Electronic Supporting Information (ESI)

Sonochemical synthesis of poly(methyl methacrylate) core/surfactin shell nanoparticles for recyclable removal of heavy metal ions and its cytotoxicity

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Fig. S1. Chemical structure of surfactin with the heptapeptide ring purified from *Bacillus clausii* BS02.
Fig. S2. Experimental setup for (a) cavitation reactor designed for acoustic atomized microemulsion polymerization and (b) conventional atomized microemulsion.
Determination of monomer conversion, solid content, molecular weights and polydispersity index (PDI)

The total number of latex particles in the system \(N_P\) and the number of polymer chains per particle \(N\) as well as the conversion \(X_m\) are calculated according to the following equations:

\[
N_P = \frac{6 \rho_0 VX_m}{\rho \pi D^3} \tag{1}
\]

\[
N = \frac{4}{3} \frac{\rho \pi (D/2)^3 N_A}{M_n} \tag{2}
\]

\[
X_m(\%) = \frac{W_1}{W_2} \times 100 \tag{3}
\]

where \(\rho_0\) is the density of MMA (0.94 g cm\(^{-3}\) at 25 °C), \(V\) is the total volume of MMA, \(X_m\) is polymerization conversion, \(\rho\) is the density of PMMA (g cm\(^{-3}\) at 25 °C), \(D\) is the diameter of the particle, \(N_A\) is 6.02×10\(^{23}\) mol\(^{-1}\), \(M_n\) is the number-average molecular weight, and \(W_1\) and \(W_2\) are the weights of the polymer and MMA, respectively.

The number-average-molecular weight \(\bar{M}_n\) and weight-average molecular weight \(\bar{M}_w\) as well as the PDI were determined by gel permeation chromatography with an Agilent GPC-Addon Rev A02.02 series HPLC system using a PL-Gel Agilent column and THF solvent. A calibration curve was constructed using standard polystyrene having a molecular weight range of 4490 to 1,112,000 g mol\(^{-1}\). The dried nPMMA was dissolved in tetrahydrofuran at a concentration of 0.3% w/v and then filtered with a nylon membrane (pore size 0.45 µm) before injection.
Energy calculations

1. Energy delivered during conventional atomized microemulsion method

Voltage input in magnetic stirrer (Model 5 MLH DX, Remi, India) = 230 V.

Current measured using digital multimeter (Model 801, Meco Instruments Pvt. Ltd., India) = 37 mA = 37 × 10^{-3} A.

Power input in overhead stirrer = voltage input × current measured = 230 (V) × 37 × 10^{-3} (A) = 8.51 W (J/s).

Time required for completion of reaction = 1 h (3600 s).

Net energy delivered during conventional method = power input in magnetic stirrer × time required for completion of reaction = 8.51 J/s × 1 h × 3600 s/h = 30636 J = 30.636 kJ.

Energy supplied in form of heat to maintain reaction temperature 55 °C = mC_{p,mix} (T_{process} - T_{ref}) = 130.38 × 4.0058 × (55 - 25) = 15668.3 J = 15.67 kJ.

Total energy supplied during conventional method = 46.31 kJ.

Quantity of material processed = quantity of [water + KPS + surfactin + MMA] = 100 ml + 0.25 g + 0.025 g + 5 g = 105.28 g.

Net energy supplied for processing of material using conventional method = net energy delivered during conventional method/quantity of material processed = 46.31 (kJ) / 105.28 (g) = 43.98 × 10^{-2} (kJ/g).

2. Energy delivered during acoustic atomized microemulsion polymerization

Energy delivered during sonication = energy required to synthesize nPMMA.

Electrical energy delivered during sonication (indicated by the power meter) = 53.5 kJ.

Efficiency of horn taken for the calculation = 18.9% (estimated independently using calorimetric studies).

Actual energy delivered by horn during sonication = energy delivered during sonication using horn × efficiency of horn = 53.5 × 18.9/100 = 10.11 kJ.
Quantity of material processed = quantity of [water + KPS + surfactin + MMA] = 100 ml + 0.25 g + 0.025 g + 5 g = 105.28 g.

Net energy supplied for processing of material using sonochemical method = actual energy delivered by horn during sonication/quantity of material processed = 10.11 (kJ) / 105.28 (g) = $9.60 \times 10^{-2}$ (kJ/g). (B)

3. Energy saved

Net energy saved = [net energy supplied for processing of material using atomized microemulsion method (A)] - [net energy supplied for processing of material using sonochemical emulsion polymerization (B)] = $43.98 \times 10^{-2}$ (kJ/g) - $9.60 \times 10^{-2}$ (kJ/g) = $34.38 \times 10^{-2}$ (kJ/g).

**Calculation of cavitation yield**

1. Conventional atomized microemulsion

Rate of polymerization = 1.26 g l$^{-1}$

Power density (J l$^{-1}$) = supplied total electrical energy = 46.31 kJ = 46310 J l$^{-1}$

Cavitational yield = $1.26$ (g l$^{-1}$) / $46310$ (J l$^{-1}$) = $0.27 \times 10^{-4}$ g J$^{-1}$

2. Acoustic atomized microemulsion polymerization

Rate of polymerization = 1.51 g l$^{-1}$

Power density (J l$^{-1}$) = supplied total electrical energy = 10.11 kJ = 10110 J l$^{-1}$

Cavitational yield = $1.51$ (g l$^{-1}$) / $10110$ (J l$^{-1}$) = $1.5 \times 10^{-4}$ g J$^{-1}$
**Fig. S3.** The pH dependence of zeta-potential of nPMMA\textsubscript{US} and nPMMA\textsubscript{AM} particles.

(Reaction conditions: nPMMA\textsubscript{US}: MMA, 5 wt.%; KPS, 3% of MMA; surfactin, 0.5% of MMA; temperature, 55 °C; power output, 50% amplitude; nPMMA\textsubscript{AM}: MMA, 5 wt.%; KPS, 3% of MMA; surfactin, 0.5% of MMA; temperature, 55 °C; agitation, 250 rpm).
The diffraction peak observed at 15.8° is assigned to the amorphous phase of PMMA. This peak is more pronounced in nPMMA\textsubscript{US}. It suggests the crystalline nature of nPMMA\textsubscript{US} is more than nPMMA\textsubscript{AM} and bulk PMMA.

![XRD patterns of (a) nPMMA\textsubscript{US}, (b) nPMMA\textsubscript{AM} and (c) bulk PMMA.](image)

\textbf{Fig. S4.} XRD patterns of (a) nPMMA\textsubscript{US}, (b) nPMMA\textsubscript{AM} and (c) bulk PMMA.
It was observed that first scan of nPMMA\textsubscript{US} showed two step exothermic peaks at 130 and 136 °C that are attributed to T\textsubscript{g1} along with respective peaks of T\textsubscript{m} arising due to the presence of little amount of surfactin (Fig. S7a). This finding corroborates with the thin shell layer of biosurfactants observed in TEM. The lower value of T\textsubscript{g1} (Fig. S7b) for nPMMA\textsubscript{AM} (115 °C) was due to its relatively large size and lower surface area as compared to nPMMA\textsubscript{US}. Moreover, the peak for surfactin shell could not be detected due to poor grafting of surfactin onto nPMMA core in case of nPMMA\textsubscript{AM}. Bulk PMMA shows regular T\textsubscript{g} at 106 °C like commercial grade PMMA (Fig. S7c). The reason for high T\textsubscript{g} of polymer nanoparticles than bulk PMMA might be a decrease in particle size to nano-scale that results in an increase in surface area and higher surface energy.

**Fig. S5.** DSC curves of (a) nPMMA\textsubscript{US} and (b) nPMMA\textsubscript{AM} and (c) bulk PMMA.
A remarkable change in thermal behavior between nPMMA\textsubscript{US}, nPMMA\textsubscript{AM} and bulk PMMA was observed. The nPMMA\textsubscript{US} showed higher thermal stability [$d_{on} = 367 \, ^\circ\text{C}$ and $d_{off} = 412 \, ^\circ\text{C}$ with $\%\text{ weight loss (W}_L\_L = 100\%$] than nPMMA\textsubscript{AM} [$d_{on} = 349 \, ^\circ\text{C}$ and $d_{off} = 402 \, ^\circ\text{C}$ with $\%\text{ weight loss (W}_L\_L = 100\%$] and bulk PMMA [$d_{on} = 283 \, ^\circ\text{C}$ and $d_{off} = 360 \, ^\circ\text{C}$ with 100% $W_L\_L$. Thus, the thermal stability pattern followed the order: nPMMA\textsubscript{US} > nPMMA\textsubscript{AM} > bulk PMMA.
Fig. S7. Overlay of XPS C 1s spectra of nPMMA$_{AM}$ and nPMMA$_{US}$ before and after exposure to the heavy metals.
Fig. S8. Plots of (a) pseudo first-order and (b) pseudo second-order model for adsorption of the tested heavy metals onto nPMMA$_{US}$ particles.
**Adsorption kinetics model**

In order to determine the rate constants, the pseudo-first order (Eq. 4) and pseudo-second order model (Eq. 5) were used:

\[
\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1t
\]

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}
\]

where, \(k_1\) is the rate constant of pseudo first-order adsorption (h\(^{-1}\)), \(q_e\) (mg g\(^{-1}\)) is the amount of metal adsorbed on the surface at equilibrium, \(q_t\) (mg g\(^{-1}\)) is the amount of solute adsorbed at any time \(t\) and \(k_2\) is the equilibrium rate constant of pseudo second-order sorption (g mg h\(^{-1}\)).

**Adsorption isotherms models**

Langmuir equation:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}b}
\]

Freundlich equation:

\[
\log q_e = \frac{\log C_e}{n} + \log k_f
\]

where, \(q_{\text{max}}\) (mg g\(^{-1}\)) is the theoretical maximum heavy metal adsorption amount, \(q_e\) (mg g\(^{-1}\)) is the equilibrium adsorption amount at heavy metal equilibrium concentration \(C_e\) (mg l\(^{-1}\)), \(k_f\) is the Freundlich coefficient characteristic of the adsorption affinity of the adsorbent, and \(n\) is the linearity index.
Thermodynamic parameters

\[
\ln\left(\frac{q_{e,m}}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}
\]

\[
\Delta G^\circ = \Delta H^\circ - TS^\circ \tag{9}
\]

where \( m \) is the adsorbent dose (mg l\(^{-1}\)), \( C_e \) is the equilibrium concentration (mg l\(^{-1}\)) of the metal ion in solution and \( q_{e,m} \) is the solid-phase concentration (mg l\(^{-1}\)) at equilibrium. \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature (K).
**Fig. S9.** Effect of adsorbent dosage on adsorption of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Fe$^{2+}$ onto (a) nPMMA$_{US}$ and (b) nPMMA$_{AM}$ particles (initial metal ion: 30 mg l$^{-1}$; pH: 6.0; contact time: 30 min). Values reported as the mean ± S.D. ($n = 3$).
Fig. S10. Effect of initial metal ion concentration on adsorption of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Fe$^{2+}$ onto (a) nPMMA$_{US}$ and (b) nPMMA$_{AM}$ particles (adsorbent loading: 200 mg l$^{-1}$; pH: 6.0; contact time: 30 min). Values reported as the mean ± S.D. ($n = 3$).
**Fig. S11.** Influence of pH on adsorption of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, and Fe$^{2+}$ onto nPMMA$_{US}$ particles. Values reported as the mean ± S.D. ($n = 3$).
Fig. S12. Effect of humic acid on Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Fe$^{2+}$ adsorption by nPMMA$_{US}$ particles (adsorbent loading: 200 mg l$^{-1}$; initial metal ion: 30 mg l$^{-1}$; pH: 6.0; contact time: 30 min). Values reported as the mean ± S.D. ($n = 3$).
Fig. S13. Effect of the background electrolytes on the adsorption capacity of nPMMA\textsubscript{US} particles: (a) Na\textsuperscript{2+}; (b) K\textsuperscript{+}; and (c) Mg\textsuperscript{2+}. Values reported as the mean ± S.D. (n = 3).
Fig. S14. The plot of $\ln \left( \frac{q_m}{C_0} \right)$ vs. $1/T$ for the adsorption of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Fe$^{2+}$ onto nPMMA$_{US}$ particles.
Fig. S15. Five consecutive adsorption-desorption cycles of nPMMAUS particles for (a) Pb$^{2+}$, (b) Cd$^{2+}$, (c) Cu$^{2+}$ and (d) Fe$^{2+}$ by HCl or EDTA. Initial metal ion concentration: 30 mg l$^{-1}$; adsorbent loading: 200 mg l$^{-1}$. 
### Table S1. The physico-chemical characteristics of surfactin used in this study.

<table>
<thead>
<tr>
<th>Biosurfactant</th>
<th>Molecular formula</th>
<th>Molecular weight (g mol(^\text{-1}))</th>
<th>CMC (μM)</th>
<th>Interfacial tension (mN m(^\text{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactin</td>
<td>C(<em>{53})H(</em>{93})N(<em>7)O(</em>{13})</td>
<td>1036</td>
<td>7.5-9.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Element</td>
<td>nPMMA&lt;sub&gt;AM&lt;/sub&gt;</td>
<td>nPMMA&lt;sub&gt;US&lt;/sub&gt;</td>
<td>nPMMA&lt;sub&gt;US&lt;/sub&gt; - Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>nPMMA&lt;sub&gt;US&lt;/sub&gt; - Cd&lt;sup&gt;2+&lt;/sup&gt;</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>BE (eV)</td>
<td>AC(%)</td>
<td>BE (eV)</td>
<td>AC(%)</td>
</tr>
<tr>
<td>C 1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C/C-H</td>
<td>284.6</td>
<td>34.7</td>
<td>284.8</td>
<td>38.5</td>
</tr>
<tr>
<td>β-shifted C</td>
<td>285.2</td>
<td>11.6</td>
<td>285.3</td>
<td>14.4</td>
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<tr>
<td>C-O-C/O-C</td>
<td>286.8</td>
<td>17.1</td>
<td>286.9</td>
<td>18.13</td>
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<td>O-C-O</td>
<td>287.9</td>
<td>6.2</td>
<td>288.0</td>
<td>7.1</td>
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<tr>
<td>O-C=O</td>
<td>288.8</td>
<td>12.7</td>
<td>288.9</td>
<td>13.87</td>
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<td>O 1s</td>
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<td></td>
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<td></td>
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<tr>
<td>ether-type (C-O)</td>
<td>532.3</td>
<td>7.4</td>
<td>532.6</td>
<td>1.3</td>
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<tr>
<td>carbonyl-type</td>
<td>534.0</td>
<td>6.3</td>
<td>534.2</td>
<td>1.7</td>
</tr>
<tr>
<td>N 1s</td>
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<td></td>
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<td></td>
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<tr>
<td>amine/amide</td>
<td>399.8</td>
<td>4.0</td>
<td>399.9</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Table S2.** Assignments of main spectral bands based on their binding energies (BE) and atomic concentration (AC) for nPMMA<sub>AM</sub> and nPMMA<sub>US</sub> before and after heavy metals adsorption.
<table>
<thead>
<tr>
<th>Polymeric adsorbents</th>
<th>Maximum sorption capacities (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb²⁺</td>
<td>Cd²⁺</td>
</tr>
<tr>
<td>Iminodiacetate chelating resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(MMA-MAGA)</td>
<td>65.2</td>
<td>28.2</td>
</tr>
<tr>
<td>Poly(GMA-co-EGDMA)-en</td>
<td>1.06</td>
<td>0.67</td>
</tr>
<tr>
<td>GMA/DVB magnetic resin</td>
<td>2.3</td>
<td>2.0</td>
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<tr>
<td>Polystyrene</td>
<td>0.36</td>
<td></td>
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<td>HA immobilized-Am-PAA-B (HA-Am-PAA-B)</td>
<td></td>
<td>108.06</td>
</tr>
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<td>2-hydroxyethyl acrylate (HEA) and 2-acrylamido-2-methylpropane sulfonic (AMPS) acid hydrogels</td>
<td>180</td>
<td>120</td>
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<tr>
<td>poly(hydroxyethyl methacrylate/maleamic acid) hydrogel</td>
<td>50.6</td>
<td>20.2</td>
</tr>
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<td>poly(acrylamide-co-sodium methacrylate)</td>
<td>35</td>
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<tr>
<td>non-crosslinked chitosan-coated bentonite beads</td>
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<td>12.21</td>
</tr>
<tr>
<td>poly(guanidine modified 2-acrylamido-2-methylpropan sulfonic acid/acrylic acid/N-vinylpyrrolidone/2-hydroxyethyl methacrylate)</td>
<td>27</td>
<td></td>
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<tr>
<td>P(N-isopropylacrylamide-co-benzo-18-crown-6-acrylamide)</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>xanthate-modified magnetic chitosan</td>
<td>76.9</td>
<td>34.5</td>
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<tr>
<td>Crosslinked chitosan</td>
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<td>Crosslinked starch gel</td>
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<td>135</td>
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<tr>
<td>Alumina/chitosan composite</td>
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<td>200</td>
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**Table S3.** Adsorption capacities of some selected polymeric adsorbents for heavy metals removal from aqueous media.
References


