



Mordenite zeolite–Polyethersulfone composite fibers developed for decontamination of heavy metal ions



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ABSTRACT

Mordenite zeolite was composited in polyethersulfone fibers with mordenite zeolite loading of 27.0, 45.5, 58.8, and 69.0 wt%. Phase inversion was used to prepare porous composite fibers. During the process, mordenite zeolite powders were mixed in polyethersulfone (PES) – *N*-methyl-2-pyrrolidone (NMP) solution. Then the PES mixed solution was coagulated in water to prepare composite fibers. The composite fiber morphology provided evidence that mordenite zeolite powders were embedded well in the PES scaffold. Characterization results implied that mordenite zeolite interacted and composited with PES matrix. With increased mordenite zeolite loading amounts, the composite fiber surface was increased respectively by 11.7 and 145 m²/g for 0 and 69.0 wt% loading. Their composite fibers exhibited thermostability and heavy metal adsorbability. The adsorption behavior of heavy metal ions, especially to Pb²⁺, was investigated because their composite fibers were immersed in a batch solution of single or quaternary mixed heavy metal ions of Pb²⁺, Cd²⁺, Cu²⁺, and Ni²⁺. Composite fibers with 58.8 wt% and 69.0 wt% of mordenite zeolite showed high adsorption capacity to lead by fitting with the Langmuir isotherm model. The maximum adsorption capacity and Langmuir constant of heavy metal ions follows the order of Pb²⁺ > Cd²⁺ > Cu²⁺ > Ni²⁺ at pH 5. Adsorption selectivity of Pb²⁺ was observed in a heavy metal mixed solution and high concentration of KNO₃ solution using composite fiber.

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1. Introduction

Advancement of human capabilities to use energy has spurred economic growth and industrial development but it has also brought about environmental pollution among other adverse effects. These effects on ecological systems and human health are now recognized as extremely severe. Such environmental pollution is caused mainly by emissions from hazardous wastes and contaminant chemicals from landfills. Among them, wastewater containing heavy metals is an important type of waste, although heavy metal concentrations in them are low. Wastewater containing heavy metals has been discharged from many industries such as mining operations, glass production industries, and metal plating facilities [1,2]. Eventually, problems arise related to accumulation of these heavy metals in the environment and in the human body via bioaccumulation in the food chain. Ultimately, such accumulation can cause anemia, encephalopathy, and cancer

[3,4]. Therefore, techniques of removing heavy metals from wastewater are fundamentally important.

Various techniques have been developed to date for the removal of heavy metals from water, including electrolytic methods, chemical precipitation, membrane processing, and adsorption [5]. Of them, adsorption is particularly effective, providing benefits that include ease of handling and low costs for chelating polymers [6], activated carbon [7], bio-sorbent [8], metal oxide [9], and zeolite [10]. Among these adsorbents, zeolites are suitable adsorbents that have large cation exchange capacity and high affinity for cationic heavy metal ions [11]. Zeolite, which has a three-dimensional and tetrahedral structure in the silica and alumina groups, has linkage to oxygen atoms and the structure of partial Si⁴⁺ and Al³⁺. Therefore, negatively charged sites can attract positively charged solutes in the concentration. Naturally, zeolite has unique cation exchange and adsorption abilities [12]. Depending on the composition and crystalline structure, several zeolites might be used. Among natural zeolites, mordenite zeolite having (Na⁺)₈[(AlO₂)₈(SiO₂)₄₀]·24H₂O was found by Meier [13] for the building framework units linked edge-sharing 12-membered ring [13]. Its two-dimensional pore structure consists of 12-membered ring channels (7 × 6.5 Å) connected by 8-membered ring channels (3.4 × 4.8 Å) [14]. Such porous

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zeolite behaves as a molecular sieve, therefore, mordenite zeolite has been used for catalysis, gas absorbance, and water treatment [15]. It is well known for natural zeolites that the decontaminant performance of heavy metals from water reportedly derives from the selectivity and removability of various positively charged metal ions [16–18]. Ion exchange in mordenite zeolite was reported by Golden etc. [19] and for lead ion [20].

Active studies have been conducted for zeolites composited with polymer materials and have been applied for gas separation membranes [21] and adsorbents [22]. Demet et al. prepared a polyacrylamide – Y-zeolite composite by polymerization of acrylamide in zeolite to overcome unfavorable zeolite properties [23]. For other zeolite–polymer composites, Yilmaz et al. fabricated zeolite nanoparticles with an impregnated polysulfone membrane. Such a composite enhanced adsorption and the membrane filtration performance by impregnation of zeolite in the membrane scaffold [24]. In the adsorbents, these composites offer the potential for practical properties in their application. For instance, powder adsorbents are recovered only slightly after operating; bead-shaped adsorbents and membranes cause a high-pressure drop under column operation. Especially, the membrane treatment increases energy costs through high-pressure operation, although its separation efficiency is high. Therefore fibrous adsorbents are advantageous in the separation process and proposed as one solution to overcome these problems. Young and co-workers synthesized chelating fibers for high adsorption capacity of heavy metals. They reported chelating fibers as having contact efficiencies with water that are higher than those of resin beads [25]. Also, Mahapatra and co-workers fabricated $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ nanocomposite having small fibrous structure to removal efficiently of heavy metals [26]. The advantage of these fibrous adsorbents is high removal efficiency because it has small mesh structures consisting of small fiber filaments. However, the natural field water sometimes contain suspended solids which are trapped in small mesh structures of conventional fibrous adsorbents. Eventually, trapped solids causes high pressure loss and low removal efficiency. Thus, fibrous adsorbent that is sustainably able to applied under like this hard environment condition is necessary. To break through this problem, our research group developed zeolite – polymer composite fiber using phase inversion with polyether sulfone (PES) for decontamination of radioactive cesium from environment [27]. This composite fiber consists of mordenite zeolite embedded on porous PES matrix. In addition, it showed high and stable adsorption ability even though it was used in the natural field water such as rice field side river, water pool and marsh. However, its adsorption properties of heavy metal ions including lead, cadmium, copper and nickel have not been investigated though the composite fibers has a great potential for practical using in various environmental condition. Thus, for this work, mordenite zeolite was composited in PES fibers to fabricate mordenite zeolite – polymer composite fibers when phase inversion was modified to form a porous polymer scaffold in a fiber shape. The purpose of the present work is to examine the adsorption behavior of the mordenite zeolite – polymer composite fibers for decontamination of heavy metal ions in comparison with powder mordenite

zeolite. For the mordenite zeolite powders were embedded in the fibrous PES scaffold with different loading amounts and the adsorption behavior of heavy metal ions was investigated when single or quaternary mixed heavy metal ions were used for batch binding experiments in details.

2. Experimental

2.1. Reagents and qualification processes

Mordenite zeolite powder was obtained from Nitto Funka Trading Co. Ltd., Japan. Also, *N*-Methyl-2-pyrrolidone (NMP) and other chemicals were purchased from Nacalai Tesque Inc. (Japan) and were used without purification. Before the experiment, the natural mordenite zeolite was washed with NMP and deionized water. Then it was dried under vacuum. The dried mordenite zeolite powder was crushed and passed through a No. 230 sieve. Polyethersulfone (PES, Ultrason E2010) was a product of BASF Co. Ltd. (Germany). Aqueous heavy metal ion solutions of Pb^{2+} , Cd^{2+} , Cu^{2+} and Ni^{2+} were prepared by dissolving their nitrate salts in deionized water. For each stock solution (Nacalai Tesque Inc.), the concentration of each ion was diluted before the adsorption experiment. When 0.1 M HNO_3 and 0.1 M NaOH solutions were used, the pH value of each heavy metal solutions was adjusted. 0.1 M KNO_3 solution was used for batch binding experiments.

2.2. Preparation of mordenite zeolite–polymer composite fibers

The mordenite zeolite–polymer composite fibers were fabricated by modified phase inversion of the PES–NMP solution to solid PES in water, according to procedures explained in earlier reports [28,29]. The PES was dissolved in NMP to prepare PES–NMP solution containing 30 wt% of PES concentration. Subsequently, specified amounts of the mordenite zeolite powders were added to the PES–NMP solution. Here, the mordenite zeolite powders were dispersed in the PES–NMP solution at concentrations of 10, 20, 30, and 40 wt%. Then, the mixed solution was stirred for several hours. After preparing the mordenite zeolite–polymer mixed solution, the mixture was extruded through a cylindrical needle with 0.6 cm needle-hole diameter by 0.42 MPa of air pressure. The extruded mixture was dropped into a 298 K of water coagulation bath. The composite fibers were immersed in a water coagulation bath for a day and were washed with 353 K in hot water to remove residual NMP. Finally, the composite fibers were dried under vacuum. As Table 1 shows, the composition of loaded mordenite zeolite in PES and the contents (%) of mordenite zeolite powders in the PES are listed.

2.3. Characterization of mordenite zeolite–polymer composite fibers

As presented in Table 1, several tests were conducted for the mordenite zeolite–PES composite fibers. The apparent volume of the composite fibers was obtained using Archimedes method. A dry sample with known mass was immersed in excess methanol

Table 1
Properties of composite fibers, PES and mordenite zeolite.

Sample	Mordenite zeolite contents [wt%]	Apparent specific volume [cm^3/g]	BET Surface area [m^2/g]	Tensile strength [MPa]	T_g [K]
PES	0	0.81	11.7	23	493.3
CF-27	27.0	0.78	32.7	21	499.5
CF-46	45.5	0.75	68.2	16	500.1
CF-59	58.8	0.68	136	6.6	500.5
CF-69	69.0	0.54	145	2.4	501.2
Mordenite zeolite	100	–	263	–	–

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