

# Adsorption of Cu<sup>2+</sup> Ions with Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) Micro/Nanoparticles

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**ABSTRACT:** Chelation efficiency of stimuli-responsive poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAAm-MAA) nanoparticles with Cu<sup>2+</sup> ions from CuSO<sub>4</sub>·5H<sub>2</sub>O solution and from wood treated with copper-based preservatives was studied. It was shown that particle size played a very important role in the adsorption process. The nano-scale particles showed much improved Cu ion adsorption efficiency, compared with the micro hydrogels. The amount of Cu ion adsorption increased with increase of MAA ratio in copolymers and adsorption efficiency decreased with increased particle size. Further-

more, the adsorption amount varied with adsorption temperature at temperatures both below and above the corresponding low critical solution temperature (LCST). The high adsorption efficiency of Cu ions by PNIPAAm-MAA polymer particles provides an effective technique for recovering metal ions (e.g., Cu<sup>2+</sup>) from wood treated with metal-based preservatives. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3470–3476, 2008

**Key words:** PNIPAAm-MAA; nanoparticle; particle size; Cu<sup>2+</sup> adsorption

## INTRODUCTION

Smart polymer, also called intelligent hydrogel, shows a phase transition behavior to external stimuli such as temperature, pH, and ions. Among the most studied hydrogels, poly(*N*-isopropylacrylamide) is a typical thermoresponsive polymer that has a low critical solution temperature (LCST) at about 32°C.<sup>1</sup> By introducing hydrophobic/hydrophilic groups, or pH sensitive groups, the phase transition of pNIPAAm-based copolymers could be controlled to a desired temperature range as well as being sensitive to pH environment.<sup>2</sup> Based on this property, hydrogels are widely studied for potential applications in drug delivery, sensing, fabrication of photonic crystals, template-based synthesis of inorganic nanoparticles, and separation and purification technologies.<sup>3–5</sup>

It is well-known that some ionized polymers can capture multivalent ions in cooperation with several ionized side chains, (i.e., chelation).<sup>6–8</sup> The chelation behavior of gel is very useful in detecting and/or capturing toxic multivalent ions in waste solutions

and can be used to design ionized-gel sensor, which is sensitive to multivalent metal ions. Furthermore, the ion-capture property of the ionized-gel is very useful in environmental purification technology.

Several studies have been reported with stimuli-responsive polymer gels that adsorb metal ions by forming an ionic bond.<sup>9–14</sup> To design and develop a polymer gel that can selectively absorb and release metal ions, the polymer should consist of two monomer groups, each having a different role. One group forms a complex with the target (adsorption part) and the other allows the polymers to stretch and shrink reversibly in response to environmental change (the responsive part). Generally, *N*-isopropylacrylamide is chosen as the responsive monomer. The adsorption monomers that have been reported include acrylic acid,<sup>9</sup> acrylamide, 2-acrylamido-2-methyl-1-propanesulfonic acid,<sup>10</sup> imidazole,<sup>11</sup> carboxylic acid (–COOH) groups,<sup>11</sup> iminodiacetic acid (–IDA) groups,<sup>11</sup> 4-(vinylbenzyl) ethylenediamine (VBEDA),<sup>12</sup> and sodium acrylate.<sup>13</sup> Hydrogels with interpenetration network structure were also studied to investigate adsorption of heavy metal ions.<sup>14</sup> Generally, for hydrogel to adsorb metal ions, the monomer with inherent properties that incorporate onto gelatin acts as determinant of the water-absorption part, and metal ions are adsorbed by effectively partitioning between hydrogels and solution phase. Apart from the nature of metal ions, the structural aspects of hydrogels also determine the quantum of

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metal ion uptake. One of the advantages with stimuli-responsive copolymers for target metal adsorption is that it can potentially be a temperature swing process. The rates of adsorption and desorption are dominated by diffusion within the gel.

It has been shown that bivalent ions such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$ , can interact with methacrylic acid and form metal-polyacid complexes involving two carboxylate groups for each ion in a large domain of pH values.<sup>15,16</sup> Furthermore, stimuli-responsive polymer with nanostructure is expected to be more efficient in capturing or detecting metal ions because of their much greater contact areas. To our knowledge, there have been very few investigations on the ion-capturing feature of the stimuli-responsive polymer with nanostructure. Such investigations are very important because these systems are stabilized with a balance of the interactions in a nanoscopic scale as mentioned above. It is of great practical interest to show how the particle size affects the metal ion adsorption process.

In 2003, the wood protection industry stopped using chromated copper arsenate (CCA) as a major wood preservative, which resulted in significant changes in the U.S. wood preservatives market. The market for wood protection industry was \$500 to \$600 million in 2005, and it is reported that US demand for wood protection and preservatives is forecast to increase 3.1% per year to \$3.2 billion in 2011.<sup>17</sup> Among the metal-based formulations, Alkaline Copper Quaternary (ACQ) is currently the one of the most common wood preservatives for wood processed.<sup>18</sup> After the life cycle of the wood products, the treated wood needs further treatment before they can be disposed or used as a substantial wood fiber resource. Furthermore, it is of great significance to recover expensive metals such as Cu and Zn from treated wood. Research work has been done with metal recovery, CCA treated wood using techniques such as acid extraction to chemically leach Cu from wood,<sup>19,20</sup> and biochemical treatment.<sup>21</sup> After acid extraction, heavy metal remediation is usually achieved by electrolytic method,<sup>22</sup> which is inefficient and energy consuming. Thermoresponsive polymer with chelation agents can provide an easy and low-cost way for recovering heavy metal ions from wood treated with metal-based preservatives.

In our early work, PNIPAAm-MAA particles with different ratios of MAA contents, surfactants, and crosslinker were synthesized.<sup>23</sup> It is shown that the polymer particle size varied with contents of monomer ratio, surfactant, and crosslinker. As monomer ratio and crosslinker content increased and the amount of surfactants decreased, the particle size increased. The objective of the current work was to study the effect of monomer ratio, particle size, and temperature of poly(*N*-isopropylacrylamide-co-

methacrylic acid) (PNIPAAm-MAA) nanoparticles on the adsorption process of  $\text{Cu}^{2+}$  ions from  $\text{CuSO}_4$  and extracted solutions from treated wood.

## EXPERIMENTAL

### Materials

Research grade methacrylic acid (MAA), *N*-isopropylacrylamide (NIPAAm), *N,N'*-methylenebisacrylamide (BIS), sodium dodecyl sulfate (SDS), and potassium persulfate (KPS) were purchased from Sigma-Aldrich (St. Louis, MO) and were used without any further purification. Sodium phosphate dibasic and sodium phosphate monobasic for PBS buffer, and Spectrum Spectra/Por 2 RC Dialysis Membrane Tubing with 12,000 to 14,000 Da MWCO were purchased from Fisher Scientific (Pittsburg, PA).  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was purchased from VWR International (West Chester, PA).

Three sets of wood samples treated commercially with alkaline copper quaternary (ACQ) preservative were selected for extraction for  $\text{Cu}^{2+}$  solution. The samples were randomly designated as groups A, B, and C and they were ground to pass a 20-mesh screen prior to use. X-ray fluorescent (XRF) measurements showed that actual copper contents of the three wood samples by weight (wt %) were A: 1.075%, B: 0.738%, and C: 0.309%.

### Preparation of PNIPAAm-MAA

The polymerization process of the PNIPAAm-MAA particles was discussed in our former paper.<sup>23</sup> Target amount of NIPAAm, MAA, BIS, and SDS was added to 120-g deionized water in a 250-mL reactor. NIPAAm and MAA served as the monomers, BIS as the crosslinking agent, and SDS as surfactant. To control particle size, different MAA to NIPAAm ratios (by mole), and loading levels of SDS were used. The formed particles were purified by membrane dialysis against distilled deionized (DDI) water using Spectra/Pros with a molecular weight cut-off of 12,000–14,000. The formulation for synthesizing PNIPAAm-MAA particles are summarized in Table I for reference.

### Preparation of $\text{CuSO}_4$ solution and $\text{Cu}^{2+}$ solution from treated wood

$\text{CuSO}_4$  solution was prepared by adding proper amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  into aqueous solution for a concentration of 5 mM. The extraction of Cu from treated wood was processed with two methods. One was extraction in water and the other was extraction in sulfuric acid solution. The same amount of ground wood particles (20 g) was placed inside into

**TABLE I**  
**Summary of the PNIPAAm-MAA Formulation and Cu<sup>2+</sup> Adsorption with Different MAA/NIPAAm Ratios and Particle Sizes from CuSO<sub>4</sub> Solutions**

<i>M/N</i>	BIS (g)	SDS (g)	<i>D</i> (nm)	<i>q<sub>t</sub></i> (mmol/g dry gel)	Adsorption amount (mmol/g-drygel)					
					pH = 5		pH = 5.5		pH = 6	
					3°C	50°C	3°C	50°C	3°C	50°C
0.025	0.033	0.075	259.1	0.107	0.079	0.069	0.109	0.084	0.097	0.082
0.050			310.6	0.211	0.164	0.113	0.178	0.170	0.183	0.181
0.075			358.2	0.311	0.269	0.174	0.232	0.255	0.235	0.257
0.100			369.0	0.407	0.339	0.241	0.275	0.290	0.390	0.360
0.400			408.4	1.346	0.649	0.517	0.542	0.449	0.697	0.501
0.700	0.033	0.100	505.8	2.006	0.564	0.522	0.690	0.547	0.742	0.765
0.025			228.7	0.107	0.105	0.091	0.100	0.087	0.096	0.076
			118.2	0.107	0.090	0.093	0.091	0.088	0.096	0.083
			44.9	0.107	0.103	0.100	0.092	0.088	0.093	0.088
			38.3	0.107	0.104	0.100	0.103	0.088	0.096	0.089
0.025	0.017	0.075	274.1	0.108	0.087	0.083	0.104	0.088	0.102	0.079
			260.1	0.107	0.106	0.104	0.105	0.087	0.095	0.081
			255.7	0.106	0.104	0.103	0.102	0.086	0.097	0.097

*M/N*, molar ratio of methacrylic acid over *N*-isopropylacrylamide; BIS, *N,N'*-methylenebisacrylamide; SDS, sodium dodecyl sulfate; *D*, particle size at 25°C; *q<sub>t</sub>*, theoretical adsorption amount.

a flask with 200-mL distilled water (plus 30 mL H<sub>2</sub>SO<sub>4</sub> for the acid extraction) solution for 2 days with continuous stirring. The solutions were then filtered to remove the solid; the filtered solutions were used for Cu<sup>2+</sup> ion adsorption. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian, Palo Alto, CA) analysis of the solutions showed that the Cu<sup>2+</sup> concentrations with water and H<sub>2</sub>SO<sub>4</sub> extraction were 2.45 and 16.80 mM from treated wood sample A (represented by A1 and A2), 0.67 and 8.08 mM from sample B (B1 and B2), 0.71 and 4.48 mM from sample C (C1 and C2). Filtered solutions were directly used for PNIPAAm-MAA particle adsorption.

### Cu<sup>2+</sup> ion adsorption and analysis

To test adsorption capacity of PNIPAAm-MAA particles to Cu<sup>2+</sup> ion, a sample of 2 mL of polymerized PNIPAAm-MAA gel solution was put into 20 mL of 5 mM CuSO<sub>4</sub> aqueous solution in a test tube. The adsorption experiments were carried out at two temperatures, 5 and 50°C. These two temperatures were chosen because they represented one temperature level below LCST and one temperature level above LCST for all studied particles. The LCSTs varied with particle formulations.<sup>23</sup> It is of interest to investigate if the temperature had a significant effect on the adsorption process. Samples in test tubes were kept for 2 days for Cu<sup>2+</sup> adsorption, which was sufficient time for reaching equilibrium. After adsorption, samples were centrifuged to separate the particle and the solution. The pH of the CuSO<sub>4</sub> solution was adjusted with Clark-Lubs buffer solution. The initial and equilibrium concentrations of

Cu<sup>2+</sup> ions in solution were measured by an ICP-AES system.

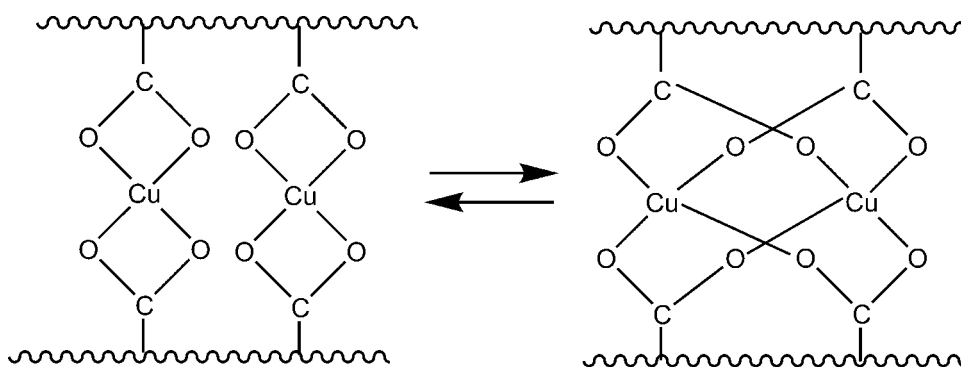
Experimental method of adsorption capacity of PNIPAAm-MAA particle to Cu<sup>2+</sup> ion from treated wood solution was similar to that from CuSO<sub>4</sub> solution. Only particles with MAA/NIPAAm = 0.1 (369 nm), 0.4 (408 nm), and 0.7 (505 nm) were used for adsorption from treated wood solutions. A sample of 2 mL of polymerized PNIPAAm-MAA gel solution was put into 20 mL of aqueous solution at 5°C (below LCST) and one at 50°C (above LCST) separately. Adsorption time was kept at 2 days for reaching equilibrium and the solutions were then centrifuged for separation. Initial and equilibrium concentrations of Cu<sup>2+</sup> ions in solution were measured by ICP-AES.

The equilibrium amount of Cu adsorbed by the particles, which was the net amount of Cu<sup>2+</sup> interacted with copolymer, was determined from the mass balance between the initial and equilibrium Cu<sup>2+</sup> ion contents in solutions, assuming that the concentration of the nonreacted Cu<sup>2+</sup> ion was retained in the equilibrium solution. The equilibrium adsorption amount, *q<sub>e</sub>* (mmol/g-drygel), was determined as follows:

$$q_e = \frac{V_l}{W_g} (C_0 - C_e) \quad (1)$$

where *V<sub>l</sub>* (mL) is the volume of the adsorption solution and *W<sub>g</sub>* (g) is the weight of the corresponding dry gel adsorbent, *C<sub>0</sub>* and *C<sub>e</sub>* (mol/L) are the initial and equilibrium Cu<sup>2+</sup> ion contents, respectively.

The adsorption efficiency (*η*, %), which is based on the actual adsorption amount (*q<sub>e</sub>*) and the theoretical adsorption amount (*q<sub>t</sub>*), was calculated as:



**Figure 1** Mechanism of the  $\text{Cu}^{2+}$  adsorption with PNIPAAm-MAA particles.

$$\eta = \frac{q_e}{q_t} \times 100\% \quad (2)$$

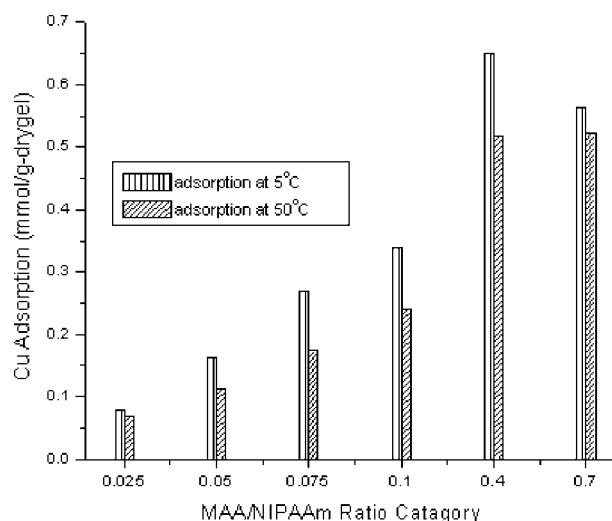
The theoretical adsorption amount,  $q_t$  (mmol/g-drygel), was calculated based on 2 mol of  $\text{Cu}^{2+}$  chelating with 4 mol of the  $-\text{COOH}$  group of PNIPAAm-MAA (Fig. 1), as described in Subramanian's work.<sup>24</sup>  $\text{Cu}^{2+}$  can chelate with  $-\text{COOH}$  groups in PNIPAAm-MAA. Generally, a copper cation can chelate with two PNIPAAm-MAA molecules and two copper cations can further link four or more PNIPAAm-MAA molecules to form an interlocking structure.

## RESULTS AND DISCUSSION

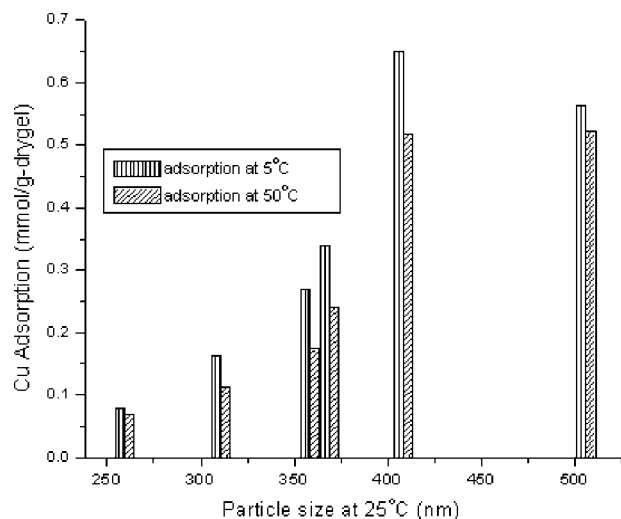
### $\text{Cu}^{2+}$ ion adsorption from $\text{CuSO}_4$ solution

The MAA/NIPAAm ratio dependence for the amount of  $\text{Cu}^{2+}$  adsorbed from  $\text{CuSO}_4$  solution to the PNIPAAm-MAA copolymer particles with different levels of pH (i.e., 5, 5.5, and 6) is summarized in Table I, and a representative graph at pH = 5 is shown in Figure 2. It is obvious that the adsorbed amount increased in a stepwise manner with the increase of MAA/NIPAAm ratio. Furthermore, the adsorbed amount at  $5^\circ\text{C}$  was only slightly higher than that at  $50^\circ\text{C}$  for most cases. This could be due to the fact that at temperatures higher than its LCST, the copolymer shrunk, thus decreased the effective contact area of the MAA unit with  $\text{Cu}^{2+}$  ions. The similar adsorption amount at temperatures below and above LCST suggested that there was no obvious temperature dependence of the adsorption process, and thus direct temperature control for adsorption might not be an efficient way for controlling adsorption amount. However, this does not necessarily suggest that the temperature-sensitive property is not useful in this system. Yamashita et al. showed a method for recycling the hydrogel with the temperature-sensitive results.<sup>14</sup> With the temperature sensitive behavior of PNIPAAm, it is easier to separate the polymer particles adsorbed with Cu

ions from solution, which could provide a convenient way for further releasing Cu with acid treatment. For pH change from 5 to 6,  $\text{Cu}^{2+}$  adsorption amount increased slightly at low MAA ratios. However, for higher MAA ratios (MAA/NIPAAm = 0.1–0.7), no apparent trend of  $\text{Cu}^{2+}$  adsorption amount with pH was detected. This is consistent with results reported by other groups,<sup>11</sup> which demonstrated that pH = 5–6 was not a sensitive region of adsorption. The equilibrium adsorption amount,  $q_e$ , ranged from 0.1 to 0.7 mmol/g-drygel, depending on different MAA contents. The absorbed amount is much higher than the published adsorption data in the literature. For example, the adsorption amount with PNIPAAm-VBEDA ranged from 0.001 to 0.012 mmol/g-drygel,<sup>12</sup> and that of PNIPAAm-MEP ranged from 0.015 to 0.035 mmol/g-drygel.<sup>25</sup> The magnificent increase of adsorption should ascribe to the nano-scale particle size. The PNIPAAm-MAA particle size ranged from 30 to 500 nm, which greatly increased the effective contact area of the MAA and  $\text{Cu}^{2+}$  ions.



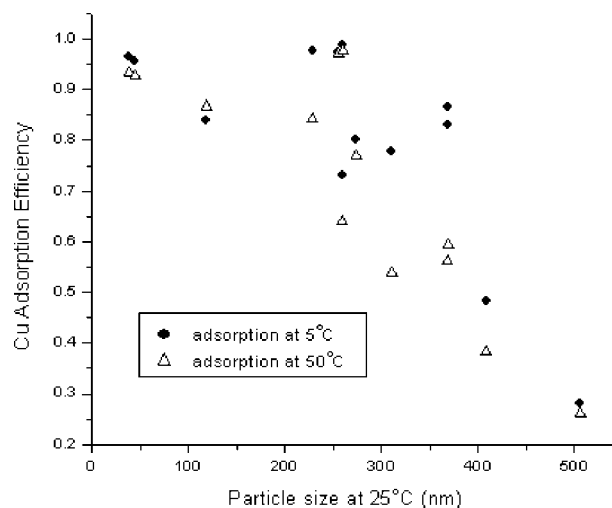
**Figure 2** PNIPAAm-MAA particle  $\text{Cu}^{2+}$  adsorption with different MAA/NIPAAm ratios at pH = 5 from  $\text{CuSO}_4$  solution.



**Figure 3** PNIPAAm-MAA particle  $\text{Cu}^{2+}$  adsorption with different particle sizes at pH = 5 from  $\text{CuSO}_4$  solution.

This is a beneficial and important factor of PNIPAAm-MAA particles for its potential application in purification processes.

The particle size effect on the amount of  $\text{Cu}^{2+}$  adsorbed to the PNIPAAm-MAA copolymer particles from  $\text{CuSO}_4$  solution with different pH levels is summarized in Table I and a representative graph at pH = 5 is shown in Figure 3. The adsorbed amount at temperatures below LCST was higher than that above LCST, as discussed before. For particles with size in range of 30–300 nm, the amount of  $\text{Cu}^{2+}$  adsorbed onto particles showed no significant change, the equilibrium adsorption amount was about 0.1 mmol/g-drygel. For these samples, the MAA/NIPAAm ratios were the same (i.e., MAA/NIPAAm = 0.025). As the particle size increased from 300 to 500 nm, the total adsorbed amount increased. However, this does not necessarily suggest that increasing particle size increased the adsorption amount since the MAA contents in the copolymer particles also increased significantly.



**Figure 4** Adsorption efficiency of  $\text{Cu}^{2+}$  with PNIPAAm-MAA with different particle sizes at pH = 5 from  $\text{CuSO}_4$  solution.

The adsorption of Cu ions onto PNIPAAm-MAA particles is a balance between the particle size and MAA contents.

As mentioned before, particles within 20- to 300-nm size range were synthesized with the same MAA/NIPAAm ratio, but different crosslinker or surfactants contents, leading to different particle sizes. Particles with size range of 300–500 nm represented increasing MAA/NIPAAm ratio with the same crosslinker and SDS contents. As shown in Figure 4, with small particle sizes, the adsorption efficiency was in the 80–98% range for most of the samples. With increased particle sizes, although the absolute adsorption amount per g-drygel increased, the adsorption efficiency decreased dramatically. This strongly suggested that particle size played an important role in the adsorption of metal ions with the copolymer particles. By controlling surfactant contents, PNIPAAm-MAA particles can be synthesized with higher MAA ratios, but smaller particle sizes,

**TABLE II**  
Summary of PNIPAAm-MAA Particles  $\text{Cu}^{2+}$  Adsorption with Different MAA/NIPAAm Ratios from Treated wood  $\text{Cu}^{2+}$  Solutions

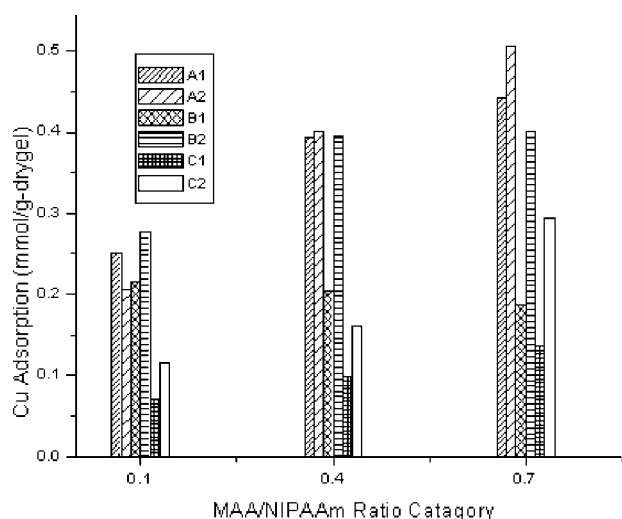
M/N	BIS (g)	SDS (g)	D (nm)	Sample group					
				A1	A2	B1	B2	C1	C2
Adsorption amount (mmol/g-drygel) at 5°C									
0.1	0.033	0.075	369.0	0.251	0.206	0.216	0.278	0.071	0.115
0.4			408.4	0.394	0.401	0.204	0.395	0.099	0.161
0.7			505.8	0.442	0.505	0.187	0.401	0.137	0.295
Adsorption amount (mmol/g-drygel) at 50°C									
0.1	0.033	0.075	369.0	0.235	0.202	0.200	0.299	0.140	0.124
0.4			408.4	0.527	0.460	0.217	0.371	0.146	0.353
0.7			505.8	0.607	0.750	0.200	0.425	0.151	0.384

M/N, molar ratio of methacrylic acid over *N*-isopropylacrylamide; BIS, *N,N'*-methylenebisacrylamide; SDS, sodium dodecyl sulfate; *D*, particle size at 25°C; and  $q_i$ , theoretical adsorption amount.

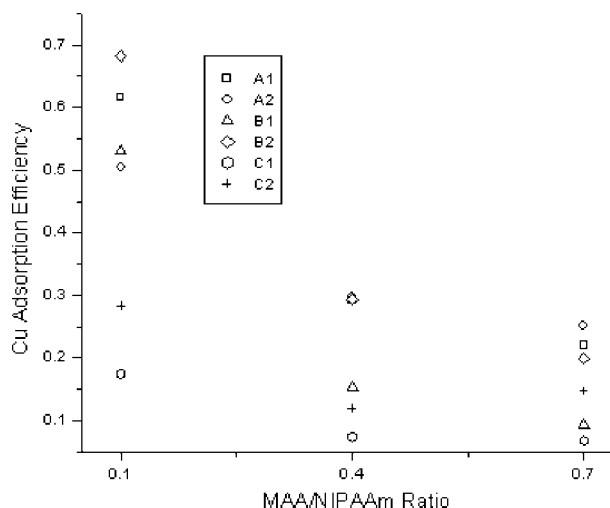
which can be used to enhance the adsorption efficiency of metal ion adsorption with the copolymer.

**$\text{Cu}^{2+}$  ion adsorption from solution extracted from treated wood**

For  $\text{Cu}^{2+}$  adsorption with PNIPAAm-MAA particles from solutions extracted from treated wood, the results are summarized in Table II and adsorption data at 5 and 50°C are plotted in Figures 5 and 6, respectively. Basically,  $\text{Cu}^{2+}$  adsorption from treated wood solutions was slightly less than the amount adsorbed with 5 mM  $\text{CuSO}_4$  solution with the same amount of PNIPAAm-MAA particles. The adsorption amount per gram dry gel was much higher than its hydrogel counterpart reported by other researchers.<sup>12,24</sup> With the increased MAA amount in the particle, although the particle size became larger, the  $\text{Cu}^{2+}$  adsorption (mmol/g-drygel) increased for most samples except B1 and C1. For these two solutions, the  $\text{Cu}^{2+}$  concentration of the stock solution was low. Adsorption efficiencies were also similar to the adsorption data with 5 mM  $\text{CuSO}_4$  solution. This might ascribe to the fact that there were other covalent ions in the treated wood sample solutions and part of the MAA was consumed for chelation with those ions, thus decreased  $\text{Cu}^{2+}$  adsorption amount and efficiency compared to pure  $\text{CuSO}_4$  solution adsorption. The pH level could be another factor leading to the less adsorption amount of  $\text{Cu}^{2+}$  compared with adsorption result from  $\text{CuSO}_4$  solution. The acid extraction from treated wood led to a much lower pH of the solution. Similar to adsorption from  $\text{CuSO}_4$  solution, there was no great difference for adsorption amount at 5 and 50°C, although there was a slight trend that adsorption at 5°C was less



**Figure 5** PNIPAAm-MAA particles  $\text{Cu}^{2+}$  adsorption with different MAA/NIPAAm ratios from treated wood Cu solution at 5°C.



**Figure 6** Adsorption efficiency of  $\text{Cu}^{2+}$  with PNIPAAm-MAA with different MAA/NIPAAm ratios from treated wood Cu solution at 5°C.

than that at 50°C. This might be due to less interaction of other ions at the higher temperature level.

The ability of PNIPAAm-MAA particles to adsorb  $\text{Cu}^{2+}$  ions from extracted treated wood solutions provides an efficient way to recover metal ions from treated wood. The recovered metal ions, together with PNIPAAm-MAA particles can be further used to formulate new wood preventatives, leading to a closed loop recycling process of treated wood.

**CONCLUSION**

PNIPAAm-MAA particles with different MAA/NIPAAm ratios and particle sizes were synthesized and used to adsorb  $\text{Cu}^{2+}$  ions from  $\text{Cu}^{2+}$  ion solutions. The results indicated that with increasing MAA contents, the adsorption amount increased, but the adsorption efficiency decreased as the particle size increased. The equilibrium adsorption amount was a balance between particle size and MAA ratio. Compared with published data, the adsorption amount increased dramatically, due to increase of the effective contact area of the micro- to nano-particles. By controlling the surfactant and MAA ratio, particles with higher MAA and smaller size can be synthesized to improve the adsorption of heavy metal ions with the stimuli-responsive based copolymer. PNIPAAm-MAA particles provide an efficient way for  $\text{Cu}^{2+}$  recovery from treated wood, and could lead to new preservative formulations. Future work will deal with efficiency of the PNIPAAm-MAA-Cu preservatives for wood treatments.

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