In fact, the application of MOFs as adsorbents for metal removal has been limited by several factors. The preparation of MOFs with desired ligands capable of cesium coordination needs specific designed. However, most reported calixarene derivatives-based MOFs are initially intended for gas storage [82], not for cesium removal from aqueous solutions. Additionally, their stability in different aqueous solutions still remain to be seen, which may lead to secondary pollutions. Therefore, several MOFs, although not based on calixarene derivatives, were presented here for showing their application prospect in cesium adsorption.

5. Concluding remarks and perspectives

The utilization of nuclear power required the development of separation technology to address environmental damage from the release of radionuclides. Due to its relative long half-life, radio-cesium is the major radioactive source of radioactive wastewater in later periods of the nuclear decay. However, the removal of cesium ions is not that easy, due to the high concentration of background ions, especially Na^+ and K^+, and the instinct nature of the monovalent alkali metal ions the cesium ions belong to.

Different methods such as chemical precipitation, coagulation/co-precipitation, solvent extraction, membrane process, chemical reduction, and adsorption have been used to remove radioactive cesium from aqueous solution. Recently, crown ethers and calixarenes derivative, which are promising coordinating structures for cesium ions, have been extensively studied for cesium extraction and adsorption.

For cesium extraction, crown ethers and calixarene derivatives were the most widely studied extractants. So far, particular attention has been given to calix[4]arenes with appended crown ethers. The unique guest-host structure enriches calix[4]arenes with a high cesium selectivity and a high decontamination factor in spite of the extreme pH condition and interference from the high concentration of background ions. Considering the high efficiency of

calix[4]arenes for cesium extraction, more work should be done to decrease its cost, as well as develop more environmental friendly diluents, such as ionic liquids and supercritical carbon dioxide. Furthermore, more types of crown ether or calixarene-based extractants with high a discrimination towards cesium ions should be developed, together with the corresponding efficient processes for industrial application.

For cesium adsorption, a new strategy has also been developed by introducing coordinative structure for cesium ions onto adsorbents. In this review, particular attention has been given to adsorbents bearing coordinating groups (e.g. crown ether and calixarenes) and coordinating polymers (e.g. MOFs) due to their unique coordination ability and selectivity for cesium ions. Adsorbents grafting with these coordinating groups by physicochemical methods showed high adsorption capacity for cesium ions. However, the further improvement of its adsorption capacity is limited by the grafting ratio, as well as the space resistance. Additionally, the widely adopted chemical grafting method may deteriorate their coordination ability, which is bad for cesium adsorption. More research works should be done to get insights into their coordination mechanisms and to provide guidance in grafting method and route for the synthesis of crown ether or calixarene-based adsorption materials. On the other hand, the new star coordinating polymers, MOFs, also showed great potential in cesium removal with several kinds of MOFs been reported. Coordination polymers based on calixarene derivatives have been extensively studies, although not yet reported for cesium removal. It should be noted that the design and formation of coordination polymers based on calixarene derivatives is still challenging. Compared to grafting method, the highly ordered porous structures are rich in coordinating ligands, which can be pre-organized or post-modification. In addition, their luminescence properties may enrich the adsorbents with detecting function for cesium ions. It will be a promising direction for future research. Furthermore, in future work, the attention should also be paid to the identification of the adsorption process with novel technology, such as XANES, which will provide deep understanding on the adsorption process and mechanisms of cesium separation from radioactive wastes.

Acknowledgments

References

[1] J.L. Wang, S.T. Zhuang, Y. Liu, Metal hexacyanoferrates-based adsorbents for cesium removal, Coord. Chem. Rev. 374 (2018) 430–438.

[2] J.L. Wang, S.T. Zhuang, Removal of cesium ions from aqueous solutions using various separation technologies, Rev. Environ. Sci. Biotechnol. 18 (2019) 231–269.

[3] Y.-H. Koo, Y.-S. Yang, K.-W. Song, Radioactivity release from the Fukushima accident and its consequences: a review, Prog. Nucl. Energy 74 (2014) 61–70.

[4] B.C. Russell, I.W. Croudace, P.E. Warwick, Determination of ^{135}Cs and ^{137}Cs in environmental samples: a review, Anal. Chim. Acta 890 (2015) 7–20.

[5] J. Beyea, E. Lyman, F.N. von Hippel, Accounting for long-term doses in "worldwide health effects of the Fukushima Daiichi nuclear accident", Energy Environ. Sci. 6 (2013) 1042–1045.

[6] J.E. Ten Hoeve, M.Z. Jacobson, Worldwide health effects of the Fukushima Daiichi nuclear accident, Energy Environ. Sci. 5 (2012) 8743–8757.

[7] T.P. Valsala, M.S. Sonavane, S.G. Kore, N.L. Sonar, V. De, Y. Raghavendra, S. Chattopadyaya, U. Dani, Y. Kulkarni, R.D. Changrani, Treatment of low level radioactive liquid waste containing appreciable concentration of TBP degraded products, J. Hazard Mater. 196 (2011) 22–28.

[8] K. Kosaka, M. Asami, N. Kobashigawa, K. Ohkubo, H. Terada, N. Kishida, M. Akiba, Removal of radioactive iodine and cesium in water purification processes after an explosion at a nuclear power plant due to the Great East Japan Earthquake, Water Res. 46 (2012) 4397–4404.

[9] A. Zhang, W. Zhang, Y. Wang, X. Ding, Effective separation of cesium with a new silica-calix[4]biscrown material by extraction chromatography, Separ. Purif. Technol. 171 (2016) 17–25.

[10] X.J. Liu, J.L. Wu, J.L. Wang, Removal of Cs(I) from simulated radioactive wastewater by three forward osmosis membranes, Chem. Eng. J. 344 (2018) 353–362.

[11] F. Jia, J.L. Wang, Separation of cesium ions from aqueous solution by vacuum membrane distillation process, Prog. Nucl. Energy 98 (2017) 293–300.

[12] F. Jia, J.F. Li, J.L. Wang, Y.L. Sun, Removal of cesium from simulated radioactive wastewater using a novel disc tubular reverse osmosis system, Nucl. Technol. 197 (2017) 219–224.

[13] H.Y. Liu, J.L. Wang, Treatment of radioactive wastewater using direct contact membrane distillation, J. Hazard Mater. 261 (2013) 307–315.

[14] Y.M. Hu, X. Guo, C. Chen, J.L. Wang, Algal sorbent derived from Sargassum horneri for adsorption of cesium and strontium ions: equilibrium, kinetics, and mass transfer, Appl. Microbiol. Biotechnol. 103 (2019) 2833–2843.

[15] J.L. Wang, S.Z. Wang, Preparation, modification and environmental application of biochar: a review, J. Clean. Prod. 227 (2019) 1002–1022.

[16] Y.N. Yin, J. Hu, J.L. Wang, Removal of Sr^{2+}, Co^{2+}, and Cs^+ from aqueous solution by immobilized *saccharomyces cerevisiae* with magnetic chitosan beads, Environ. Prog. Sustain. Energy 36 (2017) 989–996.

[17] J.L. Wang, S.T. Zhuang, Removal of various pollutants from water and wastewater by modified chitosan adsorbents, Crit. Rev. Environ. Sci. Technol. 47 (2017) 2331–2386.

[18] L.J. Xu, J.L. Wang, The application of graphene-based materials for the removal of heavy metals and radionuclides from water and wastewater, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1042–1105.

[19] Y.W. Chen, J.L. Wang, Removal of cesium from radioactive wastewater using magnetic chitosan beads cross-linked with glutaraldehyde, Nucl. Sci. Tech. 27 (2016) 1–6.

[20] J.L. Wang, C. Chen, Chitosan-based biosorbents: modification and application for biosorption of heavy metals and radionuclides, Bioresour. Technol. 160 (2014) 129–141.

[21] J.L. Wang, C. Chen, Biosorbents for heavy metals removal and their future, Biotechnol. Adv. 27 (2009) 195–226.

[22] J.L. Wang, C. Chen, Biosorption of heavy metals by Saccharomyces cerevisiae: a review, Biotechnol. Adv. 24 (2006) 427–451.

[23] D. Cui, J. Low, K. Spahiu, Environmental behaviors of spent nuclear fuel and canister materials, Energy Environ. Sci. 4 (2011) 2537–2545.

[24] R.D. Shannon, Revised effective ionic radii and systematic studies of inter-atomic distances in halides and chalcogenides, Acta Crystallogr. A 32 (1976) 751–767.

[25] D. Alby, C. Charnay, M. Heran, B. Prelot, J. Zajac, Recent developments in nanostructured inorganic materials for sorption of cesium and strontium: synthesis and shaping, sorption capacity, mechanisms, and selectivity-A review, J. Hazard Mater. 344 (2018) 511–530.

[26] J.C. Fanning, The solubilities of the alkali-metal salts and the precipitation of Cs^+ from aqueous-solution, Coord. Chem. Rev. 140 (1995) 27–36.

[27] S.T. Zhuang, Y.N. Yin, J.L. Wang, Removal of cobalt ions from aqueous solution using chitosan grafted with maleic acid by gamma radiation, Nucl. Eng. Technol. 50 (2018) 211–215.

[28] R.J. Ellis, B. Reinhart, N.J. Williams, B.A. Moyer, V.S. Bryantsev, Capping the calix: how toluene completes cesium(I) coordination with calix[4]pyrrole, Chem. Commun. 53 (2017) 5610–5613.

[29] C.J. Pedersen, Cyclic polyethers and their complexes with metal salts, J. Am. Chem. Soc. 89 (1967) 7017–7036.

[30] P.V. Bonnesen, L.H. Delmau, B.A. Moyer, G.J. Lumetta, Development of effective solvent modifiers for the solvent extraction of cesium from alkaline high-level tank waste, Solvent Extr. Ion Exch. 21 (2003) 141–170.

[31] J.F. Dozol, M. Dozol, R.M. Macias, Extraction of strontium and cesium by dicarbollides, crown ethers and functionalized calixarenes, J. Inclusion Phenom. Macrocycl. Chem. 38 (2000) 1–22.

[32] W.W. Schulz, L.A. Bray, Solvent extraction recovery of byproduct ^{137}Cs and ^{90}Sr from HNO$_3$ solutions—a technology review and assessment, Separ. Sci. Technol. 22 (1987) 191–214.

[33] B.J. Mincher, G. Modolo, S.P. Mezyk, Review article: the effects of radiation chemistry on solvent extraction: 2. A review of fission-product extraction, Solvent Extr. Ion Exch. 27 (2009) 331–353.

[34] N.A. Bezhin, I.I. Dovhyi, Sorbents based on crown ethers: preparation and application for the sorption of strontium, Russ. Chem. Rev. 84 (2015) 1279–1293.

[35] M.R. Awual, T. Yaita, T. Taguchi, H. Shiwaku, S. Suzuki, Y. Okamoto, Selective cesium removal from radioactive liquid waste by crown ether immobilized new class conjugate adsorbent, J. Hazard Mater. 278 (2014) 227–235.

[36] I.V. Kolesnichenko, E.V. Anslyn, Practical applications of supramolecular chemistry, Chem. Soc. Rev. 46 (2017) 2385–2390.

[37] T.A. Hanna, L. Liu, A.M. Angeles-Boza, X. Kou, C.D. Gutsche, K. Ejsmont, W.H. Watson, L.N. Zakharov, C.D. Incarvito, A.L. Rheingold, Synthesis, structures, and conformational characteristics of calixarene monoanions and dianions, J. Am. Chem. Soc. 125 (2003) 6228–6238.

[38] T.G. Levitskaia, L. Maya, G.J. Van Berkel, B.A. Moyer, Anion partitioning and ion-pairing behavior of anions in the extraction of cesium salts by 4,5'-Bis(tert-octylbenzo)dibenzo-24-crown-8 in 1,2-dichloroethane, Inorg. Chem. 46 (2007) 261–272.

[39] C. Xu, J.C. Wang, J. Chen, Solvent extraction of strontium and cesium: a review of recent progress, Solvent Extr. Ion Exch. 30 (2012) 623–650.

[40] P. Jagasia, P.K. Mohapatra, P.S. Dhami, P.M. Gandhi, P.K. Wattal, Evaluation of novel solvent systems containing calix-crown-6 ligands in a fluorinated solvent for cesium extraction from nitric acidic feeds, Separ. Sci. Technol. 49 (2014) 2151–2157.

[41] P. Jagasia, P.S. Dhami, P.K. Mohapatra, S.A. Ansari, S.Y. Jadhav, G.K. Kalyankar, P.M. Gandhi, U.K. Kharul, Recovery of radio-cesium from actual high level liquid waste using solvents containing calix[4]arene-crown-6 ligands, J. Environ. Chem. Eng. 5 (2017) 4134–4140.

[42] D.R. Raut, P.K. Mohapatra, S.A. Ansari, A. Sarkar, V.K. Manchanda, Selective transport of radio-cesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier, Desalination 232 (2008) 262–271.

[43] T.A. Todd, T.A. Batcheller, J.D. Law, R.S. Herbst, Cesium and Strontium Separation Technologies Literature Review, Idaho Falls, Idaho, 2004.

[44] S.K. Kim, J.L. Sessler, Calix[4]pyrrole-based ion pair receptors, Acc. Chem. Res. 47 (2014) 2525–2536.

[45] S.K. Kim, H.G. Lee, G.I. Vargas-Zuniga, V.M. Lynch, C. Kim, J.L. Sessler, Naphthocrown-strapped calix[4]pyrroles: formation of self-assembled structures by ion-pair recognition, Chemistry 20 (2014) 11750–11759.

[46] J. Yoo, M.S. Kim, S.J. Hong, J.L. Sessler, C.H. Lee, Selective sensing of anions with calix[4]pyrroles strapped with chromogenic dipyrrolylquinoxalines, J. Org. Chem. 74 (2009) 1065–1069.

[47] Q. He, G.M. Peters, V.M. Lynch, J.L. Sessler, Recognition and extraction of cesium hydroxide and carbonate by using a neutral multitopic ion-pair receptor, Angew. Chem., Int. Ed. Engl. 56 (2017) 13396–13400.

[48] C. Liu, D.X. Zhao, L.T. Zhao, P. Zhang, X. Lu, S.N. He, Extraction property of p-tert-butylsulfonylcalix 4 arene possessing irradiation stability towards cesium(I) and strontium(II), Appl. Sci. 6 (2016) 212–219.

[49] P.K. Mohapatra, S.A. Ansari, A. Sarkar, A. Bhattacharyya, V.K. Manchanda, Evaluation of calix-crown ionophores for selective separation of radio-cesium from acidic nuclear waste solution, Anal. Chim. Acta 571 (2006) 308–314.

[50] Y. Dai, R. Lv, Z. Liu, Q. Tao, Z. Zhang, Y. Liu, Extraction behavior of cesium from nitric acid medium with calix[4]-bis[(4-tert-butyl-1,2-phenylene)-crown-6], J. Radioanal. Nucl. Chem. 318 (2018) 2079.

[51] M. Simonnet, Y. Miyazaki, S. Suzuki, T. Yaita, Quantitative analysis of Cs extraction by some dialkoxycalix[4]arene-crown-6 extractants, Solvent Extr. Ion Exch. 37 (2019) 81–95.

[52] X. Chi, G.M. Peters, C. Brockman, V.M. Lynch, J.L. Sessler, Controlling structure beyond the initial coordination sphere: complexation-induced reversed micelle formation in calix[4]pyrrole-containing diblock copolymers, J. Am. Chem. Soc. 140 (2018) 13219–13222.

[53] W.J. McDowell, G.N. Case, J.A. McDonough, R.A. Bartsch, Selective extraction of cesium from acidic nitrate solutions with didodecylnaphthalenesulfonic acid synergized with bis(tert-butylbenzo)-21-crown-7, Anal. Chem. 64 (2002) 3013–3017.

[54] M.L. Dietz, E. Philip Horwitz, M.P. Jensen, S. Rhoads, R.A. Bartsch, A. Palka, J. Krzykawski, J. Nam, Substituent effects in the extraction of cesium from acidic nitrate media with macrocyclic polyethers, Solvent Extr. Ion Exch. 14 (2007) 357–384.

[55] A. Zhang, Q. Hu, Removal of cesium by countercurrent solvent extraction with a calix[4]crown derivative, Separ. Sci. Technol. 52 (2017) 1670–1679.

[56] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R.J.M. Egberink, F. de Jong, D.N. Reinhoudt, Synthesis, complexation, and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: a new class of cesium selective ionophores, J. Am. Chem. Soc. 117

(1995) 2767–2777.

[57] R. Yi, New Magnetic Composites for Adsorption toward Stronitum and Cesium: Synthesis and Adsorption Behavior Study, Tsinghua University, 2016, p. 128.

[58] M. Kvíčalová, E. Makrlík, S. Böhm, P. Vaňura, Z. Asfari, Protonation of calix[4]arene-(2,3-naphthylene-crown-6,crown-6): experimental and theoretical study, J. Mol. Struct. 1134 (2017) 722–727.

[59] T. Takahashi, T. Ito, S.Y. Kim, Selective extraction of Cs(I) using 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene in ionic liquid solvents and its application to the treatment of high-level liquid waste, J. Radioanal. Nucl. Chem. 316 (2018) 1067–1073.

[60] J.L. Sessle, S.K. Kim, D.E. Gross, C.-H. Lee, J.S. Kim, V.M. Lynch, Crown-6-calix[4]arene-capped calix[4]pyrrole: an ion-pair receptor for solvent-separated CsF ions, J. Am. Chem. Soc. 130 (2008) 13162–13166.

[61] S.K. Kim, J.L. Sessler, D.E. Gross, C.H. Lee, J.S. Kim, V.M. Lynch, L.H. Delmau, B.P. Hay, A calix[4]arene strapped calix[4]pyrrole: an ion-pair receptor displaying three different cesium cation recognition modes, J. Am. Chem. Soc. 132 (2010) 5827–5836.

[62] T. Ito, Y. Xu, S.-Y. Kim, R. Nagaishi, T. Kimura, Adsorption behavior and radiation effects of a silica-based (Calix(4)+Dodecanol)/SiO$_2$-P adsorbent for selective separation of Cs(I) from high level liquid waste, Separ. Sci. Technol. 51 (2015) 22–31.

[63] M.A. Olatunji, M.U. Khandaker, H.N.M.E. Mahmud, Y.M. Amin, Influence of adsorption parameters on cesium uptake from aqueous solutions- a brief review, RSC Adv. 5 (2015) 71658–71683.

[64] M.T. Albelda, J.C. Frias, E. Garcia-Espana, H.J. Schneider, Supramolecular complexation for environmental control, Chem. Soc. Rev. 41 (2012) 3859–3877.

[65] A. Ovsyannikov, S. Solovieva, I. Antipin, S. Ferlay, Coordination polymers based on calixarene derivatives: structures and properties, Coord. Chem. Rev. 352 (2017) 151–186.

[66] P.K. Parhi, Supported liquid membrane principle and its practices: a short review, J. Chem. 2013 (2013) 1–11.

[67] N. Kumar, I. Leray, A. Depauw, Chemically derived optical sensors for the detection of cesium ions, Coord. Chem. Rev. 310 (2016) 1–15.

[68] M.R. Awual, T. Yaita, Y. Miyazaki, D. Matsumura, H. Shiwaku, T. Taguchi, A reliable hybrid adsorbent for efficient radioactive cesium accumulation from contaminated wastewater, Sci. Rep. 6 (2016) 19937.

[69] R. Yi, G. Ye, F. Wu, D. Lv, J. Chen, Magnetic solid-phase extraction of strontium using core–shell structured magnetic microspheres impregnated with crown ether receptors: a response surface optimization, J. Radioanal. Nucl. Chem. 308 (2015) 599–608.

[70] H.-R. Yu, J.-Q. Hu, Z. Liu, X.-J. Ju, R. Xie, W. Wang, L.-Y. Chu, Ion-recognizable hydrogels for efficient removal of cesium ions from aqueous environment, J. Hazard Mater. 323 (2017) 632–640.

[71] Z. Liu, Y. Zhou, M. Guo, B. Lv, Z. Wu, W. Zhou, Experimental and theoretical investigations of Cs$^+$ adsorption on crown ethers modified magnetic adsorbent, J. Hazard Mater. 371 (2019) 712–720.

[72] A. Zhang, C. Chen, Y. Ji, S. Liu, S. Guo, Uptake of cesium and some typical metals onto hybrid calix[4]crown adsorbent with silica carrier by host–guest recognition, J. Chem. Eng. Data 63 (2018) 1578–1587.

[73] A. Leoncini, J. Huskens, W. Verboom, Ligands for f-element extraction used in the nuclear fuel cycle, Chem. Soc. Rev. 46 (2017) 7229–7273.

[74] P. Jagasia, S.A. Ansari, D.R. Raut, P.S. Dhami, P.M. Gandhi, A. Kumar, P.K. Mohapatra, Hollow fiber supported liquid membrane studies using a process compatible solvent containing calix[4]arene-mono-crown-6 for the recovery of radio-cesium from nuclear waste, Separ. Purif. Technol. 170 (2016) 208–216.

[75] A. Jo, G. Jang, H. Namgung, C. Kim, D. Kim, Y. Kim, J. Kim, T.S. Lee, Simultaneous detection and removal of radioisotopes with modified alginate beads containing an azo-based probe using RGB coordinates, J. Hazard Mater. 300 (2015) 227–234.

[76] J.Y. Kim, H.J. Kim, N.H. Heo, K. Seff, Progress toward zeolite-based self-luminous sensors for radioactive isotopes such as ^{201}Tl and ^{137}Cs: structures and luminescence of Hf, Cl, Tl-A and Hf, Cl, Cs, Na-A, J. Phys. Chem. C 121 (2017) 19619–19633.

[77] N. Ding, M.G. Kanatzidis, Selective incarceration of caesium ions by Venus flytrap action of a flexible framework sulfide, Nat. Chem. 2 (2010) 187–191.

[78] S. Naeimi, H. Faghihian, Performance of novel adsorbent prepared by magnetic metal-organic framework (MOF) modified by potassium nickel hexacyanoferrate for removal of Cs$^+$ from aqueous solution, Separ. Purif. Technol. 175 (2017) 255–265.

[79] Y. Wang, Z. Liu, Y. Li, Z. Bai, W. Liu, Y. Wang, X. Xu, C. Xiao, D. Sheng, D. Juan, J. Su, Z. Chai, T.E. Albrecht-Schmitt, S. Wang, Umbellate distortions of the uranyl coordination environment result in a stable and porous polycatenated framework that can effectively remove cesium from aqueous solutions, J. Am. Chem. Soc. 137 (2015) 6144–6147.

[80] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, Chem. Soc. Rev. 47 (2018) 2322–2356.

[81] C. Xiao, M.A. Silver, S. Wang, Metal-organic frameworks for radionuclide sequestration from aqueous solution: a brief overview and outlook, Dalton Trans. 46 (2017) 16381–16386.

[82] Z. Zhang, A. Drapailo, Y. Matvieiev, L. Wojtas, M.J. Zaworotko, A calixarene based metal organic material, calixMOM, that binds potassium cations, Chem. Commun. 49 (2013) 8353–8355.