1	Electronic Supporting Information (ESI)								
2	Sonochemical synthesis of poly(methyl methacrylate) core/surfactin shell nanoparticles for								
3	recyclable removal of heavy metal ions and its cytotoxicity								
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2 Fig. S1. Chemical structure of surfactin with the heptapeptide ring purified from *Bacillus*3 *clausii* BS02.





Speed regulator (1), US probe (2), jacket (3), thermocouple (4), water-biosurfactantinitiator solution (5), monomer mists (6), pressure gauge (7), small low pressure metering pump (8), atomizer (9), safety attachment-rupture disc (10), sight glass (11), baffles (12), butterfly valve (13), heating coil (14), nitrogen cylinder (15), nitrogen flow adjustment valve (16), vent valve (17), distillation column (18), nitrogen inlet (19), PID type controller (20), and energy regulator network for temperature control (21) Speed regulator (1), agitator impellor (2), jacket (3), thermocouple (4), waterbiosurfactant-initiator solution (5), monomer mists (6), pressure gauge (7), small low pressure metering pump (8), atomizer (9), safety attachment-rupture disc (10), sight glass (11), baffles (12), butterfly valve (13), heating coil (14), nitrogen cylinder (15), nitrogen flow adjustment valve (16), vent valve (17), distillation column (18), nitrogen inlet (19), PID type controller (20), and energy regulator network for temperature control (21)

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:

$$N_P = \frac{6\rho_0 V X_m}{\rho \pi D^3} \tag{1}$$

$$N = \frac{4}{3} \frac{\rho \pi (D/2)^3 N_A}{\overline{M}_n} \tag{2}$$

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

where ρ_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, ρ is the <u>density</u> 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_I and W_2 are the weights of the polymer and MMA, respectively.

The number-average-molecular weight $(\overline{M_n})$ and weight-average molecular weight $(\overline{M_w})$ 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) =

 $37 \text{ mA} = 37 \times 10^{-3} \text{ A}.$

Power input in overhead stirrer = voltage input × current measured = $230 (V) \times 37 \times 10^{-3} (A)$ = 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 = $8.51 \text{ J/s} \times 1 \text{ h} \times 3600 \text{ s/h} = 30636 \text{ J} = 30.636 \text{ kJ}$.

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) = $43.98 \times 10^{-2} (kJ/g)$. (A)

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 \times efficiency of horn = 53.5 \times 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)] = 43.98×10^{-2} (kJ/g) - 9.60×10^{-2} (kJ/g) = 34.38×10^{-2} (kJ/g).

Calculation of cavitational yield

1. Conventional atomized microemulsion

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

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 = $1.51 \text{ g } \text{l}^{-1}$

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) = 1.5×10^{-4} g J⁻¹



Fig. S3. The pH dependence of zeta-potential of $nPMMA_{US}$ and $nPMMA_{AM}$ particles. (Reaction conditions: $nPMMA_{US}$: MMA, 5 wt.%; KPS, 3% of MMA; surfactin, 0.5% of MMA; temperature, 55 °C; power output, 50% amplitude; $nPMMA_{AM}$: MMA, 5 wt.%; KPS, 3% of MMA; surfactin, 0.5% of MMA; temperature, 55 °C; agitation, 250 rpm).



Fig. S4. XRD patterns of (a) $nPMMA_{US}$, (b) $nPMMA_{AM}$ and (c) bulk PMMA.

The diffraction peak observed at 15.8° is assigned to the amorphous phase of PMMA. This peak is more pronounced in nPMMA_{US}. It suggests the crystalline nature of nPMMA_{US} is more than nPMMA_{AM} and bulk PMMA.



Fig. S5. DSC curves of (a) nPMMA_{US} and (b) nPMMA_{AM} and (c) bulk PMMA.

It was observed that first scan of nPMMA_{US} showed two step exothermic peaks at 130 and 136 °C that are attributed to T_{g1} along with respective peaks of T_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_{g1} (Fig. S7b) for nPMMA_{AM} (115 °C) was due to its relatively large size and lower surface area as compared to nPMMA_{US}. Moreover, the peak for surfactin shell could not be detected due to poor grafting of surfactin onto nPMMA core in case of nPMMA_{AM}. Bulk PMMA shows regular T_g at 106 °C like commercial grade PMMA (Fig. S7c). The reason for high T_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. S6. TGA thermogram of (a) $nPMMA_{US}$ and (b) $nPMMA_{AM}$ and (c) bulk PMMA.

A remarkable change in thermal behavior between nPMMA_{US}, nPMMA_{AM} and bulk PMMA was observed. The nPMMA_{US} showed higher thermal stability $[d_{on} = 367 \text{ °C} \text{ and } d_{off} = 412 \text{ °C}$ with % weight loss $(W_L) = 100\%$] than nPMMA_{AM} $[d_{on} = 349 \text{ °C}$ and $d_{off} = 402 \text{ °C}$ with % weight loss $(W_L) = 100\%$] and bulk PMMA $[d_{on} = 283 \text{ °C} \text{ and } d_{off} = 360 \text{ °C} \text{ with } 100\% \text{ W}_L]$. Thus, the thermal stability pattern followed the order: nPMMA_{US} > nPMMA_{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 pseudosecond order model (Eq. 5) were used:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{5}$$

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:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{C_{\rm e}}{q_{\rm max}} + \frac{1}{q_{\rm max}b} \tag{6}$$

Freundlich equation:

$$\log q_{\rm e} = \frac{\log C_{\rm e}}{n} + \log k_{\rm f} \tag{7}$$

where, q_{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.

$$\ln(q_{\rm e}m/C_{\rm e}) = \Delta S^{\circ}/R - \Delta H^{\circ}/RT$$
(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_em 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 Pb²⁺, Cd²⁺, Cu²⁺ and Fe²⁺ 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 \pm S.D. (*n* = 3).



Fig. S10. Effect of initial metal ion concentration on adsorption of Pb²⁺, Cd²⁺, Cu²⁺ and Fe²⁺ 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 \pm S.D. (*n* = 3).



Fig. S11. Influence of pH on adsorption of Pb²⁺, Cd²⁺, Cu²⁺ and Fe²⁺ onto nPMMA_{US} particles. Values reported as the mean \pm S.D. (n = 3).



Fig. S12. Effect of humic acid on Pb²⁺, Cd²⁺, Cu²⁺ and Fe²⁺ 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 \pm S.D. (*n* = 3).



Fig. S13. Effect of the background electrolytes on the adsorption capacity of nPMMA_{US} particles: (a) Na²⁺; (b) K⁺; and (c) Mg²⁺. Values reported as the mean \pm S.D. (*n* = 3).



Fig. S14. The plot of ln $(q_e m/C_e)$ vs. 1/T for the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ and Fe²⁺ onto nPMMA_{US} particles.



Fig. S15. Five consecutive adsorption-desorption cycles of $nPMMA_{US}$ 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.

Biosurfactant	Molecular formula	Molecular weight (g mol ⁻¹)	СМС	Interfacial tension (mN m ⁻¹)
Surfactin	C ₅₃ H ₉₃ N ₇ O ₁₃	1036	7.5 - 9.5 μM	1.0

 Table S1. The physico-chemical characteristics of surfactin used in this study.

Element	nPMMA _{AM}		nPMMA _{US}		nPMMA _{US} - Pb ²⁺		nPMMA _{US} - Cd ²⁺		nPMMA _{US} - Cu ²⁺		nPMMA _{US} - Fe ²⁺	
	BE (eV)	AC(%)	BE (eV)	AC(%)	BE (eV)	AC(%)	BE (eV)	AC(%)	BE (eV)	AC(%)	BE (eV)	AC(%)
C 1s												
С-С/С-Н	284.6	34.7	284.8	38.5	284.4	38.3	284.2	38.1	284.1	37.8	284.1	37.5
β-shifted C	285.2	11.6	285.3	14.4	285.1	14.1	285.0	16.5	284.8	16.6	284.8	15.8
C-O-C/O-C	286.8	17.1	286.9	18.13	286.6	17.8	286.4	17.5	286.2	17.1	286.2	17.0
0-C-0	287.9	6.2	288.0	7.1	287.8	6.9	287.5	6.7	287.3	6.5	287.3	6.3
O-C=O	288.8	12.7	288.9	13.87	288.7	13.5	288.5	13.3	288.2	13.1	288.1	13.0
01s												
ether-type	532.3	7.4	532.6	1.3	531.3	2.8	531.2	2.7	531.1	2.6	530.7	3.4
(C-O)												
carbonyl-	534.0	6.3	534.2	1.7	532.5	2.2	532.3	2.4	532.2	2.5	531.8	3.1
type												
N 1s												
amine/amide	399.8	4.0	399.9	5.0	400.1	4.4	399.7	2.8	399.8	4.0	399.8	3.9

Table S2. Assignments of main spectral bands based on their binding energies (BE) and atomic concentration (AC) for nPMMA_{AM} and $nPMMA_{US}$ before and after heavy metals adsorption.

Polymeric adsorbents	Maximu	im sorption	g g ⁻¹)	References	
-	Pb ²⁺	Cd ²⁺	Cu ²⁺	Fe ²⁺	
Iminodiacetate chelating			3.257		[1]
resins					
Poly(MMA-MAGA)	65.2	28.2			[2]
Poly(GMA-co-EGDMA)-	1.06	0.67	1.10		[3]
en					
GMA/DVB magnetic	2.3	2.0			[4]
resin					
Polystyrene	0.36				[5]
HA immobilized-Am-			108.06		[6]
PAA-B (HA-Am-PAA-B)					
2-hydroxyethyl	180	120	100	110	[7]
acrylate (HEA) and 2-	100	120	100	110	
acrylamido-2-					
methylpropane sulfonic					
(AMPS) acid hydrogels					
noly(hydroxyethyl	50.6	20.2	14.5		[8]
motheorylate/maleeria	30.0	20.2	14.5		٢٥١
nietilaci ylate/inaleanne					
acid) hydroger	25				[0]
poly(acrylamide-co-	35				[9]
sodium methacrylate)					54.03
non-crosslinked chitosan-			12.21		[10]
coated bentonite					
beads					
poly(guanidine modified	27				[11]
2-acrylamido-					
2-methylpropan sulfonic					
acid/acrylic acid/N-					
vinylpyrrolidone/					
2-hydroxyethyl					
methacrylate)					
P(N-isopropylacrylamide-	143				[12]
co-benzo-18-crown-6-					
acrylamide)					
xanthate-modified	76.9		34.5		[13]
magnetic chitosan					
Crosslinked chitosan		150			[14]
Crosslinked starch gel	433	-	135		[14]
Alumina/chitosan			200		[14]
composite					r1

Table S3. Adsorption capacities of some selected polymeric adsorbents for heavy metals removal

from aqueous media.

References

- 1 M.V. Dinu, E.S. Dragan, React. Funct. Polym. 2008, 68, 1346-1354.
- 2 A. Denizli, N. Sanli, B. Garipcan, S. Patir, G. Alsancak, *Ind. Eng. Chem. Res.* 2004, **43**, 6095-6101.
- 3 A. Nastasovic, S. Jovanovic, D. Dordevic, A. Onjia, D. Jakovljevic, T. Novakovic, *React. Funct. Polym.* 2004, **58**, 139-147.
- 4 A.A. Atia, A.M. Donia, A.M. Yousif, Sep. Purif. Technol. 2008, 61, 348-357.
- 5 B.L. Rivas, S.A. Pooley, H.A. Maturana, S. Villegas, J. Appl. Polym. Sci. 2001, 80, 2123-2127.
- 6 T.S. Anirudhan, P.S. Suchithra, J. Ind. Eng. Chem. 2010, 16, 130-139.
- 7 Z. Li, Y. Wang, N. Wu, Q. Chen, K. Wu, Environ. Sci. Pollut. Res. 2013, 20, 1511-1525.
- 8 N. Wu, Z. Li, Chem. Eng. J. 2013, 215-216, 894-902.
- 9 M.K. Krusic, N. Milosavljevic, A. Debeljkovic, O.B. Uzum, E. Karadag, Water Air Soil Poll. 2012, 223, 4355-4368.
- 10 M.L.P. Dalida, A.F.V. Mariano, C.M. Futalan, C.C. Kan, W.C. Tsai, M.W. Wan, *Desalination* 2011, 275, 154-159.
- 11 E.K. Yetimoglu, M. Firlak, M.V. Kahraman, S. Deniz, *Polym. Adv. Technol.* 2011, 22, 612-619.
- 12 X.J. Ju, S.B. Zhang, M.Y. Zhou, R. Xie, L. Yang, L.Y. Chu, J. Hazard. Mater. 2009, 167, 114-118.
- 13 Y.H. Zhu, J. Hu, J.L. Wang, J. Hazard. Mater. 2012, 221, 155-161.

14 G. Crini, Prog. Polym. Sci. 2005, 30, 38-70.