A Perylenediimide-Based Organic Microcrystal for the Efficient Removal of Uranium Dissolved in Aqueous Solution

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1. Introduction

Since the tragedies in Chernobyl and Fukushima, the removal of radionuclides from nuclear wastes including nuclear fuel effluent and gaseous radioactive wastes has become even more critical due to their toxicity for the nature and human. Many types of materials have been studied as sorbents to capture radionuclides such as cesium, iodide and uranium [1, [2, [3]. In this study, an organic microcrystals derived from perylenediimide was synthesized and tested for the removal of uranium dissolved in acidic aqueous solution. The resultant adsorption capacity towards uranium was among the highest ever reported. Other characteristics including selectivity, kinetics and pH dependence is under investigation.

2. Methods and Results

2.1 Synthesis of an Organic Microcrystal Sorbent

In general, perylenediimide derivatives are hardly soluble in any kind of solvents including water due to their pronounced capabilities of self-assembly by means of π - π stacking [4]. Therefore they can be considered as light-weight supporting materials comprising functional groups to capture uranium in aqueous solution. Aminoisophthalic acid with two carboxylic acid groups can provide the strong binding sites to uranium. Thus we designed and synthesized organic microcrystals as a high capacity sorbent derived from condensation reaction between perylenediimide and aminoisophthalic acid. For the synthesis of N,N'-Di-(phenyl-3,5-dicarboxylic acid)-perylene-3,4:9,10-tetracarboxylic acid diimide (T-PR), perylene-3,4,9,10-tetracarboxylic dianhydride, 5-aminoisophthalic acid, and imidazole were mixed and heated at 127 °C for 6 hours under nitrogen atmosphere (Fig. 1). The mixture was further refluxed after addition of ethanol for 6 hours and then kept for overnight to be crystallized out. The crystalline precipitate was filtered and washed thoroughly with ethanol.

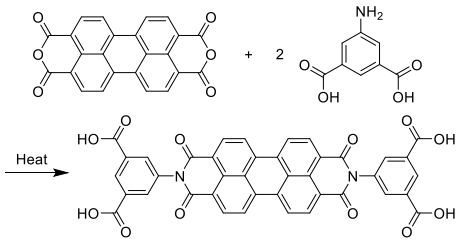

Fig. 1. Synthesis of T-PR.

2.2 Uranium Adsorption Test

$UO_2(NO_3)_2{\cdot}2H_2O$ was dissolved in deionized water to prepare uranium solutions for batch test. In order to test uranium adsorption by T-PR at various uranium concentrations, solutions with 6, 12, 25, 50, 100, 200, 400 and 1000 ppm U were prepared. pH of each solution was adjusted to 5 by adding NaOH solution. 2 mg of T-PR was added to a glass vial with 3 mL of uranium solution, and then the mixture was thoroughly stirred with magnetic stir bar for 5 hours. The resultant solution was centrifuged at 10,000 g for 5 min, and the supernatant was collected for metal analysis using inductively-coupled plasma mass spectrometry.

3. Results and Discussion

The amount of UO_2^{2+} adsorbed per the amount of adsorbent (q, mg U/g T-PR) was plotted against equilibrium concentration (C_e, ppm). The adsorption data can be fitted very well with Langmuir-Freundlich isotherm model [5]. This model describes adsorption of adsorbate onto a homogeneous surface with assumption that a maximum uptake is given. The Langmuir-Freundlich isotherm can be expressed as eq. 1:

$$q = q_m \frac{(bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \quad \text{(eq. 1)}$$

where q (mg/g) is the amount of uranium adsorbed at equilibrium concentration C_e (ppm), q_m is the maximum uranium adsorption capacity (mg/g), b (L/mg) a constant related to the free energy of the adsorption representing affinity of adsorbate and adsorbent, and n is a constant characterizing the system heterogeneity.

From the fitting, the maximum uranium adsorption capacity of T-PR was determined, and it was close to the highest value among physicochemical adsorbents ever reported.

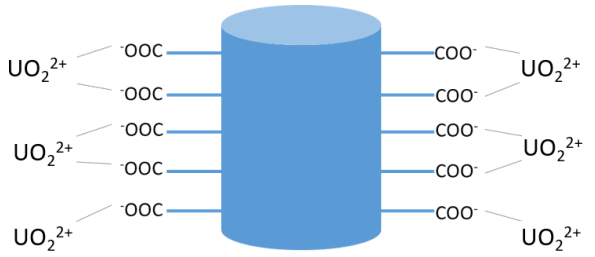

Fig. 2. Schematic model of the uranium adsorption onto the organic microcrystal.

3. Conclusions

A preliminary experiment for applying an organic microcrystal to uranium capture from aqueous solution has been performed successfully. T-PR microcrystal exhibited an excellent capability to remove a large amount of uranium from water and its capacity was among the highest reported so far. We hypothesize that positively charged uranyl ions bind to negatively charged carboxylates on the organic microcrystals. In order to figure out the adsorption mechanism, deliberate studies are required, utilizing spectroscopic and structural analysis tools such as infrared and X-ray diffraction spectroscopies. Nevertheless, perylene-diimide derivatives as sorbent materials appear to be one of the good research targets for the remediation of the uranium contaminated environment.

REFERENCES

[1] D. Yang, S. Sarina, H. Zhu, H. Liu, Z. Zheng, M. Xie, S.V. Smith and S. Komarneni, Capture of Radioactive Cesium and Iodide Ions from Water by Using Titanate Nanofibers and Nanotubes, Angew. Chem. Int. Ed. 50 (2011) 10594-10598

[2] B. Li, C. Bai, S. Zhang, X. Zhao, Y. Li, L. Wang, K. Ding, X. Shu, S. Li and L. Ma, An adaptive supramolecular organic framework for highly efficient separation of uranium via an in situ induced fit mechanism, Journal of Materials Chemistry A 3 (2015) 23788-23798

[3] M.-L. Feng, D. Sarma, X.-H. Qi, K.-Z. Du, X.-Y. Huang and M.G. Kanatzidis, Efficient Removal and Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate, J. Am. Chem. Soc. 138 (2016) 12578-12585

[4] P.K. Sukul, D. Asthana, P. Mukhopadhyay, D. Summa, L. Muccioli, C. Zannoni, D. Beljonne, A.E. Rowan and S. Malik, Assemblies of perylene diimide derivatives with melamine into luminescent hydrogels, Chem. Commun. 47 (2011) 11858-11860

[5] D.D. Do, Adsorption Analysis : Equilibria and Kinetics, Series on Chemical Engineering 2 (1998) 57-63