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研究課題名(和文) Development of A Coordination Polymer based Electro-Dialytic K Recovery System

研究課題名(英文) Development of A Coordination Polymer based Electro-Dialytic K Recovery System

研究代表者

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研究成果の概要(和文)：陰極と陽極の両方に最適化された材料を使用した電気透析システムの作成を目的としていた。しかし、いくつかの制限により、陽イオン、NH<sub>4</sub>イオン、Kイオンの吸着の半分のみが最適化出来た。目標結果は部分的に達成されたが、エネルギー効率とコスト効率も高く、汚染除去と資源の持続可能性に利用できるシステムが確立された。研究で最も困難だったのは、水中と電圧印加中に優れた安定性を維持する均一導電性セルを確立することでした。カーボンブラックなどの導電性材を追加すると、全体的なパフォーマンスが向上しますが、過剰に使用すると選択性が低下する可能性があります。

研究成果の学術的意義や社会的意義

In the field of ion recovery using ion-selective materials, a counter anion that can elute or desorb the adsorbed ion becomes necessary. With the use of electrochemical system, the desorption and material regeneration can be done using the electric voltage. This can be a truly green approach.

研究成果の概要(英文)：The research was aimed at the preparation of an electro-dialytic system with the optimized material for both cathode and anode. However, due to several limitations only half-cell of the adsorption of cations, ammonium and/or potassium ions was optimized. Though the target outcome was partly achieved, a system that can be utilized for decontamination and resource sustainability, which should be energy and cost-effective as well, was established. The most challenging part of the research was to establish a homogeneously conductive cell that holds good stability in water and during the application of voltage. The addition of some conducting materials like carbon black could enhance the overall performance, yet the overuse might lead to compromised selectivity. This work is still in the starting phase from the application point of view. Yet, the outcome provides enormous hope for the area of removal, recovery, and desalination.

研究分野：材料化学

キーワード：電気化学 水処理 イオン分離・回収

## 様式 C - 19、F - 19 - 1 (共通)

### 1. 研究開始当初の背景

Ion adsorption, separation, and recovery always involve the actions of anions and cations. In general ion exchange separations, anions or cations in the material are exchanged with target ions in the liquid, so the ion balance in the liquid can be naturally maintained. However, in electrochemical methods, electric current is passed through the electrodes to separate and recover ions, but the release of less selective ions from the electrode does not happen, in general. For having a charge balanced system, both anode and cathode should work in synergy. Therefore, by having both the cathode and anode work simultaneously, the ion balance in the liquid can be maintained, and the target ions can be recovered without causing unnecessary electrolysis. Therefore, utilizing the experience of synthesis of ion selective porous aromatic frameworks (PAF) and monovalent cation selective metal hexacyanoferrate or the Prussian blue analogs (PBA), an electrodialytic system with the selectivity for potassium ion and common counter ion, chloride was aimed.

### 2. 研究の目的

The purpose of the research was to establish a electrochemical cell for the selective separation and concentration of monovalent cations, mainly potassium in the seawater. The material PBA has strong selectivity for potassium against sodium and has good conductivity in thin film, are the already established facts. In connecting with this, a dual electrode system with positively charged and negatively charges electrodes for the large scale recovery of potassium was aimed.

### 3. 研究の方法

Preparation and characterization of PBA for the adsorption of potassium from seawater: this was done first in thin film and thicker films were gradually prepared. Since a natural ion exchange adsorption was considered at the first hand and the target ion is K, a series of PBA with either K or Na in the form of  $KM[Fe(CN)_6] \cdot H_2O$  or  $NaM[Fe(CN)_6] \cdot H_2O$ , where  $M = Mn, Fe, Co, Ni, Cu, \text{ or } Zn$ , were prepared. In all the cases, the synthesis composition was varied as  $M:Fe(CN)_6 = 0.5, 1, \text{ and } 1.5$ . The purpose of varying the metal and the composition was to find the best alternative with highest number of alkali metal ion in the molecule as well as the water stability. In addition, the purpose of varying the alkali metal between K and Na is to know the changes in the molecular structure when Na is replace by K during the natural adsorption, as it is known that all the PBA are more selective towards K compared to Na. Preparation of the thin films and optimizing the material for the best outcome is yet to be done. Material characterization: commonly used tools like XRD, TG-DTA, SEM-EDX, and the conductivity of the supernatant after the separation of the MHCF nanoparticles were used for knowing the composition of the respective products.

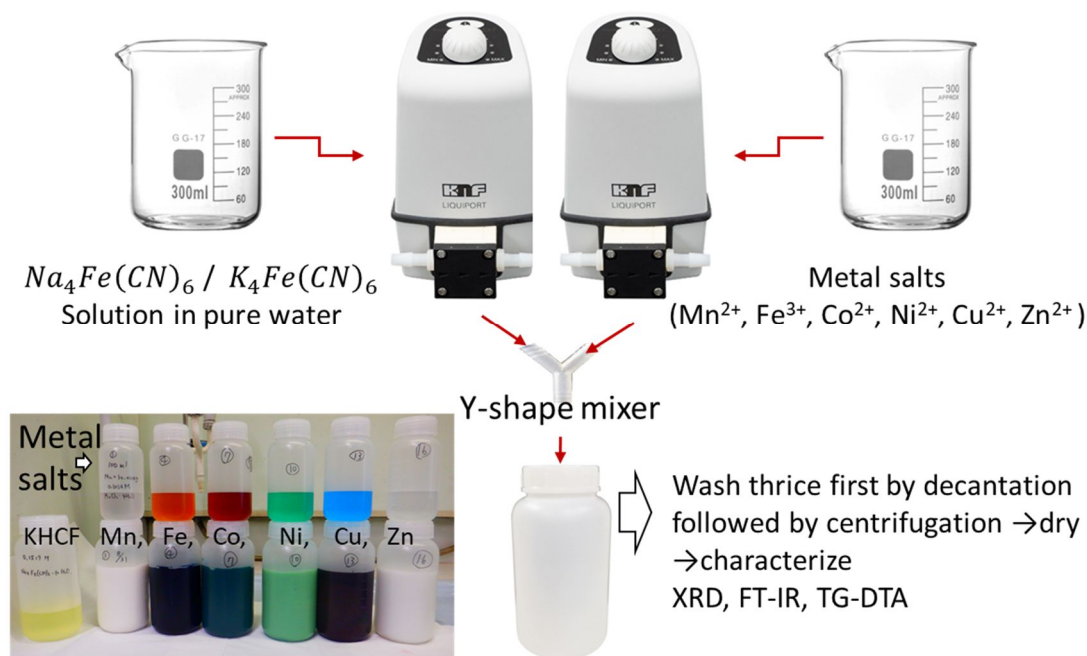


Figure 1. Synthesis process of various MHCF using a Y-mixer system in which a homogeneous slurry of the products were obtained.

#### 4 . 研究成果

- MHCF with different transition metal: PBA with Mn, Fe, Co, Ni, Cu, or Zn with Fe(CN)<sub>6</sub> were prepared in different molar ratios using a micromixing system. The preliminary result is summarized as below.

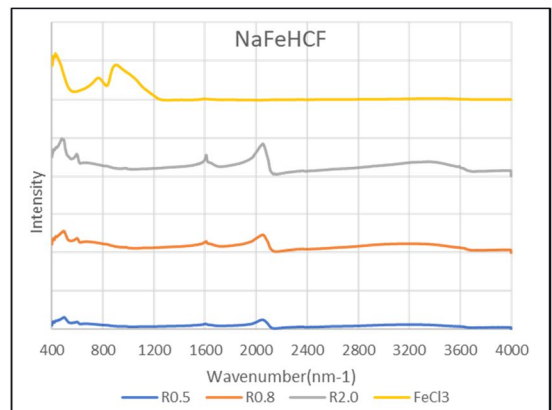
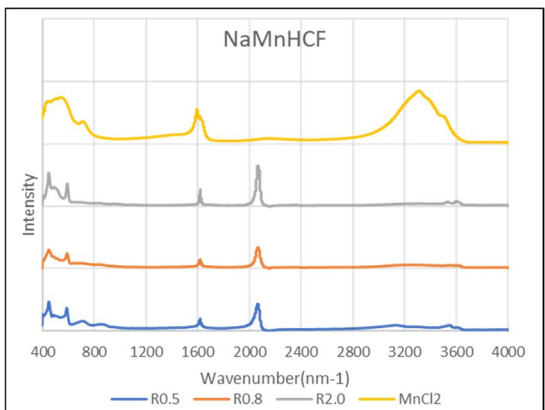
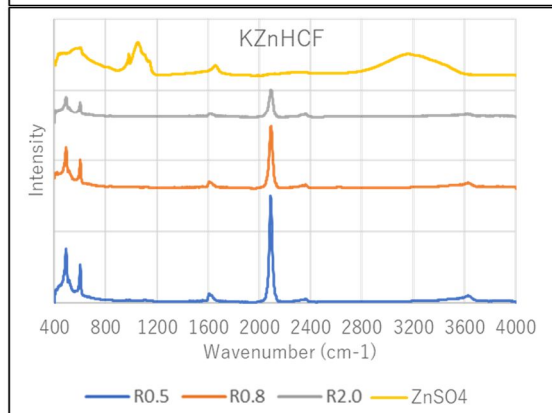
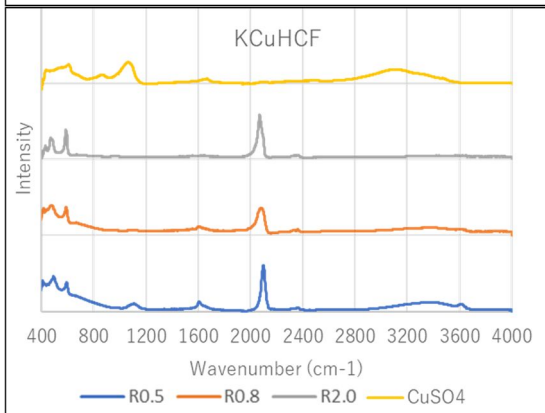
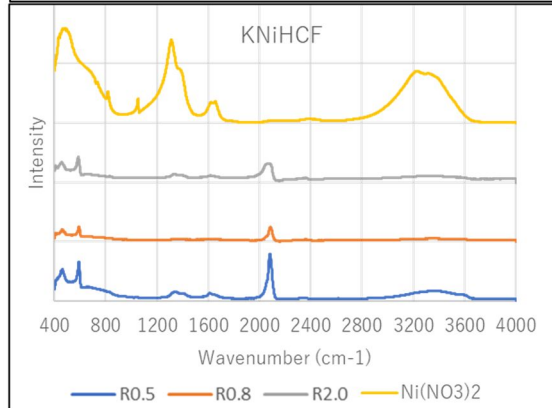
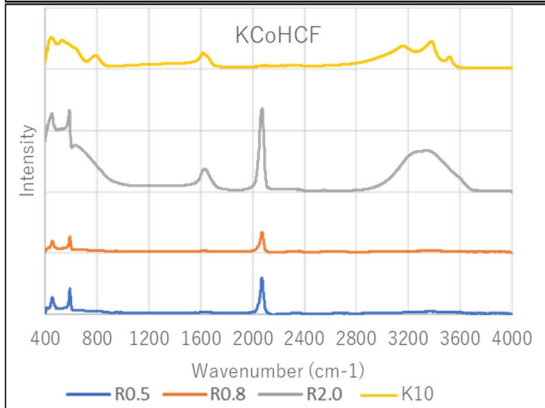
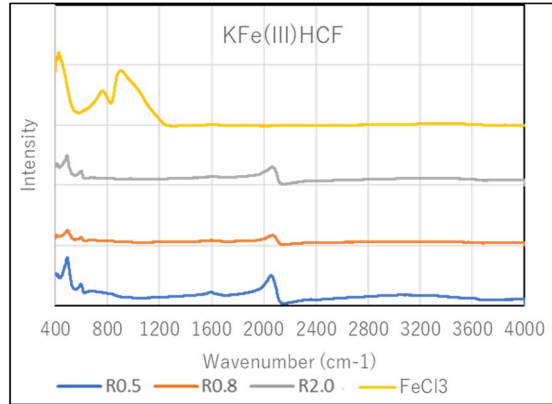
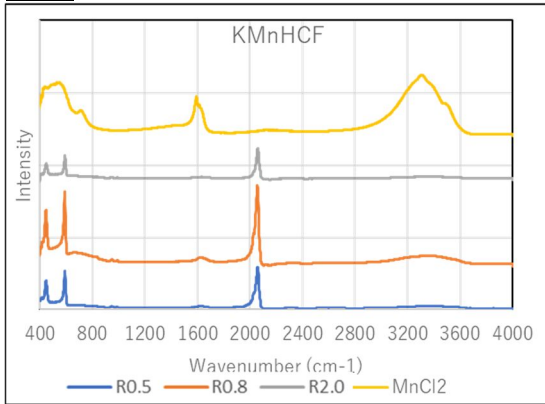
Table: Expected and observed tentative molecular

Cation	Metal, M	M:HCF	Expected composition, M = Fe(III); M(II)	Observed composition (SEM-EDX)	
<b>K</b>	Mn	0.5	Mn[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K1.37Mn[Fe(CN) <sub>6</sub> ]0.91	
		0.75	KMn[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K1.34Mn[Fe(CN) <sub>6</sub> ]0.90	
		1	K <sub>2</sub> Mn[Fe(CN) <sub>6</sub> ]	K1.51Mn[Fe(CN) <sub>6</sub> ]0.91	
	Fe	0.5	Fe[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K0.09Fe[Fe(CN) <sub>6</sub> ]0.00	
		0.75	KFe[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K0.26Fe[Fe(CN) <sub>6</sub> ]0.12	
		1	K <sub>2</sub> Fe[Fe(CN) <sub>6</sub> ]	K0.54Fe[Fe(CN) <sub>6</sub> ]0.14	
	Co	0.5	Co[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K1.15Co[Fe(CN) <sub>6</sub> ]0.86	
		0.75	KCo[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K1.45Co[Fe(CN) <sub>6</sub> ]0.95	
		1	K <sub>2</sub> Co[Fe(CN) <sub>6</sub> ]	K1.25Co[Fe(CN) <sub>6</sub> ]0.87	
	Ni	0.5	Ni[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K0.95Ni[Fe(CN) <sub>6</sub> ]0.69	
		0.75	KNi[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K1.05Ni[Fe(CN) <sub>6</sub> ]0.78	
		1	K <sub>2</sub> Ni[Fe(CN) <sub>6</sub> ]	K2.40Ni[Fe(CN) <sub>6</sub> ]1.12	
	Cu	0.5	Cu[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K0.26Cu[Fe(CN) <sub>6</sub> ]0.67	
		0.75	KCu[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K1.24Cu[Fe(CN) <sub>6</sub> ]1.08	
		1	K <sub>2</sub> Cu[Fe(CN) <sub>6</sub> ]	K1.40Cu[Fe(CN) <sub>6</sub> ]0.81	
	Zn	0.5	Zn[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	K0.53Zn[Fe(CN) <sub>6</sub> ]0.62	
		0.75	KZn[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	K1.00Zn[Fe(CN) <sub>6</sub> ]1.58	
		1	K <sub>2</sub> Zn[Fe(CN) <sub>6</sub> ]	K1.25Zn[Fe(CN) <sub>6</sub> ]1.54	
	<b>Na</b>	Mn	0.5	Mn[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.05Mn[Fe(CN) <sub>6</sub> ]0.51
			0.75	NaMn[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na0.60Mn[Fe(CN) <sub>6</sub> ]0.65
			1	Na <sub>2</sub> Mn[Fe(CN) <sub>6</sub> ]	Na0.88Mn[Fe(CN) <sub>6</sub> ]0.72
		Fe	0.5	NaFe[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.02Fe[Fe(CN) <sub>6</sub> ]0.43
			0.75	NaFe[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na0.09Fe[Fe(CN) <sub>6</sub> ]0.34
			1	Na <sub>2</sub> Fe[Fe(CN) <sub>6</sub> ]	Na0.31Fe[Fe(CN) <sub>6</sub> ]0.56
Co		0.5	Co[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.43Co[Fe(CN) <sub>6</sub> ]0.59	
		0.75	NaCo[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na0.79Co[Fe(CN) <sub>6</sub> ]0.78	
		1	Na <sub>2</sub> Co[Fe(CN) <sub>6</sub> ]	Na0.78Co[Fe(CN) <sub>6</sub> ]0.90	
Ni		0.5	Ni[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.13Ni[Fe(CN) <sub>6</sub> ]0.58	
		0.75	NaNi[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na0.70Ni[Fe(CN) <sub>6</sub> ]0.75	
		1	Na <sub>2</sub> Ni[Fe(CN) <sub>6</sub> ]	Na1.57Ni[Fe(CN) <sub>6</sub> ]1.13	
Cu		0.5	Cu[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.00Cu[Fe(CN) <sub>6</sub> ]0.96	
		0.75	NaCu[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na0.62Cu[Fe(CN) <sub>6</sub> ]1.20	
		1	Na <sub>2</sub> Cu[Fe(CN) <sub>6</sub> ]	Na1.59Cu[Fe(CN) <sub>6</sub> ]2.47	
Zn		0.5	Zn[Fe(CN) <sub>6</sub> ] <sub>0.5</sub>	Na0.78Zn[Fe(CN) <sub>6</sub> ]0.66	
		0.75	NaZn[Fe(CN) <sub>6</sub> ] <sub>0.75</sub>	Na1.04Zn[Fe(CN) <sub>6</sub> ]0.83	
		1	Na <sub>2</sub> Zn[Fe(CN) <sub>6</sub> ]	Na1.09Zn[Fe(CN) <sub>6</sub> ]0.69	

Observation:

1. Only a few materials were obtained closer to the expected composition.
2. The variation among these three compositions for each MHCF reflects the possibility of varying the water stable composition as per the requirements.
3. Amongst, CuHCF both with K or Na shows a wider composition range.
4. In general, NaMHCF have wider composition range compared to KMHCF.

FT-IR



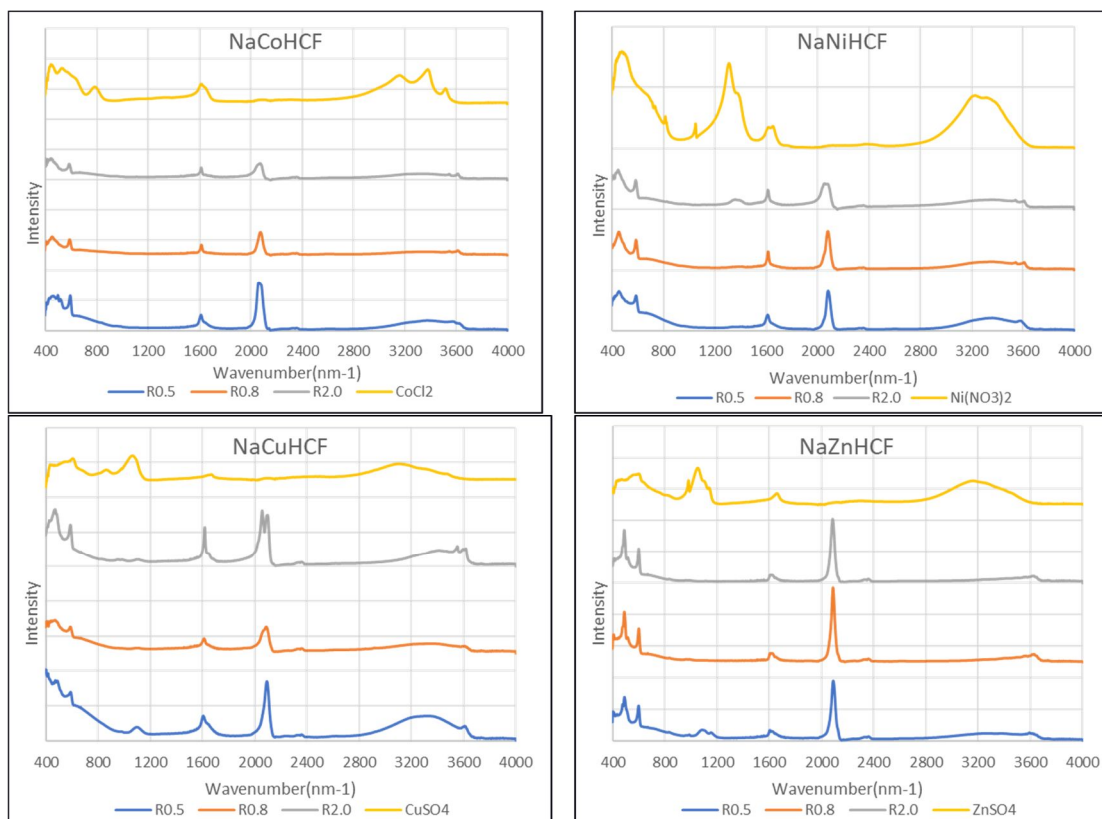


Figure 2. FT-IR spectrum showing the characteristic MHCf peaks with a water hump around 3600  $\text{cm}^{-1}$  for some NaMHCFs, which are absent in the KMHCfs.

#### Further work.

For various reasons the planned proposal had been largely delayed. Therefore, an incomplete report is being submitted, so far. A manuscript focused on the comparative account of the composition variation of various MHCf with K or Na as charge balancing cations in under drafting. Further, based on the water stable composition and their cation content and the primary particle sizes, thin film followed by thick film electrodes would be prepared and characterized for the recovery of K or  $\text{NH}_4$  in various solutions including the seawater.

## 5. 主な発表論文等

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

1. 著者名 Zhang Nan, Kawamoto Tohru, Watanabe Hiroshi, Jiang Yong, Zhang Zhenya, Lei Zhongfang, Parajuli Durga	4. 巻 14
2. 論文標題 Selective Adsorption of Potassium in Seawater by CoHCF Thin Film Electrode and Its Electrochemical Desorption/Regeneration	5. 発行年 2021年
3. 雑誌名 Materials	6. 最初と最後の頁 3592 ~ 3592
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/ma14133592	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 該当する

〔学会発表〕 計4件（うち招待講演 1件/うち国際学会 4件）

1. 発表者名 Durga Parajuli
2. 発表標題 Prussian blue analog for the electrochemical recovery / removal of ions
3. 学会等名 5th International Conference on Materials Science, Engineering and Technology（招待講演）（国際学会）
4. 発表年 2024年

1. 発表者名 Durga Parajuli
2. 発表標題 Prussian blue analog used electrochemical system for the separation of monovalent cations
3. 学会等名 ACS Fall 2022（国際学会）
4. 発表年 2022年

1. 発表者名 Durga Parajuli
2. 発表標題 Cobalt hexacyanoferrate for the recovery of potassium from seawater
3. 学会等名 Pacifihem 2020 (postponed to 2021/12)（国際学会）
4. 発表年 2021年

1. 発表者名 Durga Parajuli
2. 発表標題 Cobalt hexacyanoferrate for the recovery of potassium from seawater
3. 学会等名 Pacifihem 2020 (postponed to 2021/12) (国際学会)
4. 発表年 2021年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

At least one more academic publication covering the outcome of the proposed research will be published until FY2025.

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