

Preparation of alumina-zirconia (Al-Zr) ceramic nanofiltration (NF) membrane for the removal of uranium in aquatic system

Youngkun Chung, Yeo-Myeong Yun, Yeo-Jin Kim, Yu Sik Hwang and Seoktae Kang

ABSTRACT

In this research, ceramic nanofiltration (NF) membranes were prepared by depositing alumina-zirconia (Al-Zr) nanoparticles into the pores of ceramic ultrafiltration (UF) membranes for the removal of radioactive uranium in an aquatic system. The modified ceramic membranes showed NF membrane performance with around 1,000 Da molecular weight cut-off (MWCO) and 58% CaCl_2 rejection. The removal efficiencies of uranium species by these successfully modified ceramic NF membranes exhibited differences depending on the pH conditions (pH 5.0, 7.4, and 10.0), and achieved the highest rejection of 91% at pH 7.4. This behavior is due to the dominant aqueous species of uranium in pH 7.4, $(\text{UO}_2)_2\text{CO}_3(\text{OH}_3)^-$, which has the largest molecular weight among the conditions and the negatively charged species having electrostatic attraction to the positively charged ceramic NF membranes. The ceramic NF membrane prepared here is expected to be feasible in the advanced water treatment process to remove radioactive compounds.

Key words | ceramic nanofiltration (NF) membrane, filtration-coating, uranium

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INTRODUCTION

In nature, uranium, known as one of the most common radioactive materials, is often found in trace amounts which are not of concern with regard to radiation protection. For decades, however, anthropogenic activities such as mining, milling, nuclear testing, and the disposal of spent nuclear fuel have led to the accumulation of uranium in groundwater, thus posing a public health risk through the drinking water supply system. The maximum acceptable uranium concentration in drinking water recommended by the World Health Organization (WHO) is 30 $\mu\text{g}/\text{L}$, and the maximum contaminant level (MCL) regulated by the United States Environmental Protection Agency (USEPA) for standard drinking water is also 30 $\mu\text{g}/\text{L}$ (Broder & Alireza 2015).

To remove uranium in an aquatic system, various methods of water treatment process can be used, such as

adsorption, ion exchange, sedimentation, thermal evaporation, and membrane technologies (Kang *et al.* 2002; Keum *et al.* 2002). Among these, membrane technologies, especially nanofiltration (NF) and reverse osmosis (RO), are most feasible, particularly for a wide range of contaminants, including uranium (Choong *et al.* 2007). NF membranes are a proven technology, providing higher levels of flux than RO at lower operating pressures. Because of ease of fabrication, polymeric NF membranes have been increasingly applied for the treatment of low molecular weight dissolved organic matter and multivalent ions such as Ca^{2+} and Mg^{2+} by the mechanism of size and electrostatic exclusion (Chakraborty *et al.* 2013). However, one significant limitation is that polymeric NF membranes can easily be damaged by high-energy radiation such as

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gamma rays from radioactive materials in the aquatic system. Previous research has shown that radiation can degrade the amide and ester bonds in the active layers of polymeric NF membranes (Combernoux *et al.* 2016).

Meanwhile, ceramic NF membranes have good thermal, mechanical, and chemical stability and are suitable for use in water treatments under harsh conditions such as contamination by radioactive materials. However, their application in advanced water treatments has been limited due to issues related to the NF membrane fabrication process and reduced pore sizes from ultrafiltration (UF) to nanoscale dimensions when using several coating methods (Aegerter & Mennig 2004). For instance, dip-coating, which is the most commonly used method, is known to cause cracks which readily form due to the high surface tension of the coated layer during the drying and calcination steps. Spray- and spin-coating also have limitations related to the formation of irregular surfaces and the use of only flat-shape membranes, respectively.

Based on this research background, the purpose of this study is to evaluate the feasibility of utilizing a ceramic NF membrane for the removal of uranium by fabrication via a novel coating method. The change of physico-chemical properties from ceramic UF membranes to prepared ceramic NF membranes were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and through zeta (surface) potential analyses. The molecular weight cut-off (MWCO) values and the calcium chloride (CaCl_2) removal efficiency of the prepared NF membranes were then evaluated for the performance of NF membranes. Finally, different species of uranium under different pH conditions were used to evaluate the applicability of ceramic NF membranes for removal of radioactive materials in the natural aquatic system.

MATERIALS AND METHODS

Preparation and characterization of nanoparticles

Alumina-zirconia (Al-Zr) nanoparticles were prepared from aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich), zirconium (IV) oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Sigma Aldrich), and polyvinyl alcohol

(PVA, KAN) in an aqueous solution. Here, 15 vol% of 0.5 M Al and 0.01 M Zr were added to 69 vol% of deionized (DI) water in a dropwise manner at room temperature. After gentle stirring for 6 hours, amounts of 1 vol% of 0.5 wt% of PVA were added as a dispersant. The nanoparticles were then peptized at 90 °C (pH 2.4) for 6 hours by adding 0.01 M hydrochloric acid (HCl). The physical and chemical properties of the prepared nanoparticles were analyzed by dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern Instruments, UK) and SEM-energy dispersive spectrometry (EDS) at room temperature (Magellan 400, FEI Co., USA).

Preparation of Al-Zr ceramic NF membranes using filtration-coating

Tubular UF membranes of α -aluminium oxide (Al_2O_3) were prepared by a slip-casting technique, starting from an aqueous suspension of commercially available Al_2O_3 powder. After shaping of the support material by isostatic pressing, oxidation was performed at 1,000 °C. The prepared tubular UF membranes had outer diameters of 1.7 mm, lengths of 8 cm, and were 0.3 mm thick.

To fabricate the ceramic NF membrane, the surfaces of ceramic UF membranes were modified by the novel method of filtration-coating with prepared Al-Zr nanoparticles in an operating membrane module. A cross-flow velocity (CFV) of 15 cm/sec was set to prevent the nanoparticles from piling up on the membrane surface. During the coating process, the trans-membrane pressure (TMP) and flux were measured by a digital pressure gauge and an electronic scale, respectively. The coating periods were determined as 6 hours as the flux stabilized at 10 bar of TMP. The coated ceramic NF membranes were then dried using a microwave to prevent the formation of cracks, and this was followed by calcination at 700 °C for 3 hours with the temperature increasing at a rate of 5 °C/min.

Physico-chemical properties of prepared ceramic NF membranes

The morphology and homogeneity of the membrane surface were analyzed by SEM. The chemical properties were examined by XPS (K-alpha, Thermo VG Scientific, USA) and surface (zeta) potential measurements (SurPASSTM 3

device, Anton Paar, Austria). XPS was used to confirm the coated Al-Zr nanoparticles. The surface charge characteristics of the membranes were examined to evaluate the effect of electrostatic exclusion by uranium species. A solution of 5 mM of sodium chloride (NaCl) was circulated to determine the pH dependence of the zeta potential by measuring the cells containing the membrane samples.

Performance of prepared ceramic NF membranes

The permeability tests were conducted using a laboratory-scale membrane system (with 4.17 cm² as the effective membrane surface area) fed by DI water, polyethylene glycol (PEG) solution, and calcium chloride (CaCl₂) solution to evaluate the performance of pure water flux, MWCO, and the multivalent salt rejection, respectively. After the feed solution was purged by nitrogen gas (99.99% purity) for 10 minutes to eliminate the dissolved gas, the membrane systems were stabilized with 0.1 m/s of CFV for 20 minutes. At this time, to set the initial water flux as 150 L/m²·h (LMH), the operation of the ceramic UF and NF membranes were conducted at 0.5 bar and 10 bar of TMP, respectively. During the tests, the pH was maintained at 7.4 ± 0.2 as natural levels of the aquatic system. Initially, for the MWCO test of fabricated ceramic NF membranes, different molecular weights (200, 400, 1,000, 2,000, and 6,000 Da) of 3 g/L PEG were used. The PEG concentration was measured using a total organic carbon (TOC) analyzer (TOC-L, Shimadzu, Japan). The prepared ceramic NF membranes were then characterized by multivalent salt rejection experiments fed with 15 mM CaCl₂. The concentration of CaCl₂ was measured using a conductivity meter. To confirm the reproducibility, all experiments were performed at least three times. Between each filtration test, procedures of backwashing and chemical cleaning using 1 wt% sodium hydroxide (NaOH) were conducted.

Uranium rejection by prepared ceramic NF membranes

To evaluate the rejection of various uranium species, the uranyl nitrate (UO₂(NO₃)₂·6H₂O, Sigma Aldrich) feed solution (2 mg/L) was prepared at pH 5.0, 7.4, and 10.0 with the addition of 0.1 M HCl or NaOH and was buffered with 1 mM sodium bicarbonate (NaHCO₃). To evaluate the

effect of natural organic matter (NOM) with uranium, 5 mg/L SR-NOM was added to uranium solution at pH 7.4. The ionic strength of each feed solution was held to 5 mM by adding NaCl. The uranium in solution was measured by the arsenazo-III method using UV-visible spectroscopy (DR 5000, HACH, USA) (Jauberty *et al.* 2013). The dominant speciation of uranium was measured using Visual Minteq 3.1 (KTH, Sweden). Based on the ion composition of the experimental solutions, the degree of speciation was determined for each pH. The predicted dominant species at each pH were then selected for a 'sweep test' performed from pH 1 to 14 at 23 °C. The adsorbed mass of uranium on the ceramic NF membrane was also calculated based on the mass balance.

RESULTS AND DISCUSSION

Characterization of prepared Al-Zr nanoparticles

Physical and chemical properties (DLS and SEM-EDS)

The size of the Al-Zr nanoparticles with 0.5 wt% of PVA is 44.4 ± 1.9 nm by DLS analysis (data not shown). This can be also be confirmed by the SEM images (42.1 ± 14.1 nm). According to Zhang & Glasser (1993), regarding the formation of Al-Zr nanoparticles, it was discovered that the hydrolysis and condensation of Al and Zr occurred under acid conditions. Subsequently, oxo-bridges are generated between the two metal cations. The EDS results show a composition ratio of 87.5% (Al), 1.6% (Zr), and 10.9% (O). The distribution ratio corresponds to the concentration ratio of Al and Zr, which is 1/50 times lower in a sol condition.

Physico-chemical properties of prepared ceramic NF membranes

Physical properties (SEM)

The SEM images of the ceramic UF membrane (Figure 1(a)) show typical ceramic membranes with a pore size exceeding 300 nm before the coating process. After the filtration-coating process, the pores of the ceramic NF membranes were successfully reduced from 303.2 ± 118.3 nm to 4.3 ± 0.7 nm

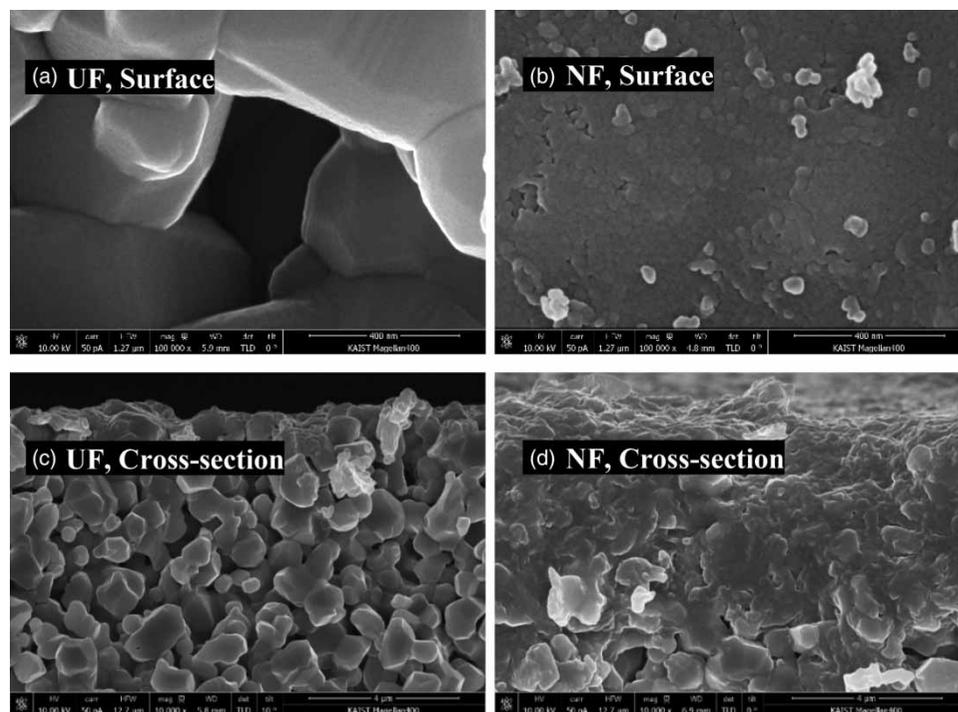


Figure 1 | SEM images of the surface and cross-section of the ceramic UF (a, c) and ceramic NF (b, d) membranes.

with the nanoparticles, and crack-free membranes could then be obtained, as shown in [Figure 1\(b\)](#). [Figure 1\(c\)](#) and [1\(d\)](#) show SEM cross-section images taken before and after the filtration-coating process. According to a comparison of these figures, the distinct packed layer was formed on the surfaces of the ceramic membranes as an active layer of polymeric membrane. Moreover, the smooth membrane surface could be obtained with a combination of high CFV (15 cm/s). The thickness of the coated layer inside the membrane support is approximately 5 μm .

Chemical properties (XPS and surface potential)

The XPS results in [Figure 2](#) show changes of the chemical properties of the membrane surfaces. There are no Zr peaks in the range 180–300 eV on the bottom line of the ceramic UF membrane in [Figure 2](#). This sample is clearly composed of aluminium (Al) (Al2p: 75.9 eV and Al2s: 120.8 eV). Meanwhile, after the filtration-coating process using Al-Zr nanoparticles, Zr peaks appeared on the surface of the ceramic NF membrane. These results were in good agreement with the findings of previous results in which

there appeared Zr peaks (Zr3d: 182.6 eV, Zr3p3: 333.1 eV, and Zr3p1: 346.8 eV) (Brenier *et al.* 1999; Kim *et al.* 2017). Therefore, the simple filtration-coating method can be used successfully to modify the chemical properties of membrane surfaces through the penetration of nanoparticles.

[Figure 3](#) depicts the surface charge of the membranes as a function of the pH from 4.0 to 11.0. The trend of the

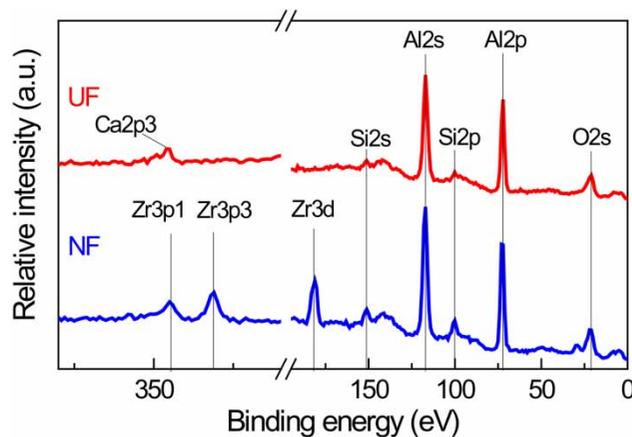


Figure 2 | The results of X-ray photoelectron spectroscopy (XPS) measurements on the ceramic UF and NF membrane surfaces.

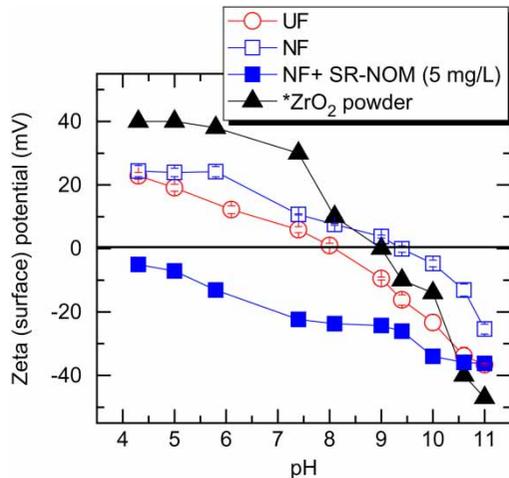


Figure 3 | The results of surface (zeta) potentials of the ceramic UF and NF membranes (*Figiel et al. 2013).

surface potential is such that both ceramic UF and NF membranes had positive charges when the pH was less than 7.4 and negative charges over pH 10.0, as shown in Figure 3. The isoelectric point (IEP) of the ceramic UF membrane was approximately pH 8.0. The IEP of the ceramic NF membrane was shifted from pH 8.0 to 9.4 by the Al-Zr nanoparticles on the membrane surface (Figiel et al. 2013). In addition, the surface potential of the ceramic NF membrane changed from positively (+10.7 mV) to negatively charged (-22.4 mV) when SR-NOM was present at pH 7.4, the condition used in uranium rejection experiments.

Performance of prepared ceramic NF membranes

MWCO

As a result of MWCO with 200, 400, 1,000, 2,000, and 6,000 Da of PEG, in this case, 90% PEG rejection of the ceramic NF membrane was obtained around 1,000 Da. Furthermore, the ceramic NF membrane shows the feasibility of removing low-molecular weights of 200 and 400 Da with 24% and 42%, respectively. Meanwhile, the ceramic UF membrane was below 5% in all ranges of molecular weights of the PEG.

Pure water flux and multivalent salt rejection (CaCl₂)

The pure water flux (J_{0-UF}) values of the ceramic UF membrane were 364 ± 14 LMH at 1 bar. The membrane

resistance (R_{m-UF}) was determined to be 9.87×10^{11} /m in the experimental conditions used here. After filtration-coating, the pure water flux (J_{0-NF}) value was 141 ± 2 LMH at 10 bar. The membrane resistance (R_{m-NF}) of the ceramic NF membrane (2.57×10^{13} /m) corresponded to the level of NF membranes, i.e., between 10^{12} and 10^{13} /m. In addition, the removal efficiency of CaCl₂ was increased from $4.1\% \pm 0.5\%$ to $58.2\% \pm 0.6\%$.

Uranium (U) rejection by prepared ceramic NF membrane

Uranium rejection was found to vary under the three different pH conditions in Figure 4. The highest rejection of $91\% \pm 2\%$ was found at pH 7.4, i.e., in a natural groundwater condition. The result containing SR-NOM shows the same removal efficiency at pH 7.4. In addition, at pH 10.0, $84\% \pm 2\%$ of uranium was removed by the ceramic NF membrane. In the acid condition, the removal efficiency was the lowest at $73\% \pm 2\%$ (at pH 5.0). Because the dominant uranium species could be changed under different pH conditions, it is important to evaluate uranium complexation under all experimental conditions to understand the removal mechanism of uranium (Barton et al. 2004).

The dominant uranium species according to Visual Minteq are UO_2CO_3 , $(UO_2)_2CO_3(OH_3)^-$, and $UO_2(CO_3)_3^{4-}$ at pH levels of 5.0, 7.4, and 10.0, respectively (Favre-Réguillon et al. 2008; Schulte-Herbrüggen et al. 2016). Obviously,

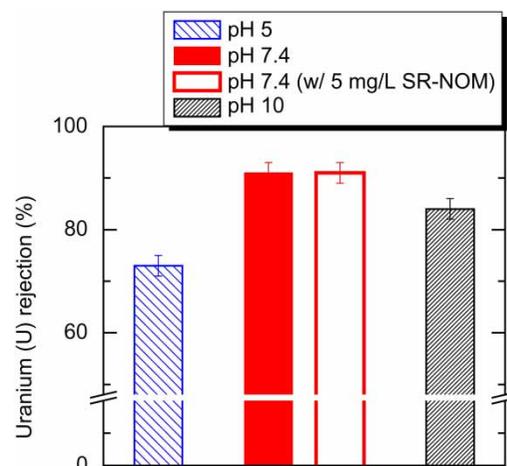


Figure 4 | Rejection of uranium (U) species by alumina-zirconia (Al-Zr) ceramic NF membranes.

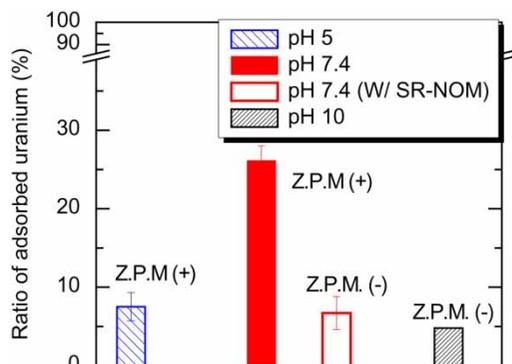


Figure 5 | The rate of adsorbed uranium (U) on the alumina-zirconia (Al-Zr) ceramic NF membranes according to pH 5.0, pH 7.4, and pH 10.0 (zeta potential of the membrane (ZPM)).

the uranium species tend to be positively charged in water as the pH increases. The molecular weights of UO_2CO_3 , $(\text{UO}_2)_2\text{CO}_3(\text{OH}_3)^-$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$, the major uranyl carbonate species, were found to be 330, 651, and 450 g/mol, respectively (Schulte-Herbrüggen et al. 2016). These results revealed that the various rejections were related to the size exclusions of the ceramic NF membrane.

In Figure 5, the rate of adsorbed uranium was $7.5\% \pm 2.0\%$, $26.1\% \pm 2.0\%$, and $4.7\% \pm 2.0\%$ at pH 5.0, 7.4, and 10.0, respectively, without containing SR-NOM. When the SR-NOM exists at pH 7.4, the rate of adsorbed uranium was 6.7%. The rate of adsorbed uranium on the ceramic NF membrane was the highest at pH 7.4 without SR-NOM, because of electrostatic attraction between the negatively charged $(\text{UO}_2)_2\text{CO}_3(\text{OH}_3)^-$ and the positively charged surfaces of the ceramic NF membrane in Figure 3. In other experimental conditions, the opposite phenomenon was obtained. Therefore, this outcome proves that the removal mechanisms of uranium species are the size exclusion and Donnan effect for ceramic NF membranes (Chakraborty et al. 2013).

CONCLUSION

In conclusion, Al-Zr ceramic NF membranes were successfully fabricated using a novel and simple method known as filtration-coating to remove radioactive materials. The performance capabilities of the ceramic NF membranes fabricated by novel filtration-coating were proved to be comparable to those of other ceramic NF membranes. In

terms of the application of prepared ceramic NF membranes, the uranium species were successfully rejected by prepared ceramic NF membranes by the mechanism of size exclusion and Donnan effect. Specifically, the most common uranium species $(\text{UO}_2)_2\text{CO}_3(\text{OH}_3)^-$ in a natural aquatic system could be effectively removed by the fabricated ceramic NF membranes. The ceramic NF membrane fabricated here is expected to be feasible in the advanced water treatment process to remove radioactive compounds released from the wastewater generated by nuclear power plants and mining to groundwater for reducing a public health risk through the drinking water supply system.

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