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Removal of Zirconium (Zr) from Aqueous Solution by Polymer Enhanced Ultrafiltration

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ABSTRACT

Although the world output of zirconium has been declining, increasing zirconium consumption cannot compete with this situation. For this reason, removal and recovery of zirconium become important. This work is focused on the removal of Zirconium (as ZrO_2^{2+}) ions from an aqueous solution using polymer-enhanced ultrafiltration (PEUF) techniques with water-soluble Poly (sodium-p-styrene sulfonate, SSS) sorbent. The negatively charged sulfonic acid groups in the polymer interact with positively charged ZrO_2^{2+} cation thereby enabling the efficient removal of ZrO_2^{2+}through ultrafiltration. The effect of polymer: zirconium mole ratio, initial solution pH, and the presence of interfering ions on the removal of zirconium was investigated. The obtained results demonstrated that ZrO_2^{2+} can be removed from the aqueous solution by the PEUF technique with more than 99% efficiency at pH ≥ 2 using polymer: Zr molar ratio of 5:1. The presence of interfering ions did not affect the percent removal of ZrO_2^{2+}.

Keywords: Polymer-enhanced ultrafiltration, Heavy metal removal, Ion Exchange, water treatment, Zirconium

1.0 INTRODUCTION

Zirconium (Zr) is widely distributed in the earth's crust. It is a significant material for nuclear energy application due to its high transparency to neutrons. It is widely used in industry as secondary metal as it has outstanding chemical, thermal and optical properties [1–3]. "The recovery and purification of nuclear-grade zirconium from spent nuclear fuel cladding have been of great interest due to vast economic and environmental benefits, which result in ~$40 million/year due to the high cost of nuclear-grade zirconium and nuclear waste disposal savings" [4].

Various separation techniques such as biosorption, adsorption, ion exchange, solvent extraction were applied for the removal and recovery of Zr from aqueous solutions or real samples [2,5–8].

The PEUF is a hybrid process that combines water-soluble polymers and ultrafiltration (UF) techniques. In PEUF, water-soluble polymers have a relatively high molecular weight cut-off (MWCO) that allows the UF membrane to reject. Such polymers also have functional groups to bind ions/small molecules. In this process, unwanted ions/small molecules are first complexed by a polymer to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained whereas permeate water is then purified from the unwanted molecules/ions [9–12].

So far, various metal ions were removed from water by PEUF. For example, Chen *et al.* [13] used the

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PEUF system to remove Na^+, K^+, Li^+, H^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, and Ni^{2+} from an aqueous solution by using the SSS a water-soluble polymer. The selectivity sequence of cation affinity for PSS was found to be $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$.

The authors also concluded that the concentration of water-soluble polymer in the solution has an important effect on the removal rate and when it was adjusted to 3 g/L, the 80% Pb^{2+} and 71% Cu^{2+} removal were obtained. Hamhami *et al.* [14] studied the recovery of samarium (Sm^{3+}) from aqueous solutions by poly(sodium 4-styrene sulfonate) assisted ultrafiltration. The removal of Sm^{3+} increased with the increment of polymer concentration in the solution. However further increment in polymer concentration led to a decrease in Sm^{3+} removal. The authors stated that such decrement caused by several phenomena such as concentration polarization, membrane fouling, osmotic pressure, and precipitation. The solution pH was also affected the Sm^{3+} removal rate. At pH 1, about 10% Sm^{3+} removed. When the pH of the solution was increased to 6, removal of Sm^{3+} reached 94%.

Rivas and Moreno-Villoslada [15] studied the removal of Cd^{2+} from an aqueous solution in the presence of Na^+ ion by PEUF using SSS water-soluble polymer. In the absence of Na^+ the complete removal of Cd^{2+}achieved. In the presence of 0.4 M $NaNO_3$ removal of Cd^{2+} decreased.

However, to the best of our knowledge, the removal of Zr by PEUF has not been reported. This work aims to investigate the optimum conditions for the removal of Zr by PEUF. In the PEUF procedure, polymer dose (i.e. polymer: target element ratio), initial solution pH, ionic strength (interfering ion), temperature, and applied pressure are the parameters that affect the removal rate [16]. For this purpose, the effect of rpolymer: Zr ratio, initial solution pH, and interfering ions on the removal of Zr was investigated.

2.0 METHODS

2.1 Materials

The water-soluble Poly (sodium-p-styrene sulfonate, SSS) with average MWCO 70 kDa was obtained from Across. Zirconyl chloride octahydrate was obtained from Sigma-Aldrich. Merck Biomax 10 kDa UF disc membrane was used in the experiments. The Amicon UFSC40001 dead-end stirred cell (400 mL capacity) was used in the experiments. The pH of the solutions was adjusted by using HCl or NH_3 solutions.

2.2 PEUF Procedure

The 250 mL of zirconium containing (5 mg/L) solution and SSS polymer were stirred in UF cell for the polymer-Zr ion-exchange reaction. After 60 minutes, the cell pressurized by using compressed nitrogen gas with an operating pressure of 1 bar to start the ultrafiltration test. The 100 mL permeate was collected (10 mL x 10 tubes) in permeate probes. The concentration of zirconium in the permeate was measured. The schematic diagram of the process is shown in Figure 1.

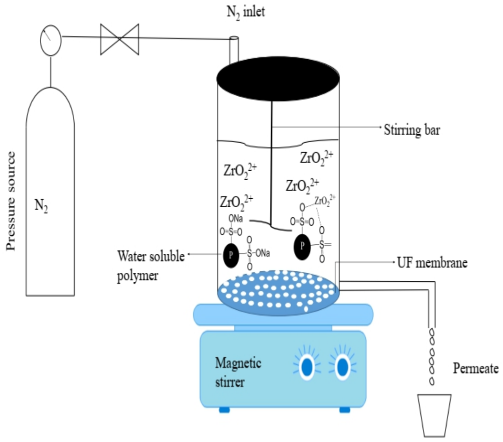

Figure 1 Scheme of the polymer-enhanced ultrafiltration, PEUF

The zirconium removal conditions were optimized by changing the PEUF parameters; polymer: Zr mole ratio (1:1, 5:1, 10:1), initial solution pH (1-4), and presence of interfering ions (Na^+, K^+, $Ca^{2+,}$ and Mg^{2+}) were optimized.

The Zr removal, R, (i.e. rejection) was calculated as shown in Equation 1.

$$R = \frac{C_0 - C_p}{C_0} * 100 \text{ …….. (1)}$$

where C_o and C_p are concentrations of ZrO_2^{2+} ions in the feed and permeate solutions, respectively.

2.3 Characterization of SSS

Fourier transform infrared (FT-IR) measurements (KBr discs) were recorded in the region of 4000–400 cm^{-1} on PerkinElmer spectrophotometer.

2.4 Analyses

The Alizarin Red S method [17] was used to determine the concentration of ZrO_2^{2+} by UV/VIS spectrophotometer (Agilent, Cary). The pH of the solution was measured by a pH meter (FG2 model, Mettler-Toledo).

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 displays the FTIR peaks of the polymer used in this experiment. The significant peak at 3434 cm^{-1} is related to intermolecular hydrogen bonding. The peak at around 2922 cm^{-1} is the C–H vibration. The peaks at 1600 – 1400 cm^{-1} are attributed to aromatic ring C-H in-plane bending. The main characteristic band of SSS at 1038 and 1008 cm^{-1} (due to —SO_3Na group) [18–21].

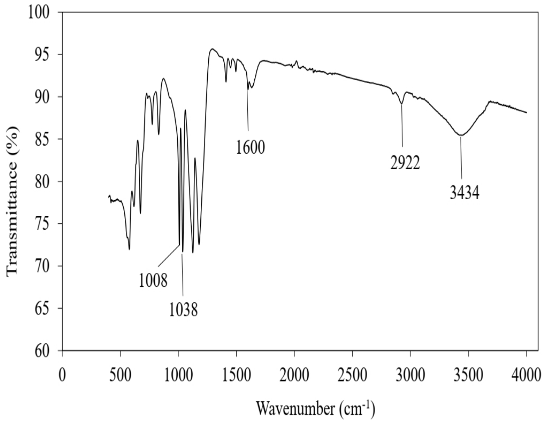

Figure 2 FTIR spectra of SSS

The elemental analysis of polymer was carried out by the Leco Truspec Micro CHNS analyser. Results showed that the polymer consists of 35 % carbon, 3.6 % hydrogen and 9.2% sulphur.

3.2 Effect of Polymer: Zr Mole Ratio on the Removal

The various dose of the polymer was added to Zr containing solutions (5 mg-Zr/L, pH 4) before filtration and the resulting removal rate is depicted in Figure 3.

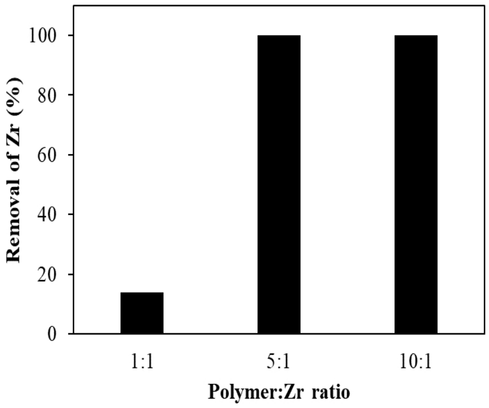

Figure 3 Removal of Zr as a function of polymer: Zr ratio

As can be seen from the Figure the percent removal of Zr increased with an increment on polymer dose. This finding was coincident with the results of Barakat and Schmidt [9] and Sánchez *et al.* [22]. They also observed that increment in polymer: metal ion ratio improved the removal rate.

The increasing the polymer: Zr ratio allows more available ion-exchange sites and in turn increases the removal efficiency. The ion-exchange reaction between the polymer and Zr is shown in Equation 2.

$$2R - SO_3^-Na^+ + ZrO_2^{2+} \leftrightarrows (R - SO_3^-)_2ZrO_2^{2+} + 2Na^+ \text{ .... (2)}$$

The optimum polymer: Zr dose was found to be 5:1 and such ratio was used in the further experiment.

3.3 Effect of Initial Solution pH on the Removal

In this series of experiment, initial solution pH varied from 1 to 4 while Zr concentration (5 mg-Zr/L) and polymer: Zr ratio was adjusted to 5:1. The removal rate of Zr versus different solution pH is depicted in Figure 4. It is clear from the figure that at pH 1, the SSS polymer could not remove the Zr. When the pH of the solution was increased, the percent removal of Zr increased also.

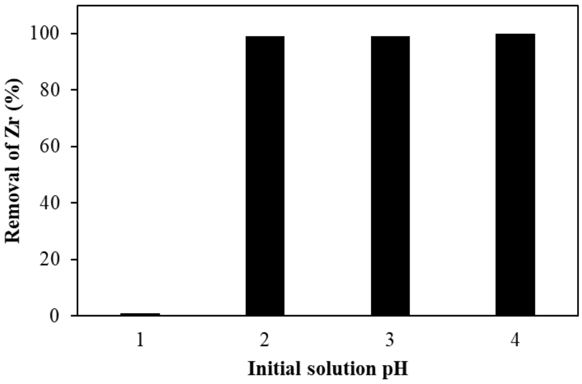

Figure 4 Removal of Zr as a function of initial solution pH

This behaviour can be explained that there is a competition between H^+ and ZrO_2^{2+} ions for the available functional groups of SSS. At pH 1, the concentration of H^+ is larger than Zr and this leads to an increase in the ion-exchange reaction rate of H^+ and leads to a low removal rate for Zr [21]. The optimum pH range was found as ≥2.

Similar results have been found in the literature for heavy metal removal using SSS polymer. Chen *et al.* [13] applied PEUF for Cu^{2+} removal. They found that removal of Cu^{2+} was 64.7% at pH 2.2 and it was increased to 96.6 at pH 7. A much the same trend was observed for the removal of Sm^{3+} ion [14].

3.3 Effect of Interfering Ions on the Removal

The interferences of ions were determined at pH 4 with polymer: Zr ratio 5:1. The concentration of Zr was adjusted as 5 mg/L and obtained results summarized in Table 1.

Table 1 Effect of interfering ions on the removal of Zr

Interfering ion	**The concentration of interfering ion (mg/L)**	**Removal of Zr (%)**
Na^+	5	> 99
K^+	5	> 99
Ca^{2+}	5	> 99
Mg^{2+}	5	> 99

It is clear from Table 1 that; the removal rate was not affected at a low concentration of interfering ions.

Similar findings were reported by Verbych *et al*. [23]. They stated that at low concentration of Na^+ and Ca^{2+} in the solution removal of Cu^{2+} was almost constant, when the Na^+ and Ca^{2+} in the solution 400 times higher than the Cu^{2+} concentration, the removal rate of Cu^{2+} decreased.

Lam *et al*. [24] investigated the effect of Na^+ on Ni^{2+} removal. The authors concluded that the presence of $2x10^{-1}$ M Na^+, Ni^{2+} removal tended towards zero.

4.0 CONCLUSION

The water-soluble SSS polymer was tested for the removal of Zr with PEUF. The optimum conditions for the Zr removal were found as polymer Zr: ratio 5:1 and pH ≥2. The presence of interfering ions at low concentrations did not affect the removal rate.

In a conclusion, PEUF may be an alternative method for the removal of Zr from solutions.

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