Facile synthesis of thermosensitive magnetic nanoparticles as "smart" draw solute in forward osmosis

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Experimental section

Materials:

Iron (III) acetylacetonate (Fe(acac)₃, 99.9%), triethylene glycol (98%), and poly(Nisopropylacrylamide) (PNIPAM, Mw=10k, 98%) were purchased from Sigma-Aldrich. Ethanol (99%) and ethyl acetate (99%) were obtained from Acros Organics. All the chemicals above were used as received.

Synthesis of PNIPAM/TRI-MNP:

0.02 mmol poly(N-isopropylacrylamide) was firstly mixed with 30 ml triethylene glycol under a flow of argon and magnetically stirring. 2 mmol Fe(acac)₃ was added when poly(N-isopropylacrylamide) was complete dissolved in triethylene glycol. The mixture was slowly heated to 190°C for 30min and then quickly heated to reflux at 275 °C under a blanket of argon. By removing the heat source, the black homogeneous colloidal suspension was cooled down to room temperature. An excess amount of ethyl acetate was added to the mixture resulting in black precipitation that was separated via centrifugation. The black product was

re-dissolved in ethanol and re-precipitated in ethyl acetate to remove residuals thoroughly. The residue was redispersed in DI water and for further characterizations.

Characterizations:

The measurements of size distribution of nanoparticles were conducted by a Nanoparticle Size Analyzer (Nano ZS, ZEN3600). Nanoparticles were imaged using a Transmission Electron Microscope (TEM, JEOL: JEM-2010 model) by drying a dispersion of magnetic nanoparticles on amorphous carbon coated copper grids. Thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer TGA 7 at a constant heating rate of 5 °C/min from room temperature to 650 °C in a nitrogen environment. The magnetic properties of functionalized magnetic nanoparticles were recorded in a vibrating sample magnetometer (VSM, LakeShore 450-10) with a saturating field of 1.7 T. An X-ray diffractiometer (GADDS XRD system, Bruker AXS) with a Cu*Ka* source (λ =1.54 Å) was employed to examine the core material of the nanoparticles.

FO Tests using PNIPAM/TRI-MNP as Draw Solute

The performance of PNIPAM/TRI-MNP as draw solutes in the FO system was carried out on a lab-scale circulating filtration unit, as depicted in Figure S1. The commercially available HTI membrane (Hydration Technologies Inc. previously Osmotek Inc.) and DI water were employed as the FO membrane and feed solution, respectively. A crossflow permeation cell was designed in a plate and frame configuration with a rectangular channel on either side of the membrane. The velocities of both draw and feed solutions, which co-currently flowed through the permeation cell channel, were maintained at 6.4 cm/s during the FO testing. The temperature of the whole FO system was kept at 22 ± 0.5 °C. The water permeation flux (J_v , $L \cdot m^{-2} \cdot h^{-1}$, abbreviated as LMH) was calculated from the volume change of the feed solution.

$$J_{\rm v} = \Delta V / (A\Delta t) \tag{3}$$

Where ΔV (L) is the permeation water collected over a predetermined time Δt (h) in the FO process duration; *A* is the effective membrane surface area (m²).



Figure S1. Schematic diagram of a laboratory-scale FO set-up combined with a magnetic separator.



Figure S2. XRD patterns for PNIPAM/TRI-MNP.



Figure S3. TGA profile of PNIPAM/TRI-MNP and TRI-MNP.



Figure S4. Size distributions of PNIPAM/TRI-MNP after each regeneration.