Characteristics of cesium ion sorption from aqueous solution on plasma-induced chitosan grafted magnetic bentonite composites

<u>Shubin Yang</u>^{1,2)}, Naoya Okada³⁾, Xiangke Wang²⁾, Masaaki Nagatsu^{1,3)} 楊 樹斌^{1,2)}, 岡田 直也³⁾, 王 祥科²⁾, 永津 雅章^{1,3)}

¹Graduate School of Science and Technology, Shizuoka University, Hamamatsu 432-8561, Japan ²Institute of Plasma Physics, Chinese Academy of Science, China ³Graduate School of Engineering, Shizuoka University, Japan ¹静岡大学創造科学技術大学院,〒432-8561 浜松市中区城北3-5-1 ²中国科学院・プラズマ物理研究所 ³静岡大学大学院工学研究科,〒432-8561 浜松市中区城北3-5-1

The effective removal of $^{137}Cs^+$ ions from seawater and from radioactive nuclear waste solutions is crucial for public health and for the continuous operation of nuclear power plants. Various $^{137}Cs^+$ adsorbents have been developed, but more effective material that can be used in practical application are still needed. A novel magnetic bentonite grafted with chitosan (denoted as CS-g-MB) was designed by the plasma-induced grafting method. The experimental results clearly showed that the CS-g-MB composites had an excellent ability for Cs⁺ capture in contaminated stimulated groundwater and real seawater. And this material is superior to other known materials in terms of magnetic property, turbidity, and stability in aqueous solution. The cesium ion exchange reaction of CS-g-MB is pH- and ionic strength-dependent, and it is mainly controlled by the cation exchange mechanism. The results indicated that the composites cannot only chemisorb Cs+ ions but efficiently trap them for safe disposal. And this is useful for its potential application of nuclear waste.

1. Introduction

The technology development of Cs^+ capture from aqueous solution is crucial for the disposal of nuclear waste and still remains a significant challenge.[1] Bentonite has the capacity to withstand intense radiation, elevated temperatures, and high cation exchange capacity, which had been proven to be promising materials for the cesium contamination management.[2]

Color and turbidity are very important factors for drinking water. Therefore, novel material with good adsorption property and poor dispersion, which can avoid increasing turbidity of water when remediate contaminated water is required and call for in the water treatment process. Previous studies showed that chitosan is an eco-friendly coagulant and flocculant.[3]

Plasma treatment is an efficient method in the field of surface modifications as its solvent-free, time-efficient, versatile, and environmentally friendly properties.[4]

With these in mind, we firstly used the RF-driven Ar plasma-induced method to synthesize CS-g-MB. The objectives of this CS-g-MB composite are: 1) to decorate chitosan to bentonite; 2) to separate easily from the medium by the simple magnetic separation process; 3) to achieve low turbidity in aqueous solution; 4) to stable in groundwater and real

seawater ; and 5) to realize high-efficiency in the removal of Cs^+ ions. This combination makes it possible to take advantage of the abundant functional groups of chitosan and the spatial structure of bentonite as well as the magnetic nanoparticles. The prepared CS-g-MB composites are applied to adsorb cesium ions from aqueous solution to evaluate their application in environmental pollution cleaning. A comparison of stability of CS-g-MB composite in the two different water systems containing simulated water and real seawater was also evaluated.

2. Experimental Section



Fig. 1. Synthesis route of CS-g-MB and the design for exchange experiment.

The plasma induced grafting procedures consist of two successive processes: surface activation and

chitosan grafting. For instance, magnetic bentonite was treated using Ar plasma for 10 min at a pressure of 50 Pa, and an RF power of 80 W. Then 150 mL 1.5g/L chitosan solution was immediately injected into the plasma treated magnetic bentonite to anchor chitosan at 80 °C. After stirring vigorously for 24 hours, the CS-g-MB composites were gathered by a permanent magnet, washed several time with 0.01 mol/L H₃PO₄ solution and Milli-Q water, and finally dried at 60 °C. The schematic of the formation of CS-g-MB and the exchange processes are shown in Fig. 1.

3. Results and Discussion

The XPS spectra of (Fig. 2a) show the spectrum of CS-g-MB composite exists the characteristic peaks of N 1s (402.6 eV), as the nitrogen only exists in chitosan, this is an indication of the effective connection of chitosan onto bentonite structure.[5] And a twin-peak is the feature of the XPS spectrum of Fe 2p peak as shown in Fig. 2b. This is indicative of the magnetic bentonite.

The C 1s spectra of bentonite in Fig. 2c can be deconvoluted into three components: (1) the C=C peak (284.4 eV); (2) the C-O peak (286.2 eV); and (3) the carboxylate carbon peak (O-C=O, 289.2eV). Besides, it is a remarkable fact the C 1s spectra of CS-g-MB composite in Fig. 2d is quite different from those of bentonite. The carboxylate carbon peak (O-C=O, 289.2eV) was replaced by the amide peak (N-C=O, 289.2eV), indicating the existence of chitosan can graft on bentonite through the reaction of amino group with carboxylate. These results indicated the CS-g-MB composite is synthesized successfully.



Fig.2. XPS spectra of survey scan (a); Fe 2p spectrum (b); and C 1s spectrum of (c and d).

The seawater used in present research was taken from the Pacific Ocean near Hamamatsu city, Japan.

And the concentrations of Na⁺, Mg²⁺, Ca²⁺, and K⁺ were detected to be 4381, 1002, 545, 403 ppm, respectively (pH =7.6). The simulated water used in this study was prepared by Na⁺:230, Mg²⁺:240, Li⁺:70, K⁺: 390 ppm (pH =5.0).



Fig.3. Adsorption isotherms (a) and removal efficiency
(b) for Cs⁺ ions by CS-g-MB composite in real seawater and simulated water (m/V=1.0 g/L).

Two very similar curves of Cs⁺ adsorption isotherm in contaminated real seawater and simulated water in Fig. 3a were observed as well as the removal efficiency of Cs^+ on CS-g-MB in Fig. 3b with the concentrations of CsCl(aq) ranged from 1.0 ppm to 150 ppm. The maximum adsorption capacity of Cs^+ on CS-g-MB composite in contaminated simulated water (1.21 mmol/g) was close to that in contaminated seawater (1.19 mmol/g). The designed material can remove 50% of Cs⁺ ions from the two contaminated water systems with concentrations of CsCl_(a0) up to 100 ppm (Fig. 3b). We considered these phenomena were closely related to the stability of the CS-g-MB composite. The material could remain stable in the contaminated seawater in a long period of time that similar with it in contaminated simulated water. Thus, we consider the simulated water can be used as the model of real seawater.

Acknowledgments

This work has been supported in part by a Grant-in-Aid for Challenging Exploratory Research (No. 25600120) from the Japan Society for the Promotion of Science (JSPS).

References

- S. J. Datta, W. K. Moon, D. Y. Choi, I. C. Hwang, K. B. Yoon: *Angew. Chem. Int. Ed.* 53 (2014), 7203.
- [2] S. Yang, C. Han, X. Wang, M. Nagatsu: J. Hazard. Mater. 274 (2014), 46.
- [3] T. Chatterjee, S. Chatterjee, S. H. Woo: Chem. Eng. J. 148 (2009), 414.
- [4] C. L. Chen, B. Liang, D. Lu, A. Ogino, X. K. Wang, M. Nagatsu: *Carbon* 48 (2010), 939.
- [5] M. H. Yang, S. B. Jong, C. Y. Lu, Y. F. Lin, P. W. Chiang, Y. C. Tyan, T. W. Chung: *Analyst* 137 (2012), 4921.