# Application of Ordered Nanoporous Silica for Removal of Uranium Ions from Aqueous Solutions

Hyung Ik Lee[1], Jin Hoe Kim[1], Ji Man Kim[1, *], Seok Kim[2], Jung-Nam Park[1],
Jae Sik Hwang[3], Jei-Won Yeon[3], and Yongju Jung[3, *]

[1] Department of Chemistry, BK21 School of Chemical Materials Science, Department of Energy Science, and
SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-746, Korea
[2] Department of Chemical and Biochemical Engineering, Pusan National University, Pusan, 609-735, Korea
[3] Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon, 305-353, Korea

Ordered nanoporous silica (MSU-H) with high surface area has been utilized as a solid substrate of a surface-modified hybrid sorbent for the application to the removal of U(VI). Carboxymethylated polyethyleneimine (CMPEI) with a strong complexing property has been introduced to the pore surface of MSU-H substrate. CMPEI-modified MSU-H (CMPEI/MSU-H) has been characterized by scanning electron microscopy and nitrogen sorption. In a kinetic experiment for 12.5 ppm U(VI) solution at pH 4.0, 99% U(VI) was removed from solution by the hybrid sorbent within less than 10 min, indicating that the sorption of U(VI) on the CMPEI/MSU-H proceeds very rapidly. It was evident that a U(VI) sorption capacity increased with pH in the range of 2.0 to 4.0. The CMPEI/MSU-H showed a high sorption capacity of 153 mg/g-sorbent at pH 4.0. In particular, the CMPEI/MSU-H showed a significantly high uranium loading stability. Only about 1% U(VI) was released out of CMPEI/MSU-H during 4 months, when the CMPEI/MSU-H was treated with polyacrylic acid.

**Keywords:** Nanoporous Silica (MSU-H), U(VI), Carboxymethylated Polyethyleneimine (CMPEI), Hybrid Sorbent.

## 1. INTRODUCTION

A variety of polymer resins and ligand modified resins have been developed for the application to the separation or recovery of radioactive species from waste solutions.[1–5] In general, these sorbents exhibit lower sorption capacity than the theoretically expected value and very slow sorption rates due to inaccessibility to sorption sites in the core of sorbents.[6] In order to overcome these weak points, hybrid sorbents with core–shell structure have been synthesized.[6–10] These hybrid sorbents are made by functionalizing the surface of solid substrate such as silica and organic resins. This approach has greatly improved sorption kinetics as well as accessibility to sorption sites. Particularly, utilizing inorganic solid substrate such as silica has an additional advantage in that sorbents containing radioactive species can be converted to vitrified waste forms for permanent disposal.[10] However, the hybrid sorbents did not show high sorption capacity in terms of the total weight of a sorbent, since the content of complexing ligands was relatively low.[6, 7] Nanoporous materials (e.g., silica and carbon) have

recently been used for the adsorption study of biomaterials such as proteins, enzymes and vitamins.[11, 12] However, the practical application of these materials has been limited due to the insufficiency of functional groups. For this reason, the synthesis of nanoporous materials with functional polymer–silica hybrid frameworks has attracted a great deal of attention.[13] More recently, we reported the preliminary results of the uranium adsorption performance of nanoporous silica-based hybrid sorbents.[14] The nanoporous silica (MSU-H) with both high accessible surface area and uniform pore size distribution played role of a substrate, which contributed to an increase in the content of functional ligands immobilized within hybrid sorbents. The silica-based hybrid sorbents were prepared by modifying the surface of a nanoporous silica with functional polymers such as polyethyleneimine (PEI), carboxymethylated polyethyleneimine (CMPEI) and polyacrylic acid (PAA). A CMPEI-modified silica showed the best performance in U(VI) uptake characteristics. Scheme 1 shows a schematic diagram for the CMPEI–silica hybrid sorbent and the interaction between the sorbent and uranium ions. In this study, the CMPEI-modified silica sorbent has been more extensively investigated from the aspects of pore structure and sorption characteristics toward U(VI). Furthermore,

---

*Authors to whom correspondence should be addressed.
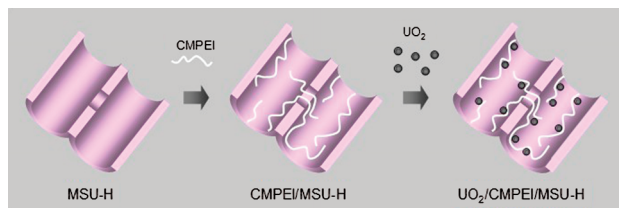
**Scheme 1.** Schematic diagram for the MSU-H, CMPEI/MSU-H hybrid sorbent and the interaction between uranium ions and the sorbent.

preliminary study on leaching behavior of the hybrid sorbent containing U(VI) has been carried out for ultimate immobilization of U(VI) within a single sorbent particle.

## 2. EXPERIMENTAL DETAILS

### 2.1. Preparation of Complexing Ligand-Modified Nanoporous Silica sorbents

A nanoporous silica (MSU-H) with a high specific surface area of ca. 305 m²/g, which was synthesized according to the method described elsewhere,[15] was used as a substrate of hybrid sorbents. CMPEI (Trilon P, $M_w =$ ca. $5.0 \times 10^4$) was purchased from BASF. A stock solution of 10,000 ppm CMPEI was prepared by diluting the Trilon P liquid in distilled water. 100 mg of MSU-H was added to 80 mL of polymer solution with 200 mg of CMPEI. The mixture solution was stirred at pH 3 or 5 for 24 h. The solution pH was adjusted using 0.1 M HCl solution. The resulting suspension was filtered through a membrane with a pore diameter of 200 nm and the polymer modified silica retained by the membrane, denoted as CMPEI/MSU-H, was thoroughly washed with a large amount of water in order to remove free CMPEI. The content of CMPEI in CMPEI/MSU-H was analyzed by thermal gravimetric analysis (TGA), after completely drying in a vacuum oven at 100 °C for 24 h. CMPEI contents were about 27% and 12% at pH 3.0 and 5.0, respectively. The MSU-H and two CMPEI/MSU-H hybrid sorbents were characterized by scanning electron microscopy (SEM) and nitrogen sorption. SEM images were collected using a Hitachi 4300SE field emission scanning electron microscope with an accelerating voltage of 15 kV. Nitrogen sorption–desorption isotherms were obtained using Micromeritics ASAP 2000 at liquid N₂ temperature. Specific surface area and total pore volume were estimated according to the Brunauer-Emmett-Teller (BET) method. Pore size distribution was calculated by the BJH (Barrett-Joyner-Halenda) method from the adsorption branch of the nitrogen sorption isotherms.

### 2.2. Sorption of U(VI) on CMPEI/MSU-H Sorbent

A 1000 ppm U(VI) solution was prepared from uranyl nitrate (Merck) in distilled water and used as a stock

solution for every sorption experiment. For U(VI) sorption tests, a CMPEI/MSU-H sorbent with polymer content of 27% was used. A sorption study of U(VI) on the CMPEI/MSU-H and MSU-H was carried out in the pH range of 2.0 to 4.0 by agitating 80 mL of suspension solution containing both U(VI) and the sorbent for 24 h. The final pH of the solutions was adjusted to a desired value with 0.1 M HCl solution. Sorption isotherm data were obtained from seven solutions containing 0.5 to 20 mg of U(VI) and 35 mg of CMPEI/MSU-H. U(VI) sorption amount by the CMPEI/MSU-H was calculated from analysis of the permeate passing through a membrane. Uranium concentrations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Horiba Ultima 2). The obtained isotherm data were analyzed by the Langmuir isotherm model. In addition, kinetic experiments were performed to determine reaction time to reach equilibrium, employing a suspension solution with 1.0 mg of U(VI). Furthermore, uranium leaching behavior of CMPEI/MSU-H has been examined as a feasibility study on uranium immobilization within a single sorbent particle. First, 40 mg of uranium-loaded sorbent (U(VI) content: 11%) was treated with 5 mL of 3.5% polyacrylic acid solution to take off uranium weakly bound to the sorbent and washed with a large amount of water. It was found that 55% of U(VI) finally remains in the sorbent. Next, the resulting uranium-loaded CMPEI/MSU-H (U(VI) content: 6%) was dispersed and stirred in an aqueous solution of pH 4.0. Finally, the amount of U(VI) leached out of the CMPEI/MSU-H was measured during 4 months in order to examine the uranium loading stability of the CMPEI/MSU-H. All the experiments were carried out at 22 °C.

## 3. RESULTS AND DISCUSSION

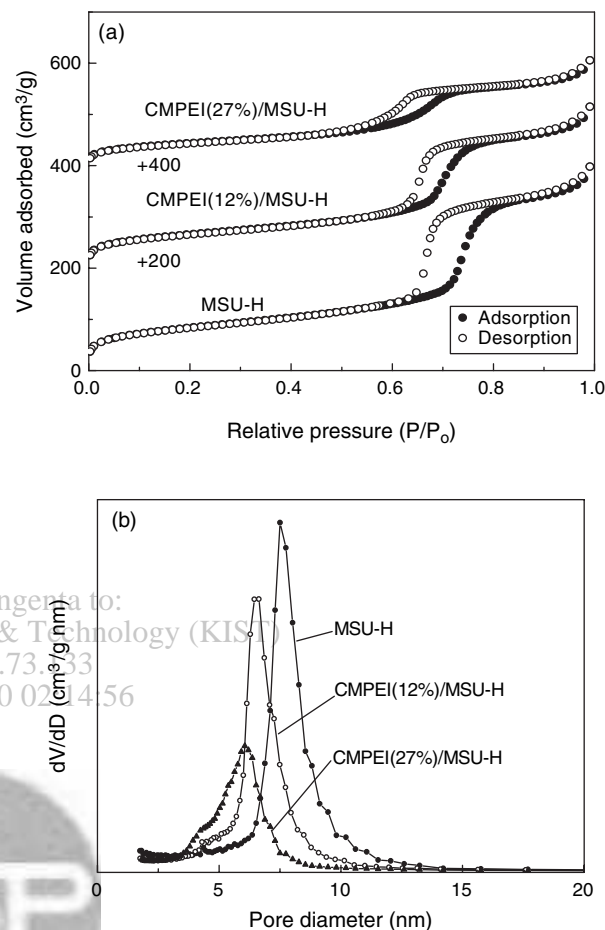### 3.1. Characterization of CMPEI-Modified MSU-H

Figure 1 shows the SEM images of the nanoporous silica (MSU-H) and two CMPEI-modified silicas. It was observed that the MSU-H has a submicron-scale primary particle size in the range of 100 to 300 nm. Careful observation by SEM revealed that the surface morphology of the MSU-H did not greatly change after forming a hybrid sorbent with CMPEI. This implies that most of CMPEI exists in the interior of MSU-H particles, more exactly in the pore surface of MSU-H rather than in the outer surface of MSU-H.

Figures 2(a and b) show the N₂ sorption isotherms and the corresponding pore size distribution curves of the MSU-H and the CMPEI/MSU-H hybrid sorbents, calculated from the adsorption branch by the BJH method, respectively. The values for BET surface area, total pore volume and pore size of these materials are listed in Table I. One of the most noteworthy features is that the BET surface area and total pore volume gradually
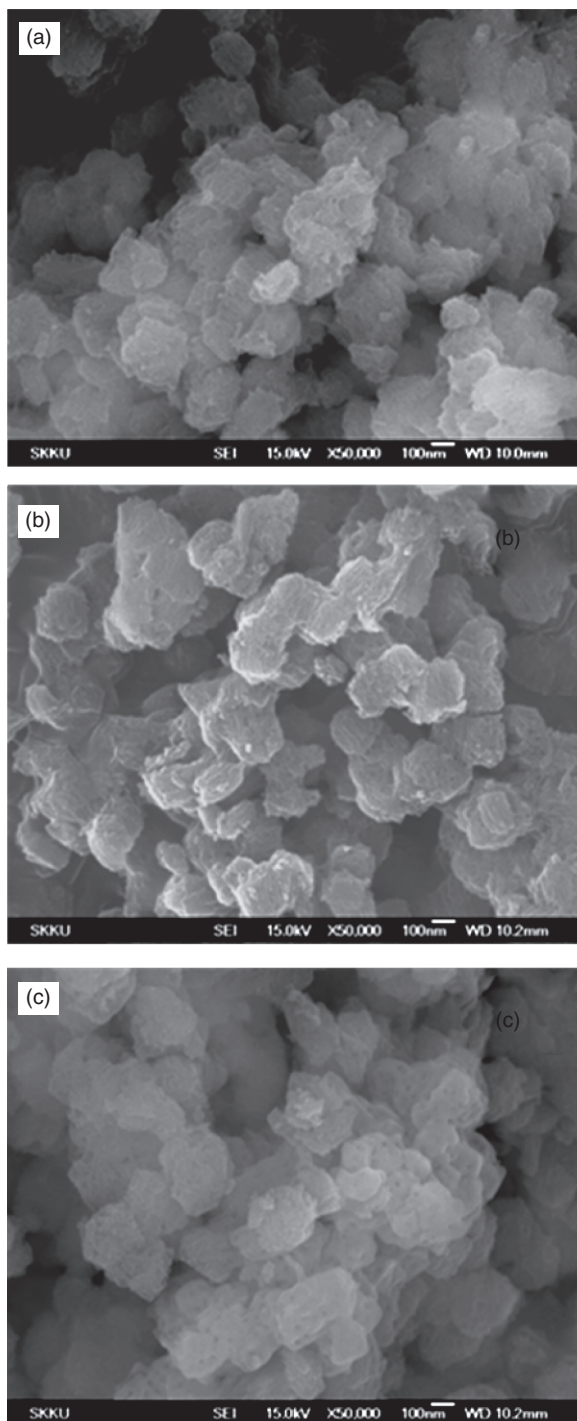
**Fig. 1.** SEM images of the MSU-H (a), CMPEI(12%)/MSU-H (b), and CMPEI(27%)/MSU-H (c).



**Fig. 2.** N$_2$ adsorption–desorption isotherms (a) and the corresponding pore size distribution (b) for the MSU-H, CMPEI(12%)/MSU-H and CMPEI(27%)/MSU-H.

Overall results indicate that the surface of the nanopores of MSU-H was quite uniformly modified with CMPEI, maintaining accessible mesopores (>3 nm), which would be crucial for the application of CMPEI/MSU-H as U(VI) sorbent.

### 3.2. U(VI) Sorption on the CMPEI-Modified MSU-H

Figure 3 shows the sorption behavior of U(VI) on the CMPEI/MSU-H sorbent versus time. It was observed that 99% U(VI) was removed by the sorbent within less than

decreased to about half the level of pristine MSU-H by the introduction of CMPEI. Figure 2(b) shows that the pore size distribution curves of the MSU-H significantly changed in terms of both the distribution shape and peak maximum, as CMPEI content increased. Particularly, it was observed that the pore size of the MSU-H substrate greatly decreased with the addition of CMPEI.

**Table I.** Structural characteristics of the MSU-H and CMPEI/MSU-H sorbents.

| Sample | BET surface area (m$^2$ g$^{-1}$) | Total pore volume[a] (cm$^3$ g$^{-1}$) | Pore size[b] (nm) |
|---|---|---|---|
| MSU-H | 305 | 0.57 | 7.6 |
| CMPEI(12%)/MSU-H | 241 | 0.45 | 6.5 |
| CMPEI(27%)/MSU-H | 162 | 0.29 | 5.9 |

[a]Total pore volume calculated at P/Po = 0.990. [b]Pore size at the peak of pore size distribution curve calculated by the BJH method on the basis of the adsorption branch of the nitrogen isotherms.
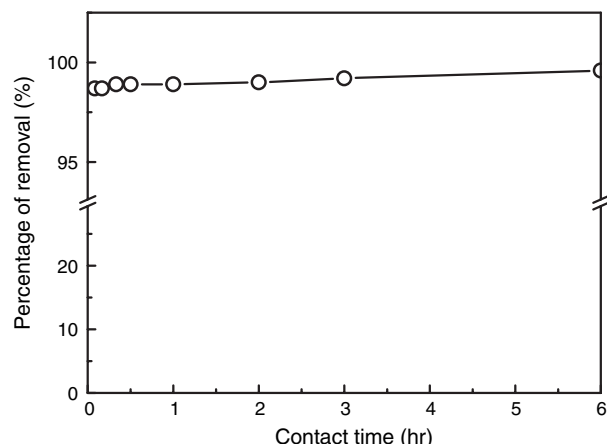
**Fig. 3.** The percentage of removal with contact time for 12.5 ppm U(VI) solution by the CMPEI(27%)/MSU-H.

10 min for 12.5 ppm U(VI) solution at pH 4.0, implying that the sorption reaction had already reached equilibrium. This indicates that the sorption of U(VI) on the CMPEI/MSU-H proceeds much faster, as compared to that on Duolite ES467 which needs 10 to 12 h.[16] Figure 4(a) shows the sorption isotherms of U(VI) on the pristine MSU-H and the CMPEI/MSU-H at pH 2.0, 3.0 and 4.0. The CMPEI/MSU-H presented much higher sorption capacities at all tested pHs, when compared with those of the pristine MSU-H. Particularly, it was evident that the U(VI) sorption capacity of the CMPEI/MSU-H increased with pH. It is thought that this is mainly caused by the chemical structure of CMPEI depending on pH. The complexing efficiency of CMPEI increases with pH, as its functional groups (i.e., imine and carboxylate group) become more deprotonated with an increase of pH. The adsorption isotherms were analyzed by the linearized Langmuir equation which is given as follows:

$$C_e/q_e = 1/(Q_0 K_L) + C_e/Q_0$$

where $q_e$ is the adsorbed sorbate amount per a sorbent at an equilibrium, $C_e$ is the concentration of a sorbate at an equilibrium, $Q_0$ is the maximum sorption capacity, and $K_L$ is a constant.[17] Figure 4(b) shows the Langmuir plots for the sorption data of U(VI) on the CMPEI/MSU-H at pH 2.0, 3.0 and 4.0 and the linear regression lines. The Langmuir isotherms showed excellent fits to the experimental data with very high correlation coefficients ($R^2 > 0.995$), as shown in Table II. This suggests that the sorption of U(VI) on the CMPEI/MSU-H obeyed the Langmuir model. The CMPEI/MSU-H showed much larger $Q_0$ value (145 mg/g-sorbent) at pH 4.0, as compared to that of the PEI-coated silica (52.4 mg/g-sorbent).[6]

It is of great concern to uranium immobilization research to investigate uranium leaching behavior of a sorbent. In the previous study, uranium loading stability of the CMPEI/MSU-H was examined without any treatment. About 20% of U(VI) was released from the
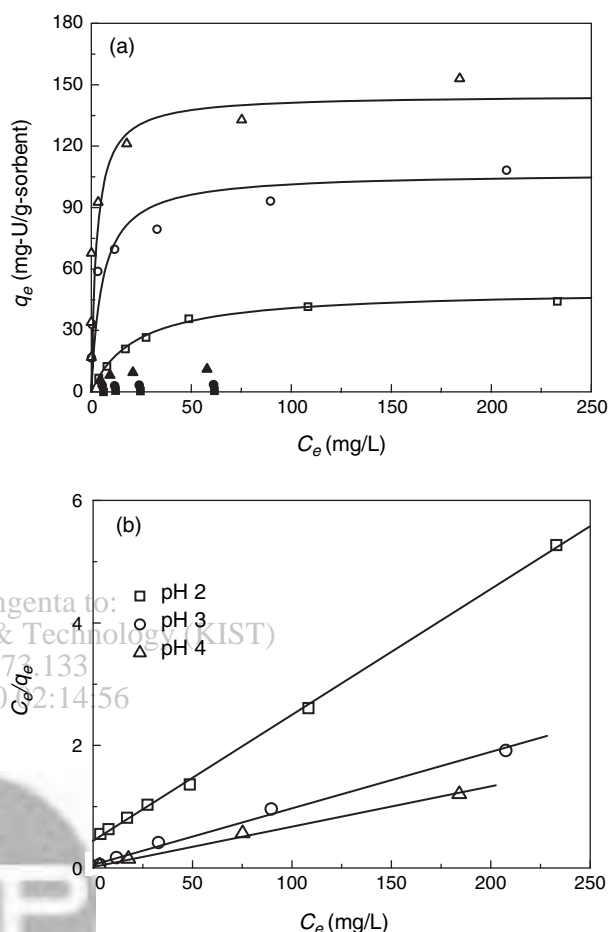


**Fig. 4.** Sorption isotherms (a) of U(VI) on the MSU-H (■: pH 2.0, ●: pH 3.0, ▲: pH 4.0) and the CMPEI(27%)/MSU-H (□: pH 2.0, ○: pH 3.0, △: pH 4.0). Solid lines (a) represent curve fitting results of the nonlinear regression analysis based on the Langmuir equation, and Langmuir isotherm plots (b) for the U(VI) adsorption on the CMPEI(27%)/MSU-H. Solid lines (b) represent the linear regression line by the linearized Langmuir equation.

CMPEI/MSU-H sorbent in less than 2 weeks. It is thought that this can be attributed mainly to the weakly sorbent bound U(VI). To completely retain uranium within the sorbent, U(VI)-loaded sorbent was treated with polyacrylic acid (PAA) and thoroughly washed with distilled water. Figure 5 shows uranium leaching behavior of the PAA-treated CMPEI/MSU-H with 6% U(VI) content. Surprisingly, it was found that over 99% of uranium was retained within the CMPEI/MSU-H particles during 4 months.

**Table II.** Regression analysis results for the sorption isotherm of U(VI) on the CMPEI(27%)/MSU-H, based on the linearized Langmuir equation.

| | Langmuir isotherm | | |
|---|---|---|---|
| pH | $Q_0$ (mg g$^{-1}$) | $K_L$ (L mol$^{-1}$) | $R^2$ |
| 2 | 50.0 | $1.22 \times 10^4$ | 0.999 |
| 3 | 107 | $5.02 \times 10^4$ | 0.995 |
| 4 | 145 | $1.18 \times 10^5$ | 0.998 |
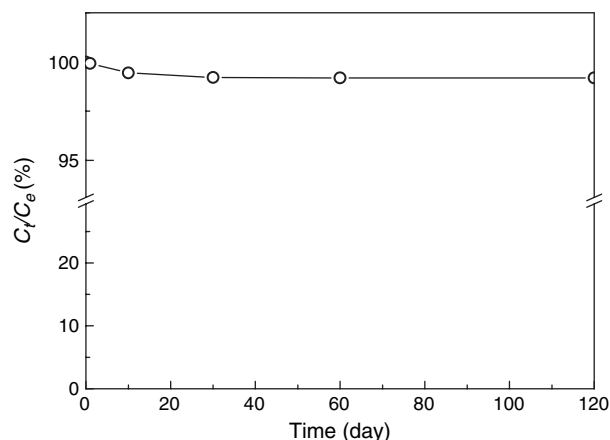
**Fig. 5.** Uranium leach behavior of the CMPEI/MSU-H in an aqueous solution of pH 4.0, after the treatment with polyacrylic acid. $C_t$ and $C_o$ mean U(VI) content at a given time and the initial U(VI) content, respectively.

## 4. CONCLUSION

Ordered nanoporous silica (MSU-H) was modified with carboxymethylated polyethyleneimine (CMPEI) for the separation of U(VI). From the analysis results of scanning electron microscopy and nitrogen sorption, it was verified that the nanopore surface of the MSU-H was quite uniformly modified with CMPEI rather than the outer surface of the MSU-H. In a kinetic experiment of 12.5 ppm U(VI) solution at pH 4.0, the sorption reaction reached equilibrium within less than 10 min, indicating that the CMPEI/MSU-H with highly accessible surface of CMPEI is capable of exceedingly fast sorption of U(VI). In addition, the CMPEI-modified MSU-H (CMPEI/MSU-H) exhibited much higher sorption capacity at pH range of 2.0 to 4.0, as compared with that of pristine MSU-H. It was obvious that the U(VI) sorption capacity of the CMPEI/MSU-H increased with pH, which may be attributed to the change in the complexation efficiency of CMPEI. It is thought that the complexation efficiency increase with pH as the functional groups of CMPEI become more deprotonated with increasing pH. In particular, it was observed that only about 1% U(VI) was released out of the CMPEI/MSU-H during 4 months, when the CMPEI/MSU-H was treated with polyacrylic acid.

## References and Notes

1. K. E. Geckeler and K. Volchek, *Environ. Sci. Technol.* 30, 725 (**1996**).
2. E. Guibal, I. Saucedo, J. Roussy, and P. Le Cloirec, *React. Polym.* 23, 147 (**1994**).
3. D. Leroy, L. Martinot, P. Mignonsin, D. Strivay, G. Weber, C. Jérôme, and R. Jérôme, *J. Appl. Poly. Sci.* 88, 352 (**2003**).
4. A. Zhang, G. Uchiyama, and T. Asakura, *React. Funct. Polym.* 63, 143 (**2005**).
5. A. Denizli, R. Say, B. Garipcan, and S. Patir, *React. Funct. Polym.* 58, 123 (**2004**).
6. M. Chanda and G. L. Rempel, *React. Polym.* 25, 25 (**1995**).
7. D. E. Bryant, D. I. Stewart, T. P. Kee, and C. S. Barton, *Environ. Sci. Technol.* 30, 4011 (**2003**).
8. F. Barbette, F. Rascalou, H. Chollet, J. L. Babouhot, F. Denat, and R. Guilard, *Anal. Chim. Acta* 502, 179 (**2004**).
9. M. Ghoul, M. Bacquet, and M. Morcellet, *Water Res.* 37, 729 (**2003**).
10. K. A. Venkatesan, V. Sukumaran, M. P. Antony, and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.* 260, 443 (**2004**).
11. A. Vinu, T. Mori, and K. Ariga, *Sci. Tech. Adv. Mater.* 7, 753 (**2006**).
12. A. Vinu, M. Miyahara, and K. Ariga, *J. Nanosci. Nanotechnol.* 6, 1510 (**2006**).
13. Y.-S. Kang, H. I. Lee, Y. Zhang, Y. J. Han, J. E. Yie, G. D. Stucky, and J. M. Kim, *Chem. Commun.* 1524 (**2004**).
14. Y. Jung, S. Kim, S. J. Park, and J. M. Kim, *Colloids Surf. A: Physicochem. Eng. Aspects* 313–314, 162 (**2008**).
15. H. I. Lee, J. H. Kim, D. J. You, J. E. Lee, J. M. Kim, W. S. Ahn, C. Pak, S. H. Joo, H. Chang, and D. Seung, *Adv. Mater.* 20, 757 (**2008**).
16. M. Streat, *React. Polym.* 2, 79 (**1984**).
17. Y. S. Ho, *Water Res.* 37, 2323 (**2003**).

**RESEARCH ARTICLE**