A Multisite-Functionalised Polymer for the Extraction of Thorium(IV) from Water

Journal:	*RSC Advances*
Manuscript ID:	RA-COM-02-2015-002622.R2
Article Type:	Communication
Date Submitted by the Author:	14-Apr-2015
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A Multisite‒Functionalised Polymer for the Extraction of Thorium(IV) from Water[†]

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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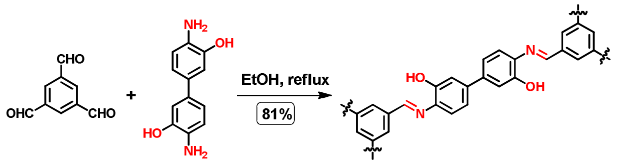
A multisite functionalised polymer (MFP-1) was synthesized and applied in the effective extraction of Thorium (Th(IV)) ions from water, which exhibits a maximum Th(IV) sorption capacity of 0.39 mmol/g at 298 K and pH 3.8. Moreover, MFP-1 can be easily recycled for at least 3 times and the radioactive Th(IV) could be enriched via this process.

During the last century, the radioactive pollution has induced more and more public concerns because of their high toxicity. Accordingly, great efforts are being made to develop the methods for the separation of the radioactive ions from the waste waters. The developed methods include chemical precipitation[1, 2], sorption[3-5], ion exchange[6, 7], liquid extraction[8, 9], supercritical fluid extraction[10], and extraction chromatography[11]. Among them, the method based on the sorption is highly effective and economical, and many types of materials have been used as sorbents[12-15]. For example, the inorganic zeolites have been utilized to separate and recover the uranium and thorium ions from the aqueous solutions[3]. Nevertheless, most of the developed sorbents exhibit a low adsorption capacity[12-15], and new materials are being explored as sorbents for the separation of the radioactive ions. Accordingly, we reported herein the construction of a functional organic polymer as a sorbent for the separation of radioactive ions.

In the design of such sorbents, the basic concern is their chelating ability and stability[16]. The chelating ability of the sorbents directly determines their sorption capacity, while the stability affects their recycle use. In this regard, organic polymers, which are made by linking organic building blocks together using covalent bonds, might be ideal candidates as efficient sorbents for the separation of radioactive ions. Careful selection of the constituents can yield organic polymers with diverse functionalities. Various strong chelating ligands can be incorporated into the organic polymers, which may lead to sorbents with a high sorption capacity. The imine-type ligands have been well-established as one of the strongest chelating ligands in the field of coordination chemistry[17-19]. Given their strong chelating ability, the imine-based materials are widely used in environmental chemistry for the sorption and recovery of contaminants[17, 19]. Accordingly, we synthesized a novel multisite functionalised polymer (MFP-1) with large amounts of imine and hydroxyl groups. The imine and hydroxyl groups of MFP-1 could provide large amounts of chelating sites for the efficient separation of the radioactive ions.

As an example, MFP-1 was applied in the sorption of thorium (Th(IV)) ions because Th(IV) represents one of the most important radioactive ions. Meanwhile, Th(IV) is extremely dangerous because of its severe radioactivity and toxicity even at very low level. In addition, Th(IV) can accumulate in living organisms and thus causing diseases[20, 21]. The effect of pH, ionic strength, and temperature were examined in the sorption of Th(IV) by MFP-1. The sorption experiments revealed that MFP-1 exhibits a maximum Th(IV) sorption capacity of 0.39 mmol/g at 298 K and pH 3.8. Furthermore, MFP-1 could be easily reused for at least 3 times and the radioactive Th(IV) could be enriched via this process. The excellent sorption performance of MFP-1 toward Th(IV) ions is mainly due to the strong chelating ligands (imine and hydroxyl groups) and the robust imine linkages.



1 **2** **MFP-1**

Scheme 1. Facile synthesis of the imine and hydroxyl-functionalised organic polymer (MFP-1) via the condensation of **1** and **2** under solvothermal conditions with a high yield of 81%.

As shown in Scheme 1, the functional organic polymer, MFP-1, was “bottom-up” constructed from benzene-1,3,5,-tricarbaldehyde (**1**) and 3,3'-dihydroxybenzidine (**2**) in alcohol. The synthetic conditions are quite mild and the monomers can be facilely obtained from the cheap and commercially available compounds (see SI for details). Thus, MFP-1 can be easily prepared in a large scale manner for further practical applications. With the robust covalent linkage in its structure, MFP-1 is stable and insoluble in water and in common organic solvents (such as tetrahydrofuran (THF), acetone, dimethyl sulfoxide (DMSO), and *N*, *N*-dimethylformamide (DMF)). Importantly, MFP-1 is also stable in hydrochloric acid with the concentration of 0.01-0.10 mol/L (Fig. S2). The Fourier-transform infrared (FT-IR) spectrum of MFP-1 exhibits a stretching vibration band at 1620 cm^{-1}, indicating the successful condensation of **1** and **2** via the formation of C=N bonds (Fig. S1).

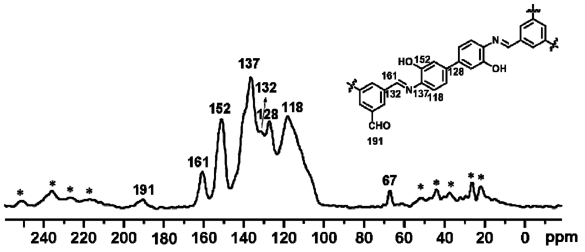


Fig. 1 ^{13}C CP/MAS NMR spectrum of MFP-1. Asterisks denote spinning sidebands. The assignments of ^{13}C chemical shifts of MFP-1 were indicated in the chemical structure. The minor signal at 67 ppm originated from the solvent.

The atomic-level structure of MFP-1 was further characterised by ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy (Fig. 1). The presence of a signal at *ca.* 161 ppm in the ^{13}C NMR spectrum of MFP-1 further confirm the successful condensation of **1** and **2** via the formation of C=N bonds. The signals at *ca.* 118, 128, 132, 137, and 152 ppm can be ascribed to the carbon atoms of the phenyl groups, while the minor peak at *ca.* 191 ppm is assigned to the carbon atoms of the terminal aldehyde groups in the MFP-1 network. Thus, MFP-1 was constructed through covalent bonds with large amounts of imine and hydroxyl groups.

As mentioned above, the imine and hydroxyl groups have strong chelating ability toward various metal ions. Th(IV) ions has been recognized as one of the most significant radioactive metal ions in environmental, which can accumulate in living organisms and thus causing several disorders and diseases. Therefore, new sorbents are being developed for the sorption and separation of Th(IV) ions from the waste waters. In this regard, MFP-1, which is functionalised by the imine and hydroxyl groups, could be utilized as new solid sorbents for Th(IV) ions. Therefore, MFP-1 was applied in the separation of Th(IV) ions from water.

The sorption of Th(IV) ions on MFP-1 as a function of pH was firstly investigated in 0.010 mol/L $NaClO_4$ solution (Fig. 2). The pH value from 2.0 to 12.0 was selected to find the optimum pH value for the sorption experiments. As shown in Fig. 2, when the pH value increases from 3 to 4, the sorption of Th(IV) ions on MFP-1 was greatly increased, indicating that the sorption of Th(IV) on MFP-1 is strongly dependent on pH. The large amount of Th(IV) ions absorbed on MFP-1 at slightly acidic conditions may be attributed to the complex formation between the Th(IV) ions and the chelating sites (imine and hydroxyl groups) on MFP-1. As the pH decrease, the chelating sites are protonated and their ability for coordination with Th(IV) ions decreases. The surface of MFP-1 would be covered by hydronium ions (H_3O^+) which could strongly affect the complex formation between the Th(IV) ions and the MFP-1. With the increase of the pH, the chelating sites on MFP-1 are released, resulting in the significant increase of the sorption. However, at higher pH (pH > *ca.* 4), the precipitation of $Th(OH)_4$ may be formed, which could contribute the rapid increase of Th(IV) sorption. Based on the species simulation (Fig. S6), the precipitation of $Th(OH)_4$ is formed at pH > *ca.* 4.3. In the case of MFP-1, more than 90% of Th(IV) has been absorbed below pH 3.8, indicating that the increase of the sorption of Th(IV) is mainly contributed by MFP-1 and the pH 3.8 was chosen as the standard conditions in the following tests.

To assess the effect of the amount of MFP-1, the sorption of Th(IV) with the solid-to-liquid (MFP-1 : solvent) ratio at 0.50, 0.25 and 0.01 g/L was examined. As shown in Fig. 2A, the sorption of Th(IV) by MFP-1 was increased with the increasing of the solid-to-liquid ratio at pH < 4, indicating that the sorption of Th(IV) by MFP-1 was strongly influenced by the solid-to-liquid ratio.

The concentration of ionic strength would also influence the sorption capacity of Th(IV) on MFP-1. Fig. 2B illustrated the removal percentage of Th(IV) by MFP-1 as a function of pH in 0.001, 0.010, and 0.100 mol/L $NaClO_4$ solutions. The sorption of Th(IV) on MFP-1 were almost the same in the different concentration of $NaClO_4$, indicating that the concentration of cation (Na^+) insignificantly influenced the sorption capacity of MFP-1.

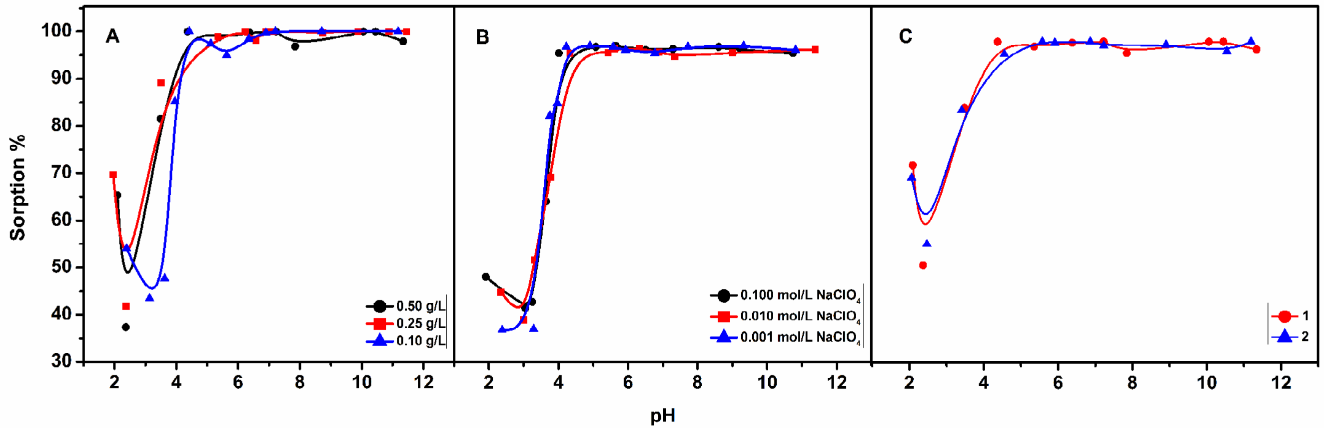


Fig. 2 The effect of pH on Th(IV) sorption by MFP-1. (A) solid-to-liquid ratio(S/L), I = 0.01 mol/L $NaClO_4$(black S/L = 0.50 g/L blue S/L = 0.25 g/L red S/L = 0.10 g/L). (B) Ionic strength, m/V = 0.10 g/L(black I = 0.100 mol/L blue I = 0.010 mol/L red I = 0.001 mol/L). (C) Pre-equilibrium process, m/V = 0.10 g/L; I = 0.010 mol/L $NaClO_4$. (1. Adding MFP-1, DDW, $NaClO_4$ and Th(IV) to a polyethylene tubing at the same time; 2. The mixture of MFP-1, DDW, $NaClO_4$ was vibrated for 24 h in a polyethylene tubing and then the Th(IV) ions was added.)

The pre-equilibrium tests was further conducted to verify whether the pre-equilibrium process would influence the sorption of Th(IV) on MFP-1. As shown in Fig. 2C, the sorption of Th(IV) with the addition of MFP-1 in different sequence were almost the same, indicating the pre-equilibrium process has no effect on the the sorption of Th(IV) on MFP-1.

Temperature was another important parameter to understand the sorption of radionuclides (Fig. S3). As shown in Table 1, the sorption capacity of MFP-1 increased from 0.41 to 10.5 mmol/g with the increasing of the temperature from 298 to 338 K at pH 3.8, indicating that the integrative sorption process of Th(IV) is endothermic[22-24]. With the increasing of the initial concentration of Th(IV), the sorption capacity of MFP-1 was also increased (Fig. S3). The increased sorption capacity of MFP-1 in these conditions may be attributed to the acceleration of the diffusion of Th(IV) ions from the bulk solution to the adsorbent surface of MFP-1.

To further analyse the sorption process, both the Langmuir and Freundlich models are evaluated based on the sorption isothermals[25, 26]. Langmuir sorption isotherm model is commonly used for monolayer sorption onto a surface containing amount of identical sites, while the Freundlich equation is basically empirical in nature and it assumes the sorption occurs on the heterogeneous surfaces[27, 28]. The Langmuir (Fig. 3) and Freundlich **(**Fig. S4) model for MFP-1 in the sorption of Th(IV) were obtained based on the experimental data. As shown in Table 1, the values of the correlation coefficient (R^2) showed that the Langmuir model gave a better fit to the sorption isotherm. From the Langmuir sorption isotherm model, the theoretical value Q_{max} for MFP-1 was 0.41 mmol/g at 298K and pH 3.8, which fitted the experimental value Q of 0.39 mmol/g[29]. This value represents an excellent sorption of Th(IV), which is superior to many other materials[16, 30, 31]. Relevant data calculated from these equations were listed in Table 2. ΔS^0 and ΔH^0 were calculated from the intercept and slope of the plot of $\ln K_d$ vs. 1/T (Fig. 4), respectively. The value of ΔH^0 = 59.22 kJ/mol indicates that the removal of ions from water was essentially an endothermic process, *i.e.*, the sorption of Th(IV) ions on MFP-1 are more efficient at higher temperature. The values of ΔG^0 were -12.65, -14.06, -14.91, -18.36 and -22.67 kJ/mol at 298, 308, 318, 328 and 338 K, respectively. The values of K_{sp} were 2×10^{-45} and 2×10^{-30} at T = 298 K and T = 338 K(SI), respectively, indicating that Th(IV) might not precipitate out of the solution at the selected pH and different temperature. All the values of ΔG^0 at different temperature are below 0 indicating that the sorption was a spontaneous process. The decrease in the value of ΔG^0 with the increase of the temperature indicated that the sorption was more favorable at higher temperature. The positive values of entropy change (ΔS^0) may be attributed to some of the structure of MFP-1 changed in aqueous solutions, which resulting from the affinity of MFP-1 toward Th(IV) ions[32].

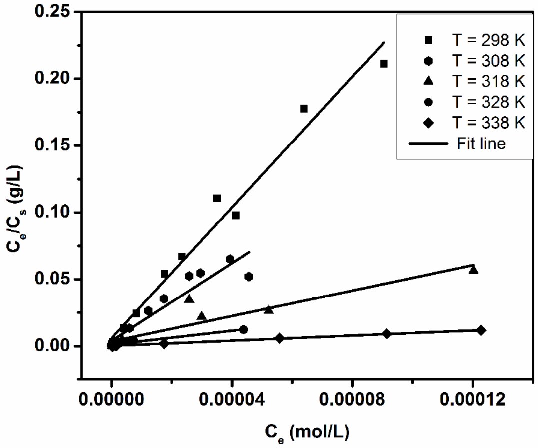


Fig. 3 Fitting lines of the Langmuir sorption isotherms of Th(IV) by MFP-1 at different temperatures (m/V = 0.10 g/L, pH = 3.8 ± 0.05, and I = 0.010 mol/L $NaClO_4$).

To examine the selectivity of MFP-1 in the separation of Th(IV) ions, the sorption capacity of UO_2^{2+} ions on MFP-1 was further tested (Fig. S8). The results show that there was a platform on the UO_2^{2+} adsorption curve at the sorption percentage of 35% at the pH 3.8–4.3, while the sorption percentage of Th(IV) was 70–90% under the same conditions. This result indicated that the MFP-1 can selectively adsorb Th(IV) at the pH range of 3.8–4.3.

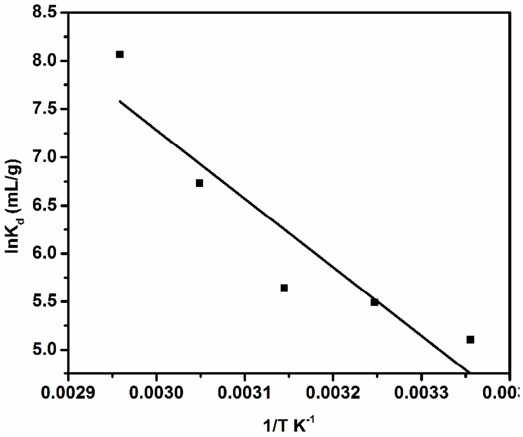


Fig. 4 Effect of temperature on the distribution coefficients of Th(IV) on MFP-1 (m/V = 0.10 g/L, pH = 3.8 ± 0.05, I = 0.010 mol/L $NaClO_4$).

Table 1 Parameters of Langmuir and Freundlich models at different temperatures.

	Langmuir				Freundlich	
T(K)	C_{max} (mmol/g)	*b*[a]	R^2	K_F[b]	1/n[c]	R^2
298	0.41	4.03×10^5	0.9784	0.0021	5.9587	0.6596
308	0.75	3.24×10^5	0.8989	0.0069	4.2900	0.7420
318	2.11	1.34×10^5	0.8672	0.0436	2.9584	0.7220
328	3.86	2.18×10^5	0.9674	1.0661	1.8506	0.8307
338	10.38	3.07×10^5	0.9839	1.0290	2.2143	0.4971

[a] *b* is Langmuir constant. [b] K_F is the Freundlich constant, which indicates the sorption capacity. [c] n is the surface heterogeneity factor.

Table 2 The thermodynamic data of Th(IV) sorption on MFP-1.

T (K)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
298	59.22	0.24	-12.65
308	59.22	0.24	-14.06
318	59.22	0.24	-14.91
328	59.22	0.24	-18.36
338	59.22	0.24	-22.67

The recycle use of MFP-1 in the separation of Th(IV) was further examined. The batch tests of pH effect indicated that the adsorbed Th(IV) on MFP-1 could be released to the acidic solution. The strong complexation could occur between the Th(IV) ions and the chlorine ions, the desorption tests were thus conducted with various concentrations (0.01, 0.10 and 1.00 M) of HCl solutions. The loading operations were carried out by adding 50 mg of MFP-1 and 60 mL of Th(IV) ions in a 100 mL polyethylene pipe at pH = 3.8 ± 0.05, and shaking for 24h. The desorption operations were carried out by shaking the polymer with 30 mL of HCl solutions in 100 mL polyethylene pipes. As shown in Fig. 5, MFP-1 could be reused successively at least for three times without significant loss of sorption capacity. The Fig. S7 also shown that the chemical composition and the connection was stable at the sorption-desorption recycle. The FT-IR spectra of MFP-1 before and after the recycle indicates that MFP-1 is stable in the sorption tests (Fig. S2). Therefore, the 0.01 mol/L solution of HCl could be used as the efficient desorbent for the recycle use of MFP-1. Moreover, the radioactive Th(IV) could be enriched via this process

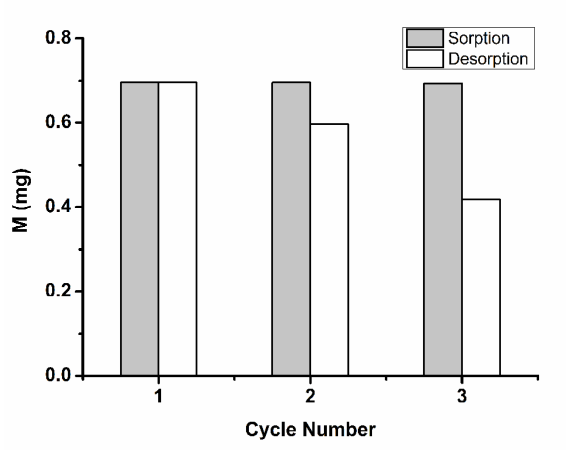


Fig. 5 Recycle use of MFP-1 in the separation of Th(IV) (pH = 3.8 ± 0.05, I = 0.010 mol/L $NaClO_4$).

Conclusion

In conclusion, we have demonstrated that a multisite-functionalised polymer (MFP-1) can be constructed from simple starting materials and applied in the separation of Th(IV) ions. The maximum Th(IV) sorption capacity for MFP-1 was 0.39 mmol/g at 298 K and pH 3.8, which is superior to many other materials. The high sorption capacity of Th(IV) ions is mainly attributed to the abundant functional groups (imine and hydroxyl groups) within MFP-1. Furthermore, MFP-1 could be easily recycled for at least 3 times and the Th(IV) could be readily enriched via this process. Therefore, it is believed that MFP-1 could be utilized as effective absorbents for the removal and recovery of Th(IV) from water. In addition, this research highlights the construction of various functional organic polymers for the separation of diverse radioactive ions.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NO. J1210001 and 21327801) and the Fundamental Research Funds for the Central Universities (lzujbky-2013-235). We thank Prof. Wei Wang (Lanzhou University) for helpful discussion.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: Additional experimental characterizations details, FT-IR, absorption curves, TEM. See DOI: 10.1039/c000000x/

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