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Metal oxide enhanced microfiltration for the selective removal of Co and Sr ions from nuclear laundry wastewater

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ABSTRACT

The present study investigated the potential use of a hybridized adsorption/microfiltration system for the selective removal of hazardous cobalt and strontium ions from nuclear power plant laundry wastewater, which is essential for managing low-level radioactive wastes. A crystalline silicotitanate (CST) and four different iron oxides were fabricated and used as adsorbents, which had different crystal structures and adsorptive mechanisms, such as ion exchange and surface coordination. CST showed the greatest affinity for Co and Sr ions (e.g., the Freundlich isotherm constant, K_F=23.5 mg/g and 33.9 mg/g, respectively, at pH 7) and its adsorption capacity was independent of solution pH (pH 5–9), whereas the iron oxides removed substantive amounts of Co ions at neutral and alkaline pH levels, but only marginal amounts of strontium. Background species (e.g., K^+, Na^+, Ca^{2+}, and Mg^{2+}) had no significant impact on the affinities of the adsorbents for Co and Sr ions. The selectivity coefficients of CST for both Co and Sr ions ranged from 3 to 130. CST and ferrihydrite adsorbents were successfully regenerated using NaCl and HCl solutions, respectively, and their post-regeneration adsorption capacities were unchanged without any sign of significant inactivation after multiple adsorption and regeneration cycles. The addition of adsorbents to the microfiltration system enhanced the membrane permeability (> 30%), probably because the cobalt species were removed prior to precipitation at the membrane surface. Substantial and stable metal removals (> 90% for both Co and Sr) were achieved during 50 h of continuous system operations.

1. Introduction

Nuclear power plants produce large quantities of hazardous low-level radioactive wastes (LLRWs) during routine nuclear power plant operations, such as laundry wastewater and floor sweepings, which account for > 85% of all radioactive wastes generated [1]. Laundry wastewater resulting from the decontamination of irradiated components and work clothing accounts for most LLRW [2], and contains long-lived radioactive nuclides (*e.g.*, Co, Sr) and non-radioactive species, such as surfactants, electrolytes, and particulate matter. Thus, the volume reduction of nuclear wastes by selectively removing radioactive species is an important aspect of laundry wastewater management [3].

Various treatment methods, such as thermal treatments, extraction, adsorption, ion exchange, and membrane separation, have been applied to LLRWs [4]. Thermal treatments, such as evaporation, incineration, and vitrification, achieve significant volume reductions and destroy organic compounds. Vitrification used to be popular for treating high-level radioactive wastes, and in recent years, it has been applied to LLRWs [5,6]. A combination of plasma incineration and vitrification technologies has also been attempted [7], whereby thermal plasma removes the combustible portions and vitrification transforms non-combustible components into a glassy slag. However, these thermal methods have high operation costs because of their substantial energy requirements, and because the concentration of all non-evaporable materials, irrespective of radioactivity, is unavoidable. Extraction using diamides or supercritical fluids has been used to remove and concentrate radioactive actinides [8], but inadequate extraction and waste solvent generation were problematic. Furthermore, supercritical fluid extraction requires extreme operating conditions in terms of pressure and temperature [9].

On the other hand, the use of adsorption processes to remove metal ions from wastewater is both economically feasible and attractive, and thus, a variety of adsorbents, such as activated carbon [10–12], agricultural biomass [13–15], clinoptilolite [16], iron oxides [17], and ammonium molybdophosphate-polyacrylonitrile [18], have been investigated with respect to cobalt and strontium uptake from aqueous solutions. However, further investigations are needed to determine the adsorption rates, capacities, and selectivities. Furthermore, the chemical and thermal stabilities of bio-adsorbents are another concern because large quantities of waste sludge

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(*i.e.*, biosolids) are produced. Inorganic ion exchangers have been reported to effectively decontaminate low salinity LLRW [19,20]. In another study, chemically synthesized zeolite A was used as an ion exchanger to remove cesium and strontium ions from water, but its adsorption capacity was found to be dependent on a fixed bed depth and water flow rate [21]. However, selectivity and regeneration remain important issues with respect to the extensive, long-term use of ion exchange processes.

Several mineral adsorbents, such as iron oxides [17,22], aluminum oxides [23], silica-based composites [24], natural zeolites [25], and crystalline silicotitanate (CST), have been used to remove metal ions from aqueous streams [26–28]. Of these adsorbents, iron oxides and CST are the most stable chemically and thermally, and have been used to remove radioactive materials. Nevertheless, few studies have been done to evaluate and compare the performances of iron oxides and CST for nuclear waste treatment. The separation of these adsorbents used is another challenging issue.

Membrane processes have been reported to be effective for separating and concentrating radioactive materials from nuclear waste streams [1,4,29–33], and reverse osmosis (RO) membranes have been examined for the treatment of laundry and simulated liquid wastes with low-level radioactivity to reduce disposal volumes [29]. RO is able to concentrate wastes, but has the disadvantages of low permeability, high operating pressure, large energy consumption, and non-selectivity. Nanofiltration (NF) membranes are more selective for radioactive species [1], but still require relatively high operating pressures. Low-pressure membranes have been alternatively tested in various process configurations, such as co-precipitation followed by microfiltration (MF) [31], membrane distillation using a porous membrane [30], the combined use of iron oxides and crossflow microfiltration [22], and processes involving the addition of polyelectrolytes to ultrafiltration systems [34,35]. It is evident that combined adsorption and microfiltration offers an attractive option if selective, regenerable adsorbents are available. The combined process has the advantages of low operating pressure and energy requirements while providing superior treatment capabilities. More importantly, adsorbents that remove target materials can be completely separated and recovered after the treatment by the membrane, which is particularly important in nuclear waste management. In addition, this process array is more attractive and flexible for selective removal.

In the present study, hybridized adsorption/microfiltration processes were investigated for the treatment of simulated nuclear power plant laundry wastewater containing Co and Sr ions. The performances of CST and iron oxides with respect to target metal removals, selectivities, and regeneration efficiencies as well as membrane fouling control were evaluated and compared. More specifically, the effects of solution chemistry, such as solution pH, background species, and competing ions, on metal removal were examined, and membrane permeabilities were evaluated at different solution pH values in the absence and presence of adsorbents.

2. Experimental

2.1. Nuclear power plant laundry wastewater

The simulated nuclear power plant laundry wastewaters used were prepared in the laboratory by dissolving $Co(NO_3)_2 \cdot 6H_2O$ and/or $Sr(NO_3)_2$ (both analytical grade from Sigma-Aldrich) at 1.0 mg L^{-1} in deionized water. The concentrations of the background species (*e.g.*, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^-) are provided in Table 1. Counter anions and cations for such species were chloride and sodium ions, respectively. The basic recipe of the synthetic wastewater was recommended by the Korea Hydro & Nuclear Power Co., Ltd.

Table 1
Quality of the simulated nuclear power plant laundry wastewater.

Parameter	Value
pH	7.0
Conductivity (μS/cm)	152
Turbidity (NTU)	13.0
Nonionic surfactants (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).

Table 2
Characteristics of the adsorbents used.

Adsorbent	Particle size (μm) [a]	Surface area (m^2/g)	Shape [b]	Point of zero charge
CST	62.8	37.0	Spherical	7.9 ± 0.1
Ferrihydrite	47.2	338	Amorphous	6.3 ± 0.1
Goethite	14.3	47.7	Rod	7.0 ± 0.1
Hematite	6.20	22.5	Hexahedron	7.1 ± 0.1
Magnetite	19.8	37.7	Spherical	7.0 ± 0.1

[a] Mean diameter when dispersed in water.
[b] Based on SEM pictures (Fig. S1 in Supplementary Material).

2.2. Adsorbents and adsorption tests

The five different mineral oxide adsorbents used were prepared in the laboratory as follows (see Fig. S1). Crystalline silicotitanate was prepared by mixing 1.12 g of tetraethyl orthosilicate (Sigma-Aldrich, USA) with 1.62 g of titanium isopropoxide (Sigma-Aldrich, USA) in a Teflon-lined pressure vessel. Then, 1.825 g of sodium hydroxide (Kanto Chemicals, Japan) and 15 mL of deionized water were added to the mixture, which produced a white precipitate. The mixture was then stirred vigorously for 30 min, and the Teflon bomb was placed in a stainless steel vessel, sealed, and heated in an oven at 185 °C for 84 h. Solid crystals of silicotitanate were collected by filtration using a Millipore 0.45-μm filter, washed once with deionized water, several times with pure ethanol, and again with deionized water. Finally, the crystals having sodium ions in the cavity were dried at 65 °C in an oven.

Iron oxide particles (IOPs), that is, ferrihydrite, goethite, and hematite, were prepared using ferric nitrate salts [22,36]. Briefly, a ferrihydrite stock slurry was produced by neutralizing a 1 M ferric nitrate solution with 2 M sodium hydroxide solution. Goethite was synthesized by heating freshly precipitated ferrihydrite at 70 °C for 60 h under alkaline conditions ($pH > 12$), and the hematite was synthesized by heating a ferrihydrite aqueous suspension at 90 °C for 48 h under slightly alkaline conditions (pH 8). Magnetite was prepared by aging 1 M ferrous sulfate solution under alkaline conditions (pH 11–12) for 20 h. The physical and chemical properties of the synthesized adsorbents are summarized in Table 2.

Adsorption kinetics and isotherm tests were conducted in a batch reactor. Briefly, 100 mL of simulated wastewater containing a single metal (Co or Sr) was placed in 250-mL bottles. Predetermined amounts of each adsorbent (0.1–0.6 g/L of CST or 1–5 g/L of IOP as Fe) were added to simulated wastewater and placed in a