Electronic Supplementary Information (ESI)

Micro-hydrogel Particles Consisting of Hyperbranched Polyamidoamine for the Removal of Heavy Metal Ions from Water

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**General Information**

All chemicals were purchased from Sigma-Aldrich. The materials used in the inverse suspension polymerization experiments were ethylenediamine (EDA), N,N’-methylenebisacrylamide (MBA), sorbitan monostearate (Span® 60), and toluene. All reactants were used as received without further purification. EDA and MBA are monomers for Michael addition reaction, and Span 60 is a suspension stabilizer. Also, CdCl₂, CuCl₂, PbCl₂, NiCl₂, ZnCl₂, CoCl₂ were used for the preparation of Cd(II), Cu(II), Pb(II), Ni(II), Zn(II), Co(II) stock solutions.

¹H NMR spectra were recorded on a Bruker Fourier Transform Avance 400 spectrometer for the polymers dissolved in deuterium oxide. FT-IR spectra were obtained with a Bruker EQUINOX-55 spectrometer. Thermal stability studies of the particles were carried out using a TA 2200 thermal analyzer system with a scan rate of 10 °C min⁻¹ under a flow nitrogen gas. The morphology of the polymer particles was examined by optical microscopy (OM) and scanning electron microscopy (SEM). Copper ion binding capacities were measured by inductively coupled plasma optical emission spectrometer (Agilent ICP-OES 720).

**Measurement of Swelling Ratio**

We measured the swelling ratio (Q) by following procedure. The dry HPAMAM particles (W_{dry}) were placed in distilled water and kept there for at least 2 days to reach swelling equilibrium at room temperature. Equilibrated swollen HPAMAM particles were then removed from water and tapped with filter paper to dry the particle surface. And then the particles were collected and weighted (W_{s}). Swelling ratio (Q) was calculated from the following equation (1).

\[
\text{Swelling ratio (Q)} = \left[ \frac{(W_{s} - W_{\text{dry}})}{W_{\text{dry}}} \right]
\]

where W_{dry} and W_{s} are the weights of the dry sample and the swollen particles, respectively.
Measurement of Copper Ion Adsorption Capacity

Binding experiments were carried out in batches as follow. Stock copper solution was prepared as 10,000 ppm in distilled deionized water. The dry HPAMAM particles were placed in the stock heavy metal solution and kept there for at least 1 days to reach equilibrium at room temperature. The HPAMAM particles were separated from the metal solutions by filtration with cellulose nitrate membrane filters with a pore size of 0.45 μm. The concentration of metals in the filtrate was determined by using inductively coupled plasma optical emission spectrometer (Agilent ICP-OES 720). Copper ion binding capacity (A) was calculated from the following equation (2).

\[
\text{Copper ion binding capacity (A)} = \frac{[(C_0 - C_e)V]}{m} \quad (2)
\]

where \(m\) (g) is the weights of the dry sample, \(V\) (L) is the volume of the stock copper solution, \(C_0\) and \(C_e\) (g/L) are the initial and equilibrium copper ion concentrations, respectively.

Measurement of Gel Fraction

The dry HPAMAM particles (\(W_{\text{before}}\)) were placed in distilled water and stirred for at least 2 days to dissolve unreacted monomers and oligomers at room temperature. HPAMAM particles were then removed from water and tapped with filter paper and then dried under vacuum for 24hr at 60 °C. Then the weight of dry HPAMAM particles were measured (\(W_{\text{after}}\)). Gel fraction was calculated from the following equation (3).

\[
\text{Gel fraction} = \frac{W_{\text{after}}}{W_{\text{before}}} \times 100 \quad (3)
\]

Metal Ion Adsorption Test Using Column Method

Glass column (Spectra/Chrom™ LC Column, diameter: 2.5 cm, volume: 4.91ml/cm) was prepared for our fixed-bed column adsorption test. 25g of P-M12/8S0.5R0.3k-500 particles were
placed in glass column. In order to pack the PAMAM particles in glass column, water was injected to percolate through the column at the flow rate of 2.0 mL/min. Then, Cu\(^{2+}\) aqueous solution was allowed to flow at each flow rate.

**EDX analysis**

Frozen HPAMAM particles with liquid nitrogen were broken by spatula, then cut HPAMAM particles were prepared for element analysis of inner part of HPAMAM particles. Element composition was determined by Hitachi SU8230.

**XPS analysis**

HPAMAM particles, Cu\(^{2+}\) adsorbed HPAMAM particles, and Cu\(^{2+}\) solution were prepared on silicon wafer. XPS spectra were recorded by Thermo VG Scientific Sigma Probe.

**Table S1. Properties of PAMAM particles**

|               | [MBA]/[EDA] \(^a\) | Span 60 (wt%) \(^b\) | Agitation speed (rpm) \(^c\) | Size (μm) \(^d\) | Gel fraction (%) \(^e\) | Swelling ratio (g/g) \(^f\) | Cu\(^{2+}\) adsorption capacity (g/g) \(^g\) |
|---------------|-------------------|---------------------|---------------------------|----------------|-----------------|---------------------|-----------------------------|
| P-M\(_9\)/S\(_{0.5}\)R\(_{1k}\) | 1.000             |                     |                           | 50–250         | 88.020          | 11.017              | 0.199                      |
| P-M\(_9\)/S\(_{0.5}\)R\(_{1k}\) | 1.125             | 0.5                 | 1000                      | 50–250         | 96.298          | 5.198               | 0.188                      |
| P-M\(_{10}\)/S\(_{0.5}\)R\(_{1k}\) | 1.250             |                     |                           | 50–250         | 97.514          | 3.637               | 0.176                      |
| P-M\(_{11}\)/S\(_{0.5}\)R\(_{1k}\) | 1.375             |                     |                           | 50–250         | 97.251          | 3.184               | 0.163                      |
| P-M\(_{12}\)/S\(_{0.5}\)R\(_{1k}\) | 1.500             |                     |                           | 50–250         | 97.908          | 2.870               | 0.156                      |
| Sample            | Initial Feed Ratio | Weight % | Agitation Speed (rpm) | Size Range (μm) | Gel Fraction (%) | Swelling Ratio (g/g) | Cu²⁺ Adsorption Capacity (g/g) |
|-------------------|--------------------|----------|------------------------|------------------|------------------|-----------------------|-------------------------------|
| P-M13/8S0.5R1k    | 1.625              | 50–250   | 97.968                 | 2.374            | 0.138            |
| P-M14/8S0.5R1k    | 1.750              | 50–250   | 97.741                 | 2.143            | 0.125            |
| P-M15/8S0.5R1k    | 1.875              | 50–250   | 98.852                 | 2.015            | 0.110            |
| P-M16/8S0.5R1k    | 2.000              | 50–250   | 99.102                 | 2.027            | 0.109            |
| P-M12/8S1.0R1k    | 1.0                | 50–200   | -                      | 2.889            | 0.167            |
| P-M12/8S2.0R1k    | 2.0                | 30–150   | -                      | 3.005            | 0.171            |
| P-M12/8S5.0R1k    | 1.500              | 5–50     | -                      | 2.844            | 0.168            |
| P-M12/8S0.5R0.5k  | 0.5                | 500      | 60–400                 | -                | 2.934            | 0.169                 |
| P-M12/8S0.5R1.5k  | 1500               | 30–180   | -                      | 3.002            | 0.170            |

\(^a\) Initial molar feed ratio of MBA to EDA ([MBA]/[EDA]). \(^b\) Weight concentration of Span 60 (Wt%). \(^c\) Agitation speed (rpm). \(^d\) Size range of micro-hydrogel particles (μm). \(^e\) Gel fraction (%). \(^f\) Swelling ratio (g/g). \(^g\) Cu²⁺ adsorption capacity (g/g).

**Fig. S1** FT-IR spectra for 1 and P-M₈/₈S₀.₅R₁k
Fig. S2 Thermogravimetric analysis

Fig. S3 Gel fraction of HPAMAM particles with feed compositions
Fig. S4 SEM image of P-M₈/₈S₀.₅R₁k
Fig. S5 OM images of (a) P-M_{8/8S0.5R1k}; (b) P-M_{9/8S0.5R1k}; (c) P-M_{10/8S0.5R1k}; (d) P-M_{11/8S0.5R1k}; (e) P-M_{12/8S0.5R1k}; (f) P-M_{13/8S0.5R1k}; (g) P-M_{14/8S0.5R1k}; (h) P-M_{15/8S0.5R1k}; (i) P-M_{16/8S0.5R1k}.

Fig. S6 OM images of (a) P-M_{12/8S0.5R1k}; (b) P-M_{12/8S1.0R1k}; (c) P-M_{12/8S2.0R1k}; (d) P-M_{12/8S5.0R1k};
**Fig. S7** OM image of (a) P-M12/8S0.5R0.5k; (b) P-M12/8S0.5R1k; (c) P-M12/8S0.5R1.5k;

**Fig. S8** Effect of feed compositions of monomers on (a) swelling ratio and (b) Cu\textsuperscript{2+} absorption
Fig. S9 Effect of amount of stabilizer (a) and agitation speed (b) on a swelling ratio
| Absorbent                                                                 | Absorption capacities (mg/g) | Ref |
|--------------------------------------------------------------------------|------------------------------|-----|
| Anatase nanoabsorbent                                                   | 23.74                        | 1   |
| Mesoporous carbon                                                        | 56.62                        | 2   |
| Polystyrene-supported chitosan                                           | 99.8                         | 3   |
| Polyaniline graft chitosan beads                                         | 100                          | 4   |
| Polyacrylonitrile fiber functionalized iminodiacetic acid                | 119.39                       | 5   |
| Poly(vinylbenzyl chloro-co-styrene-co-divinyl benzene) bead              | 61.2                         | 6   |
| N(2-sulfoethyl) chitosan                                                 | 99.8                         | 7   |
| Carboxylic acid functionalized poly(glycidyl methacrylate)              | 37.5                         | 8   |
| Deacetylated konjac glucomannan confugated soy protein isolate           | 62.5                         | 9   |
| DowexTM M4195                                                            | 54                           |     |
| Purolite TM S-930Plus                                                    | 48                           |     |
| Diaion TM Cr11                                                           | 48                           |     |
Table S3. Properties of PAMAM and PAMAM particles

|                | Volume of organic phase (mL) | Span 60 (wt%) | Agitination speed (rpm) | Size (μm) | Swelling ratio (g/g) | Cu$^{2+}$ absorption capacity (g/g) |
|----------------|-------------------------------|---------------|--------------------------|------------|----------------------|-----------------------------------|
| P-M$_{12/8}$S$_{0.5}$R$_{1k}$-15 | 15                            |               |                          |            | 2.870                | 0.156                             |
| P-M$_{12/8}$S$_{0.5}$R$_{1k}$-30  | 30                            |               |                          |            | 2.905                | 0.160                             |
| P-M$_{12/8}$S$_{0.5}$R$_{1k}$-100 | 100                           | 1000          |                          | 50–250     | 3.103                | 0.169                             |
| P-M$_{12/8}$S$_{0.5}$R$_{1k}$-150 | 150                           | 0.5           |                          | 300        | 3.052                | 0.175                             |
| P-M$_{12/8}$S$_{0.3}$R$_{0.3k}$-300| 300                           |               |                          | 50–250     | 2.958                | 0.169                             |
| P-M$_{12/8}$S$_{0.3}$R$_{0.3k}$-500| 500                           |               |                          | 300        | 3.153                | 0.181                             |
| P-M$_{12/8}$S$_{0.3}$R$_{0.3k}$-750| 750                           |               |                          |            | 3.033                | 0.172                             |
| P-M$_{12/8}$S$_{0.3}$R$_{0.3k}$-2000| 2000                          |               |                          |            | 3.019                | 0.178                             |
| P-M$_{12/8}$S$_{0.3}$R$_{1k}$-10000| 10000                         |               |                          |            | 2.974                | 0.171                             |

$^a$ Volume of organic solvent (mL). $^b$ Weight concentration of Span 60 (wt%). $^c$ Agitation speed (15–300–stirring bar, 500–10000–mechanical stirrer); (rpm). $^d$ Size range of micro-hydrogel particles (μm). $^e$ Swelling ratio (g/g). $^f$ Cu$^{2+}$ adsorption capacity (g/g).
Fig. S10 Effect of the reaction scale on swelling ratio (a) and Cu$^{2+}$ absorption capacity (b)
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