様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月 １６ 日現在

機関番号：１１３０１
研究種目：研究活動スタート支援
研究期間：2020～2021
課題番号：２０Ｋ２２３２０

研究課題名（和文）Adsorption and separation behaviors of Cs-137 from high level liquid waste by a novel porous covalent organic frameworks (COFs) based adsorbent

研究課題名（英文）Adsorption and separation behaviors of Cs-137 from high level liquid waste by a novel porous covalent organic frameworks (COFs) based adsorbent

研究代表者
呉　昊（Wu, Hao）

東北大学・工学研究科・助教

研究者番号：７０８８１７９６

交付決定額（研究期間全体）：（直接経費）　　2,200,000円

研究成果の概要（和文）：高レベル放射性廃液中に含まれている発熱性を有する核分裂生成物であるセシウム（Cs）を目標とする元素は新型共有結合性有機構造体（COF）による分離回収が期待される。本研究では、まず、優れた耐酸化性特性を有するCOF構造を設計して合成した。次は、Csに親和性の高い1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (calix[4]arene-R14)抽出材をCOFの穴に含浸したことで合成した吸着剤を用いることで本目標を達成することができる。

研究成果の学術的意義や社会的意義
Cesium (Cs) as one of the heat-generating fission products of a nuclear power plant has a long half-life of around 30 years and is also a strong gamma (γ) radiation emitter. The method developed in this study provides a new viewpoint for the efficient recovery of Cs from nitric acid solution.

研究成果の概要（英文）：An acid-stable 2D covalent organic framework (COF) was synthesized by a reversible Schiff base reaction and the following irreversible enol-keto tautomerism. Then, a novel composite was prepared by impregnating the 1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene(calix[4]arene-R14) analogues and their molecule modifiers into the pores of the prepared COFs support. Next, the adsorption performances of the prepared adsorbent for selective separation of cesium (Cs) from simulated high-level liquid waste and simulated radioactive contaminated wastewater were investigated under the effect of contact time, adsorption capacity, acid concentration etc.

研究分野：原子力化学

キーワード：共有結合性有機構造体　セシウム

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

1. 研究開始当初の背景

The high-level liquid waste (HLLW) generated by the plutonium uranium reduction extraction reprocessing process contains numerous nonvolatile fission products, long-lived minor actinides, trace amounts of uranium and plutonium, and corrosion products. Cesium (Cs) as one of the heat-generating (0.42 W/g) fission products of a nuclear power plant, has a long half-life of around 30 years, and is also a strong gamma (γ) radiation emitter. In particular, the chemical activity and high solubility of ^{137}Cs make it extremely harmful to human body, wherein it leads to the damage of tissues, and even cancer. Thus, the presence of Cs in HLLW is a matter of great public concern for the whole of society, and urgent measures should therefore be taken to remove it from the HLLW.

On the other hand, from previous studies, although silica, active carbon, zeolite, metal–organic framework (MOFs) etc. have been widely used in the extraction chromatography as a support in the separation of ^{137}Cs from HLLW, to find a more promising support is still urgent. Covalent organic framework (COF), which are mainly composed of light H, C, N, O elements through covalent bonding, have been attracted much attention in recent years as a novel kind of porous crystalline materials and exhibit a great potential in various fields such as catalysis, gas storage and separation, and drug carriers etc. While, synthetic procedures of COF have been mainly focused on reversible condensation reactions, such as the Schiff base reaction, Spiro-borane condensation, Knoevenagel condensation and imide condensation etc., the gradual collapse of predesigned crystalline framework structure of COF in highly acidic condition makes its application to be frustrating in the practical reprocessing process of HLLW.

2. 研究の目的

① Try to develop an acid-stable COF structure that could be applied even in highly acidic condition;

② Try to prepare a COF based adsorbent which can be applied to selectively recover Cs from nitric acid solution.

3. 研究の方法

①COF is firstly prepared by a combination of reversible and irreversible reactions using 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1). The first reversible Schiff base reaction facilitates to the formation of a crystalline framework. Exceptional resistance toward acid treatment could be realized through enhancing its chemical stability by the following irreversible enol-to-keto tautomerization (Fig. 1).

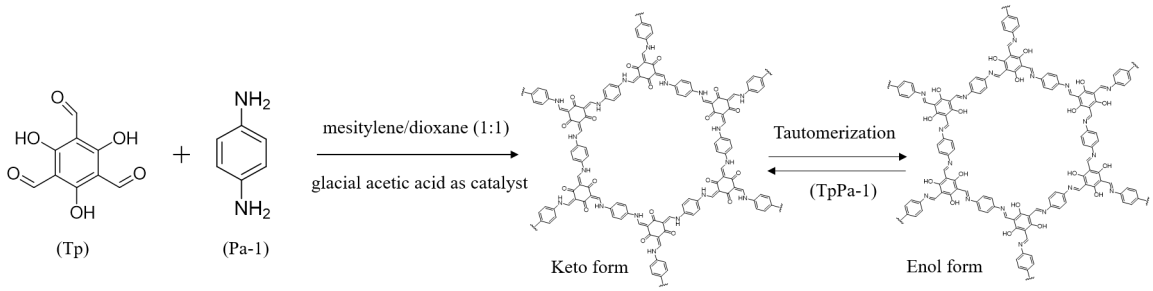

Fig. 1 Synthesis procedure of the acid-stable COF

② The extractant of 1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) and its modifier of 1-Dodecanol are selected as the materials used in this study for the selective recognition of Cs. Next, they are dissolved in dichloromethane in glass conical flash. Then the quantity of synthesized COFs support is added. The mixtures are stirred mechanically by a rotary evaporator. Calix[4]+1-Dodecanol will be impregnated into the pores of the prepared COF particles by evaporation and immobilization as shown in Fig. 2.

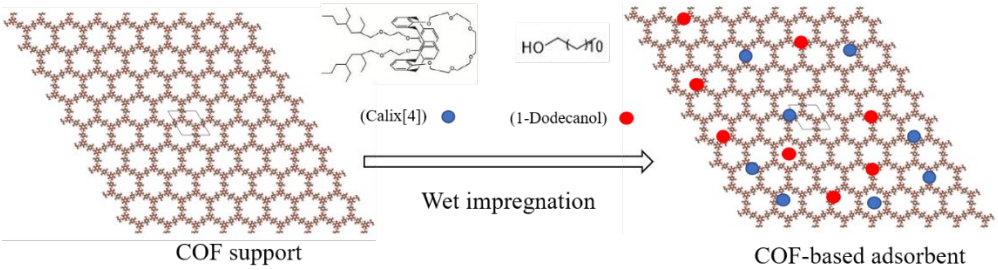

Fig. 2 Synthesis schematic of COF based adsorbent

4. 研究成果

① The prepared adsorbent exhibited fast adsorption kinetics toward Cs and the adsorption equilibrium could be attained within 1 h.

② With an increase in the nitric acid concentration, the adsorption performance toward Cs decreased gradually. While the structure of the prepared COF support could be remained intact in as high as 1 M HNO_3 condition.

The prepared COF based Calix[4] impregnated adsorbent exhibited good recognition toward Cs due to the impregnation of Calix[4] extractant. The prepared COF structure could be well-maintained in 1 M HNO_3 condition. The obtained experimental results support that the utilization of this type of acid-stable COF based adsorbent in HLLW to recover Cs is considered to be feasible.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　0件／うちオープンアクセス　1件）

１．著者名 Hao Wu, Seong-Yun Kim	４．巻 37
２．論文標題 Adsorption performances of an acid-stable 2D covalent organic framework towards palladium(II) in simulated high-level liquid waste	５．発行年 2021年
３．雑誌名 Analytical Sciences	６．最初と最後の頁 1～3
掲載論文のDOI（デジタルオブジェクト識別子） 10.2116/analsci.21C001	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Wu Hao、Kudo Tatsuya、Kim Seong-Yun、Miwa Misako、Matsuyama Shigeo	４．巻 54
２．論文標題 Recovery of cesium ions from seawater using a porous silica-based ionic liquid impregnated adsorbent	５．発行年 2021年
３．雑誌名 Nuclear Engineering and Technology	６．最初と最後の頁 1～9
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.net.2021.10.026	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Wu Hao、Kudo Tatsuya、Takahashi Tadayuki、Ito Tatsuya、Kim Seong-Yun	４．巻 330
２．論文標題 Impregnation of covalent organic framework into porous silica support for the recovery of palladium ions from simulated high-level liquid waste	５．発行年 2021年
３．雑誌名 Journal of Radioanalytical and Nuclear Chemistry	６．最初と最後の頁 1065～1074
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s10967-021-07971-x	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計1件（うち招待講演　0件／うち国際学会　0件）

１．発表者名 Hao Wu, Tatsuya Kudo, Seong-Yun Kim
２．発表標題 Adsorption Performance of Cs(I) by Silica-based Adsorbent Impregnating with Calixcrown and Ionic Liquid from Simulated High-level Liquid Waste
３．学会等名 日本原子力学会東北支部 第4 4 回研究交流会
４．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

―

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関