REMOVAL OF HEAVY METAL IONS FROM AQUATIC ENVIRONMENT USING GAMMA-IRRADIATION-MODIFIED CARBOXYMETHYL CELLULOSE HYDROGELS

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論文題名　：**REMOVAL OF HEAVY METAL IONS FROM AQUATIC ENVIRONMENT USING GAMMA-IRRADIATION-MODIFIED CARBOXYMETHYL CELLULOSE HYDROGELS**
(ガンマ線照射で修飾したカルボキシメチルセルロースハイドロゲルによる水性環境からの重金属イオンの除去)

区　　分　：甲

論　文　内　容　の　要　旨

Heavy metal contamination in water has caused unending concern for environment and human health. Upon entering the human body, the metallic ions discharged from the industrial processes can cause many serious complications such as brain damage, shrinkage of muscle bundles, death, and hereditary deformities and teratogenicity. The treatments of these toxic elements have become the objectives of many studies for decades. Under these circumstances, the author has been developing new organic-hydrogel adsorbents by utilizing the gamma irradiation method.

Among the technologies adopted to eliminate the toxic elements, the adsorption method utilizing organic hydrogels has been considered an effective and user-friendly approach from the viewpoints of high cost performance and availability, which are attributed to their light-element(C, H, O, N, etc.) polymer network made from inexpensive and common natural substances, such as green plants and crab/shrimp shells, massively disposed as wastes in daily life. As for the method producing organic hydrogels from these easily obtainable materials, the gamma irradiation method is the most suitable one due to unnecessity of toxic reaction-initiator and cross-linker agents, which are generally used in the ordinary chemical-reaction methods for forming gel-network and for grafting functional-groups to the network.

In the present study, the author has newly developed organic-hydrogel adsorbents derived from readily obtainable cellulose-based materials by utilizing Cobalt-60 gamma radiation, and has evaluated their capabilities as recyclable metal-ion adsorbents by performing repetitive adsorption-and-desorption experiments. The thesis compiles these author’s investigations and is composed of 6 chapters.

Chapter 1 provides overviews of heavy metal pollutants in waste water and available removal techniques, including the previous studies on the utilization of organic hydrogels as adsorbents with emphasis on Carboxymethyl-Cellulose(CMC)-based hydrogels.

Chapter 2 explains on the fabrication of the CMC-based hydrogels by utilizing the gamma irradiation, and on the experimental methods to characterize the hydrogels. In the present study, three types of CMC-based hydrogels have been newly synthesized: (1) the CMC-hydrogels grafted with sodium sulfonate styrene (SSS) monomer, (2) the SSS-grafted CMC-hydrogels reinforced by Bis[2-(Methacryloyloxy) Ethyl] Phosphate (BMEP) monomer, and (3) the CMC-based hydrogel with an interpenetrating network produced by gamma irradiation after infusing carboxymethyl chitosan (CMCts) polymer into the SSS-grafted CMC-hydrogels.

Chapter 3 reports on the SSS-grafted CMC-hydrogels’ capabilities of extracting metal ions from their

aqueous mixture (Cr, Mn, Mo, Ni, Cu, Zn, Fe, U, Cd, Pb). In the experiments, the SSS-grafted CMC-hydrogels were demonstrated to adsorb all kinds of the metal ions in the solution around twice the amounts by the CMC-hydrogel without showing significant difference by the elements. It was also noticed that the SSS-grafted CMC-hydrogel with CMC:SSS=1:2 of weight-ratio shows the highest removal efficiency for all of the metal ions in the solution, indicating strong electrostatic interaction between SSS and the metal ions: the adsorbed metal-ion weight per that of the adsorbent were 40.7 and 15.0 μg/g for Fe and Cr, respectively, and 7.00 μg/g for both of Cu and Zn. However, it was also revealed that the capturing ability of CMC:SSS=1:2-hydrogel after 2 cycles decreased to a half by the disintegration of the surface parts resulted from the large volume change caused by the SSS's strong electrostatic force, which indicated the necessity of reinforcement of the hydrogel's structure.

Chapter 4 describes an attempt to improve the reusability of the SSS-grafted CMC-hydrogel by introducing a network reinforcer, Bis[2-(Methacryloyloxy)Ethyl] Phosphate (BMEP). In the simultaneous multi-ion capturing experiments in the above-mentioned conditions, the reinforced SSS-grafted CMC-hydrogels (CSB hydrogels) revealed different capturing-efficiencies for the coexisting metal ions in the order of Mo < V < Zn < Cr < Cu < Mn < Cd < Co < Ag < Ni. As for the mechanical strength, the CSB hydrogels showed higher elasticities {in a range from 5.75 kPa of Young's Modulus (E) with the addition of 12.9 mM of BMEP to E: 3.41 kPa with 2.6 mM of BMEP} than that without the reinforcement (E: 2.76 kPa). Though the adsorption capacity decreased with the BMEP addition increment, the CSB hydrogel with 2.6 mM of BMEP (CSB2.6 hydrogel) showed a high adsorption capability comparable to the hydrogel without the reinforcement as well as showing no disintegration in the repetitive adsorption-and-desorption experiments. In addition, the CSB2.6 hydrogel also demonstrated a high desorption capacity, even for Ni (~81 % after the 4th iteration) exhibiting the highest affinity to the CSB hydrogels, which indicated a possibility as a recyclable adsorbent.

Chapter 5 gives the investigations on the SSS-grafted CMC-hydrogel modified to have an interpenetrated network composed of CMC and CMCts. By the modification, the SSS-grafted CMC-hydrogel was found to show a high selectivity for Ag^+ among the 10 metal ions described previously: the modified-hydrogel{(CMC+CMCts):SSS=4:2}'s adsorption capacity for Ag is 4 times higher (>40 μg/g) than those for other metal ions. Besides, it was also found that decrease in the Ag-capturing efficiency is less than 15 % after the 4th repetition of the adsorption-and-desorption cycle, indicating the possibility as an element-selective resource-recycling material.

Chapter 6 summarizes the results obtained in the present study and discusses the subjects to be solved in future investigations.