学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Encapsulation of adsorptive particles into CNT-reinforced alginate gels for the development of high-performance adsorbent for cesium and strontium eliminations

(吸着性粒子をカーボンナノチューブ補強アルギン酸ゲルに内包するアプローチを用いたセシウムとストロンチウムを除去するための高性能吸着材の開発)

Radioactive cesium and strontium are the inevitable medium lived fission products have half-lives of 30.17 and 28.8 years respectively. Until today, simultaneous removal of these extremely hazardous elements is an unsolved problem. For decades, scientists are familiar with various transition metal cyano ferrates as well as zeolites to decontaminate water from radioactive cesium and strontium. However, it is unfeasible to use such material directly in water because of their small particle size, leads to further decontamination. More over their low permeability made their large-scale application in fixed-bed columns impractical.

Hence, the caging of those scavenger materials in nontoxic and inexpensive alginate vesicle will be a promising method for the safe and effective use. In order to enhance further stableness and efficiency of encapsulated beads under extreme adverse conditions highly dispersed multi walled carbon nanotubes (MWCNT) are the versatile supporter because of their intense strength, networking ability and surface area.

Ferric hexacyanoferrate (Prussian blue), sodium cobalt hexacyanoferrate and zeolite-A were successfully synthesized and firmly encapsulated in calcium alginate beads individually along with MWCNTs for decontaminating water from cesium and strontium ions. The novel beads were stable and showed sensational removal capability in all possible unfavorable conditions more effectively.

This dissertation consists of introduction, experimental, results and discussion and conclusions. First, a brief introduction about environmental problems related to radioactive cesium and strontium were described. The significance of their removal from water was also pointed out. A comprehensive literature review also delineated the previous contributions to the field. The deep knowledge on literatures provided a theoretical framework towards the current problems that lead to a suitable original idea of encapsulation in alginate vesicle with MWCNT. The experimental section describing the methodologies that adopted to accomplish the problem solving research. The key adsorbing materials such as Prussian blue, sodium cobalt hexacyanoferrate and zeolite-A were synthesized and purified scientifically. The physical and chemical characterization of the prepared samples was systematically done using various techniques such as scanning electron microscope (SEM), x-ray diffraction (XRD) measurement, Fourier transform infrared spectroscopy (FT-IR), thermo gravimetric analysis (TG-DTA) etc. Then the three materials were encapsulated in micro-porous beads using sodium alginate as the immobilizer and calcium ion (Ca^{2+}) as the cross-linker. In each case two types of beads were prepared one was without MWCNTs and another with MWCNTs. The bead preparation was further optimized. The newly developed adsorbent beads could withstand in extreme pH, temperature and ionic strength without any break and leak. The developed beads were further examined by means of SEM and Brunauer–Emmett–Teller (BET) analysis to understand the morphological and porous peculiarities. A series of experiments were done to analyze the practical application of high performing adsorbent for the removal of cesium and strontium from aqueous solutions under batch and continuous flow conditions in the fixed bed adsorbent column. Later detailed kinetic, equilibrium and column breakthrough studies were performed. The research further extended to determine the effect of pH and ionic competition on adsorption of cesium and strontium.

The major results obtained and the healthy discussions with valid points were done. Usually immobilization decrease the availability of adsorbent towards adsorbate, but CNTs enhanced the encapsulation efficiency along with making the enclosed materials fully available for adsorption. Multipurpose MWCNTs make a supporting physical network over the caged crystals that help them to remain more firmly inside the beads for risk free use. The adsorption behavior and rate were carefully examined by means of different isothermal and kinetic models. Mathematical fitting of experimental data on the adsorption isotherm model was in the order Langmuir isotherm greater than Freundlich isotherm. MWCNT modified Prussian blue, sodium cobalt hexacyanoferrate and zeolite-A bead´s Cs^{+}/Sr^{2+} maximum adsorption capacity were 143/55 mg/g, 133/72 mg/g and 113/107 mg/g, and that of without MWCNT were 131/53 mg/g, 121/70 mg/g and 102/96 mg/g respectively. Similarly, in kinetic models pseudo second order gave better fitting than pseudo first order. The adsorption was monolayer site-to-site attachment and immediate. The investigation to understand the effect of pH and ionic competition on adsorption brought into a conclusion that the performance of beads was consistent with a broad range of pH values as well as ionic competition. The fixed bed column adsorption analysis showed that beads could be used for large scale treatment.

In conclusion, the performance of this economic beads with respect to their stability, simplicity and removal capacity is innovative than currently available adsorbent. Their relevance ranges from low to high level of contaminant concentration as well as much suitable for both household and industrial scale design. Consequently, this newly developed bead will be a potential solution for the existing radiation problem.