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Synergistic combination of metal oxide adsorbents for enhanced fouling control and metal removal in a submerged membrane adsorber



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ABSTRACT

Selective contaminant removal and concentration methods are essential for low level radioactive waste management. Herein, the synergy achieved by dosing a mixture of metal oxide adsorbents (crystalline silicotitanate (CST) and ferrihydrite (FH)) into a submerged membrane adsorber for the removal of key metal species (Co^{2+} , Sr^{2+} , and Cs^+), and the degree of membrane fouling control in nuclear plant laundry wastewater treatment were investigated. Substantial and stable removal of metal ions (> 90%) was achieved when the concentration of CST in the reactor was maintained at levels as high as 0.3 g/L, whereas the effect of FH varied significantly depending on the target metals. High and constant metal removal by CST was attributed to the ion exchange based sorption reaction in the CST cavities. CST itself did not mitigate membrane fouling, whereas the use of FH prevented fouling even at high dosages. Interestingly, the combination of CST and FH effectively eliminated fouling, which could not be achieved with CST alone. Combination of even small amounts of FH (0.1 g/L as Fe) with CST effectively reduced fouling. Thus, the synergistic effect of the CST and FH mixed adsorbent system on fouling control can be ascribed to the contribution of FH particles. FH exhibited high capacity for sorption of a key foulant in the feedwater constituents, i.e., the nonionic surfactant Tween 80. FH had a much greater sorption capacity for Tween 80 than CST. Possible binding of multivalent metal ions to the surfactant anchored on FH could furnish further repulsive forces between the FH particles, thereby making the cake layer looser. Dosing of the CST and FH adsorbent mixture into the membrane adsorber enabled enhanced metal removal with simultaneous fouling control.

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1. Introduction

Low level radioactive waste (LLRW) is of great concern because of the large quantities generated during nuclear power plant operation. ^{60}Co , ^{90}Sr , and ^{137}Cs are the three major radionuclides found in LLRW [1]. Conventional approaches, such as chemical precipitation [2], solvent extraction [3], and thermal evaporation [4], have been widely employed for the removal of such radioactive species, as well as for volume reduction of LLRW. More recently, pressure-driven dense-membrane processes, such as reverse osmosis and nanofiltration, have also been applied to treatment of LLRW, and substantial decontamination and volume reduction have been achieved using these techniques [1,5,6]. However, these technologies are hampered by the critical issue of non- or low-selectivity in metal removal, especially when the concentration of the target species is relatively low compared to that of background species. Thus, developing a protocol for achieving more selective removal of target metals along with volume reduction is required in LLRW management. In this

respect, the use of low-pressure membranes in combination with adsorbents or complexation agents would be attractive if the additives are sufficiently selective [7–10].

Ultrafiltration membranes employing soluble polymers as complexation agents have been utilized to bind metal ions, including Cs and Co ions [9,11,12]. A major issue associated with this hybridized system is the recovery and regeneration of the complexation agent used. Serious membrane fouling caused by polymers is inevitable and requires further efforts to overcome the problem [9]. The selectivity of functional groups (e.g., carboxyl and sulfonate groups) in polymers is also questionable.

On the other hand, various types of adsorbents have been investigated for application to radionuclide uptake from aqueous solutions [13,14]. Very high sorption capacities (e.g., 0.507 mmol/g for Sr) were achieved when activated carbons were applied to removal of radionuclides from aqueous medium [15] and seawater [15,16]; however, these adsorbents were not highly selective. Low-cost biosorbents have been prepared and applied to removal of radionuclides, such as Cs and Co [17,18], but they are chemically and thermally unstable. Disposable biosorbents also produce a vast amount of waste, which creates a secondary environmental problem. The sorption properties of several clay minerals, such as clinoptilolite,

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chabazite, natural and synthetic mordenite, NaA-X zeolite, and montmorillonite have been evaluated [19–22]. These mineral adsorbents were found to be ineffective for removal of radionuclides (e.g., Cs⁺) in the presence of competitive cations (e.g., Na⁺ and K⁺). Additionally, they were able to sorb metals effectively only within a limited pH range of 6–9. Transition metal ferrocyanides exhibit a large sorption capacity (distribution coefficient = 2.94×10^3 L/g) as well as a high selectivity for Cs ions over the wide pH range of 2–10 [23–25]. However, these species are too fine to be separated by gravity. Silicotitanates are another class of adsorbents with selective ion exchange capabilities and have also been applied to metal removal [26,27]. Previous studies investigated the sorption behavior of crystalline silicotitanate (CST) for application to the adsorptive removal of radionuclides, such as Co, Sr, and Cs [28–30]. CST particles were found to be highly selective towards Cs ions, even in the presence of background ions (e.g., Na⁺, K⁺, Ca²⁺, and Mg²⁺) [31]. However, separation of the exhausted CST particles was a secondary issue that restricted their direct application to wastewater treatment.

The combined use of adsorbents with low-pressure membranes is a prospectively applicable technique. Potassium zinc hexacyanoferrate has been combined with a microfiltration (MF) process for removal of Cs ions from aqueous solution, and successful removal of more than 99% of the initial Cs ions was achieved. However, severe membrane fouling occurred with the formation of a dense cake layer. In our previous study, five different types of mineral oxide adsorbents containing CST and ferrihydrite (FH) combined with MF [31] were evaluated. By dosing the CST (0.3 g/L) into a batch MF unit, >90% removal of Co as well as Sr ions from nuclear power plant wastewater was achieved. However, membrane fouling occurred with CST addition, an issue that must be resolved for practical applications. Previous studies reported that certain mineral adsorbents, such as iron oxide and aluminum oxide, were effective for prevention of membrane fouling in drinking water treatment when dosed into membrane systems [32,33]. This could be ascribed to differences in the structures and interactions of metal oxide adsorbents with feedwater constituents (e.g., natural organic matter), which have not been demonstrated in nuclear plant wastewater treatment. In addition, in each test, only one type of adsorbent was injected into the membrane systems; however, it is interesting to explore whether there are any combined effects on fouling control and removal efficiency when a mixture of adsorbents is utilized.

Therefore, in the present study, we investigate and compare the performance when single and mixed adsorbents are dosed into a submerged membrane adsorber for metal (Co²⁺, Sr²⁺, and Cs⁺) removal and fouling control. Two metal oxide adsorbents, CST and FH, are tested individually or in mixtures to evaluate the potential impact of synergistic effects on fouling control. The hydraulic filtration resistance, cake layer formation, and cake layer reversibility are characterized using an unstirred MF cell unit. The effects of specific wastewater constituents (e.g., metals, surfactant, and silica particles) on membrane fouling are examined while elucidating the fouling control mechanisms in the presence of adsorbents.

2. Materials and methods

2.1. Nuclear power plant laundry wastewater

Simulated synthetic wastewater was prepared as described elsewhere [31]. The chemical composition and key characteristics of the synthetic wastewater are provided in Table 1.

2.2. Synthesis of metal oxide adsorbents

Two different types of adsorbents, CST and FH, were prepared in the laboratory [31]. Briefly, CST was prepared by mixing 1.12 g of

Table 1

Parameters for nuclear power plant laundry wastewater.

Parameter	Value
pH	7.0
Conductivity (μS/cm)	152
Turbidity (NTU)	13.0
Nonionic surfactant (mg/L) ^a	100
Ca ²⁺ (mg/L)	6.0
Mg ²⁺ (mg/L)	2.0
Na ⁺ (mg/L)	14.8
K ⁺ (mg/L)	1.4
Cl ⁻ (mg/L)	25.0
SO ₄ ²⁻ (mg/L)	6.8
HCO ₃ ⁻ (mg/L)	3.0
NO ₃ ⁻ (mg/L)	0.48
SiO ₂ (mg/L)	4.57
Co ²⁺ (mg/L)	1.0
Sr ²⁺ (mg/L)	1.0

^a Tween 80 (Sigma-Aldrich), structure shown in Fig. S1.

tetraethyl orthosilicate (Sigma-Aldrich, USA) with 1.62 g of titanium isopropoxide (Sigma-Aldrich, USA) in a Teflon-lined pressure vessel. Subsequently, 15 mL of deionized water and 1.825 g of sodium hydroxide (Kanto Chemicals, Japan) were added to the mixture. The mixture was stirred vigorously for 30 min and then the Teflon vessel was placed inside a stainless steel vessel, sealed, and heated in an oven at 185 °C for 84 h. After cooling to room temperature, the CST particles were collected by filtering the solution using a 0.45 μm filter (Millipore, USA). Collected CST particles were washed once with deionized water, several times with pure ethanol, and finally with deionized water. Rinsed particles were dried for 24 h at 65 °C in an oven. FH was prepared by neutralizing 1.0 M ferric nitrate solution with 2.0 M sodium hydroxide solution. The precipitate formed was washed several times until free from electrolytes and stored in a refrigerator at 4 °C.

2.3. Membrane adsorber operation

Fig. 1 shows the laboratory-scale membrane adsorber composed of a submerged MF membrane module and an air diffuser. The membrane reactor had a working volume of 0.8 L, while the hollow fiber membrane (Kolon, Korea), made of polyvinylidene difluoride (PVDF), had a nominal pore size of 0.1 μm, an inner diameter of 0.8 mm, and an outer diameter of 2.0 mm. The membrane module installed had a bundle of 10 fibers that are 12 cm long each, providing an effective filtration surface area of 75 cm² (a photo of the membrane module is given in Fig. S2). The MF unit was operated at a constant flux of 50 L/m² h. The feed solution was supplied using a peristaltic pump while maintaining the reactor at a constant volume (0.8 L) by means of a level sensor. The hydraulic retention time (HRT) and solid retention time (SRT) were set to 115 min and 19 h, respectively. Each experiment was run for longer than 57 h (corresponding to the time required to filter three batches of reactor volumes) to ensure that the reactor reached a pseudo-steady state. Air sparging (0.5 L/min) was provided continuously using an air diffuser, which was placed underneath the membrane module to scour adsorbent particles away from the membrane surface. The transmembrane pressure (TMP) was continuously recorded on a laptop computer using a digital pressure transducer (ZSE40F, SMC, Japan) in conjunction with a digital multimeter (M-3850D, Metex, Korea). Permeate samples (final products) were collected every hour using a fraction collector (Universal Fraction Collector, Eldex, USA). A predetermined amount of adsorbent was initially added to the membrane

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