SUPPORTING INFORMATION

for

In Situ Allocation of a Monomer in Pectin-g-Terpolymer Hydrogels and Effect of Comonomer Compositions on Superadsorption of Metal Ions/Dyes

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EXPERIMENTAL SECTION

Characterization. PANIPNs were characterized by Fourier transform infrared (FTIR) spectroscopy through Spectrum-2, Singapore in the range from 4000 to 400 cm\(^{-1}\); \(^1\)H-\(^{13}\)C-nuclear magnetic resonance (\(^1\)H-\(^{13}\)C-NMR) spectroscopy using Bruker-Advance Digital 300 MHz in CDCl\(_3\) solvent with TMS as an internal reference/JEOL ECX400, at the proton frequency of 400 MHz; X-ray photoelectron spectroscopy (XPS) via ESCA+, Omicron nanotechnology, Oxford Instrument Germany, equipped with Al Source (k\(_\alpha\) radiation h\(_{\nu}\) = 1486.7 ev) monochromator, operating at 15 kv, and 20 mA; thermogravimetric analysis (TGA) using Pyris6 TGA, The Netherlands in N\(_2\) atmosphere with flow, and scanning rates of 20.0 cm\(^3\) min\(^{-1}\) and 10 °C min\(^{-1}\), respectively, from 30 to 700 °C; differential scanning calorimetry (DSC) via Pyris6 DSC, the Netherlands in N\(_2\) atmosphere with the flow rate of 20.0 cm\(^3\) min\(^{-1}\), within 30–442 °C; X-ray diffraction (XRD) by X'Pert PRO, PANalytical B.V., the Netherlands, using Ni-filtered CuK\(_\alpha\) radiation (\(\lambda = 1.5406 \, \text{Å}\)) having angle of diffraction, within 5–100°; scanning electron microscope (SEM), and energy dispersive X-ray (EDX) using ZEISS EVO-MA 10 having resolution of 3 nm with W filament and Sb as sources, and rheological analyses through Anton Paar MCR 102 rheometer. PANIPNs were also characterized by measuring network parameters, such as crosslink densities (i.e., CDs, \(\rho_c\)), and average molecular weights between crosslinks (i.e., \(M_c\)), LCST, % gel content (i.e., % GC) content, amount of % –COOH, pH at point of zero charge (i.e., pH\(_{PZC}\)), and equilibrium swelling ratios (i.e., ESRs) at different pH\(_i\) and temperature. RSM based optimization was performed by Design Expert 7.0.0. All graphics based analyses were carried out using Origin 9.0 software.
Methodology. SF and M(II/III) solutions of varying concentrations (i.e., 10–200 and 10–60 ppm for dye and M(II/III), respectively) were prepared by exact dilution of 1000 ppm stock solutions. In the present study, 0.025 g of dry PANIPNs was added to 50 mL buffered solutions of adsorbates with constant stirring at 300 rpm. The progress of adsorption was monitored by withdrawing supernatant solution after definite time intervals and measuring absorbance at λ_{max} using UV-vis spectrophotometer (PerkinElmer Lambda 365) and atomic absorption spectrometer (PerkinElmer A-ANALYST 100) for dyes and M(II/III), respectively. From the pre-calibrated equations, adsorbate concentrations (i.e., \( C_t \)) were calculated, from which \( q_t \) (mg g\(^{-1}\)) values were determined using Equation S1.

\[
q_t = \frac{(C_0 - C_t)V}{m_s}
\]

(S1)

Here, \( C_0/C_t \) (ppm), \( V \) (mL), and \( m_s \) (g) are feed dye concentrations at \( t = 0/t \), volume of dye solution and mass of PANIPNs, respectively. Equilibrium AC (i.e., \( q_e \), mg g\(^{-1}\)) was obtained via replacing \( C_t \) by \( C_e \) in Equation S1.

Swelling and pH/temperature reversibility studies of PANIPNs. For swelling and deswelling studies, hydrogels were immersed for a time period of 1 hr at of pH\(_i\) = 2 and 12, respectively. For analyzing the temperature reversibility, hydrogels were allowed to swell and deswell at 323 and 293 K, respectively. Indeed, all the cycles were continued repetitively until the loss of hydrogel stability.

Calculation of \% –COOH, pH\(_{PZC}\), \% GC, and network parameters of PANIPNs. The amount of –COOH was estimated by a method reported elsewhere using Equation S2.\(^{51}\)

\[
% -\text{COOH} = \left[ (C_{\text{NaOH}} \times V_{\text{NaOH}}) - (C_{\text{HCl}} \times V_{\text{HCl}}) \times 45 \times 10^{-3} \times 100 \right] / 0.05
\]

(S2)
The \( \text{pH}_{\text{PZC}} \) of both the PANIPNs was estimated by taking 0.05 g of xerogel in 50 mL buffer solutions of different initial pH (i.e., \( \text{pH}_i = 2 \) to 10). After 72 hrs of immersion, final pH (i.e., \( \text{pH}_f \)) of all the solutions were estimated. The difference of these \( \text{pH}_f \) and \( \text{pH}_i \) was plotted with \( \text{pH}_i \) to find the \( \text{pH}_{\text{PZC}} \).

The \% GC of the PANIPNs were estimated by the method reported elsewhere,\(^{S1}\) using Equation S3.

\[
\% \text{GC} = \frac{W_d}{W_i} \times 100
\]  \hfill (S3)

The \( M_c \) of PANIPNs was calculated, using Equation S4, based on the network theory of Flory and Rehner.

\[
M_c = -\frac{V_S \rho_p (\varphi_p^{1/3} - \frac{\varphi_p}{2})}{\ln(1 - \varphi_p) + \varphi_p + \chi \varphi_p^2}
\]  \hfill (S4)

Here, \( V_S, \rho_p, \varphi_p, \) and \( \chi \) are molar volume of water, density of PANIPNs, volume fraction of swollen PANIPNs after attending the equilibrium, and interaction parameter of PANIPNs-water, respectively. However, \( V_S \) was calculated from density and molecular weight of PANIPNs. Equation S5 was employed to calculate \( \varphi_p \) from the known value of swelling ratio (i.e., \( m_w, \text{ g g}^{-1} \)).

\[
\varphi_p = \frac{1/\rho_p}{(m_w/0.99) + (1/\rho_p)}
\]  \hfill (S5)

Indeed, \( \chi \) was calculated from the Flory-Huggins theory, using Equation S6, in which \( a_w \) is the activity of water.

\[
\ln a_w = \ln(1 - \varphi_p) + \varphi_p + \chi \varphi_p^2
\]  \hfill (S6)

For pure component system (i.e., \( a_w = 1 \)), Equation S6 can be rearranged to Equation S7.

\[
\text{or}, \quad \chi = \frac{\varphi_p}{3} + 0.5
\]  \hfill (S7)
Finally, crosslink density (i.e., $\rho_c$), in the PANIPNs network, was calculated using Equation S8.

$$\rho_c = \frac{M_0}{M_c}$$

(S8)

Here, molar mass of repeating unit per crosslink (i.e., $M_0$) is defined by Equation S9.

$$M_0 = \frac{n_{PN}M_{PN} + n_{CPOL}M_{CPOL}}{n_{PN} + n_{CPOL}}$$

(S9)

Here, $n$ and $M$ ($n_{PN}$, $n_{CPOL}$, $M_{PN}$, and $M_{CPOL}$) represent moles of repeating units, and molar masses of PN and copolymer (i.e., CPOL) in PANIPNs, respectively. In fact, $M_{CPOL}$ was taken as the average of respective contributions of the monomers in copolymer. Ignoring the marginal contribution of MBA and assuming only the presence of binary copolymerization, for incorporating PN in the matrix of CPOL by free radical solution polymerization reaction, the approximate copolymer composition of monomers was calculated using Equation S10.

$$\frac{M_{AA}}{M_{NIPAm}} = \frac{r_{AA}m_{AA}^2 + m_{AA}m_{NIPAm}}{r_{NIPAm}m_{NIPAm}^2 + m_{AA}m_{NIPAm}}$$

(S10)

Here, $r_{AA}/r_{NIPAm}$ and $m_{AA}/m_{NIPAm}$ are reactivity ratios and moles of AA/NIPAm, respectively. However, PANIPNs network was also characterized by measuring network parameters, such as $M_c$ and $\rho_c$, based on the network theory of Flory and Rehner.

**Adsorption isotherm studies of dye/M(II/III) onto PANIPN41 and PANIPN21.** ACs (i.e., $q_{\text{max}}$, mg g$^{-1}$) of PANIPNs were estimated from the correlation of equilibrium AC (i.e., $q_e$, mg g$^{-1}$) and the residual adsorbate concentration at equilibrium (i.e., $C_e$). However, in the present study, adsorption isotherm studies of PANIPNs for M(II/III), such as Hg(II), Cd(II), Cr(III), and SF, were conducted by taking 50 mL of solutions within 5–100 and 5–30 ppm at constant pH$_i$ = 7 and 9 for M(II/III) and SF, respectively, along with 0.025 g of PANIPNs at constant temperature (i.e., 293, 303, 313, and 323K) and 500 rpm. At definite time intervals, the supernatant solution
was withdrawn and the residual adsorbate concentration (i.e., $C_t$, ppm) was determined by UV-vis spectrophotometer and atomic absorption spectrometer for dye and M(II/III), respectively, via measuring absorbance (i.e., $A_t$) at $\lambda_{max}$. In fact, the adsorption data were analyzed using different isotherm models, such as Langmuir, Freundlich, and Temkin (Equations S11–S13) for the estimation of various model parameters to enlighten various aspects of adsorption mechanism.

\[
q_e = q_{max} \frac{k_t C_e}{1 + k_L C_e}
\]  
(S11)

\[
q_e = k_F C_e^{1/n}
\]  
(S12)

\[
q_e = \frac{RT}{b_T} \ln(k_T C_e)
\]  
(S13)

Here, $k_L$, $k_F$, and $k_T$ are the corresponding isotherm constants and $q_{max}$, $n$, $b_T$, and $k_T$ are the corresponding parameters of the isotherm models. $R_L$ can be defined by the Equation S14.

\[
R_L = \frac{1}{1 + k_L C_0}
\]  
(S14)

**Kinetics of adsorption.** Adsorption kinetics are carried out to identify the mechanism, rate determining step, and diffusion characteristics of the isothermal adsorption process. In the present study, kinetics studies were executed by taking 0.025 g of both PANIPNs at different initial concentrations of SF/M(II/III), constant pH, and various temperatures. The kinetic data were analyzed via non-linear pseudofirst/second order kinetics models (Equations S15/S16).

\[
q_t = q_e [1 - \exp(-k_1 t)]
\]  
(S15)

\[
q_t = q_e \left( 1 - \frac{1}{1 + k_2 q_e t} \right)
\]  
(S16)

Here, $k_1$ (min$^{-1}$)/$k_2$ (g mg$^{-1}$ min$^{-1}$) represent pseudofirst/second order rate constants.
**Thermodynamics of adsorption.** The thermodynamic parameters, such as changes in enthalpy (i.e., $\Delta H^0$), entropy (i.e., $\Delta S^0$) and Gibbs free energy (i.e., $\Delta G^0$) were measured to apprehend the effect of temperature on adsorption isotherm. The spontaneity of adsorption process is confirmed by the negative $\Delta G^0$, as expressed by Equation S17.

$$\Delta G^0 = -RT \ln k_d$$  \hspace{1cm} (S17)

Here, $k_d$, known as distribution coefficient, can be defined by the Equation S18.

$$k_d = \frac{q_e}{C_c}$$  \hspace{1cm} (S18)

Here, $\Delta H^0$ and $\Delta S^0$ can be determined from the slope and intercept of the linearized form of van’t Hoff’s equation, respectively, as expressed in Equation S19.

$$\ln k_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$  \hspace{1cm} (S19)

**Effect of temperature on adsorption kinetics.** The effect of temperature on kinetics was established by taking 25 ppm M(II/III) solutions at pH$_i$ = 7 and 0.025 g of PANIPN21/41 at 293, 303, 313, and 323 K. As all the M(II/III) followed pseudosecond order kinetics, $k_2$ at different temperatures could be interrelated by the following Arrhenius type equation.

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT}$$  \hspace{1cm} (S20)

Here, $k_0$ and $E_a$ are temperature independent factor (g mg$^{-1}$ min$^{-1}$) and activation energy of adsorption (kJ mol$^{-1}$), respectively. In fact, from the slope of the linearized $\ln k_2$ vs. $1/T$ plot, $E_a$ can be evaluated.

**RESULTS AND DISCUSSION**
Experimental design and model development for the synthesis of PANIPN

Table S1. Resolution-IV Design for Screening of Important Process Variables in Phase-I

| run no. | amount of SA (wt %) | total amount of PPS + SBS (wt %) | amount of PN (wt %) | amount of MBA (wt %) | pH<sub>i</sub> (-) | temperature (K) | ESR (-) |
|---------|---------------------|---------------------------------|---------------------|---------------------|------------------|----------------|---------|
| 1       | 66.67               | 1.00                            | 0.10                | 0.10                | 4                | 303            | 129     |
| 2       | 95.24               | 1.00                            | 0.10                | 0.10                | 12               | 303            | 203     |
| 3       | 66.67               | 4.00                            | 0.10                | 0.10                | 12               | 323            | 210     |
| 4       | 95.24               | 4.00                            | 0.10                | 0.10                | 4                | 323            | 155     |
| 5       | 66.67               | 1.00                            | 0.50                | 0.10                | 12               | 323            | 184     |
| 6       | 95.24               | 1.00                            | 0.50                | 0.10                | 4                | 323            | 155     |
| 7       | 66.67               | 4.00                            | 0.50                | 0.10                | 4                | 303            | 156     |
| 8       | 95.24               | 4.00                            | 0.50                | 0.10                | 12               | 303            | 214     |
| 9       | 66.67               | 1.00                            | 0.10                | 0.40                | 4                | 323            | 130     |
| 10      | 95.24               | 1.00                            | 0.10                | 0.40                | 12               | 323            | 204     |
| 11      | 66.67               | 4.00                            | 0.10                | 0.40                | 12               | 303            | 206     |
| 12      | 95.24               | 4.00                            | 0.10                | 0.40                | 4                | 303            | 176     |
| 13      | 66.67               | 1.00                            | 0.50                | 0.40                | 12               | 303            | 170     |
| 14      | 95.24               | 1.00                            | 0.50                | 0.40                | 4                | 303            | 140     |
| 15      | 66.67               | 4.00                            | 0.50                | 0.40                | 4                | 323            | 157     |
| 16      | 95.24               | 4.00                            | 0.50                | 0.40                | 12               | 323            | 231     |
| 17      | 80.955              | 2.50                            | 0.30                | 0.25                | 8                | 313            | 184     |
| 18      | 80.955              | 2.50                            | 0.30                | 0.25                | 8                | 313            | 184     |
| 19      | 80.955              | 2.50                            | 0.30                | 0.25                | 8                | 313            | 184     |

SA: sodium acrylate, PPS: potassium persulfate, SBS: sodium bisulfite, PN: pectin, MBA: N, N'-methylenebisacrylamide, and ESR: percent equilibrium swelling ratio
Table S2. ANOVA for Phase-1

| source                      | sum of squares | degrees of freedom | mean square | F value | p-value |
|-----------------------------|----------------|--------------------|-------------|---------|---------|
| model                       | 15098.75       | 6                  | 2516.46     | 108.23  | < 0.0001* |
| amount of SA (A)            | 1156.00        | 1                  | 1156.00     | 49.72   | < 0.0001* |
| amount of PPS + SBS (B)     | 2256.25        | 1                  | 2256.25     | 97.04   | < 0.0001* |
| pH$_i$(E)                   | 11236.00       | 1                  | 11236.00    | 483.27  | < 0.0001* |
| AB                          | 110.25         | 1                  | 110.25      | 4.74    | 0.0484*  |
| AD                          | 100.00         | 1                  | 100.00      | 4.30    | 0.0585   |
| CF                          | 240.25         | 1                  | 240.25      | 10.33   | 0.0068*  |
| curvature                   | 151.74         | 1                  | 151.74      | 6.53    | 0.0240   |
| residual                   | 302.25         | 13                 | 23.25       |         |         |
| lack of fit                 | 302.25         | 11                 | 27.48       |         |         |
| pure error                 | 0.00           | 2                  | 0.00        |         |         |
| cor. total                 | 15552.74       | 20                 |             |         |         |
| std. dev.                  | 4.82           |                    | $R^2$       | 0.9804  |         |
| mean                       | 177.47         | adj. $R^2$         | 0.9713      |         |         |
| CV %                       | 2.72           | pred. $R^2$        | 0.9386      |         |         |
| PRESS                      | 955.26         | adeq. precision    | 34.0380     |         |         |

*significant

Table S3. Central Composite Design (CCD) of Experiment

| run no. | amount of SA (wt %) | total PPS + SBS (wt %) | pH$_i$ (--) | ESR (--) |
|---------|---------------------|------------------------|-------------|----------|
| 1       | 66.67               | 2.00                   | 5.00        | 63       |
| 2       | 95.24               | 2.00                   | 5.00        | 71       |
| 3       | 66.67               | 4.00                   | 5.00        | 60       |
| 4       | 95.24               | 4.00                   | 5.00        | 75       |
| 5       | 66.67               | 2.00                   | 10.00       | 167      |
| 6       | 95.24               | 2.00                   | 10.00       | 200      |
| 7       | 66.67               | 4.00                   | 10.00       | 154      |
| 8       | 95.24               | 4.00                   | 10.00       | 200      |
| 9       | 56.93               | 3.00                   | 7.50        | 80       |
| 10      | 100.00              | 3.00                   | 7.50        | 162      |
| 11      | 80.95               | 1.32                   | 7.50        | 80       |
| 12      | 80.95               | 4.68                   | 7.50        | 70       |
| 13      | 80.95               | 3.00                   | 3.30        | 118      |
| 14      | 80.95               | 3.00                   | 11.70       | 310      |
| 15      | 80.95               | 3.00                   | 7.50        | 216      |
| 16      | 80.95               | 3.00                   | 7.50        | 216      |
| 17      | 80.95               | 3.00                   | 7.50        | 216      |
| 18      | 80.95               | 3.00                   | 7.50        | 216      |
| 19      | 80.95               | 3.00                   | 7.50        | 216      |
| 20      | 80.95               | 3.00                   | 7.50        | 216      |

SA: sodium acrylate, PPS: potassium persulfate, SBS: sodium bisulfite, and ESR: percent equilibrium swelling ratio
Calculation of LCST, % –COOH, pH<sub>PZC</sub>, % GC, and network parameters of PANIPNs

The grafting of PN within copolymer network of thermosensitive PANIPNs was envisaged by the variation of LCST. In order to determine the LCST of PANIPNs and respective copolymers, 0.01 g of hydrogels were allowed to swell in double distilled water for 24 h, followed by performing DSC in N<sub>2</sub> atmosphere within 5–100 °C at scanning rate of 5 °C min<sup>−1</sup>. In fact, the LCST of PANIPN41 and PANIPN21, appeared at 75.56 °C and 68.75 °C, were found to be slightly higher than copolymers(Figure S2g), emphasizing the relative enhancement of hydrophilic groups in PANIPNs. Thus, the increase in water swelling-deswelling reversibility of the PANIPNs, beyond the LCST of PNIPAm hydrogel, could be attributed to the presence of highly hydrophilic SA and PN moieties in the hydrogel network. The % –COOH content was found to be 9.84 and 4.95 % for PANIPN41 and PANIPN21,
respectively, resulted by the relative variation of SA in PANIPNs. However, for the used PANIPNs, pH_{PZC} was found to be 7.07 and 6.66 for PANIPN41 and PANIPN21, respectively (Figure S2h). Again, %GC of PANIPNs was found to decrease from 71.47 % of PANIPN41 to 62.49 % in PANIPN21. The network parameters, such as average molecular weight between crosslink (i.e., M_c) and crosslink density (i.e., \( \rho_c \)), were obtained from swelling data of the hydrogels using Equations S4 and S8, respectively. The decrease in \( M_c \) with an enhancement of \( \rho_c \) was observed with progressive increase in the wt % of crosslinker, ascribed to the formation of greater number of networks. Similar results were also reflected by the increase in initiator amount from 1.25 to 2.0 wt % (Table S5). Indeed, the successive increase in wt % of PN in PANIPNs from 0.25 to 0.75 wt % resulted a decrease in \( \rho_c \), attributed to the increase in viscosity of solution leading to a decrease in the efficiency of radical formation. A reverse trend of network parameters was also observed by the increase in SA:NIPAm ratio in the copolymer network from 1:1 to 10:1. In

| polymer (SA:NIPAm/MBA/PPS+SBS/PN) | density (g mL^{-1}) | swelling ratio in water (g/g) | volume fraction of swollen hydrogel (\( \phi_p \)) | polymer-water interaction parameter (\( \gamma \)) | average molar mass between crosslink (\( M_c \)) | crosslink density (\( \rho_c \)) |
|-------------------------------------|----------------------|-------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| PANIPN1 (1:1/0.20/2.00/0.50)       | 1.364                | 254.43                        | 0.0028                                        | 0.50095                                       | 2.12 \times 10^{11}                            | 4.55 \times 10^{10}                           |
| PANIPN2 (2:1/0.20/2.00/0.50)       | 1.375                | 345.64                        | 0.0021                                        | 0.50069                                       | 6.77 \times 10^{11}                            | 1.60 \times 10^{10}                           |
| PANIPN3 (4:1/0.20/2.00/0.50)       | 1.384                | 366.67                        | 0.0020                                        | 0.50065                                       | 8.66 \times 10^{11}                            | 1.18 \times 10^{10}                           |
| PANIPN4 (10:1/0.20/2.00/0.50)      | 1.394                | 373.63                        | 0.0019                                        | 0.50063                                       | 9.60 \times 10^{11}                            | 1.00 \times 10^{10}                           |
| PANIPN5 (4:1/0.10/2.00/0.50)       | 1.376                | 380.71                        | 0.0018                                        | 0.50063                                       | 9.68 \times 10^{11}                            | 1.06 \times 10^{10}                           |
| PANIPN6 (4:1/0.20/2.00/0.50)       | 1.384                | 367.63                        | 0.0019                                        | 0.50065                                       | 8.75 \times 10^{11}                            | 1.17 \times 10^{10}                           |
| PANIPN7 (4:1/0.30/2.00/0.50)       | 1.385                | 306.21                        | 0.0023                                        | 0.50078                                       | 4.49 \times 10^{11}                            | 2.28 \times 10^{10}                           |
| PANIPN8 (4:1/0.40/2.00/0.50)       | 1.391                | 239.34                        | 0.0030                                        | 0.50099                                       | 1.86 \times 10^{11}                            | 5.51 \times 10^{10}                           |
| PANIPN9 (4:1/0.20/1.25/0.50)       | 1.384                | 315.24                        | 0.0023                                        | 0.50075                                       | 4.98 \times 10^{11}                            | 2.05 \times 10^{10}                           |
| PANIPN10 (4:1/0.20/1.50/0.50)      | 1.433                | 327.03                        | 0.0021                                        | 0.50070                                       | 6.70 \times 10^{11}                            | 1.53 \times 10^{10}                           |
| PANIPN11 (4:1/0.20/2.00/0.50)      | 1.384                | 367.63                        | 0.0019                                        | 0.50065                                       | 8.75 \times 10^{11}                            | 1.17 \times 10^{10}                           |
| PANIPN12 (4:1/0.20/2.50/0.50)      | 1.373                | 255.14                        | 0.0028                                        | 0.50094                                       | 2.21 \times 10^{11}                            | 4.63 \times 10^{10}                           |
| PANIPN13 (4:1/0.20/2.00/0.25)      | 1.555                | 327.21                        | 0.0022                                        | 0.50074                                       | 5.17 \times 10^{11}                            | 1.98 \times 10^{10}                           |
| PANIPN14 (4:1/0.20/2.00/0.50)      | 1.384                | 365.63                        | 0.0020                                        | 0.50065                                       | 8.57 \times 10^{11}                            | 1.19 \times 10^{10}                           |
| PANIPN15 (4:1/0.20/2.00/0.75)      | 1.386                | 378.21                        | 0.0019                                        | 0.50063                                       | 9.77 \times 10^{11}                            | 1.05 \times 10^{10}                           |

SA: sodium acrylate, NIPAm: N-isopropylacrylamide, PPS: potassium persulfate, SBS: sodium bisulfite, and PN: Pectin
this regard, the increment of NIPAm content, a large moiety compared to SA, resulted in better population of branched multiple side chains in the PANIPNs (Table S5).

FTIR analyses

Table S6. FTIR analyses of PN, TerP41, and PANIPN41

| PN      | TerP41  | PANIPN41       | assignment                                      | ref. |
|---------|---------|----------------|------------------------------------------------|------|
| –       | –       | 3650 (w)       | weak H-bonds                                    |      |
| –       | 3434 (b)| 3343 (b)       | mutual O–H/ N–H H-bonding                       |      |
| –       | –       | 2855 (w)       | symmetric –CH2– str. of –O–CH3–                |      |
| –       | 2352 (w)| 2350 (w)       | strong O–H/ O–H H-bonding                       | S2   |
| –       | 1713 (sh)| –             | H-bonded –COOH dimer                            | S3   |
| –       | 1560 (s, b)| –         | asymmetric COO– str.                           | S3   |
| –       | –       | 1458 (w)       | –CH2– def. of –O–CH2–                          |      |
| 1444    | –       | –             | –OCH2– def. of methyl ester of PN ring          |      |
| –       | 1411 (m)| –             | symmetric COO– str.                           |      |
| –       | 1386 (m)/1365 | 1385 (m, s)/1365 (w) | doublet peaks of isopropyl groups of NIPAm | S4   |
| –       | 1280    | –             | amide-III/C–N str.                              | S5   |
| 1265    | –       | –             | C–O–C of ester                                  |      |
| 1148    | –       | –             | C–O–C str. peak of α-1,4- glycosidic link/ring  | S6, S7|
| –       | –       | 1169 (sh)     | C–O–C str. peak of β-1,4-glycosidic link/ring  | S7   |
| 1112    | –       | 1112 (w)      | C–O, C–C, C–C–H and O–C–H of PN ring           |      |
| 1080    | –       | –             | C–O str. and O–C–H bending                      |      |
| 1051    | –       | –             | C–O/C–C of PN ring                              |      |
| 1030    | –       | –             | O–C/C–C–C–C–H of PN ring                        |      |
| 1018    | –       | –             | C–2C–3/C–2O–2/C–1O–1 of PN ring                 |      |
| 985/970 | –       | –             | –OCH3 of ester of PN ring                       |      |
| –       | –       | 874 (w)       | β-D-glucose                                     |      |
| 825–860 | –       | –             | equatorial anomeric hydrogen                    |      |
| –       | 787 (w) | –             | H-bonded –COOH dimer                            | S5   |
| –       | 661 (m, s)| 669   | N–C=O in-plane bending                          | S5   |
| –       | –       | 473 (m), 460 (w), 453 | C–O–C and branching                           | S8   |

w = weak, s = sharp, b = broad, sh = shoulder, and m = medium
| PANIPN41 | Hg(II)-PANIPN41 | Cd(II)-PANIPN41 | Cr(III)-PANIPN41 | SF | SF-PANIPN41/21 | assignment | ref. |
|---------|----------------|-----------------|-----------------|----|----------------|------------|-----|
| 3435 (b)| 3585 (s), 3526 (s) | 3426 (b) | 3435 (b) | 3434 (b) | 3435 (b)/3434 (b) | modification of mutual O–H/N–H H-bonds in Hg(II)-PANIPN41 | S9 |
| –       | –              | –              | –              | – | 3119 (w) | aromatic C–H str. of SF | S10 |
| 2975    | 2973           | 2973           | 2975           | – | 2957/2956 | change in –CH₂–asymmetric str. due to C=O…H–C H-bonds | S11, S12 |
| 2925    | 2928           | 2935           | 2929           | 2926 | 2925/2925 | C–H str. peak of –CH₃ | S13 |
| 2855    | 2856           | 2855           | 2856           | 2854 | 2855/2854 | symmetric –CH₂–str. of –O–CH₂–strong O–H/O–H H-bonding | S14 |
| 2350 (w) | 2352 (w) | –              | –              | 2346 (w) | –/2379 (w), 2359 (w), 2345 (w), 2341 (w) | –/2379 (w), 2359 (w), 2345 (w), 2341 (w) | S15 |
| 1734    | 1716           | 1720           | 1730           | – | 1721/1718 | C=O str. of chelates asymmetric –COO–str. and C=O str. of secondary amide | S16 |
| 1638    | 1614           | 1635           | 1632           | – | 1632/1634 | N=O str. of SF aromatic ring C=O str. of SF | S17, S18 |
| –       | –              | –              | –              | 1611 (s) | 1530 (m)/1490 (m) | – | S19 |
| 1458 (w) | 1458 (w) | 1458 (w) | 1458 (w) | – | – | –/CH₂– def. of –O–CH₂– asymmetric COO str. | S20 |
| 1385 (m, s) | 1385 (m, s) | 1385 (m, s) | 1385 (m, b) | – | – | –/CH₂– bending of isopropyl groups of NIPAm merged with C–O and C–C str. of Cr(III) in Cr(III)–PANIPN41 one of the doublet peaks of isopropyl groups of NIPAm | S21 |
| 1365 (w) | –              | –              | –              | – | – | – | S22 |
| 1169    | 1167           | 1170           | 1168           | 1166/1168 | – | asymmetric C–O–C str. | S23, S24 |
| –       | –              | –              | 807            | – | – | Cr–O/C–O str. | S25 |
| –       | –              | 608            | –              | – | – | Cr–O bond | S26 |
| –       | –              | 519            | –              | – | – | Cr–N bond | S27 |
| –       | 509            | –              | –              | – | – | Hg–N covalent bond | S28 |

w = weak, s = sharp, b = broad, and m = medium

In Hg(II)-PANIPN41, Hg–N covalent bonds were produced via dehydrogenation of numerous N–H groups, as realized from the arrival of symbolic Hg–N peak at 509 cm⁻¹ and the
disappearance of secondary amide peak at 1638 cm\(^{-1}\) (Figure S3a). The loss of N–H groups eventually affected mutual O–H/N–H H-bonding in Hg(II)-PANIPN41, realized from the conversion of broad peak within 3000–3500 cm\(^{-1}\) into sharp O–H \textit{str.} peaks at 3585 and 3526 cm\(^{-1}\). In fact, preferential covalent bond formation among Hg(II) and amide could be attributed to the soft nature of Hg(II) cation, which was also responsible for weaker binding of Hg(II) with O–H, as reflected in the prevalence of almost undisturbed O–H/ O–H H-bonding peak at 2352 cm\(^{-1}\) in Hg(II)-PANIPN41. In contrast, unaffected mutual O–H/ N–H H-bonding and secondary amide in Cd(II)/Cr(III)-PANIPN41 was ascribed to weaker binding abilities of both Cd(II) and Cr(III) with N–H of amides (Figure S3a, Table S7), as both Cd(II) and Cr(III) ions are relatively harder than Hg(II). Accordingly, as compared to Hg(II), stronger coordinating tendencies of both Cd(II) and Cr(III) ions with O-donor ligands were apprehended from the C=O \textit{str.} of the respective chelates (Table S7) and complete disruption of strong O–H/O–H H-bonding peaks in Cd(II)/Cr(III)-PANIPN41, along with the appearance of characteristic Cr–O, Cr–N peaks in Cr(III)-PANIPN41.

Altogether, adsorptive binding of M(II/III) in PANIPN41 resulted in significant lowering of asymmetric –COO\(^{-}\) peaks, whereas both \textit{str.} and \textit{bending} peaks of –CH\(_3\) in NIPAm were unaffected in the M(II/III)-PANIPN41 (Table S7).

Intimate coulombic attractions/H-bonding between SF and PANIPN41/21 resulted in complete disappearance of three SF specific peaks in SF-PANIPN41/21 (Table S7). Consequently, significant modification of both weaker H-bonds (C=O…H–C) and mutual O–H/ N–H H-bonding was realized from substantial lowering of asymmetric –CH\(_2\)– \textit{str.}, C–O–C \textit{str.}, and C=O \textit{str.} of secondary amide/ester, along with disappearance of one of the doublet peak at 1365 cm\(^{-1}\), ascribed to restricted bending of –CH\(_3\) of NIPAm side chains in SF-PANIPN41/21. In this context, as compared to SF-PANIPN21, relatively extensive modification of the H-bonding environment in
SF-PANIPN41 could be realized from complete disappearance of strong O–H/O–H H-bonding in SF-PANIPN41, while the related characteristic peaks at 2379, 2359, 2351, 2345, and 2341 cm\(^{-1}\) remained intact in SF-PANIPN21 (Figure S3b and Table S7), with notable existence of C–N \textit{str.} peak at 1327 cm\(^{-1}\) in PANIPN41/21. Notably, PANIPN41, bearing relatively higher proportion of –COO\(^{-}\), was involved in stronger ionic interaction with SF cations, leading to possible replacement of H-bonds by coulombic attractions in SF-PANIPN41, resulting in higher AC of PANIPN41 than PANIPN21.

**Table S8. Adsorption Thermodynamics Parameters of SF at Higher Concentration**

| concentration (ppm) /temperature (K) | \(\Delta G^0\) (kJ mol\(^{-1}\)) of SF/ for PANIPN41(PANIPN21) | \(\Delta H^0\) (kJ mol\(^{-1}\)) of SF/ for PANIPN41(PANIPN21) | \(\Delta S^0\) (J mol\(^{-1}\) K\(^{-1}\)) of SF/ for PANIPN41(PANIPN21) |
|--------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 40/293                               | 6.08(2.19)                                                    | 28.66(20.93)                                                 | –76.41(–50.78)                                               |
| 40/303                               | 5.46(2.03)                                                    | 28.66(20.93)                                                 | –76.41(–50.78)                                               |
| 40/313                               | 4.77(1.74)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/293                               | 3.33(1.37)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/303                               | 5.14(1.78)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/313                               | 4.71(1.46)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/323                               | 3.69(1.06)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/323                               | 2.89(0.352)                                                   | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 50/293                               | 4.37(1.30)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 60/303                               | 3.87(0.89)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 60/313                               | 2.84(0.38)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 60/323                               | 2.05(0.69)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 60/293                               | 3.46(0.45)                                                    | 24.99(24.27)                                                 | –67.21(–65.38)                                               |
| 80/303                               | 2.52(–0.12)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 80/313                               | 1.73(–1.15)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 80/323                               | 1.01(–3.35)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 100/293                              | 2.44(–0.27)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 100/303                              | 1.72(–1.23)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 100/313                              | 1.07(–3.24)                                                   | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
| 100/323                              | 0.46(–)                                                       | 24.19(24.01)                                                 | –71.39(–71.64)                                               |
**Table S9. Comparative Table**

| types of adsorbate | name of adsorbate | adsorption capacity (mg g⁻¹) | ref. |
|--------------------|-------------------|-------------------------------|------|
| M(II/III)          | Hg(II)            | 9.02/3.0/60/298               | S20  |
|                    | chitosan derivative adsorbent |                      |      |
|                    | multifunctional mesoporous material | 21.05/–/1000/– | S21  |
|                    | PAM/ATP          | 192.50/7.0/100–900/303       | S22  |
|                    | MWCNTsb         | 84.66/6.0/400/298           | S23  |
|                    | CNTs/Fe₂O₃c      | 65.52/6.5/50/298            | S24  |
|                    | Ti(IV) iodovanadate cation exchanger (TIV) | 17.20/6.0/20/293–323 | S25  |
|                    | 4-aminantipyrine immobilized bentonite | 52.90/4.0/1/298 | S26  |
|                    | mesoporous silica-coated magnetic particles | 14.00/2.0/10–60/– | S27  |
|                    | chemically treated sawdust (Acacia arabica) | 20.62/6.0/3/– | S28  |
|                    | Si-DTCd          | 80.24/6.0/200/298           | S29  |
|                    | dithiocarbamate-anchored polymer/organosmectite composites | 71.10/7.0/50/293 | S30  |
|                    | graphene/c−MWCNTb | 93.30/–/50/298              | S31  |
|                    | graphene−MWCNTb  | 75.80/–/50/298              | S31  |
|                    | RGO−MnO₂         | 9.50/–/1/303                | S32  |
|                    | RGO−Ag           | 9.53/–/1/303                | S32  |
|                    | EDA-modified mPMMA microbeadsf | 9.08/5.0/5−700/298 | S33  |
|                    | CSTUg           | 135.00/5.0/100/303          | S34  |
|                    | PANIPN41h        | 78.44/7.0/30/303            | TS  |
|                    | PANIPN21i        | 96.78/7.0/30/303            | TS  |
| Cd(II)             | Si-DTCd          | 43.47/7.0/100/298           | S29  |
|                    | dithiocarbamate-anchored polymer/organosmectite composites | 82.20/7.0/50/293 | S30  |
|                    | CS-co-MMB-co-PAAj | 135.51/4.5−5.5/300/– | S35  |
|                    | AC-Fe₃O₄−NPs modified with DBABTk | 185.22/6.0/5/– | S36  |
|                    | graphene oxide−Al13 | 89.74/6.0/10/298          | S37  |
|                    | mesoporous MCM-41 | 210.96/7.0/250/298         | S38  |
|                    | BiOBr microsphere | 11.70/7.0/29/298          | S39  |
|                    | garden grass | 17.60/4.0/50/303          | S40  |
|                    | biomass of nonliving, dried brown marine algae Sargassum natans, Fucus vesiculosus, and Ascophyllum nodosum | 100.00/3.5/100/– | S41  |
|                    | ANMP derived from PCBsI | 230.06/3.5/450/293 | S42  |
|                    | polyaniline grafted chitosan | 12.87/6.0/20−40/303 | S43  |
|                    | dead T. viride | 10.95/6.0/26/320          | S44  |
|                    | polyvinyl alcohol-chelating sponge | 125.11/5.5/560/293 | S45  |
|                    | dithiocarbamatated-sporopollenin | 7.09/7.0/15/293 | S46  |
|                    | MGOm            | 91.29/6.0/200/298           | S47  |
|                    | RGO−Fe(O)/Fe₂O₄ | 1.91/7.0/2−6/298           | S48  |
|                    | functionalized graphene (GNSC8P) | 30.05/6.2/–/– | S49  |
|                    | functionalized graphene (GNSPF6) | 73.42/6.2/–/– | S49  |
|                    | GOa             | 14.90/5.6/–/–              | S50  |
|                    | GO−TiO₂         | 72.80/5.6/–/–              | S50  |
|                    | GOa             | 167.50/6.0/–/333           | S51  |
coupling agent to produce a magnetically magnetized with Fe propansulfonic acid poly(acrylic acid), adsorbent, a p(AMPS-c-VI), PEI grafted magnetic porous adsorbent\(^{g}\), PANIPN41\(^{h}\), PANIPN21\(^{i}\)

| Cr(III) | AC-Fe\(_3\)O\(_4\)-NPs was modified with DBABT\(^{b}\) | 188.70/6.0/25/0 | S36 |
|--------|---------------------------------------------------|-----------------|-----|
|        | AC\(^{i}\)                                        | 60.00/6.0/25/0  | S36 |
|        | AC-Fe\(_3\)O\(_4\)-NP\(^{e}\)                     | 123.50/6.0/25/0 | S36 |
|        | garden grass                                      | 38.80/4.0/50/30 | S40 |
|        | RGO\(^{c}\)-Fe(O)/Fe\(_3\)O\(_4\)                 | 31.10/7.0/2–6/298 | S48 |
|        | FABN\(^{s}\)                                      | 387.00/5.5/283–313 | S55 |
|        | AA@VTES@Fe\(_3\)O\(_4\)\(^{l}\)                  | 0.24/6.0/170/303 | S56 |
|        | poly(ami doamine) modified GO\(^{n}\)             | 4.15/−/1/298   | S57 |
|        | magnetic p(AMPS)\(^{a}\)                          | 76.87/−/500/298 | S58 |
|        | PANIPN41\(^{h}\)                                  | 99.41/7.0/30/303 | TS\(^{a}\) |
|        | PANIPN21\(^{i}\)                                  | 83.11/7.0/30/303 | TS\(^{a}\) |

| Dye | SF | hydrogels prepared with sodium polyacrylate and 6 wt% of CM PDA@SBP\(^{w}\) | 54.00/10.0/100/293 | S61 |
|-----|----|--------------------------------------------------------------------------|-----------------|-----|
|     |    | native SBP\(^{r}\)                                                      | 17.90/10.0/100/293 | S61 |
|     |    | Au-NP-AC\(^{y}\)                                                       | 50.25/7.0/18/−  | S62 |
|     |    | AC\(^{i}\)                                                               | 1.32/5.0/25/298 | S63 |
|     |    | MWCNT\(^{x}\)                                                          | 43.42/1.0/25/298 | S63 |
|     |    | Cd(OH)\(_2\)-NW-AC\(^{sa}\)                                           | 76.92/5.0/25/298 | S63 |
|     |    | MIL-101(Cr)-SO\(_4\)                                                   | 70.80/6.2/50/−  | S64 |
|     |    | AC\(^{i}\)                                                               | 19.01/6.0/10/−  | S65 |
|     |    | ZnO-NR-AC\(^{ab}\)                                                      | 55.25/6.0/10/−  | S65 |
|     |    | Ni\(_3\)-NP-AC\(^{ac}\)                                               | 46.00–52.0/8.1/5/− | S66 |
|     |    | HDTMA\(^{ud}\), modified Spirulina sp.                                   | 54.05/2.0/300/− | S67 |
|     |    | SDS/RM\(^{ae}\)                                                        | 89.40/4.0/50/308 | S68 |
|     |    | pineapple peels                                                          | 21.70/6.0/60/302 | S69 |
|     |    | NaOH-treated rice husk                                                   | 37.97/8.0/10/303 | S70 |
|     |    | CuO-NPs\(^{af}\)                                                       | 53.67/12.0/154/303 | S71 |
|     |    | CO\(_2\) neutralized activated red mud                                  | 9.77/8.3/37/302 | S72 |
|     |    | Cu-NWs-AC\(^{ae}\)                                                     | 34.00/5.5/15/−  | S73 |
|     |    | MDMLG\(^{ab}\)                                                         | 137.53/12.0/105/− | S74 |
|     |    | PANIPN41\(^{h}\)                                                        | 127.61/9.0/30/303 | TS\(^{a}\) |
|     |    | PANIPN21\(^{i}\)                                                        | 117.60/9.0/30/303 | TS\(^{a}\) |

\(^{a}\)polyacrylamide/attapulgite, \(^{b}\)multi-walled carbon nanotubes, \(^{c}\)carbon nanotube/magnetite nanocomposites, \(^{d}\)silica-supported dithiocarbamate adsorbent, \(^{e}\)reduced graphene oxide, \(^{f}\)ethylenediamine modified magnetic poly(methylmethacrylate) microbeads, \(^{g}\)cross-linked magnetic chitosan-phenylthiourea, \(^{h}\)pectin-g-(TerP41), \(^{i}\)pectin-g-(TerP21), \(^{j}\)chitosan-based hydrogel graft-copolymerized with methylenebisacrylamide and poly(acrylic acid), \(^{k}\)activated carbon magnetized with Fe\(_3\)O\(_4\) nanoparticles modified with 2-(2, 4-Dichloro-benzylidene)-amino)-benzenethiol, \(^{l}\)activated non-metallic powder derived from printed circuit boards, \(^{m}\)magnetic graphene oxide, \(^{n}\)graphene oxide, \(^{o}\)poly(2-acrylamido-2-methyl-1-propansulfonic acid-co-vinylimidazole), \(^{p}\)polyethylenimine grafted magnetic porous adsorbent, \(^{q}\)activated carbon, \(^{r}\)activated carbon was magnetized with Fe\(_3\)O\(_4\) nanoparticles, \(^{s}\)fluorinated activated boron nitride, \(^{t}\)the surface of Fe\(_3\)O\(_4\) nanoparticles via the bridging function of a silane coupling agent to produce a magnetically-separable nanoadsorbent, \(^{u}\)2-acrylamido-2-methyl-1-propansulfonic acid, \(^{v}\)Al-Mont-EnPILC,
polydopamine coated sea buckthorn branch powder, sea buckthorn branch powder, Au loaded on activated carbon, multiwalled carbon nanotube, cadmium hydroxide nanowire loaded on activated carbon, ZnO nanorod-loaded activated carbon, nickel sulfide nanoparticle-loaded activated carbon, hexadecyltrimethylammonium bromide, sodium dodecyl sulphate/red mud, copper oxide nanoparticles, copper nanowires loaded on activated carbon, MgO decked multi-layered graphene, and this study.

**Figure S1.** (a) Pareto chart, contour plots of ESR (−) vs. (b) initiator (B) and SA (A), (c) initiator (B) and pH (C), (d) SA and pH and (e) actual vs. predicted ESR
Figure S2. Swelling reversibility of TerP41, TerP21, PANIPN41 and PANIPN21 by variation of (a) pH (2/12), (b) temperature (293 K/323 K) and swelling of PANIPN41 and PANIPN21 at different (c, e) pH and (d, f) temperature; (g) LCST of TerP21, TerP41, PANIPN21 and PANIPN41; (h) pH_{PZC} of PANIPN21 and PANIPN41
Figure S3. FTIR spectra of (a) TerP41, PANIPN41, Hg(II)-, Cd(II)- and Cr(III)-PANIPN41, and (b) TerP41, PANIPN41, SF-PANIPN41, SF-PANIPN21, and SF
Figure S4. $^1$H-NMR of (a) PN, (b) NIPAm, (d) AA and (f) MBA and $^{13}$C-NMR of (c) NIPAm, (e) AA and (g) MBA
Figure S5. DSC of (a) TerP21, PANIPN21 and SF-, Hg(II)-, Cd(II)- and Cr(III)-PANIPN21, (b) TerP41, PANIPN41 and SF-, Hg(II)-, Cd(II)- and Cr(III)-PANIPN41; XRD of (c) TerP21, PANIPN21 and SF-, Hg(II)-, Cd(II)- and Cr(III)-PANIPN21, (d) TerP41, PANIPN41 and SF-, Hg(II)-, Cd(II)- and Cr(III)-PANIPN41
Figure S6. SEM photomicrographs of (a) PANIPN41, (b) PANIPN21, (c) Hg(II)-PANIPN41, (d) Hg(II)-PANIPN21, (e) Cd(II)-PANIPN41, (f) Cd(II)-PANIPN21, (g) Cr(III)-PANIPN41 and (h) Cr(III)-PANIPN21; EDX spectra of (i) Hg(II)-PANIPN21, (j) Cd(II)-PANIPN41 and (k) Cr(III)-PANIPN41.
Figure S7. Pseudosecond order kinetics plots for (a) SF-PANIPN41 and (b) SF-PANIPN21 (pH = 9, T = 303 K and adsorbent dose = 0.5 g L\(^{-1}\)), pseudosecond order kinetics plots for (c) SF-PANIPN41 and (d) SF-PANIPN21 (pH = 9, C\(_o\) = 30 ppm and adsorbent dose = 0.5 g L\(^{-1}\)), nonlinear Langmuir isotherms fitting for (e) SF-PANIPN41 and (f) SF-PANIPN21.
Figure S8. Pseudosecond order kinetics plots for (a) Hg(II)-PANIPN41, (b) Hg(II)-PANIPN21, (c) Cd(II)-PANIPN41, (d) Cd(II)-PANIPN21, (e) Cr(III)-PANIPN41 and (f) Cr(III)-PANIPN21 (pH$_i$ = 7, T = 303 K and adsorbent dose = 0.5 g L$^{-1}$), pseudosecond order kinetics plots for (g) Hg(II)-PANIPN41, (h) Cd(II)-PANIPN41 and (i) Cr(III)-PANIPN41 and inset of (g), (h) and (i) show kinetics fitting for Hg(II)-PANIPN21, Cd(II)-PANIPN21 and Cr(III)-PANIPN21, respectively (pH$_i$ = 7, $C_0$ = 30 ppm and adsorbent dose = 0.5 g L$^{-1}$) and nonlinear isotherms fitting for (j) Hg(II)-PANIPN41, (k) Cd(II)-PANIPN41, (l) Cr(III)-PANIPN41 and inset of (j), (k) and (l) show isotherm fitting for Hg(II)-PANIPN21, Cd(II)-PANIPN21, and Cr(III)-PANIPN21, respectively
Figure S9. Plot of ln k_d vs. 1/T for (a) Hg(II)-PANIPN41, (b) Hg(II)-PANIPN21, (c) Cd(II)-PANIPN41, (d) Cd(II)-PANIPN21, (e) Cr(III)-PANIPN41, (f) Cr(III)-PANIPN21, (g) SF-PANIPN41, and (h) SF-PANIPN21 (pH_i = 7, T = 303 K, and adsorbent dose = 0.5 g L^{-1})
Figure S10. Plots of ln $k_2$ vs. $1/T$ for (a) SF-PANIPN21/41 and (b) Hg(II)-, Cd(II)- and Cr(III)-PANIPN21/41
Figure S11. Synergistic removal of (a),(b),(c) and (d) SF-MO/pH$_i$ = 9/PANIPN21, (e),(f),(g) and (h) SF-MO/pH$_i$ = 2/PANIPN21 ($C_o$ = 30 ppm, $T = 303$ K and adsorbent dose = 1 g L$^{-1}$).
Scheme S1. Possible structure of MO-SF-PANIPN21 adduct (a-h) at pH$_i$ = 9/2 involving ionic interaction between I. SF dimer and MO, II. SF dimer and PANIPN21, III. SF and PANIPN21, IV. SF and MO, V. MO and SA moiety of PANIPN21 and VI. MO and NIPAm moiety of PANIPN21.
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