Highly water soluble nanoparticles as a draw solute in forward osmosis for the treatment of radioactive liquid waste

Hee-Man Yang*, Hye Min Choi, Sung-Chan Jang, Bum-Kyoung Seo, Kune Woo Lee, Jei Kwon Moon
Decontamination & Decommissioning Research Division, Korea Atomic Energy Research Institute (KAERI),
Daedeok-daero 989-111, Yuseong-gu, Daejeon, 305-353, Republic of Korea
*Corresponding author: *hmyang@kaeri.re.kr*

1. Introduction

The operation of nuclear pressurized water reactors (PWRs) results in numerous radioactive waste streams which vary in radioactivity content. Most PWR stations have experienced leakages of boric acid into liquid radioactive waste systems. These wastes contain about 0.3~0.8 wt% of boric acid. It is known that reverse osmosis (RO) membrane can eliminate boron at high pH and boron of 40~90% can be removed by RO membrane in pH condition. RO uses hydraulic pressure to oppose, and exceed, the osmotic pressure of an aqueous feed solution containing boric acid.

Forward osmosis (FO), a low energy technique based on membrane technologies, has recently garnered attention for its utility in wastewater treatment and desalination applications. In the FO process, water flows across a semi-permeable membrane from a solution with a low osmotic pressure (the feed solution) to a solution with a high osmotic pressure (the draw solution) [1]. The driving force in FO processes is provided by the osmotic gradient between the two solutions. Low energy costs and low degrees of membrane fouling are two of the advantages conveyed by FO processes over other processes, such as reverse osmosis processes that rely on a hydraulic pressure driving force [1,2].

However, the challenges of FO still lie in the fabrication of eligible FO membranes and the readily separable draw solutes of high osmotic pressures. Superparamagnetic Fe3O4 nanoparticles can be separated from water by an external magnet field easily. If Fe3O4 nanoparticles are coated with highly soluble organic substances, thus they can be used as a draw solute by concurrently generating high osmotic pressure and easy separation [2].

In this study, we introduced highly water-soluble hyperbranched caroboxylated polyglycerol-coated magnetic nanoparticles (CPG-MNPs). It is known that the highly branched, globular architecture of PG significantly increase solubility compared to linear polymer and they are eco-friendly [3]. After synthesis of CPG-MNPs, the physical properties of resulting CPG-MNPs and their performance as a draw solute in FO processes were characterized

2. Experiment

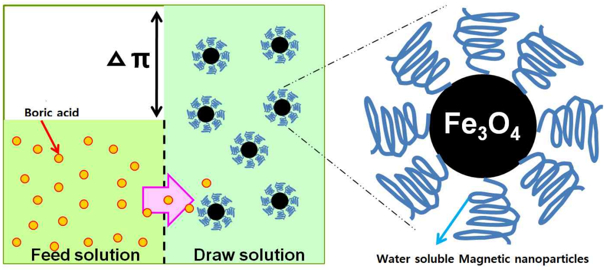

Fig. 1. Schematic diagram of the FR membrane and magnetic separation process using magnetic nanoparticles as a draw solution

Magnetic nanoparticles were prepared as follow: iron acetylacetonate (5 mmol) and triethylene glycol (100 ml) was mixed and this mixture was first heated to 110 oC for 1 hour to complete dissolved the solid. The resulting solution was heated to reflux for three hours under N^2 protection. After cooling to 120 ^oC, glycydol was added to the reaction solution, and polymerization was carried out at 120 ^oC for 12 h. The resulting suspension was added dropwise into excess acetone to obtain a black precipitate. The collected precipitate was dispersed in water and centrifuged at 6000 rpm to further remove any agglomerates, and then precipitated in excess acetone to remove the free polyglycerol polymer. The polyglycerol grafted magnetic nanoparticles were then collected by centrifugation at 6000 rpm for 10 min and dried under vacuum to obtain the polyglycerol coated magnetic nanoparticles.

Next, the polyglycerol coated magnetic nanoparticles were dissolived in 30 wt% NaOH. Then, that solution was added dropwise a solution of sodium chloroacetate in water over 30 min. The reaction mixture was heated to 80^{o}C for 2day and then cooled to room temperature, neutralized with hydrochloric acid and dialysis in distilled water.

3. Results and Discussion

As-synthesized magnetic nanoparticles were synthesized by the thermal decomposition method in an triethylene glycol solvent, according to a reported procedure [4]. Fig 2 shows the characteristic peaks of TREG at 1655, 1437, and 1069 cm^{-1} due to the O-H stretching vibration, C-H bending vibration, and C-O bending vibration, respectively. And The nanoparticles showed the characteristic absorption bands of the Fe–O bond at 570 cm^{-1}. These results suggested that the surfaces of the nanoparticles were successfully modified with the triethylene glycol.

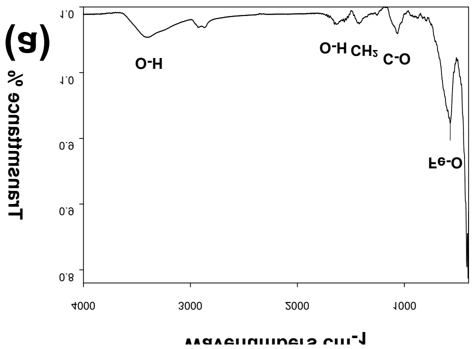

Fig. 2. FTIR spectra of triethylene glycol coated Fe3O4 nanoparticles

The caroboxylated polyglycerol coated magnetic nanoparticles morphology was confirmed by TEM imaging (Fig. 3). The average diameters calculated from TEM image was 8.2±1.4 nm. The average hydrodynamic diameter of the as-synthesized MNPs in water was measured by dynamic light scattering (DLS) to be 35 nm (Fig. 4). Furthermore, the HPG-MNPs displayed good stability in water, even after several lyophilization steps.

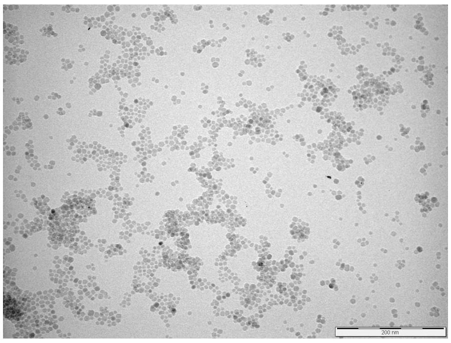

Fig. 3. TEM image of the CPG-coated MNPs.

Ths sodium chloroacetate was selected to give copious carboxylate groups for functionalization of the magnetic nanoparticle surface. These functional groups may enhance the interaction between water and magnetic nanoparticles because the free carboxylate groups extended in water may facilitate the dispersibility of carboxylated magnetic nanoparticles in the aqueous solution and increase the driving force for FO.

Furthermore, the osmotic pressures of draw solutions prepared from carboxylated polyglycerol-coated nanoparticles were also measured using an osmometer to evaluate the efficiency of them as a draw solute in FO.

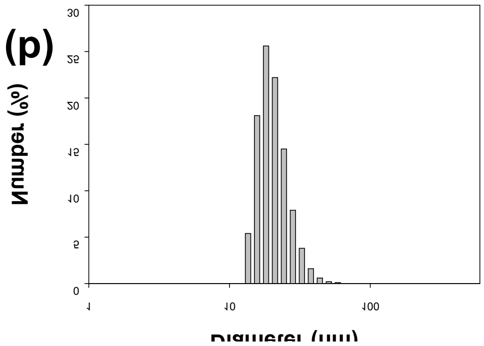

Fig. 4. Size distributions of CPG-coated MNPs

3. Conclusions

In this study, CPG-coated MNPs were successfully synthesized and examined for their utility as a new MNP based draw solute in FO processes. The CPG-MNPs showed no aggregate of particles in water even after placing external magnet, and exhibited a high water flux in FO process. The CPG-MNPs are, therefore, potentially useful as a draw solute in FO processes.

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