

## Hydrogels for Removal of Heavy Metals from Aqueous Solution

Qiang Chen<sup>1</sup>, Lin Zhu<sup>1</sup>, Chao Zhao<sup>2</sup> and Jie Zheng<sup>2\*</sup>

<sup>1</sup>School of Material Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan, China, 454003

<sup>2</sup>Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio 44325, USA

### Abstract

Significant needs and efforts have been made in the development of novel hydrogels for early detecting and effectively removing heavy metal ions from environments. In this review, three types of hydrogels used for removal of heavy metal ions and associated ion capture-release mechanisms are discussed. Well-defined three-dimensional porous structures, coupled with highly hydrated and versatile chemical groups, are the keys to developing effective hydrogels for removal of toxic heavy ions. Biomolecule-conjugated hydrogels and stimuli-responsive hydrogels are the promising next generation materials for detection and removal of toxic heavy metal ions due to their selectively binding metal ions in a controlled manner.

**Keywords:** Hydrogels; Heavy metal ions

### Introduction

Some heavy metals (e.g. Fe, Zn, Cu, Co, Mn, and Mo) in small quantities are nutritionally essential for the maintenance of human metabolism [1]. However, heavy metals are also very toxic and non-biodegradable; hence they can readily be accumulated in an ecological system to induce irreversible pollution or in human body to cause adverse health effects [2]. A number of methods including coagulation and precipitation [3], ion exchange treatment [4], membrane filtration [5], and electrochemical technologies [6] have been developed to early detect and remove toxic heavy metals from environments, but limited success has been achieved to date due to their less efficiency and further generation of toxic sludge or other waste products. Additionally, these methods require expensive equipment and involve time-consuming and laborious procedures. Alternatively, adsorption offers many potential advantages for removal of toxic heavy metals over other methods, thanks to its flexibility in design and operation, high-quality treated effluent, reversible nature for multiple uses, and many commercially available adsorbent materials, such as activated carbon [7], zeolite [8], clay [9-13], sawdust [14], bark [15], biomass [16], lignin, chitosan and other polymer adsorbents [17].

Compared to conventional adsorbent materials above, hydrogel-based adsorbents recently have attracted special attention to their highly potential for effective removal of heavy metals [18]. Hydrogels usually have physically well-defined three-dimensional porous structures and chemically-responsive functional groups, which enable to readily capture metal ions from wastewater and to release and clear these metal ions from the hydrogels upon changes in aqueous solution conditions [19]. The hydrophilic character of hydrogel adsorbents enable to form a flexible network of polymer chains, which allows metal ions to quickly penetrate into the network with water and to form stable complexes with functional groups [20].

Significant efforts have been invested in the removal of heavy metals from whole environments using a wide range of hydrogels functionalized by carboxylic acid, amine, hydroxyl, or sulfonic acid groups, which are able to form complexes with toxic metal ions [21]. Functional chemical groups are generally introduced to the hydrogel matrix using copolymerization [20], grafting [22], semi-interpenetrating polymer network (semi-IPN) [23], and IPN technologies [24]. However, most of hydrogels are able to bind to all metal ions and thus lack ability to specifically and selectively bind and removal certain metal ions of interesting. To date, very limited studies

have been reported for addressing selective removal of heavy metal ions using controllable functionalized hydrogels. In an effort to fill this gap, this review will solely focus on the development and testing of three types of hydrogels for selectively removing toxic heavy metal ions from environmental in a controlled manner. Finally, recent advances and future aspects of functionalized hydrogels will also be discussed.

### Protein or DNA-Functionalized Hydrogels

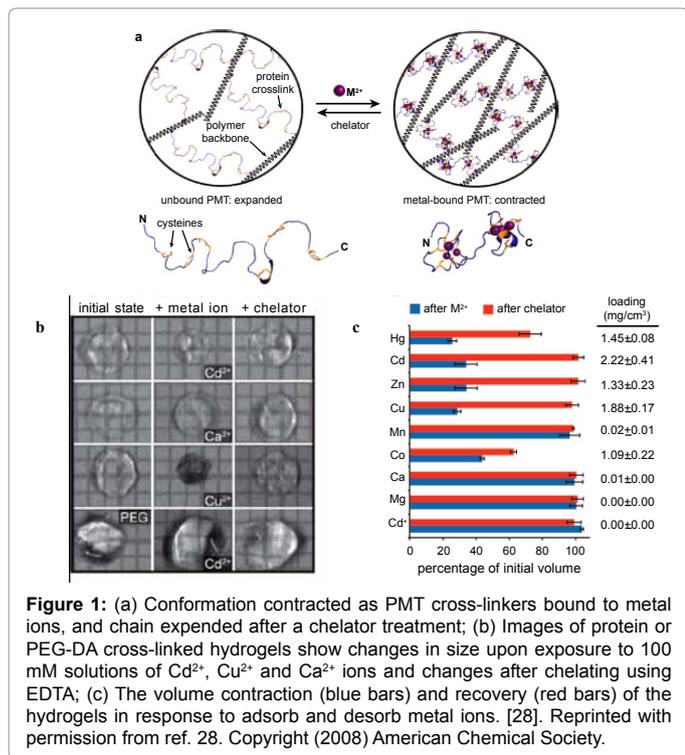
It is well known that certain heavy metal ions can form specific complexes with biomolecules containing nitrogen, sulfur, and oxygen to introduce toxicological effects on nervous system ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ); the kidneys or liver ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ); or skin, bones, or teeth ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ) [25,26]. Motivated by specific interactions between protein/peptide/ligand and metal ions, Fracis's group reported an efficient chemical synthesis method to produce a hybrid protein-polymer hydrogels using N- and C-termini of pea metallothioneins (PMTs) proteins as cross-linker. The hybrid hydrogels exhibited unique and controllable structural and mechanical properties, strongly depending on the folding state of the proteins [27]. The PMTs proteins can specifically bind to trace heavy metal ions ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  ions) [28]. As shown in Figure 1a, toxic metal ions can bind to PMTs protein, and led to chain contraction. Following isolation, the bound metal ions can be removed from the hybrid hydrogels by chelators, which allow reusing the hydrogels and the hydrogels become expansion. The dynamic volume change of the hybrid hydrogels were also characterized in the presence of a series of metal ions as shown in Figure 1b and 1c. Upon exposure to 100 mM solutions of  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  ions, the swollen hydrogels underwent large reductions in volume, as expected from the condensation of protein cross-links around the metal ions. The volume recovery of the hybrid hydrogels was almost 100% after removing bound metal ions by

**\*Corresponding author:** Jie Zheng, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio, USA, 44325, E-mail: [zhengj@uakron.edu](mailto:zhengj@uakron.edu)

**Received** June 08, 2012; **Accepted** June 21, 2012; **Published** June 23, 2012

**Citation:** Chen Q, Zhu L, Zhao C, Zheng J (2012) Hydrogels for Removal of Heavy Metals from Aqueous Solution. J Environ Anal Toxicol S2:001. doi:10.4172/2161-0525.S2-001

**Copyright:** © 2012 Chen Q, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.



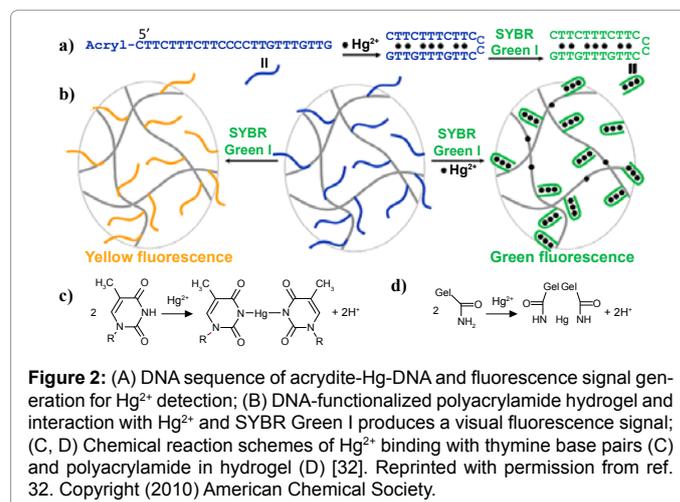
chelators. However, in the presence of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> that are common ions in drinking water, all of the hybrid hydrogels underwent minimal contraction, suggesting that PTMs have little binding affinity to Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> ions. This selectivity makes the hybrid hydrogels more appropriate for the removal of very small quantities of heavy metal contaminants from saline water. Compared to hybrid hydrogels, hydrogels using poly(ethylene glycol) (PEG)-dialdehyde (PEG-DA) as cross-linker did not produce an apparent size change in response to any ion (Figure 1c), indicating that the binding selectivity was solely due to the protein component.

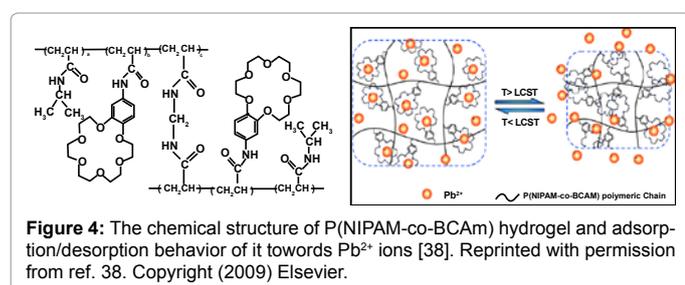
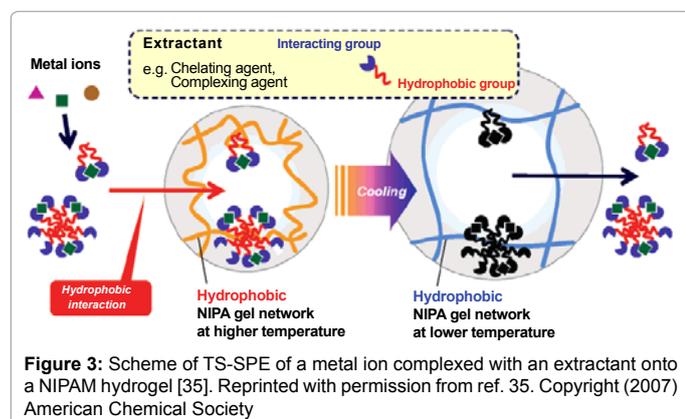
Mercury is a highly toxic and bioaccumulative heavy metal that causes serious human health problems even at low concentrations [29]. It is thus important for the development of novel materials to effectively remove Hg<sup>2+</sup> from various systems. A number of studies have shown that hydrogels can remove Hg<sup>2+</sup>, but these hydrogels are not selective for binding to Hg<sup>2+</sup> [30]. Many fluorescence-based sensors can selectively detect Hg<sup>2+</sup> as color changes being detected by the naked eyes [29,31]. However, immobilization of these sensors at a high concentration has not been demonstrated in most case, rendering it difficult to effectively remove mercury at the same time. Thus, the detection and removal of Hg<sup>2+</sup> have to be performed by separate tasks in most systems. Recently, Liu' group reported a re-generable polyacrylamide hydrogels-based sensor functionalized with a thymine-rich DNA, which offers ultrasensitive detection and effective removal of Hg<sup>2+</sup> from water simultaneously [32]. The DNA sequence, the binding and fluorescence signal generation between DNA and Hg<sup>2+</sup> were shown in Figure 2a. The acryl modified-DNA was copolymerized with acrylamide to form hybrid hydrogels. DNA-functionalized polyacrylamide hydrogel could interact with SYBR Green I to produce yellow fluorescence in the absence of Hg<sup>2+</sup>. However, in the presence of Hg<sup>2+</sup>, the hybrid hydrogel could produce green fluorescence (Figure 2b). The reaction between DNA and Hg<sup>2+</sup> was based on Hg<sup>2+</sup> binding with thymine base pairs as shown in Figure 2c. The selectivity was tested by incubating the DNA-

functionalized gels with various metal ions, but only Hg<sup>2+</sup> produced a green fluorescence, suggesting that the high selectivity of Hg<sup>2+</sup> by the DNA is well maintained within the hydrogel matrix. The removal of Hg<sup>2+</sup> from water was achieved by using DNA-functionalized hydrogels, leading to dramatic concentration decrease for Hg<sup>2+</sup> from 1 μM to ~30 nM within 6 h. Interestingly, for hydrogels prepared without the DNA, similar kinetics of Hg<sup>2+</sup> removal was also observed, which can be explained by the ability of polyacrylamide to bind Hg<sup>2+</sup> via the amide nitrogen in Figure 2d. The fact that Hg<sup>2+</sup> removal is almost independent of DNA while still retaining the lowest detection limit of 10 nM Hg<sup>2+</sup> suggests that the acrylamide gel matrix has high Hg<sup>2+</sup> adsorption capacity while the DNA has a strong Hg<sup>2+</sup> binding affinity. Such a combination offers a high sensitivity for Hg<sup>2+</sup> detection and a cost-effective capacity for Hg<sup>2+</sup> removal at the same time. Additionally, most of DNA-functionalized hydrogels can be regenerated for reuse after removal of Hg<sup>2+</sup>, dry for storage, and then rehydration.

### Temperature-Swing Hydrogels

Tokuyama's group had developed thermo-responsive gel adsorbents composed of Poly (N-isopropylacrylamide) (PNIPAM) (primary component) and a chelating or an ionic component (secondary component) for capturing heavy metals in a solution by temperature-swing adsorption [33,34]. The temperature-swing (TS) adsorption means the control of the adsorption and desorption of metal ions by changing the temperature. Although the TS method shows the benefit for controlling the adsorption and desorption of heavy metals, the hydrogels exhibit relative low adsorption capacity for metal ions. This could be due to that the secondary component was introduced in a very limited amount as compared to primary component of NIPAM, in order to maintain the gelation and thermo-sensitivity of copolymeric hydrogels. Recently, they developed a novel temperature-swing solid-phase extraction (TS-SPE) technique for removal heavy metals without secondary component [35]. As shown in Figure 3, metal ions in an aqueous solution first formed complex with an extractant. Then, the metal-extractant complexes (or micelles) were adsorbed onto the PNIPAM hydrogel through hydrophobic interactions at temperature above lower critical solution temperature (LCST). Finally, the metal-extractant complexes were desorbed from the hydrogels after temperature was reduced to a value below the LCST. They demonstrate that using TS-SPE technique, PNIPAM hydrogels can adsorb and desorb Cu (II) ions reversibly upon the temperature changes back and forth between 10 and 40°C. The amount of adsorbed





Cu (II) ions increased as temperature, and the maximum adsorption was achieved at a temperature above the LCST.

### Crown ethers-Functionalized Hydrogels

Crown ethers, the first generation of synthetic host compounds, have a remarkable ability to recognize specific metal ions such as  $K^+$ ,  $Ba^{2+}$ ,  $Cs^{2+}$  and  $Pb^{2+}$ . When the size of ions matches the cavity size of the crown ether, the ions can be specifically captured by the crown ether receptor, forming a stable “host-guest” complex [36]. But, most of crown ethers-functionalized hydrogels were used for detection, instead of removal, of metal ions [37]. Recently, Chu’s group has developed a novel polymeric  $Pb^{2+}$  adsorbent, which is prepared by incorporation of benzo-18-crown-6-acrylamide (BCAm) as metal ion receptor into the thermo-responsive PNIPAM hydrogels [38]. As ion-signal receptor, BCAM is highly selective to  $Pb^{2+}$  ions. As compared to pure PNIPAM hydrogels, the adsorption  $Pb^{2+}$  ions into P(NIPAM-co-BCAm) hydrogels exhibited a strong temperature dependence. The “swollen-shrunk” structural change of P(NIPAM-co-BCAm) networks triggered by environmental temperature has large influence in the formation of BCAM- $Pb^{2+}$  complexes. In Figure 4, at temperature lower than the LCST, the copolymer networks swollen, which makes it easier for the cavities of crown ethers to capture the guest ions, so that the P (NIPAM-co-BCAm) hydrogels exhibited higher adsorption capacity for  $Pb^{2+}$  ions. On the other hand, at temperature higher than the LCST, the networks shrunk and the cavities of crown ethers were close to each other. As a result, electrostatic repulsions among the ions affected the formation of stable BCAM- $Pb^{2+}$  complexes inside the matrix, leading to a smaller adsorbed amount of  $Pb^{2+}$ . The smart hydrogels can not only be used as adsorbents for removal of lead ions from water, but also be able to conveniently release the absorbed heavy ions as a response to external stimuli.

### Conclusions and Perspective

Development of novel hydrogels used for selective detection and

removal of toxic heavy metal ions has recently attracted considerable attention important in environments and living systems. The advantages of hydrogels include the simplicity of synthesis, ease of applicability, abundance of raw materials, and availability of functional groups. Intensive studies have been reported to detect heavy metal ions using hydrogels, but few studies have been conducted to remove heavy metal ions from targeted systems. With the understanding of specific interactions between heavy metal ions and hydrogels, future research direction could focus on the development of biomacromolecule-conjugated hydrogels. Such hybrid hydrogels possess great potentials for selectively bind to and effectively remove ions. Most importantly, the sequence of protein and DNA can be readily tuned to generate diverse binding affinity to specific metal ions. Additionally, stimuli-responsive polymeric hydrogels are alternative promising materials to specifically capture-release heavy metal ions in a controllable way upon changes in external stimulus such as temperature, pH, electric field, and chemicals.

### Acknowledgements

Q.C. thanks financial support from the Science and Technology Research Project of Education Department of Henan Province (No.12B430007), the Doctoral Foundation of Henan Polytechnic University (No.648415). J.Z. thanks the financial supports from a NSF CAREER Award (CBET-0952624) and a 3M Non-Tenured Faculty Award.

### References

- Aragay G, Pons J, Merkoci A (2011) Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection. *Chem Rev* 111: 3433-3458.
- Wan Ngah WS, Hanafiah MA (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour Technol* 99: 3935-3948.
- Charerntanyarak L (1999) Heavy metals removal by chemical coagulation and precipitation. *Water Sci Technol* 39: 135-138.
- Dabrowski A, Hubicki Z, Podkošcielny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* 56: 91-106.
- Vijayalakshmi A, Arockiasam DL, Nagendran A, Mohan D (2008) Separation of proteins and toxic heavy metal ions from aqueous solution by CA/PC blend ultrafiltration membranes. *Sep Purif Technol* 62: 32-38.
- Basha CA, Somasundaram M, Kannadasan T, Lee CW (2011) Heavy metals removal from copper smelting effluent using electrochemical filter press cells. *Chem Eng J* 171: 563-571.
- Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J Hazard Mater* 97: 219-243.
- Erdem E, Karapinar N, Donat R (2004) The removal of heavy metal cations by natural zeolites. *J Colloid Interface Sci* 280: 309-314.
- Eloussaief M, Kallel N, Yaacoubi A, Benzina M (2011) Mineralogical identification, spectroscopic characterization, and potential environmental use of natural clay materials on chromate removal from aqueous solutions. *Chem Eng J* 168: 1024-1031.
- Eloussaief M, Benzina M (2010) Efficiency of natural and acid-activated calys in the removal of Pb(II) from aqueous solutions. *J Hazard Mater* 178:753-757.
- Eloussaief M, Hamza W, Kallel N, Benzina M (2012) Wastewaters decontamination: Mechanisms of Pb (II), Zn (II) and Cd (II) competitive adsorption on Tunisian smetite in single and multi-systems. *Environmental Progress and Sustainable Energy J*.
- Eloussaief M, Sdiri A, Benzina M (2012) Modelling the adsorption of mercury onto natural and aluminium pillared clays. *Environ Sci Pollut Res*.
- Eloussaief M, Jarraya I, Benzina M (2009) Adsorption of copper ions on two clays from Tunisia: pH and temperature effects. *Appl Clay Sci* 46: 409-413.

14. Bulut Y, Tez Z (2007) Removal of heavy metals from aqueous solution by sawdust adsorption. *J Environ Sci (China)* 19: 160–166.
15. Al-Asheh S, Banat F, Al-Omari R, Duvnjak Z (2000) Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. *Chemosphere* 41: 659–665.
16. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour Technol* 98: 2243–2257.
17. Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. *Arabian J Chem* 4: 361–377.
18. Peng XW, Zhong LX, Ren JL, Sun RC (2012) Highly effective adsorption of heavy metal ions from aqueous solutions by macroporous xylan-rich hemicelluloses-based hydrogel. *J Agric Food Chem* 60: 3909–3916.
19. Zheng Y, Wang A (2009) Evaluation of ammonium removal using a chitosan-g-poly(acrylic acid)/rectorite hydrogel composite. *J Hazard Mater* 171: 671–677.
20. Yetimoglu EK, Kahraman MV, Ercan O, Akdemir ZS, Apohan NK (2007) *N*-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid based hydrogels: Synthesis, characterization and their application in the removal of heavy metals. *React Funct Polym* 67: 451–460.
21. Bekiari V, Sotiropoulou M, Bokias G, Lianos P (2008) Use of poly(*N,N*-dimethylacrylamide-co-sodium acrylate) hydrogel to extract cationic dyes and metals from water. *Colloids Surf A* 312: 214–218.
22. Wang XH, Zheng Y, Wang AQ (2009) Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgitite composites. *J Hazard Mater* 168: 970–977.
23. Chen Q, Zhu L (2012) PVA/PVAm hydrogel membranes for removal of metal ions from aqueous solution. *Appl Mechan Mater.* 130-134: 1507-1510.
24. Li XL, Li YF, Zhang SD, Ye ZF (2011) Preparation and characterization of new foam adsorbents of poly(vinyl alcohol)/chitosan composites and their removal of dye and heavy metal from aqueous solution. *Chem Eng J* 183: 88-97.
25. Hamilton JW, Kaltreider RC, Bajenova OV, Ilnat MA, McCaffrey J, et al. (1998) Molecular basis for effects of carcinogenic heavy metals on inducible gene expression. *Environ Health Perspect* 106: 1005-1015.
26. Partanen T, Heikkilä P, Hernberg S, Kauppinen T, Moneta G, et al. (1991) Renal cell cancer and occupational exposure to chemical agents. *Scand J Work Environ Health* 17: 231-239.
27. Esser-Kahn AP, Francis MB (2008) Protein-cross-linked polymeric materials through site-selective bioconjugation. *Angew Chem Int Ed* 47: 3751-3754.
28. Esser-Kahn AP, Iavarone AT, Francis MB (2008) Metallothionein-cross-linked hydrogels for the selective removal of heavy metals from water. *J Am Chem Soc* 130:15820-15822.
29. Nolan EM, Lippard SJ (2008) Tools and tactics for the optical detection of mercuric ion. *Chem Rev* 108: 3443-3480.
30. Denizli A, Senel S, Alsancak G, Tuzmen N, Say R (2003) Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine). *React Funct Polym* 55: 121-130.
31. Tchounwou PB, Ayensu WK, Ninasvili N, Sutton D (2003) Environmental exposure to mercury and its toxicopathologic implications for public health. *Environ Toxicol* 18: 149-175.
32. Dave N, Chan MY, Huang PJ, Smith BD, Liu JW (2010) Regenerable DNA-functionalized hydrogels for ultrasensitive instrument-free mercury(II) detection and removal in water. *J Am Chem Soc* 132: 12668-12673.
33. Tokuyama H, Yanagawa K, Sakohara S (2006) Temperature swing adsorption of heavy metals on novel phosphate-type adsorbents using thermosensitive gels and/or polymers. *Sep Purif Technol* 50: 8-14.
34. Tokuyama H, Kanazawa R, Sakohara S (2005) Equilibrium and kinetics for temperature swing adsorption of a target metal on molecular imprinted thermosensitive gel adsorbents. *Sep Purif Technol* 44: 152-159.
35. Tokuyama H, Iwama T (2007) Temperature-swing solid-phase extraction of heavy metals on a poly(*N*-isopropylacrylamide) hydrogel. *Langmuir* 23: 13104-13108.
36. Ju XJ, Chu LY, Liu L, Mi P, Lee YM (2008) A novel thermoresponsive hydrogel with ion-recognition property through supramolecular host-guest complexation. *J Phys Chem B* 112: 1112-1118.
37. Mayes AG, Blyth J, Millington RB, Lowe CR (2002) Metal ion-sensitive holographic sensors. *Anal Chem* 74: 3649-3657.
38. Ju XJ, Zhang SB, Zhou MY, Xie R, Chu LY (2009) Novel heavy-metal adsorption materials: ion-recognition P(NIPAM-co-BCAm) hydrogels for removal of lead(II) ions. *J Hazard Mater* 167: 114–118.

This article was originally published in a special issue, **Emerging Water Contaminants and Treatment** handled by Editor(s), Dr. Xiaoliang Cheng, Lawrence Berkeley Lab, USA.