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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

氏名：
Name
Salma Sadia

学位論文題目：
Title of Dissertation

Development of zeolite-embedded sheets for facile decontamination: radioactive cesium in soil and disease-causing bacteria in water
（簡便な除染のためのゼオライト包埋シートの開発：土壌中の放射性セシウムおよび水中の病原性微生物）

学位論文要約：
Dissertation Summary

Introduction

Soil and water contamination by toxic metals and disease-causing bacteria is a global problem, and facile and inexpensive decontamination methods are widely required. In decontaminating soil and water, powdery functional materials like activated carbons, titanium oxide, and zeolites are effective. However, powders are difficult to separate from soil and water after decontamination leading to high cost and complex procedures. Embedding the powders in water-permeable fabrics enables the separation from soil and water, and I prepared a fabric filter sheet embedding mordenite-type natural zeolite in it. This study aimed to investigate the potential of the mordenite-embedded sheet in decontaminating soil and water and is consists of two parts. First, the decontamination of a Cs-contaminated clay using a mordenite-embedded sheet, and second, the disinfection of water containing an E. coli species using a protonated mordenite-embedded sheet. Embedding mordenite powder on sheets allowed easy and effective decontamination of both pollutants.

Part 1

Radioactive elements, including ^{134}Cs and ^{137}Cs, were emitted from the Fukushima Daiichi Nuclear Power Plant in 2011, contaminating soils [1, 2]. In the Cs-decontamination, washing methods prevail due to cost and ease of use [3, 4]. The washing methods aim to release Cs^+ through a cation-exchange reaction by washing with salt solutions.

However, conventional washing methods remove little Cs^+ because the Cs^+-exchange reaction between the soil and solution phase reaches equilibrium after releasing only a few amounts of Cs^+ [5, 6].

$$[\text{soil}]\text{-}Cs^+ \rightleftarrows Cs^+$$

Here, adding a Cs^+-adsorbent to this suspension changes the reaction equation.

$$[\text{soil}]\text{-}Cs^+ \rightleftarrows Cs^+ \rightleftarrows Cs^+\text{-}[\text{adsorbent}]$$

In this system, the adsorbent removes the Cs^+ in the solution, decreases the Cs^+ concentration, and causes more Cs^+ release from the soil (shift of equilibrium). I named this the adsorbent-coexistence method. In this method, separating the adsorbent from the soil suspension is necessary after the washing process. However, the separation is usually impossible because adsorbents for Cs^+ are powdery. This study developed a technology that uses a sheet embedded with an adsorbent for easily separating the adsorbent by hand from the soil suspension. A natural mordenite was selected as the adsorbent due to its high Cs^+-adsorption selectivity and low price, and montmorillonite was used as a simulated soil. Figure 1 shows the physical appearance and SEM images of the mordenite-embedded sheet (MES) obtained by heating at 160 °C for 8 min.

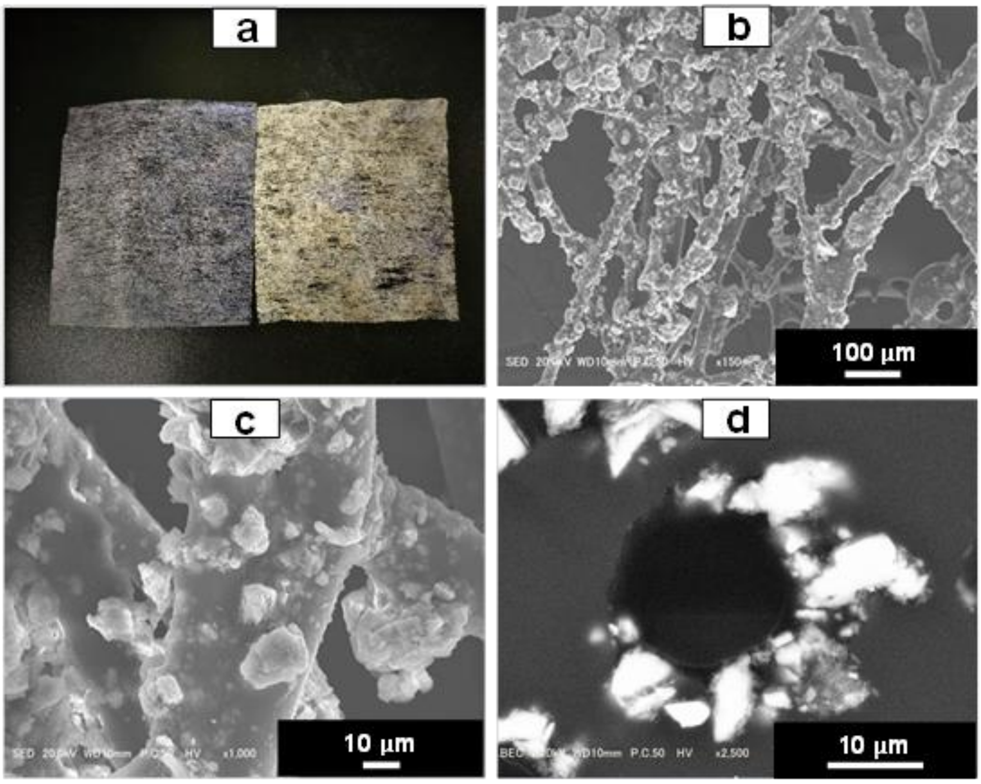

Fig. 1 Physical appearance of (a: left) the fabric filter and (a: right) MES; SEM images of MES (b) at a lower magnification and (c) at a higher magnification; (d) cross-section SEM image of a fiber of MES.

The mixtures of $^{133}Cs^+$-retaining wet/dry montmorillonite and water/0.1 mol L^{-1} KNO_3 were shaken with/without the MES. Figure 2 shows that the addition of the MES increased Cs^+ release in all cases, with the highest increase for wet montmorillonite (more than nine times). The washing solution composition of 0.1 mol L^{-1} KNO_3 and water gave similar levels of Cs decontamination. The Cs concentration in the final washing solution is lower with water than with 0.1 mol L^{-1} KNO_3, as is indicated by the preliminary isotherm experiments. Therefore, surface water or tap water is preferable as the washing solution because it is cost-effective, and the concentration of both Cs and other solutes in the resultant waste solution is low.

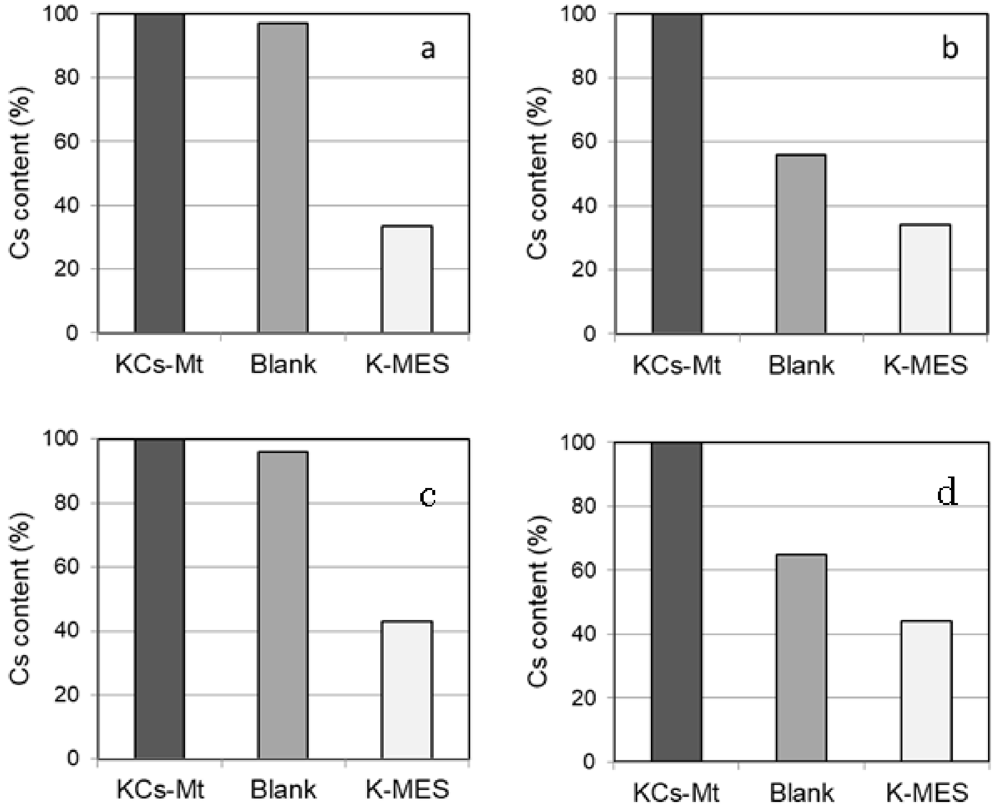

Fig. 2 The amount of Cs in KCs-Mt: untreated (KCs-Mt), washed without K-MES (Blank), and washed with K-MES (K-MES). (a) wet KCs-Mt washed with water; (b) wet KCs-Mt washed with 0.1 mol L^{-1} KNO_3; (c) dry KCs-Mt washed with water; (d) dry KCs-Mt washed with 0.1 mol L^{-1} KNO_3.

The proposed one-step washing method, the adsorbent-coexistence method, has the potential to be a manageable decontamination method for Cs-contaminated solids. When this method is applied to Cs-contaminated soils, operating in the early stages of contamination is desirable because the desorption of Cs^+ from them becomes more difficult with time.

Part 2

Safe water is essential for people to wash their hands, cook, and drink, but it is not readily available in rural areas of developing countries. The contaminants in the water are mainly heavy metals, arsenic, and pathogenic bacteria. The World Health Organization reported that at least two billion people drink fecal-contaminated water containing pathogenic bacteria, associated with 485 000 diarrheal deaths each year, most of them infants [7]. The best way to solve this problem is to develop infrastructures that provide clean water. However, in the short term, the priority should be supplying simple and effective methods to purify water for individual use.

The methods to kill pathogenic bacteria in the water besides boiling are chlorination and using heavy metals [8, 9]. This study used high concentrations of protons to kill bacteria in water because many bacterial species do not survive at low pH, below around 4, except for acidophiles [10, 11]. Adding acid solutions similarly lowers the pH, but using chemical reagents at home may not be widely recommended for safety reasons. Hence, we used a mordenite-type zeolite containing protons to lower the pH, where the zeolite releases protons into the water through cation exchange with cations in the water.

I have fabricated a protonated natural mordenite-embedded non-woven fabric sheet (H-MES) as a new tool for disinfecting drinking water at home. Proton retention amount was 1.2 mmol per gram of mordenite, 75% of its cation-exchange capacity (Fig. 3a). The H-MES released protons through cation exchange with cations in aqueous solutions, lowering the pH of the solutions to below 4 (Fig. 3b).

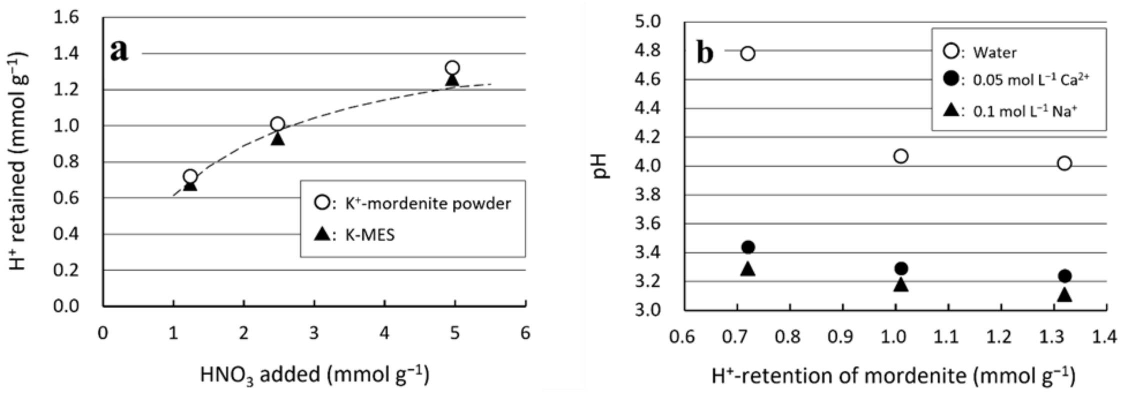

Fig. 3 Protonation and deprotonation properties of mordenite. (a) amount of H^+ retention on the K-MES and K^+-saturated mordenite with different amounts of added HNO_3. The dotted curve shows mathematically calculated values assuming equal adsorption selectivity of H^+ and K^+ towards mordenite; (b) pH of aqueous solutions with added K^+-saturated mordenite with different amounts of H^+ retention.

The low pH led to disinfecting 100 mL of 100-fold diluted TSB solutions containing an Escherichia coli species (DH5α). For example, an initial viable count of around 5000 CFU mL^{-1} decreased to 14 CFU mL^{-1} after 24 h shaking at 25 °C with added H-MES containing 0.2 g protonated mordenite; 3.8 $\times 10^7$ CFU mL^{-1} without the H-MES (Fig. 4). Adding a nitric acid solution showed a similar effect, but using chemical reagents at home might lead to unexpected accidents. Adding and removing the H-MES to and from household waterpots by hand is easy.

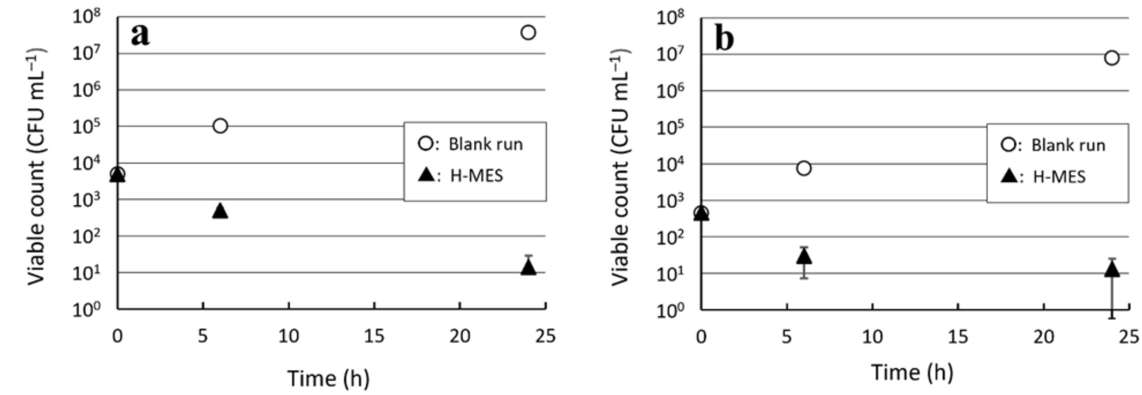

Fig. 4 Viable count of DH5α at different shaking times with added H-MES at an initial viable count of around (a) 5000 CFU mL^{-1} and (b) 500 CFU mL^{-1}. Error bars show standard deviation.

We aimed to develop a simple and effective tool for disinfecting water in household waterpots of rural residents in developing countries. A natural mordenite powder was embedded in a fabric sheet and partially protonated to form H-MES, a new type of disinfectant. The H-MES released the protons, the protons lowered the pH to below 4, killing DH5α in the aqueous solutions. The level of disinfection was high, although a few DH5α remained in the treated water even after 24 h. However, because the goal of our study is complete disinfection, we need to improve the performance of the H-MES to attain that goal.

Adding H-MES instead of adding acids for lowering the pH of water could prevent accidents due to misuse at home, and the H-MES does not affect the smell and taste of the water like chlorination does. Also, the H-MES enables simple water disinfection in batch systems because of simple removal from the treated water. Besides protonated mordenite, other materials that kill or adsorb bacteria could easily disinfect batch water at home if given a physical form like the H-MES.

Conclusion

This study showed the capacity of natural mordenite type zeolite for both the Cs-decontamination of soils and the disinfection of water. Its low price and availability make the natural mordenite a potential material for these purifications. Embedding the natural mordenite powder to give sheet-form is crucial because it enables more release of Cs^+ from coexisting Cs-contaminated soils. In addition, easy separation of the mordenite powder from soil suspensions enables low-cost decontamination of Cs-contaminated soils because the separation of mordenite is possible manually. The embedding is also crucial in the disinfection of drinking water in rural areas of developing countries because it enables facile disinfection of water in household water-pots. The use of low-cost functional materials such as natural mordenite with sheet-form like the embedded sheet may be applicable also for other cases of environmental purifications.

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