Supplementary Information:

A low-Energy Forward Osmosis Process to Produce Drinking Water

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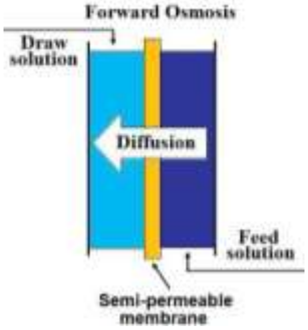

Figure S1. Principle of forward osmosis process: water naturally diffuses across a semipermeable membrane from feed solution with low solute concentration to draw solution with high solute concentration. Water diffusion is driven by osmotic pressure difference between the feed and the draw solution instead of hydraulic pressure or heat.

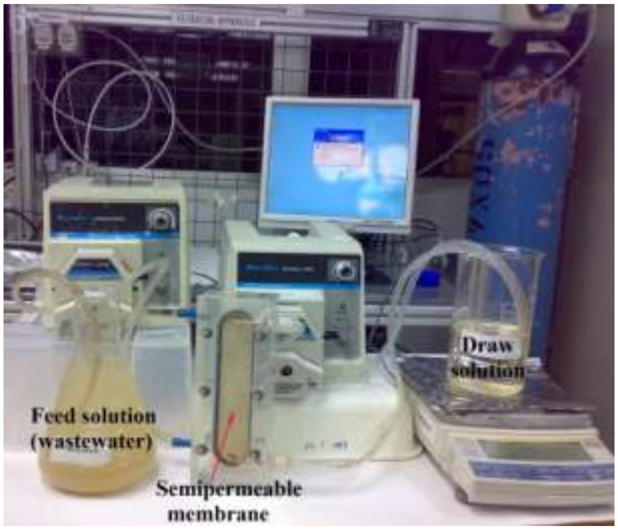

Figure S2. Laboratory setup for the forward osmosis process. Peristaltic pumps are used to circulate the feed and draw solutions which are separated by the flat-sheet semipermeable FO membrane (cellulose triacetate). Fresh water naturally diffuses from the feed solution (wastewater) to the draw solution ($Al_2(SO_4)_3$) in a forward osmosis mode without intensive energy of hydraulic pressure or heat. The weight change of the draw solution with time is recorded by an electric balance. Experimental conditions: 0.5 M $Al_2(SO_4)_3$ as draw solution, wastewater as feed solution, crossflow rate of 0.2 L/min for both feed and draw solutions, and temperature of both feed and draw solutions at 25 ^{0}C.

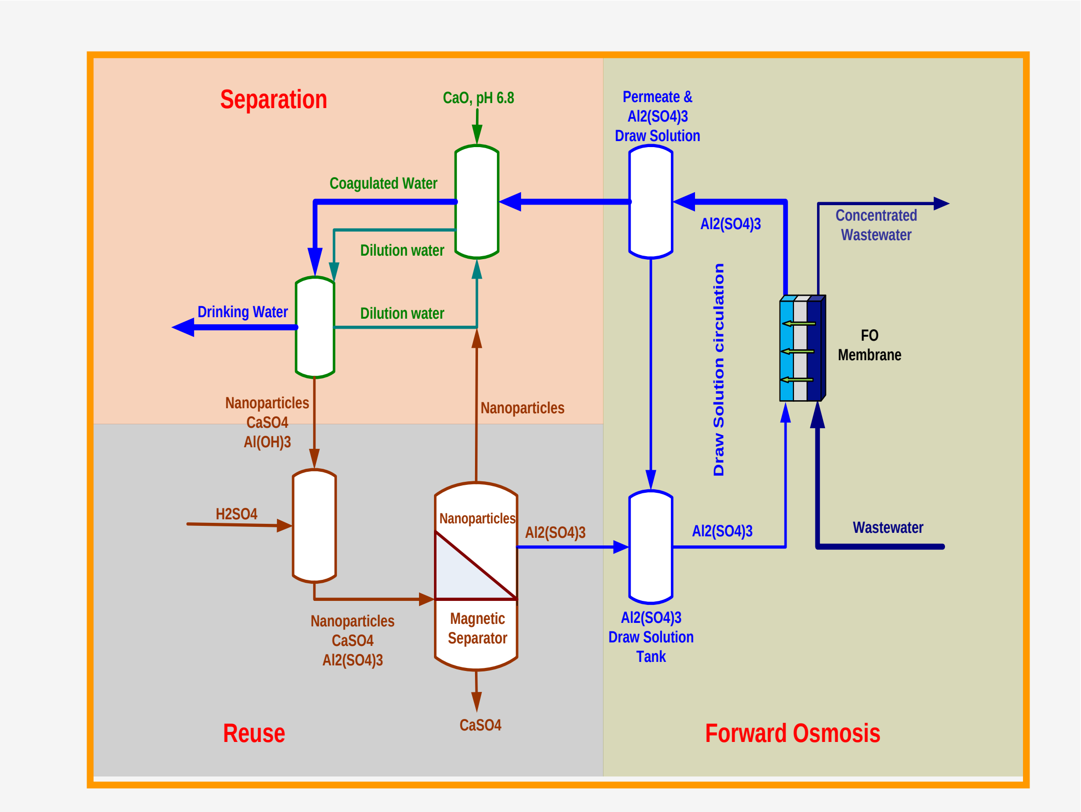

Figure S3. The detailed diagram of $Al_2(SO4)_3$ draw solution separation process with the help of nanoparticles. The whole process was illustrated in detail in Experimental details 4 “Detailed process for the separation and reuse of $Al_2(SO_4)_3$ draw solution” of Supplementary Information.

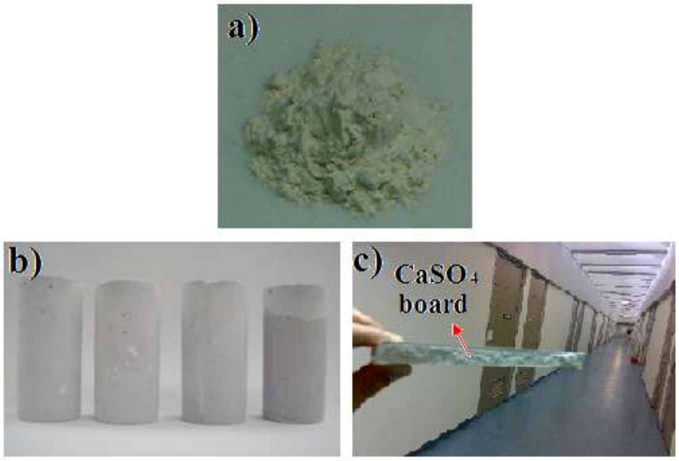

Figure S4. Photos of $CaSO_4$ products. a) $CaSO_4$ produced from the separation process of $Al_2(SO_4)_3$ draw solution; b) construction concrete made by mixing the $CaSO_4$ and cement; c) $CaSO_4$ board for walls and ceilings.

Experimental details:

1. Laboratory setup for FO

Figure S2 describes the setup used in our laboratory-scale FO experiments. The crossflow membrane unit is a flat-sheet type C-10 T (Nitto Denko Co., Ltd., Japan), which has channels on both sides of the flat-sheet FO membrane (HTI, Albany, OR). The feed solution was directed against the active layer of the membrane and the draw solution was directed against the support layer. Both the feed and draw solution were maintained at room temperature 25°C. The feed and draw solution flow tangent to the FO membrane in a crossflow mode, which doesn't have hydraulic pressure on the membrane. Peristaltic pumps (Masterflex) are used to pump the solutions.

2. Fe_3O_4@ Silica core/shell nanoparticles

2.1 Synthesis of Fe_3O_4 nanoparticles

$FeCl_3.6H_2O$ (40 mL, 1 M in HCl solution 2 M) and $FeCl_2.4H_2O$ (10 mL, 2 M in HCl solution 2 M) were mixed in an additional beaker and added dropwise within 15 min to an alkaline solution (400 mL, 0.75 M) at room temperature under magnetic stirring. The solution quickly turned black as result of magnetite formation. The magnetite particles were let to grow for 1 h under stirring and nitrogen. They were collected with a permanent magnet, and the supernatant was discarded by decantation.

Fifty milligrams of block copolymer Pluronic P127 was dissolved in 3 mL double-distilled water in a 20 mL round-bottom flask equipped with a magnetic stirring bar. 3 mL of the Fe_3O_4 nanoparticles (6 mg/mL) were then added dropwise to the copolymer solution.

2.2 Coating of Fe_3O_4 nanoparticles with silica shells

In a typical procedure, 0.3 mL of the above Fe_3O_4 nanoparticles was diluted with 4 mL deionized (DI) water and 20 mL 2-propanol. Under continuous mechanical stirring, 0.5 mL ammonia solution (30wt %) and 10 mg of TEOS were consecutively added to the reaction mixture. The reaction was allowed to proceed at room temperature for 30 min under continuous stirring. The growth of silica shells on Fe_3O_4 nanoparticles involved the base-catalyzed hydrolysis of TEOS and subsequent condensation of silica onto the surfaces of Fe_3O_4 cores. The core-shell Fe_3O_4@silica nanoparticles could be separated from the reaction medium by centrifuging at 4000 rpm and then redispersed into DI water. Due to the presence of negative charges on the surfaces of silica shells, these magnetic nanoparticles having a core-shell structure could form very stable dispersions in water without adding other surfactants. The TEM and magnetism curve of Fe_3O_4@SiO_2 nanoparticles are shown in Fig. 3a).

One commercial FO membrane (Hydration Technologies Inc., Albany, OR) was tested. The proprietary membrane is thought to be made of a cellulose triacetate top layer and a polyester supporting layer. In this paper, the membrane will be denoted as HTI.

3. Determination of solute rejection and reverse diffusion

The concentration of $Al_2(SO_4)_3$ is determined by Inductively Coupled Plasma Emission Spectrometer (ICP, PerkinElmer Optima 2000). The rejection rate of solute is calculated with the equation: R(%)=(CF-CP)/CFx100, where CF and CP are the concentration of feed and draw solutions, respectively.

4. Detailed process for the separation and reuse of $Al_2(SO_4)_3$ draw solution:

The detailed process diagram was shown in Figure S3. In forward osmosis part, fresh water diffuses through the semipermeable FO membrane into the 250ml, 0.5 M $Al_2(SO_4)_3$ draw solution, which causes an increase in the volume of $Al_2(SO_4)_3$ solution. After the volume reaches 500 ml, the diluted $Al_2(SO_4)_3$ draw solution was sent to a separation part to separate $Al_2(SO_4)_3$ solute and produce drinking water. The $Al_2(SO_4)_3$ solution was further diluted by 50 times with DI water to 25 L. This dilution water can be repeatedly used during the process. Adding 46 g CaO to the diluted solution lead to the forming of a gel-like mixture comprising of $Al(OH)_3$ gel and $CaSO_4$ crystals which stably suspend in the solution and can’t precipitated out from the solution. Adding 80 g of negatively-charged and magnetic Fe_3O_4@SiO_2 nanoparticles into the solution resulted in the forming of the rust-colored flocs comprising of Fe_3O_4@SiO_2 nanoparticles, $Al(OH)_3$ gel and $CaSO_4$ crystals.

Under an external magnetic field, the flocs can be deposited within minutes from the solution, leaving clear water behind. The clear water was decanted out as the drinking water.

The deposited flocs comprising of $Al(OH)_3$, CaSO4 and Fe_3O_3@SiO_2 nanoparticles was sent to a reuse part to recover magnetic nanoparticles and regenerate $Al_2(SO_4)_3$ solution. The flocs was added with sulfuric acid (H_2SO_4, 150 ml, 5M) to regenerate $Al_2(SO_4)_3$ solution from $Al(OH)_3$, wherein the Fe_3O_4@SiO_2 nanoparticles were collected by an external magnetic field, and the $CaSO_4$ precipitated down to the bottom of the vial, respectively. And the regenerated $Al_2(SO_4)_3$ solution was feed back to the FO process.

Chemical Route for $Al_2(SO_4)_3$ Recycle

$CaO + H_2O \rightarrow Ca(OH)_2$ …… (1)

$Ca(OH)_2 \Leftrightarrow Ca^{+2} + 2OH^-$ …… (2)

$Al_2(SO_4)_3 \Leftrightarrow 2Al^{+3} + 3SO_4^{-2}$ …… (3)

$Al^{+3} + 3OH^- \rightarrow Al(OH)_3$ …… (4)

$Ca^{+2} + SO_4^{-2} \rightarrow CaSO_4$ …… (5)

$3H_2SO_4 + 2Al(OH)_3 = 6H_2O + Al_2(SO_4)_3$……(6)

5. Determination of surface charge

Particle surface charge, represented by zeta potential, was measured by an electro-kinetic-analyser (EKA, Anton Paar).