Novel heavy-metal adsorption material: ion-recognition P(NIPAM-*co*-BCAm) hydrogels for removal of lead(II) ions

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ABSTRACT

A novel polymeric lead(II) adsorbent is prepared by incorporating benzo-18-crown-6-acrylamide (BCAm) as metal ion receptor into the thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel. Both stimuli-sensitive properties and the Pb^{2+}-adsorption capabilities of the prepared P(NIPAM-*co*-BCAm) hydrogels are investigated. The prepared P(NIPAM-*co*-BCAm) hydrogels exhibit good ion-recognition and Pb^{2+}-adsorption characteristics. When crown ether units capture Pb^{2+} and form $BCAm/Pb^{2+}$ host–guest complexes, the lower critical solution temperature (LCST) of the hydrogel shifts to a higher temperature due to both the repulsion among charged $BCAm/Pb^{2+}$ groups and the osmotic pressure within the hydrogel. The adsorption results at different temperatures show that P(NIPAM-*co*-BCAm) hydrogels adsorb Pb^{2+} ions at temperature lower than the LCST, but undergo desorption at temperature higher than the LCST due to the "stretch-to-shrink" configuration change of copolymer networks which is triggered by the change in environmental temperature. This kind of ion-recognition hydrogel is promising as a novel adsorption material for adsorption and separation of Pb^{2+} ions. The adsorption and desorption of Pb^{2+} could be rationally achieved by simply changing the environmental temperature.

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1. Introduction

Water pollution with heavy metal ions is a serious problem due to their serious toxicity to human beings and other living organisms [1,2]. Lead, one of the most common heavy metals, is well known to be a cumulative poison through water intake or food chains. Lead can cause damage to the central nervous system and dysfunction to the kidneys and immune system of human beings, especially for children [3–5]. However, lead ions are commonly found in the industrial wastewaters because of their wide applications in many industrial technologies. Examples include lead mining, battery manufacturing, smelteries, printed circuit board factories, and military bases or facilities, as well as in landfill leachate and urban rainwater runoff, etc. [1]. Therefore, lead has been classified as priority pollutant by the US Environmental Protection Agency (EPA) and the maximum contaminant level (MCL) of lead ions in drinking water has been set at a low level of $0.015 \, mg \, l^{-1}$ by EPA [6].

Effective removal of lead ions from industrial wastewater has great scientific and practical interest. To achieve that, various technologies have been developed, including chemical precipitation, membrane separation, solvent extraction, ion-exchange, and adsorption [7–9]. Among them, adsorption is a promising technique because of its high efficiency, easy handling, and availability of dif-

ferent adsorbents [9–11]. In the past few decades, a large number of cross-linked polymeric materials and chemically modified biosorbents have been reported to be used as adsorbents for removal of lead ions from aqueous solutions. These adsorbent materials usually incorporate various metal-complexing ligands including carboxyl, amide, amino acid, amidoxime, imidazole, thiol, pyridine, and triazole functional groups [12–20]. However, how to release the adsorbed lead ions from the adsorbents, which causes a decrease in the adsorption capacity, remains a major issue for currently existing ligand adsorption techniques.

To solve this problem, we have been focusing on the development of intelligent or smart polymeric materials which can not only be used as adsorbents for removal of lead ions from aqueous solutions but also be able to conveniently release the absorbed heavy ions as a response to external stimuli. Stimuli-responsive intelligent or smart polymeric materials could exhibit significant property changes in response to mild changes in environmental stimuli such as temperature, pH, electric field, and chemicals. Such materials have attracted great interests for a wide variety of applications such as sensors, controlled drug or gene delivery, biotechnology, protective coatings, recyclable absorbents, and so on [21–24]. Nevertheless, up to now, there are few reports on the development of stimuli-responsive materials for removal of heavy metals from wastewater.

Poly(*N*-isopropylacrylamide) (PNIPAM), a typical and widely studied thermo-sensitive polymer, exhibits a reversible volume change as the surrounding temperature varies across a tempera-

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ture that is called the lower critical solution temperature (LCST). Crown ethers, the first generation of synthetic host compounds, have remarkable recognition ability towards specific metal ions. When the ion diameter matches the cavity size of the crown ether, the ion could be captured by the crown ether receptor and "host–guest" complex is stably formed. In our previous works, we prepared a novel thermo-sensitive P(NIPAM-*co*-benzo-18-crown-6-acrylamide) P(NIPAM-*co*-BCAm) hydrogel with good ion-recognition property by using PNIPAM hydrogel as an actuator and benzo-18-crown-6-acrylamide (BCAm) as the ion-signal receptor [25]. As ion-signal receptor, BCAm is highly selective to Pb^{2+} ions [26,27]. Therefore, here we report the application of P(NIPAM-*co*-BCAm) hydrogel as a novel adsorbent to remove Pb^{2+} ions from aqueous solutions.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPAM; kindly provided by Kohjin Co. Ltd., Japan) is purified by recrystallization with a hexane/acetone mixture (v/v, 50/50). BCAm is synthesized according to previously reported procedures [28,29]. *N*,*N*′-Methylenebisacrylamide (MBA; Chengdu Kelong Chemical Reagent Co.) is used as a cross-linker. 2,2′-Azobisisobutyronitrile (AIBN; Shanghai Reagent Fourth Factory) is recrystallized with ethanol and used as initiator. Lead nitrate (Chongqing Jiyuan Chemicals Co. Ltd.) is used in this study as the heavy metal source by dissolving it into the deionized water. All solvents and other chemicals are of analytical grade and used as received. Deionized water (18.2 MΩ, 25 °C) from a Milli-Q Plus water purification system (Millipore) is used throughout this work, and the measured pH value of the water is around 6.9.

2.2. Preparation and Fourier transform infrared characterization of hydrogels

Cross-linked P(NIPAM-*co*-BCAm) hydrogel is prepared by thermally initiated free-radical copolymerization. The synthesis and purification are performed as described previously [25]. The preparation recipe is NIPAM (2.825 g) and BCAm (0.7161 g) monomers, MBA (0.0385 g) cross-linker, and AIBN (0.0205 g) dissolved in 25 ml of mixed solvent of H_2O/THF (v/v, 9/1).

PNIPAM hydrogel, which served as a reference, is also prepared and purified using the protocol described above, but without any addition of BCAm.

The washed P(NIPAM-*co*-BCAm) and PNIPAM hydrogels are cut into thin discs and then equilibrated in deionized water at 20 °C.

The chemical structures of both P(NIPAM-*co*-BCAm) and PNIPAM hydrogels are characterized using Fourier transform infrared spectroscope (FT-IR; Nicolet 560, PE Com., USA) in the range of 4000–400 cm^{-1} with KBr disc technique. Dried hydrogel specimens are prepared using a freeze-drying method.

2.3. Pb^{2+}-recognition and thermo-responsive behaviors of P(NIPAM-co-BCAm) hydrogels

The ion-recognition and thermo-responsive behaviors of P(NIPAM-*co*-BCAm) hydrogels are investigated by evaluating their volume-phase transition behaviors in Pb^{2+} solution and deionized water at various designed ambient temperatures ranging from 20 to 50 °C. The concentration of Pb^{2+} in the solution is 4.0 mmol l^{-1}, and the pH values of the Pb^{2+} solutions are around 5.0. We determine the volume change of hydrogel by measuring the diameter change of the hydrogel discs.

Briefly, P(NIPAM-*co*-BCAm) hydrogel discs are immersed in sufficient Pb^{2+} solution or deionized water in a transparent glass Petri

dish with a calibrated scale. Then, we let the hydrogel discs to reach swelling/deswelling equilibrium by incubating the loaded Petri dish in a temperature-controlled water bath with the temperature fluctuation less than ±0.1 °C. The diameters of hydrogel discs are measured using a digital camera, which is placed vertically to the gel surface at a fixed height. Photos of the hydrogel discs with a calibrated scale are then analyzed using graph-processing software to determine the diameter of hydrogel discs. The same measurements are carried out for at least three times and the reported data are the averages with a standard deviation less than 2%.

2.4. Temperature-dependent adsorption of Pb^{2+} ions onto P(NIPAM-co-BCAm) hydrogels

The temperature-dependent adsorption capabilities of P(NIPAM-*co*-BCAm) gel-absorbent for Pb^{2+} ions from aqueous solutions are investigated experimentally. Equilibrium adsorptions at various designed temperatures (in the range of 20–50 °C) are performed in batch experiments. In all experiments, the amount of dried gel sorbents is kept at approximately 37 mg for a 15 ml solution and the initial concentrations of Pb^{2+} are all 4.0 mmol l^{-1} (828 mg l^{-1}). The weighted gel sorbents are added into a flask containing 15 ml Pb^{2+} solution, and then the flask is placed in a thermostatic water bath shaker and operated under 150 rpm at designed temperature for 3.5 h.

The adsorption capacity of the P(NIPAM-*co*-BCAm) gels at designed temperature is expressed as follows:

$$q_T = \frac{(C_0 - C_T)V}{m} \tag{1}$$

where q_T is the amount of Pb^{2+} adsorbed onto unit mass of the P(NIPAM-*co*-BCAm) gel (mg g^{-1}) at the designed temperature T (°C), C_0 and C_T (mg l^{-1}) are the concentrations of Pb^{2+} in the initial solution and in the final solution after adsorption at T (°C), respectively, V is the volume of the aqueous phase (l), and m is the mass of the dried P(NIPAM-*co*-BCAm) gel (g). The concentration of residual Pb^{2+} remained in the aqueous solution is determined by Atomic Absorption Spectrometer (AAS; SperAA 220FS, Varian Inc., USA).

For comparison, similar adsorption experiments are also carried out with dried PNIPAM gels.

3. Results and discussion

3.1. FT-IR characterization of P(NIPAM-co-BCAm) hydrogels

Chemical structure of the cross-linked P(NIPAM-*co*-BCAm) hydrogel is shown in Fig. 1. By comparing the FT-IR spectra of BCAm monomer and PNIPAM and P(NIPAM-*co*-BCAm) hydrogels, the copolymerization of NIPAM and BCAm is confirmed. Specifically, the appearance of the following characteristic peaks in the FT-IR spectrum of P(NIPAM-*co*-BCAm) hydrogel suggests a suc-
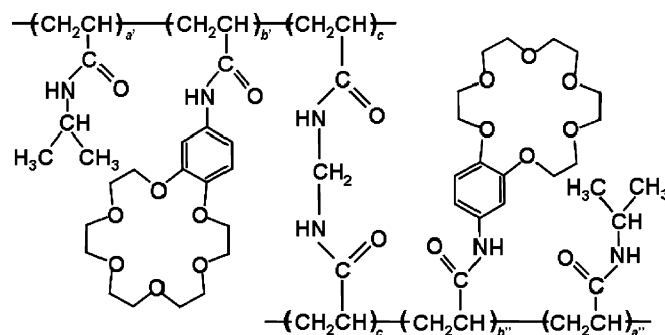

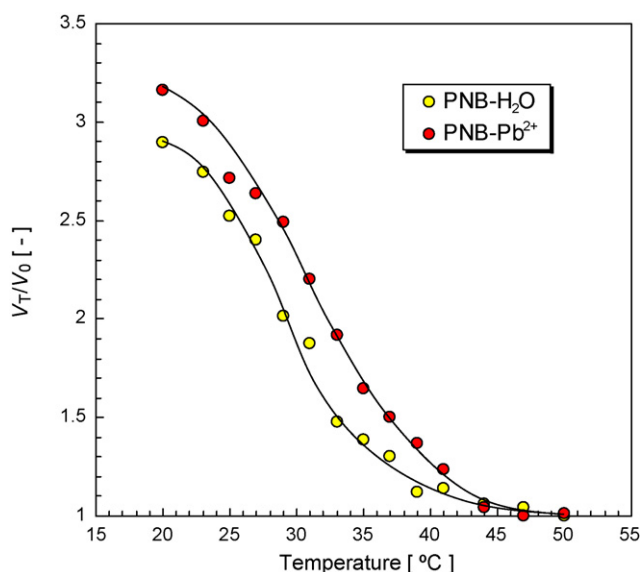**Fig. 1.** Chemical structure of the cross-linked P(NIPAM-*co*-BCAm) hydrogel.

Fig. 2. Temperature dependence of volume change ratios of cross-linked P(NIPAM-*co*-BCAm) hydrogels in Pb^{2+} aqueous solution and deionized water.

Fig. 4. Temperature dependence of the adsorption capacity of P(NIPAM-*co*-BCAm) hydrogel towards Pb^{2+} ions.

cessful copolymerization: (1) a strong 1516 cm^{-1} band for C=C skeletal stretching vibration of the phenyl ring, (2) a 1230 cm^{-1} band for C–O asymmetric stretching vibration in Ar–O–R, (3) a 1130 cm^{-1} band for C–O asymmetric stretching vibration in R–O–R′, and (4) a 1057 cm^{-1} band for C–O symmetric stretching vibration in Ar–O–R. Corresponding bands also appear in the FT-IR spectrum of BCAm. Furthermore, the characteristic double peaks at 1388 and 1366 cm^{-1} for isopropyl group of NIPAM appear in both FT-IR spectra of PNIPAM and P(NIPAM-*co*-BCAm) hydrogels. These feature peaks suggest a successful fabrication of P(NIPAM-*co*-BCAm) hydrogels.

3.2. Ion-recognition and thermo-responsive behaviors of P(NIPAM-co-BCAm) hydrogels

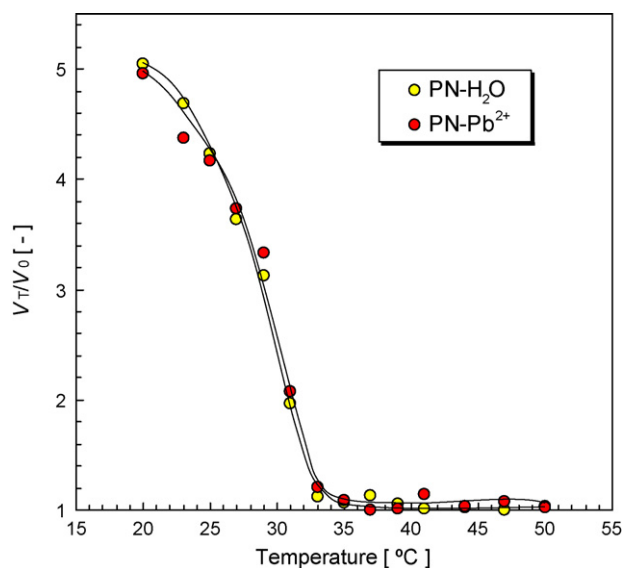In this work, we investigate the Pb^{2+}-recognition behavior of P(NIPAM-*co*-BCAm) hydrogels by studying the temperature-

induced volume phase transition in Pb^{2+} solution. We express the temperature-induced change in volume of hydrogel using the volume ratios of hydrogel disc (V_T/V_0), where V_T and V_0 are the volume of hydrogel disc in the equilibrium state at a certain temperature (T, °C) and that at the highest temperature in the measurements (50 °C), respectively. As expected, the temperature-dependent volume-change trend of P(NIPAM-*co*-BCAm) hydrogels in Pb^{2+} solution is significantly different from that in deionized water (Fig. 2). Clearly we can see that, in both Pb^{2+} solution and deionized water, P(NIPAM-*co*-BCAm) hydrogels undergo a rapid volume change when the environmental temperature changes across the respective LCST temperatures. What is significant here is that the LCST of P(NIPAM-*co*-BCAm) hydrogel shifts to a higher temperature in Pb^{2+} solution. Such an LCST shift indicates the formation of crown ether/metal ion complexes. Because the BCAm receptors in the copolymeric hydrogel can selectively recognize and effectively capture Pb^{2+} into their cavities through supramolecu-

Fig. 3. Temperature dependence of volume change ratios of cross-linked PNIPAM hydrogels in Pb^{2+} aqueous solution and deionized water.
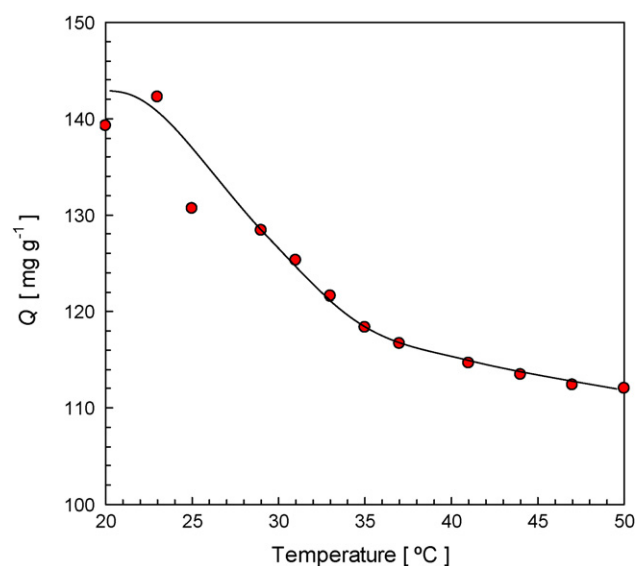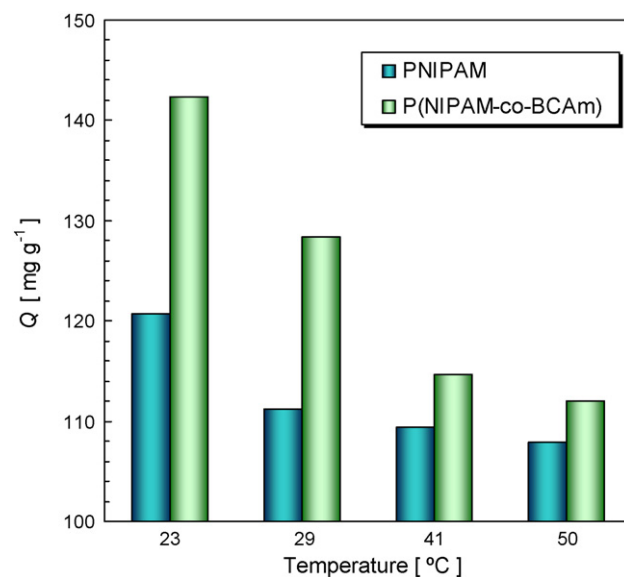

Fig. 5. Comparison of adsorption capacities of cross-linked PNIPAM and P(NIPAM-*co*-BCAm) hydrogels towards Pb^{2+} ions.
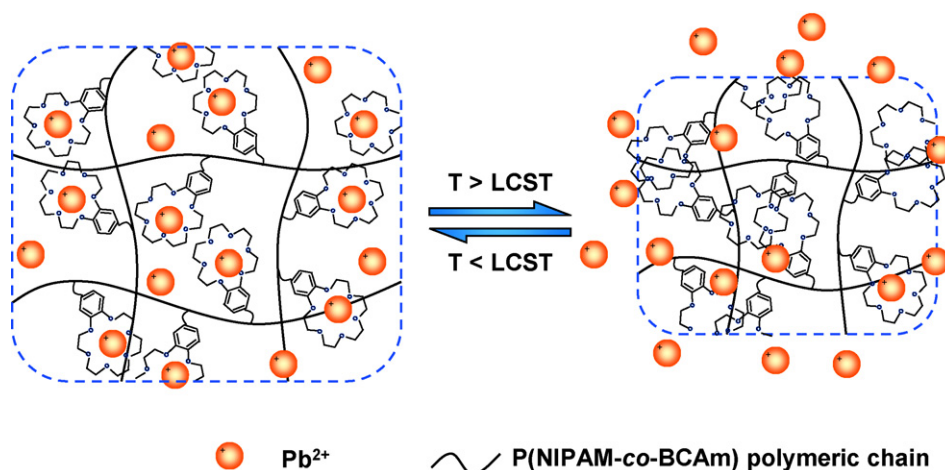
Fig. 6. Schematic illustration of the thermo-responsive adsorption/desorption behavior of P(NIPAM-*co*-BCAm) hydrogel towards Pb²⁺ ions, which exhibit "adsorption at temperature lower than the LCST and desorption at temperature higher than the LCST".

lar "host–guest" complexation, the polymer networks with such appended ionic "host–guest" complexes could behave like ionic polymer networks. The repulsion among charged BCAm/Pb²⁺ complex groups counteracts the shrinkage of the P(NIPAM-*co*-BCAm) networks during the increase of temperature. Only when the temperature is high enough, the polymeric networks could shrink due to the increase of hydrophobic associations, thereby resulting in the shift of the LCST to a higher temperature. Additionally, the osmotic pressure within the hydrogel due to a Donnan potential also makes the hydrogel swell more.

For comparison, the thermo-responsive volume-change behaviors of PNIPAM hydrogels in the absence or presence of Pb²⁺ are also studied in this work. As shown in Fig. 3, the volume-change trend of PNIPAM hydrogels in Pb²⁺ solution is almost the same as that in deionized water. The result indicates that, without presence of crown ether receptors in the polymeric networks, the metal ions scarcely affect the phase transition behaviors of PNIPAM-based hydrogels.

3.3. Temperature-dependent adsorption of Pb²⁺ ions from aqueous solutions

Effect of environmental temperature on adsorption characteristics of P(NIPAM-*co*-BCAm) hydrogels toward lead(II) ions in aqueous solutions are examined. As shown in Fig. 4, the P(NIPAM-*co*-BCAm) hydrogel shows a high adsorption capacity for Pb²⁺ at low temperature, and the adsorbed amount of metal ions per unit mass of the gels decreases with increasing the temperature. The results indicate that the P(NIPAM-*co*-BCAm) hydrogel has a better and higher adsorption capability toward Pb²⁺ ions at low temperature. From both the above-mentioned phenomena and the results illustrated in Fig. 2, the prepared P(NIPAM-*co*-BCAm) hydrogels are confirmed to exhibit an interesting behavior as that "adsorption at temperature lower than the LCST and desorption at temperature higher than the LCST". Therefore, the developed P(NIPAM-*co*-BCAm) hydrogel is a thermo-sensitive smart adsorbent material which could easily release the adsorbed substance by simply increasing the environmental temperature across the LCST.

A comparison of temperature-dependent adsorption capabilities of both P(NIPAM-*co*-BCAm) and PNIPAM hydrogels is also studied in this work (Fig. 5). Compared with the P(NIPAM-*co*-BCAm) hydrogel, the PNIPAM hydrogel obviously exhibits lower adsorption capacity for Pb²⁺ ions and its adsorption performance changes little with the temperature increase. The slight decrease of adsorbed amount on the PNIPAM hydrogel upon the temperature increase

might have resulted from the decrease of the adsorption area and the weakened force of physical attraction, because the Pb²⁺ adsorption onto the PNIPAM hydrogel mainly depends on the physical adsorption. Furthermore, acetamide groups in PNIPAM polymer networks perhaps also play some role in binding Pb²⁺ ions. As the temperature increases, the volume and the adsorption area of PNIPAM hydrogel decrease, which may reduce the adsorption of Pb²⁺ ions. Moreover, the hydrophilic-to-hydrophobic transition of polymer networks triggered by the temperature increase may also affect the adsorption of Pb²⁺ ions.

Compared with that of the PNIPAM hydrogel, the adsorption capabilities of P(NIPAM-*co*-BCAm) hydrogel towards Pb²⁺ ions exhibit a strong temperature dependence, which is due to fact that the adsorption of P(NIPAM-*co*-BCAm) hydrogel mainly depends on both the complexation of Pb²⁺ ions with pendant BCAm groups and the physical adsorption. The "swollen–shrunken" configuration change of P(NIPAM-*co*-BCAm) networks triggered by environmental temperature could influence the formation of BCAm/Pb²⁺ complexes. At temperatures lower than the LCST, the copolymer networks stretch, which makes it easier for the cavities of crown ethers to capture the guest ions (Pb²⁺), so that the P(NIPAM-*co*-BCAm) hydrogel exhibits a higher adsorption capacity. On the other hand, at temperatures higher than the LCST, the P(NIPAM-*co*-BCAm) copolymer networks shrink and the cavities of crown ethers are close to each other. As a result, the electrostatic repulsions among the ions affect the formation of stable BCAm/Pb²⁺ complexes inside the hydrogel, which leads to a smaller adsorbed amount of Pb²⁺. A schematic illustration of the thermo-responsive adsorption/desorption behavior of P(NIPAM-*co*-BCAm) hydrogel towards Pb²⁺ ions is shown in Fig. 6.

The developed ion-recognition P(NIPAM-*co*-BCAm) hydrogel could serve as a novel adsorption material for Pb²⁺ ion adsorption and separation. The adsorption and desorption of Pb²⁺ ions could be rationally achieved by simply changing the environmental temperature.

4. Conclusions

The removal of lead(II) ions from aqueous solutions is carried out using the P(NIPAM-*co*-BCAm) hydrogels. The prepared P(NIPAM-*co*-BCAm) hydrogels exhibit good ion-recognition and Pb²⁺-adsorption characteristics. The LCST of the P(NIPAM-*co*-BCAm) hydrogel shifts to a high temperature due to the formation of BCAm/Pb²⁺ host–guest complexes. The Pb²⁺-adsorption capacity of P(NIPAM-*co*-BCAm) hydrogels shows strong temperature depen-

dence and exhibits an interesting behavior as that "adsorption at temperature lower than the LCST and desorption at temperature higher than the LCST" towards Pb^{2+} ions as a result of the "stretch–shrink" configuration change of copolymer networks triggered by the change in environmental temperature. Our results suggest that the P(NIPAM-*co*-BCAm) hydrogel can be a novel thermo-responsive smart Pb^{2+} adsorbent and have great potential applications in environmental protections.

Acknowledgments

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