

# Synthesis of magnetic nanoparticles as a draw solute in forward osmosis membrane process for the treatment of radioactive liquid waste

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## 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.

As an emerging technology forward osmosis (FO) has attracted growing interest in wastewater treatment and desalination because FO operates at low or no hydraulic pressures. FO is a membrane process in which water flows across a semi-permeable membrane from a feed solution of lower osmotic pressure to a draw solution of higher osmotic pressure [1].

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  $\text{Fe}_3\text{O}_4$  nanoparticles can be separated from water by an external magnet field easily. If  $\text{Fe}_3\text{O}_4$  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].

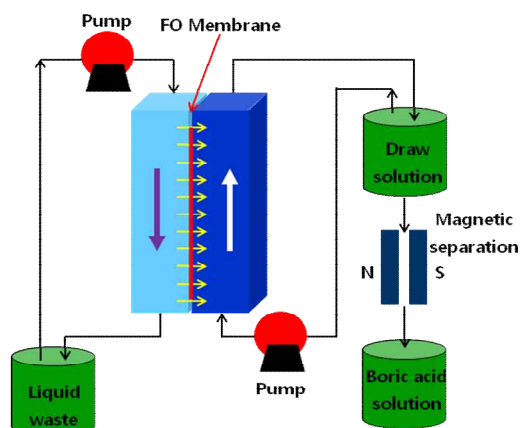


Fig. 1. Schematic diagram of the FO membrane and magnetic separation process using magnetic nanoparticles as a draw solution

The objective of this study is to synthesize the hydrophilic polymer coated  $\text{Fe}_3\text{O}_4$  nanoparticles as a

draw solute in FO for application to separate the boric acid in radioactive liquid waste. The hydrophilic  $\text{Fe}_3\text{O}_4$  nanoparticles were well characterized, and its osmolality was investigated to evaluate the possibility of nanoparticles as a new draw solute in FO application.

## 2. Experiment

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 °C for 1 hour to complete dissolved the solid. The resulting solution was heated to reflux for three hours under  $\text{N}_2$  protection. After cooling to room temperature, ethyl acetate was added to the reaction solution resulted in a black precipitation of magnetic nanoparticles. Then, the nanoparticles were magnetically collected from the solution. After washed with ethyl acetate for three times, the solid productions were obtained drying the precipitation under vacuum. Next, the magnetic nanoparticles were mixed with glycidol with aid of sonication for 1 h. the resulting dispersion was magnetically stirred at 140 °C under an  $\text{N}_2$  atmosphere for 20 h and then allowed to cool down to room temperature. The resulting gel was diluted with distilled water, and the precipitates were obtained by the centrifugation. This washing process was repeated four times to remove the by-product. The washed sample was lyophilized to obtain the polyglycerol coated magnetic nanoparticles.

Next, polyglycerol coated nanoparticles was treated with succinic anhydride at 50°C in the presence of triethylamine, in anhydrous  $\text{N,N}$ -dimethylformamide). After reaction, the residue was dialyzed by employing a 6000-8000 cut-off membrane and lyophilized to obtain the hydrophilic magnetic nanoparticles

## 3. Results and Discussion

As-synthesized magnetic nanoparticles were synthesized by the thermal decomposition method in a triethylene glycol solvent, according to a reported procedure [3]. X-Ray diffraction (XRD) analysis confirmed the crystalline natures of all nanoparticles (Fig. 2). All peaks were well matched with values previously reported for magnetite ( $\text{Fe}_3\text{O}_4$ ) crystals.

Next, we intended to initiate the ring-opening polymerization of glycidol at the hydroxyl groups on the surface of nanoparticles. The obtained nanoparticles

was characterized qualitatively by FTIR, TEM, and dynamic light scattering (DLS).

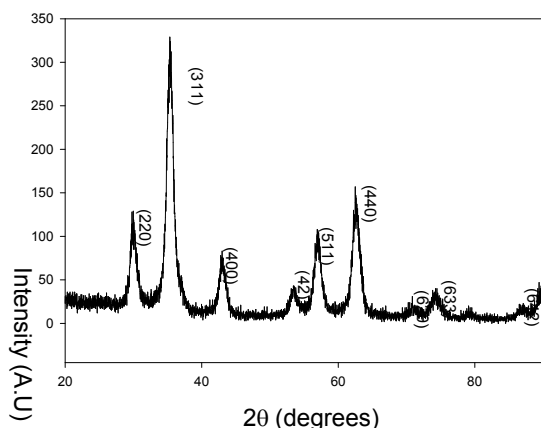


Fig. 2. X-ray diffraction patterns of triethylene glycol coated  $\text{Fe}_3\text{O}_4$  nanoparticles.

In Fig. 3, the FT-IR spectrum of the polyglycerol coated nanoparticles shows a strong band at  $1090\text{cm}^{-1}$  attributed to the C-O-C ether stretch. The spectrum also displays strong bands at around  $2895\text{cm}^{-1}$  corresponding to the  $\text{CH}_2$  stretching vibrations, and at around  $3400\text{cm}^{-1}$ , which is consistent with the large amount of surface hydroxyl groups. These absorption bands provide strong evidence that the  $\text{Fe}_3\text{O}_4$  nanoparticles have been coated with polyglycerol.

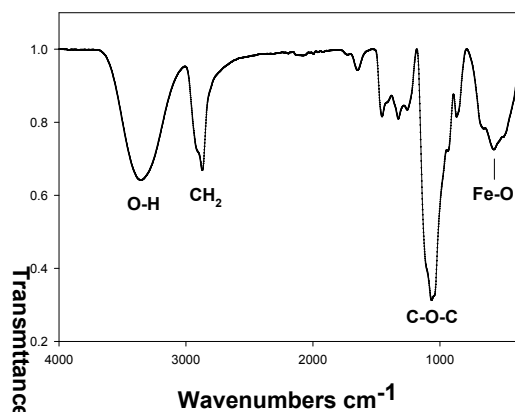


Fig. 3. FTIR spectra of polyglycerol coated  $\text{Fe}_3\text{O}_4$  nanoparticles

To improve the hydrophilicity of nanoparticles, succinic anhydride 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.

DLS data showed that the diameters of magnetic nanoparticles changed from  $20.92\pm 5.65\text{nm}$  to  $21.16\pm 5.77\text{nm}$  after reaction with succinic anhydride

(Fig. 4). The conjugation of carboxyl group on the surface of magnetic nanoparticles reduced the zeta-potential value from  $(-11.3\pm 0.61)$  to  $(-20.4\pm 1.35\text{mV})$  by ionization of carboxylic acid. Therefore, these results indicate that the polyglycerol on the surface of magnetic nanoparticles were successfully carboxylated.

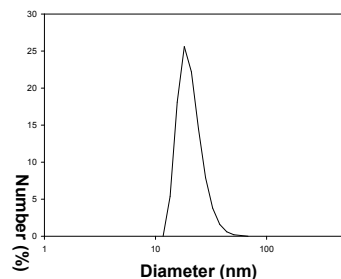


Fig. 4. Size distribution of carboxylated polyglycerol coated  $\text{Fe}_3\text{O}_4$  nanoparticles

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.

#### 4. Conclusion

The carboxylated polyglycerol coated  $\text{Fe}_3\text{O}_4$  nanoparticles have been successfully synthesized. The nanoparticles were about 50 nm in diameter and showed the good colloidal stability in aqueous solution. The osmolality and osmotic pressure were enough high to be used as a draw solute in FO. For the future work, we will investigate the performance of our magnetic draw solute in FO to remove boron in the simulated liquid waste.

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