

Removal of perchlorate from groundwater by the polyelectrolyte-enhanced ultrafiltration process

Hasina Parvin Huq, Jung-Seok Yang, Ji-Won Yang*

*Department of Chemical and Biomolecular Engineering, KAIST,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea
Tel. + 82 (42) 869-3924; Fax: +82 (42) 869-3910; email: jwyang@kaist.ac.kr*

Received 25 January 2006; Accepted 10 February 2006

Abstract

The polyelectrolyte enhanced ultrafiltration (PEUF) process for perchlorate removal from groundwater containing common co-contaminants like nitrate and sulfate was investigated. Existing processes such as ion exchange can remove perchlorate but with greater complexity, especially when applied in the presence of high nitrate and sulfate concentration. The effect of cationic polyelectrolyte, poly(diallyldimethyl ammonium chloride) (PDADMAC) concentration and the effect of nitrate and sulfate in a broader concentration range were observed. In the absence of other anions, a lower amount of PDADMAC (0.5–1 mM) can remove more than 90% of perchlorate from the aqueous phase. However, in the presence of 5 mM nitrate, perchlorate removal decreases as the available binding sites of PDADMAC for perchlorate are reduced. In the presence of both 1 mM to 10 mM nitrate and sulfate, 60–80% perchlorate was removed with 30 mM PDADMAC. The removal of sulfate and nitrate in this case was nearly 75% and 65%, respectively. The effect of other parameters such as relative flux, membrane material and pore size were also observed to study the feasibility of PEUF for perchlorate removal. Consequently, PEUF proved to be an effective perchlorate removal process owing to the high removal efficiency and suitability in groundwater remediation containing other contaminants.

Keywords: Groundwater; Perchlorate; Cationic polyelectrolyte; Ultrafiltration

*Corresponding author.

Presented at the EuroMed 2006 conference on Desalination Strategies in South Mediterranean Countries: Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean. Sponsored by the European Desalination Society and the University of Montpellier II, Montpellier, France, 21–25 May 2006.

0011-9164/07/\$– See front matter © 2007 Elsevier B.V. All rights reserved

1. Introduction

Groundwater, the major source for drinking water, is more prone to be contaminated due to the increasing toxicity impact of a most recently enlisted compound — perchlorate. Both the natural and manmade perchlorate anion is commonly associated with the solid salt of potassium, sodium and ammonium, the latter being the most popular. Ammonium perchlorate manufactured mostly in the US is widely used as the primary ingredient of solid rocket propellant. Almost 90% of perchlorate compounds are manufactured for the use in defense activities and the aerospace industry as explosives and other military munition items [1–3]. Harmful perchlorate interferes with iodide uptake into the thyroid gland, resulting in thyroid malfunctioning that extremely hinders human mental growth [3–5].

Highly soluble and mobile perchlorate can persist in the environment for many decades under typical groundwater conditions. Perchlorate is a strong oxidizing agent and kinetically a sluggish species [1]. Such eccentric characteristics of perchlorate make it reluctant to respond to the most standard physical and chemical treatment processes.

Currently, research is ongoing to determine a feasible perchlorate removal process. The anion-exchange method is currently the most commonly used perchlorate removal process. While treating water with a high concentration of sulfate and nitrate, the capacity for perchlorate removal is significantly reduced in the ion-exchange method. In the presence of co-contaminants such as sulfate and nitrate, the selection of a proper resin makes this process more susceptible for the removal of perchlorate ions. Excessive disposal of brine from the ion-exchange process and production of secondary contaminants and high costs due to multiple steps limit this process in a real field application [6–9].

Researchers have also studied biological treatments in this regard [9–12]. The biological pro-

cess is time consuming, complicated and sensitive to seasonal variation. Lastly, there has been some research in the area of phytoremediation which may only have limited application in the future [12]. Therefore, a beneficial, effective and simple removal method is a necessary step for the perchlorate contaminant.

The fundamental mechanism of membrane separation technology extending to polyelectrolyte enhanced ultrafiltration (PEUF) is recognized as one of the most meritorious technologies in which membranes with pores smaller than the used polymeric agents are employed. Thus, polymer–anion complexes can be retained and the target ions are separated from the rest of the solution process [13]. PEUF until now has been used for the removal of heavy metals [14–17]. No research results have been reported for the use of PEUF in perchlorate removal.

The simplicity of operation of single aqueous phase PEUF makes it an attractive process. The problems of multiphase separation processes such as mass-transfer limitations, interface reactions and membrane instability are not observed [15]. The binding ability and the selectivity of the polyelectrolyte can be further increased by introducing various functional groups to the polymers. Considering the afore-mentioned merits, PEUF could be an effective perchlorate removal process taking the economic and environmental aspects under serious consideration.

Polyelectrolytes used in PEUF are highly charged macromolecules or aggregates, formed in aqueous solution by dissociation of charged units. Such dissociation is typically accompanied by smaller oppositely charged counter ions that tend to neutralize the charge on the repeating units of the macromolecule preserving electroneutrality. The most frequently used water-soluble cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDADMAC) was used in the experiment as it has very low acute and chronic toxicity to environmental organisms and is readily biodegradable. The feasibility in terms of perchlorate

removal efficiency using this method was investigated based on different parameters. The perchlorate removal effect in presence of nitrate and sulfate was also observed in various concentrations, from low to extreme levels to incorporate a real field scenario.

2. Experimental

2.1. Materials and methods

Synthetic water containing perchlorate and PDADMAC was used. The technical grade of PDADMAC and sodium perchlorate were purchased from Sigma (USA). The concentration of PDADMAC was calculated based on the monomer unit, DADMAC. To observe the effect of other ions, reagent-grade sodium nitrate and sodium sulfate were purchased from Sigma-Aldrich (USA). All chemicals were used without further purification. The water used in this study was purified by the EASYpure water purification system (Barnstead, USA). Two types of membranes, regenerated cellulose (MWCO 3,000: YM3, 10,000: YM10) and polyether sulfone (MWCO 10,000: PES 10), were used.

All the perchlorate and PDADMAC solutions were shaken using a magnetic stirrer for 8 h before filtration to obtain equilibrium. Pressure and temperature were maintained at 2 bars and room temperature during filtration, respectively. Based on the analytical detection limit, 1 mM of perchlorate was used as the initial concentration in the removal process. The feed tank was filled with 200 ml of feed solution. To perform this dead-end batch filtration, a batch stirred cell (Millipore 8400, USA) was used. During the filtration the feed solution was stirred at 160 rpm to minimize membrane fouling. The permeate stream was sampled at desired time intervals and permeate flux was calculated from the permeate volume.

2.2. Analysis

The concentration of nitrate, sulfate and perchlorate were analyzed using ion chromatography

(IC, Metrohm 732, Netherlands). Shodex SI 90-4E column (for general analysis) was used and temperature was maintained at 40°C. A dose of 4 mM of Na₂CO₃ was used as eluent with 1.2 ml/min.

The removal efficiency of nitrate, perchlorate, and sulfate was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100$$

Here, R is the removal efficiency of the ions, and C_f and C_p are the concentrations of each component in the feed and permeate, respectively. The LR-COD kit (Humas, Korea) was used to analyze the concentration of PDADMAC.

3. Results and discussion

3.1. Relative flux

Relative flux is the ratio between solution flux and water flux. As shown in Fig. 1, in an absence of other ions, the flux decline is insignificant compared to other filtration process as the viscosity of the solution decreased due to the high mobility of perchlorate ion and use of low concentration of PDADMAC. The small flux decline mainly occurred due to the increase in the concentration of retained macromolecule, i.e., PDADMAC accumulation on the membrane surface with the passing of time.

Flux decline was higher in the presence of high concentrations of nitrate and sulfate ions due to higher accumulation of PDADMAC bonded with other ions on the membrane surface. Higher flux reduction was also observed due to an increase in the PDADMAC concentration which enhances the viscosity of the aqueous solution. In both cases, in the absence or presence of other contaminants, the flux reduction was less in YM 3 and PES 10 than that of YM 10. The actual

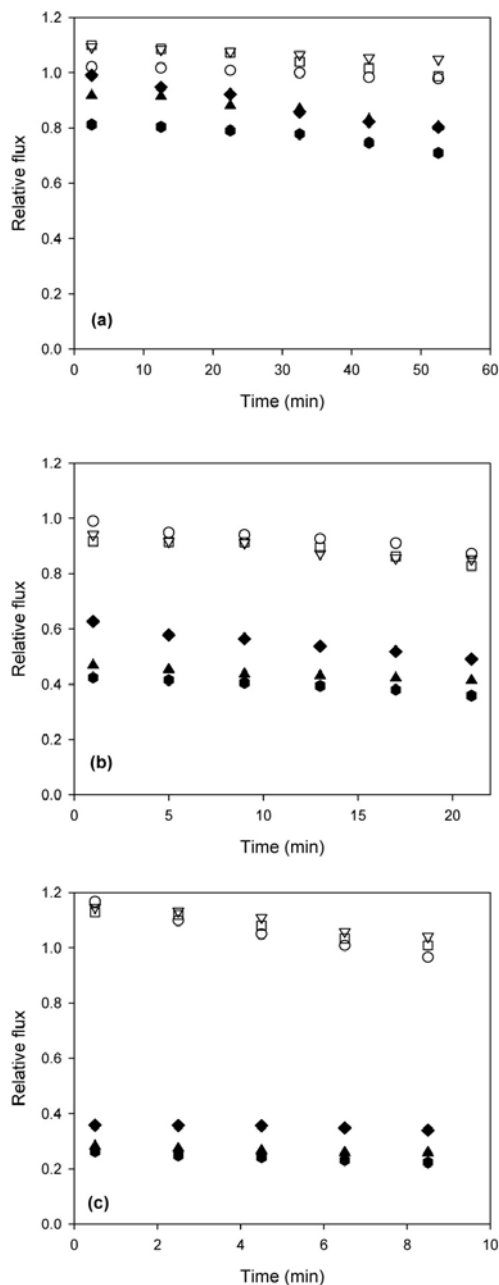


Fig. 1. Relative flux of PEUF in absence and in presence of other ions with (a) YM 3, (b) YM 10 and (c) PES 10, respectively (\circ ClO_4^- :PDADMAC = 1:0.5; ∇ ClO_4^- :PDADMAC = 1:0.7; \square ClO_4^- :PDADMAC = 1:1.0; \blacklozenge ClO_4^- :PDADMAC: NO_3^- : SO_4^{2-} = 1:30:1:1; \blacktriangle ClO_4^- :PDADMAC: NO_3^- : SO_4^{2-} = 1:30:5:5; \bullet ClO_4^- :PDADMAC: NO_3^- : SO_4^{2-} = 1:30:10:10).

flux of the YM 10 was greater than that of YM 3 or PES 10 as the accumulated amount of PDADMAC was less at higher MWCO. Therefore, the higher MWCO membrane seems to be more advantageous in permeate flux.

3.2. Effect of membrane types and pore size

In Fig. 2, the perchlorate removal in the PES type membrane showed a small decrease. However, overall, perchlorate removal efficiency is almost independent of membrane types and pore size. A regenerated membrane, YM 10, showed the most convenience in the matter of perchlorate removal efficiency and operation time. It was observed that the regenerated cellulose membrane with higher MWCO was more feasible in enhancing the capacity and efficiency of wastewater treatment per unit time under the same operating condition.

3.3. Effect of polyelectrolyte concentration

As the PDADMAC amount increased from 0.5 to 1.0 mM, the removal of perchlorate ions also increased from 85% to 95% due to the increase in the ionic interaction between perchlorate and PDADMAC (Fig. 2). Here a smaller oppositely charged counter ion, perchlorate tends to neutralize the charge on the repeating units of the PDADMAC preserving electroneutrality. However, compared to the small increase of PDADMAC concentration, perchlorate removal was high. Also the permeate concentration of PDADMAC was very low as most of the PDADMAC remained in the retentate.

3.4. Effect of presence of other contaminants

3.4.1. Effect of PDADMAC concentration in the presence of nitrate

As shown in Fig. 3, PDADMAC also absorbed certain amounts of nitrate as an oppositely charged ion which causes a significant

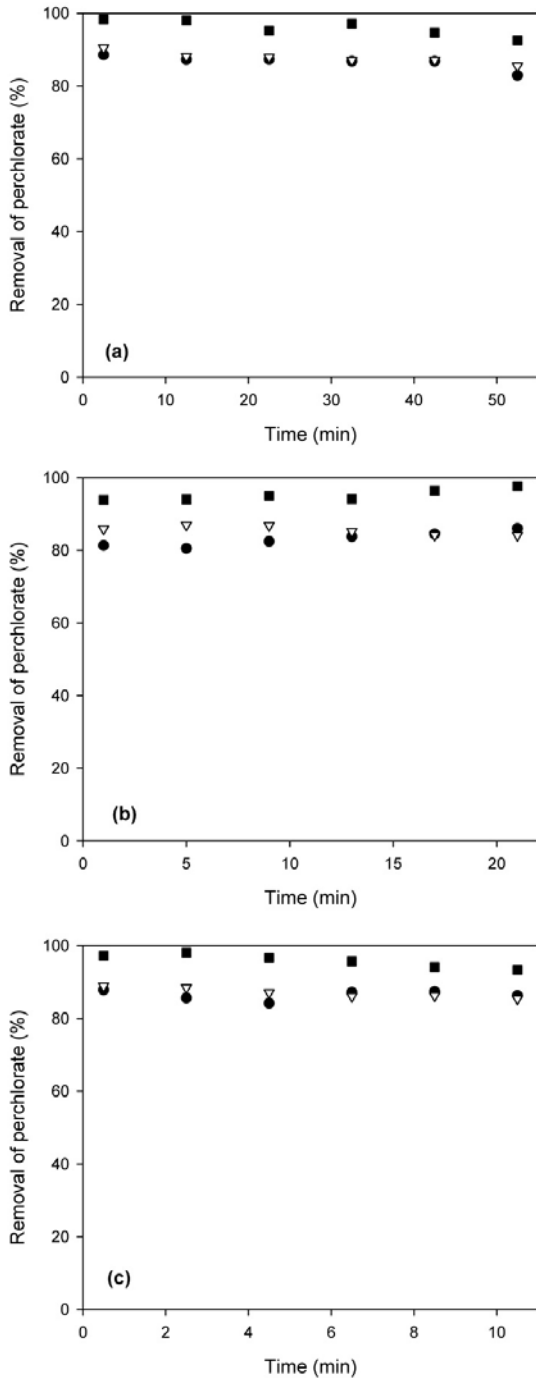


Fig. 2. Removal of perchlorate in the absence of other ions with (a) YM3, (b) YM10, and (c) PES10, respectively (● $\text{ClO}_4^-:\text{PDADMAC} = 1:0.5$; ▽ $\text{ClO}_4^-:\text{PDADMAC} = 1:0.7$; ■ $\text{ClO}_4^-:\text{PDADMAC} = 1:1.0$).

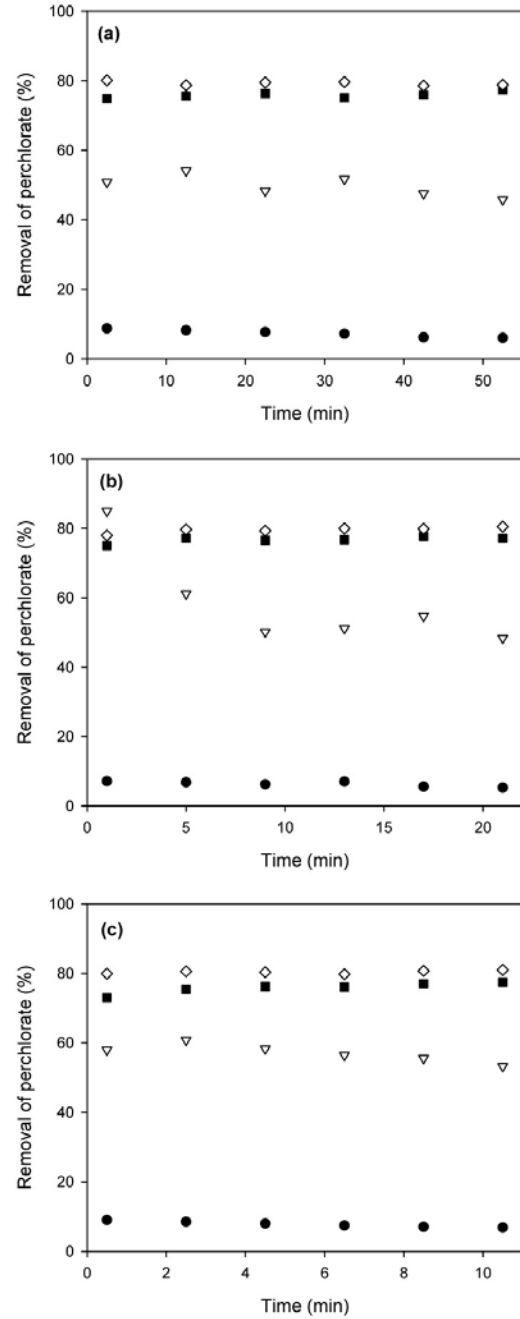


Fig. 3. Removal of perchlorate in the presence of nitrate in various ratio of perchlorate and PDADMAC with (a) YM3, (b) YM10, and (c) PES10, respectively (● $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:0.5:5$; ▽ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:10:5$; ■ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:20:5$; ◇ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:30:5$).

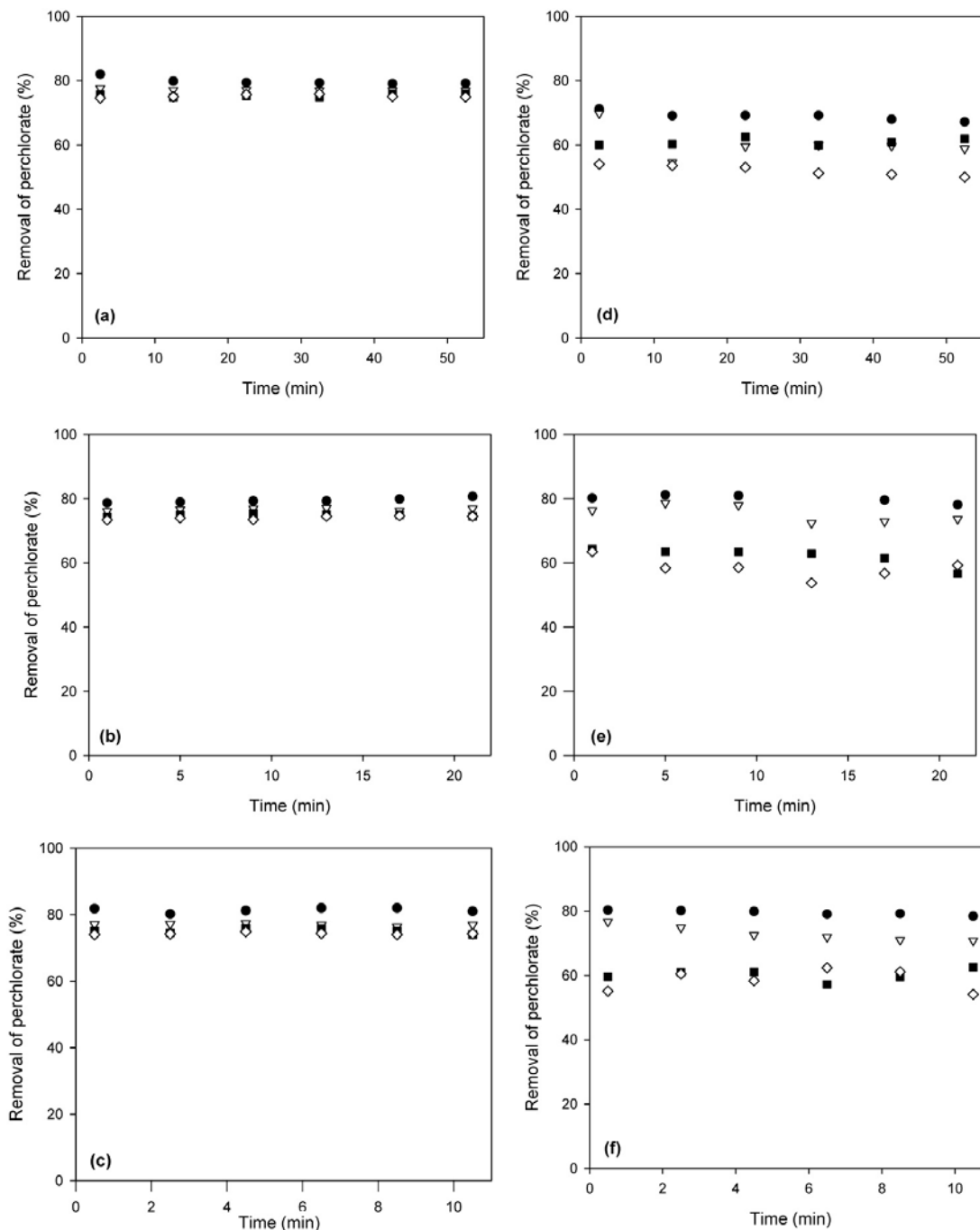


Fig. 4. Removal of perchlorate in the presence in 1:30 (mM) of perchlorate and PDADMAC with (a,d) YM3, (b,e), YM10, and (c,f.) PS10, respectively. (a,b,c) In the presence of nitrate (● $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:30:1$; ▽ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:30:5$; ■ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:30:7$; ◇ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^- = 1:30:10$) and (d,e,f) in the presence of sulfate (● $\text{ClO}_4^-:\text{PDADMAC}:\text{SO}_4^{2-} = 1:30:1$; ▽ $\text{ClO}_4^-:\text{PDADMAC}:\text{SO}_4^{2-} = 1:30:5$; ■ $\text{ClO}_4^-:\text{PDADMAC}:\text{SO}_4^{2-} = 1:30:7$; ◇ $\text{ClO}_4^-:\text{PDADMAC}:\text{SO}_4^{2-} = 1:30:10$).

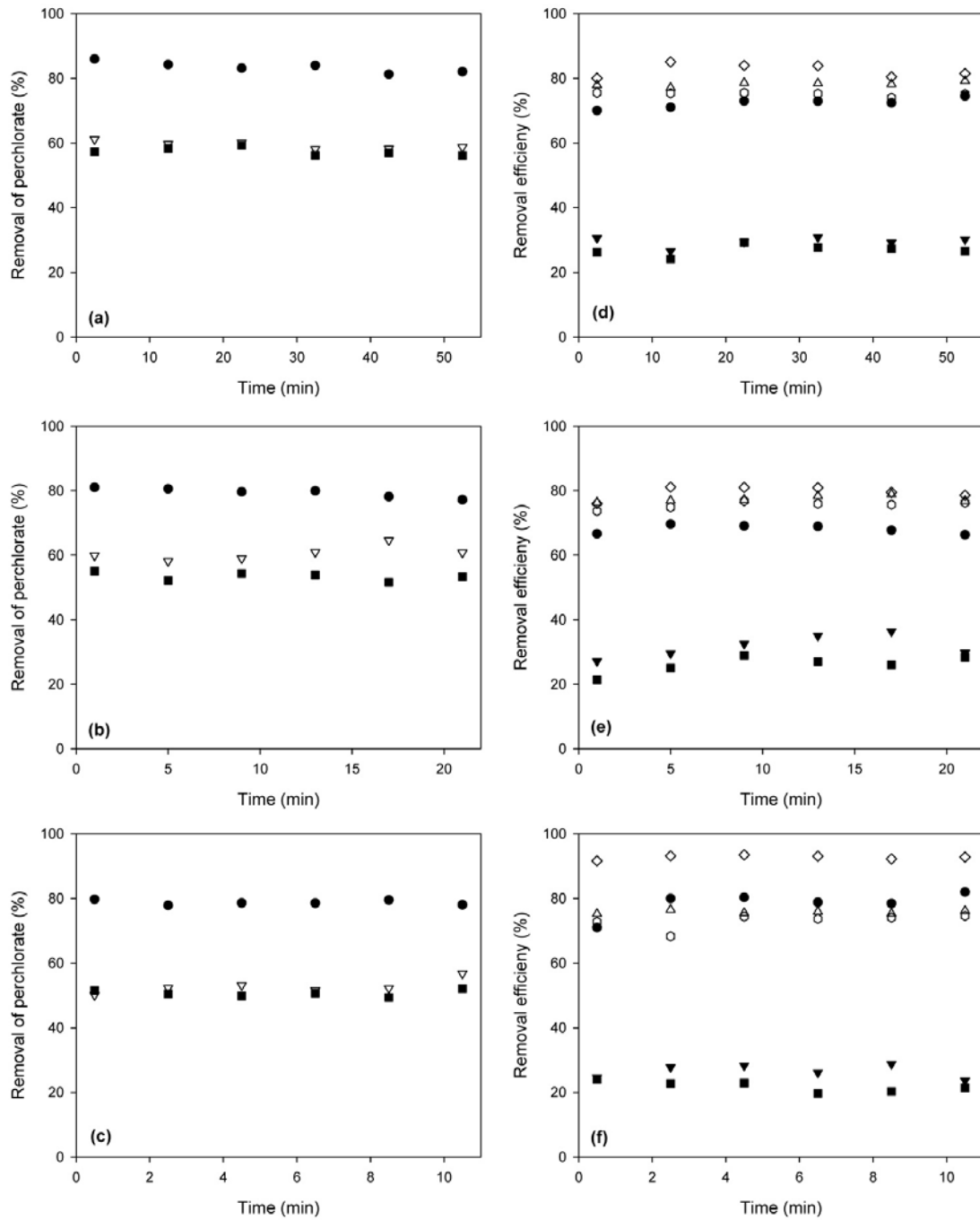


Fig. 5. Removal of (a,b,c) perchlorate (● $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:1:1$; ▽ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:5:5$; ■ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:10:10$), (d,e,f) sulfate (◇ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:1:1$; △ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:5:5$; ○ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:10:10$) and nitrate (● $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:1:1$; ▼ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:5:5$; ■ $\text{ClO}_4^-:\text{PDADMAC}:\text{NO}_3^-:\text{SO}_4^{2-} = 1:30:10:10$) in the presence of multiple ions with (a,d) YM 3, (b,e) YM10, and (c,f) PES10, respectively.

decrease in binding strength between PDADMAC and perchlorate. Hence, to obtain higher removal efficiency of perchlorate in the removal process, an excessive amount of PDADMAC should be present to enhance the effect of the nitrate concentration.

With the increase of the ratio of perchlorate and PDADMAC from 1:10 to 1:30, the removal of perchlorate also increased up to 80%. When 20 and 30 mM of PDADMAC were added, perchlorate removal showed almost a stable removal of 80%, which implies that a 1:30 mM ratio of perchlorate and PDADMAC is the optimum ratio for the removal of perchlorate in the presence of maximum 5 mM of nitrate ion. Therefore, based on these data, depending on the presence of a high concentration of other ions, the polyelectrolyte and perchlorate ratio can be increased for the optimal removal of perchlorate.

3.4.2. Effect of nitrate and sulfate in the removal of perchlorate

According to Fig. 4, up to 5 mM of nitrate has less effect in the removal of perchlorate in the presence of 30 mM of PDADMAC. As shown in Fig. 4, in the presence of sulfate the perchlorate removal efficiency decreases as the divalent ions have higher binding affinity towards the polyelectrolyte. From 1 to 5 mM of sulfate the perchlorate removal efficiency remained around 80%. However, with the increasing sulfate concentration above 5 mM, the perchlorate efficiency decreased to 65%. These data imply that using 1:30 mM of perchlorate and PDADMAC in the presence of a single ion such as only sulfate or only nitrate, 80% removal of perchlorate is the maximum value that can be achieved.

In the presence of both nitrate and sulfate, the perchlorate removal efficiency varied from 60% to 80% (Fig. 5). Data show that in the presence of 1 mM of nitrate and sulfate the removal efficiency was around 80% and nitrate and sulfate removal efficiency was also 80% and 70%

(Fig. 5), respectively. With an increase of concentration as high as 10 mM of nitrate and sulfate, removal efficiency of perchlorate seems to have less of an effect on perchlorate removal, which is within 60%. At the same time the sulfate and nitrate removal efficiency was 80% and approximately 40%, respectively (Fig. 5). It was observed that in the range of 1 mM concentration of sulfate and nitrate, it is possible to remove perchlorate above 80% along with a sufficient removal of sulfate and nitrate. As shown in Fig. 5 in the presence of sulfate and nitrate, the perchlorate removal efficiency decreased due to the competitive binding with PDADMAC.

4. Conclusions

PEUF can be an extremely effective alternative to the ion-exchange method if applied with proper engineering skills focusing on environmental aspects. This study shows that the removal of perchlorate depends on the characteristics and concentration of the polyelectrolyte. The initial perchlorate concentration (1 mM) chosen in the study, based on the detection limit of the available analytical tools, was already high and expected in extreme cases in the groundwater contaminated site. Yet the high removal of perchlorate (>90%) was possible using lower amounts of PDADMAC (~ 1 mM), which makes this single-step process very economical in the absence of other ions.

Furthermore, in the presence of other common groundwater co-contaminants like nitrate and sulfate, a high ratio of PDADMAC to perchlorate is necessary to increase the removal of perchlorate. However, addition of a higher concentration of PDADMAC does not make the process economically unstable as it can give simultaneously a high removal of co-existing contaminants such as nitrates and sulfates with perchlorate, depending on the concentration ratio. This process also decreases the possibility of secondary pollution as

the permeate concentration contains negligible amounts of PDADMAC and remains mostly in the retentate.

The operational condition and process requirement criteria are the basic parameters based on which the appropriate technology for removal was selected. The PEUF process can be used successfully with high removal efficiency using a low concentration of polyelectrolyte. However, perchlorate does not exist alone in real contaminated sites. PEUF can also be a better alternative in the cases where the simultaneous removal of perchlorate, nitrate and sulfate are needed.

Acknowledgement

This work was partially supported by a grant (M1-0412-00-0001) from the Korea Ministry of Science and Technology through the National Research Laboratory program, and by KOSEF through the Advanced Environmental Monitoring Research Center (ADEMRC) at Gwangju Institute of Science and Technology (GIST).

References

- [1] E.T. Urbansky, Perchlorate chemistry: Implications for analysis and remediation, *Bioremed. J.*, 2 (1998) 81–95.
- [2] R.Q. Gullick, M.W. Lechvallier and T.A.S. Barhorst, Occurrence of perchlorate in drinking water sources, *J. AWWA*, 93 (2001) 66–77.
- [3] J. Wolff, Perchlorate and the thyroid gland, *Pharmacol. Rev.*, 50 (1998) 89–105.
- [4] F.X. Li, L. Squartsoff and S.H. Lamm, Prevalence of thyroid diseases in Nevada counties with respect to perchlorate in drinking water, *J. Occup. Environ. Med.*, 43 (2001) 630–634.
- [5] W.L. Goleman, J.A. Carr and T.A. Anderson, Environmentally relevant concentrations of ammonium perchlorate inhibit thyroid function and alter sex ratios in developing *Xenopus laevis*, *Environ. Toxicol. Chem.*, 21 (2002) 590–597.
- [6] V. Roquebert, S. Booth, R.S. Cushing, G. Crozes and E. Hansen, Electrodialysis reversal (EDR) and ion exchange as polishing treatment for perchlorate treatment, *Desalination*, 131 (2000) 285–291.
- [7] J.R. Batista, F.X. McGarvey and A.R. Vieira, The removal of perchlorate from waters using ion exchange resins, in: *Perchlorate in the Environment*, E.T. Urbansky, ed., Plenum Press, New York, 2000, pp. 135–146.
- [8] A.R. Tripp and D.A. Clifford, The treatability of perchlorate in groundwater using ion exchange resins, in: *Perchlorate in the Environment*, E.T. Urbansky, ed., Kluwer Academic/Plenum, New York, 2000, pp. 135–146.
- [9] B.E. Logan, J. Wu and R.F. Unz, Biological perchlorate reduction in high-salinity solutions, *Water Res.*, 35 (2001) 3034–3038.
- [10] B.C. Okeke, T. Giblin and W.T. Frankenberger, Jr., Reduction of perchlorate and nitrate by salt tolerant bacteria. *Environ. Poll.*, 118 (2002) 357–363.
- [11] B.E. Logan and D. LaPoint, Treatment of perchlorate- and nitrate-contaminated groundwater in an autotrophic, gas phase, packed-bed bioreactor, *Water Res.*, 36 (2002) 3647–3653.
- [12] V.A. Nzungu and C. Wang, Influences of phytoremediation of perchlorate-contaminated water, in: *Perchlorate in the Environment*, E.T. Urbansky, ed., Kluwer Academic/Plenum, USA, 2000, pp 219–230.
- [13] S. Tabatabai, J.F. Scamehorn and S.D. Christian, Economic-feasibility study of polyelectrolyte enhanced ultrafiltration (PEUF) for water softening, *J. Membr. Sci.* 100 (1995) 193–199.
- [14] M.R. Pastor, E. Samper-Vidal, P.V. Galván and D. Prats Rico, Analysis of the variation in the permeate flux and of the efficiency of the recovery of mercury by polyelectrolyte enhanced ultrafiltration (PE-UF), *Desalination*, 151 (2002) 247–251.
- [15] J.F. Scamehorn, S.D. Christian, E.E. Tucker and B.I. Tan, Concentration polarization in polyelectrolyte-enhanced ultrafiltration, *Coll. Surf.*, 49 (1990) 259–267.
- [16] K.J. Sasaki, S.L. Burnett, S.D. Christian, E.E. Tucker and J.F. Scamehorn, Polyelectrolyte ultrafiltration of multivalent ions. Removal of Cu^{2+} by sodium poly(styrenesulfonate), *Langmuir*, 5 (1989) 363–369.
- [17] R.S. Juang and M.N. Chen, Retention of copper (II)-EDTA chelates from dilute aqueous solutions by a polyelectrolyte enhanced ultrafiltration process, *J. Membr. Sci.*, 119 (1996) 25–37.