Supporting Information for

Magnetic flocculation for nanoparticle separation and catalyst recycling

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Experimental

Materials

FeCl₃·6H₂O (Sigma-Aldrich, \geq 99%), NaH₂PO₄ (Amresco, reagent grade), NH₄OH (Sigma-Aldrich, ACS reagent, 28.0-30.0 % NH₃ basis), ethanol (EtOH, \geq 99%, ACS reagent), tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 98%), poly(diallyldimethylammonium chloride) (PDADMAC, Sigma-Aldrich, 100-200 kDA), NaOH (Sigma-Aldrich, ACS reagent), NaCl (EMD, ACS reagent), poly(sodium 4-styrenesulfonate) (PSS, Sigma-Aldrich, 70 kDa), NaBH₄ (Sigma-Aldrich, 99.99%), trisodium citrate dihydrate (Sigma-Aldrich, ≥99%), HAuCl₄·xH₂O (Sigma-Aldrich, 99.999%), hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich, \geq 99%), AgNO₃ (Sigma-Aldrich, \geq 99%), K₂PdCl₄ (Sigma-Aldrich, 98%), ethylene glycol (EG, Sigma-Aldrich, anhydrous, 99.8%), poly(vinylpyrrolidone) (PVP, Sigma-Aldrich, 40 kDa), H₂PtCl₆·6H₂O (Sigma-Aldrich, ACS reagent, \geq 37.50% Pt basis), NaNO₃ (Sigma-Aldrich, ACS reagent), dichloromethane (DCM, \geq 99.9%, HPLC grade), and TiO₂ nanoparticles (Evonik Aeroxide P25, ~21 nm particle diameter, 55 m² g⁻¹ surface area, Acros) were used as received. P25 TiO₂ nanoparticles have been extensively studied and characterized in the literature, and are often used as a benchmark photocatalyst. Poly(acrylic acid) (PAA, Sigma-Aldrich, 250 kDa), at 10 wt.% in water, was neutralized with NaOH to pH 7 before use. Chitosan (CS, Sigma-Aldrich, 50 kDa, deacetylated chain, poly(D-glucosamine)) was dissolved at 1 g/L in a 1 wt.% acetic acid (Fisher Scientific, ACS reagent) aqueous saline solution (0.5 mol/L NaCl) at 70 °C before use. Oil sands process-affected water (OSPW) was provided by Shell Canada, and stored at 4 °C in the dark. The concentrations of the organic and inorganic constituents of the OSPW are given in Table S1. Flue gas desulphurization wastewater (FGDW) was provided by by a coal-fired power plant in the southeastern United States, and stored at 4 °C in the dark. Prior to use, the OSPW and FGDW were homogenized by stirring, and filtered through glass microfiber filters (Whatman 934-AH) to remove suspended solids.

Magnetic Flocculant Synthesis

α-Fe₂O₃ ellipsoids were prepared by aging an aqueous solution of 20 mmol/L FeCl₃ and 0.2 mmol/L NaH_2PO_4 at 105 °C for 50 h,¹ washing the product thrice with deionized (DI) water, once with 1 mol/L NH₃, and thrice again with water by centrifugation. The α -Fe₂O₃ ellipsoids were then coated with silica using a modified Stöber process.^{2,3} The α -Fe₂O₃ powder was dispersed into a solution of EtOH and DI water by probe sonication. NH₄OH was then added to the dispersion, followed by the dropwise addition of 1 mol/L TEOS in EtOH solution over 1 h, under vigorous mechanical stirring, such that the final concentrations of reagents were 25 mmol/L TEOS, 0.3 mol/L NH₃, 12 mol/L H₂O, and 1.5 g/L α -Fe₂O₃. This mixture was then stirred at room temperature for 18 h, after which the product (α -Fe₂O₃@SiO₂) was washed thrice with EtOH by centrifugation. The α -Fe₂O₃@SiO₂ powder was then reduced in a tube furnace at 350 °C under 100 cm³/min of 50% H₂ in Ar for 6 h, washing the product (Fe₃O₄@SiO₂) thoroughly with DI water by magnetic decantation. The $Fe_3O_4@SiO_2$ particles were then coated with flocculant polymers using a layer-by-layer (LbL) technique.^{4,5} The Fe₃O₄@SiO₂ powder was dispersed into a pH 12 NaOH aqueous solution by probe sonication, to which a 1 g/L PDADMAC aqueous saline solution (0.5 mol/L NaCl) was added under vigorous mechanical stirring, such that the final concentrations of reagents were 0.5 g/L PDADMAC, 0.25 mol/L NaCl, and 5 g/L Fe₃O₄@SiO₂. The mixture was gently stirred for 20 min, after which the particles were washed thrice with DI water by magnetic decantation, and resuspended into DI water by probe sonication (1st layer PDADMAC). A 1 g/L PSS aqueous saline solution (0.5 mol/L NaCl) was then added under vigorous mechanical stirring, such that the final concentrations of reagents were 0.5 g/L PSS, 0.25 mol/L NaCl, and 5 g/L Fe₃O₄@SiO₂. The mixture was gently stirred for 20 min, after which the particles were washed thrice with DI water by magnetic decantation, and

resuspended into DI water by probe sonication (2nd layer PSS). A 1 g/L PDADMAC aqueous saline solution (0.5 mol/L NaCl) was then added under vigorous mechanical stirring, such that the final concentrations of reagents were 0.5 g/L PDADMAC, 0.25 mol/L NaCl, and 5 g/L Fe₃O₄@SiO₃. The mixture was gently stirred for 20 min, after which the particles were washed thrice with DI water by magnetic decantation, and resuspended into DI water by probe sonication (3rd layer PDADMAC). These three-layer coated particles (PDADMAC, PSS, PDADMAC), referred to as $Fe_3O_4@SiO_2@PDADMAC$, were used as a base to prepare the other magnetic flocculant formulations. A fourth layer was coated to prepare each of $Fe_3O_4@SiO_2@PSS$ and $Fe_3O_4@SiO_2@PAA$ formulations: either a 1 g/L PAA or PSS aqueous saline solution (0.5 mol/L NaCl) was added under vigorous mechanical stirring, such that the final concentrations of reagents were 0.5 g/L PAA or PSS, 0.25 mol/L NaCl, and 5 g/L Fe₃O₄@SiO₂. The mixture was gently stirred for 20 min, after which the particles were washed thrice with DI water by magnetic decantation, and resuspended into DI water by probe sonication (4th layer PAA or PSS). A fifth layer was coated on Fe₃O₄@SiO₂@PSS particles to prepare the Fe₃O₄@SiO₂@CS: a 1 g/L CS aqueous saline solution (0.5 mol/L NaCl in 1 wt. % acetic acid) was added under vigorous mechanical stirring, such that the final concentrations of reagents were 0.5 g/L CS, 0.25 mol/L NaCl, 0.5 wt. % acetic acid, and 5 g/L Fe₃O₄@SiO₂. The mixture was gently stirred for 20 min, after which the particles were washed thrice with DI water by magnetic decantation, and resuspended into DI water by probe sonication (5th layer CS). In all cases, the polymer designated in the sample name refers to the terminal or outermost polymer layer.

Metallic Nanoparticle Synthesis

Citrate-stabilized Au nanoparticles were prepared reductively at room temperature.^{6–8} 60 µL of freshly prepared, ice-cold 0.1 mol/L NaBH₄ were added to an aqueous solution of 2.5 x 10⁻⁴ mol/L HAuCl₄·xH₂O and 10⁻⁴ mol/L trisodium citrate dihydrate under vigorous stirring, and left overnight. Then, the solution was filtered using a 0.2 μm syringe filter and stored in the dark at 4 °C until use. CTAB stabilized Ag nanoparticles were prepared by dropwise addition of an aqueous solution of 8 mmol/L NaBH₄ and 0.5 mmol/L CTAB to an equal volume of a 2 mmol/L AgNO₃, 0.4 mol/L NH₃, and 0.5 mmol/L CTAB aqueous solution under vigorous stirring in an ice bath, followed by stirring for 4 h, and then heating the solution at 90 °C for 1 h.^{9,10} PVP stabilized Pd nanoparticles were prepared by simultaneously injecting 3 mL of a 0.157 mol/L K₂PdCl₄ solution in EG and 3 mL of a 26.67 g/L solution of PVP in EG each at 45 mL/h into 5 mL of EG at 110 °C under vigorous stirring, reacting at 110 °C for 3 h, and washing the product once with acetone and thrice with EtOH, by centrifugation, before resuspending into DI water.¹¹ PVP stabilized Pt nanoparticles were prepared by adding 1 mL of a H₂PtCl₆·6H₂O solution in EG to 7 mL of a solution of NaNO₃ and PVP in EG at 160 $^{\circ}$ C under vigorous stirring, such that the final concentrations of reagents were 10 mmol/L H₂PtCl₆, 33 mmol/L NaNO₃, and 3.33 g/L PVP.¹² The solution was stirred at 160 °C for 15 min, followed by washing the product once with acetone and thrice with EtOH by centrifugation before resuspending the into DI water.

Flocculation Experiments

The flocculation experiments were performed in triplicate in glass vials. TiO_2 nanoparticle powder was dispersed into DI water by probe sonication at a typical concentration of 100 mg/L. A sonicated suspension of magnetic flocculant (10 g/L) was rapidly added to the TiO_2 suspension, which was then rapidly mixed for 60 s by vortex mixing, followed by 20 min of slow mixing at 25 rpm on a rotary mixer. The mixture was then settled over an Nd rare earth block magnet (5.08 x 5.08 x 2.54 cm l x w x h) for 30 min, and the supernatant sampled to determine remaining TiO_2 concentration in suspension. Following

separation of the supernatant by magnetic decantation, the settled flocs were dispersed into an equal volume of aqueous HCl solution (typically pH 2.5), and sonicated for 20 min to induce deflocculation. The magnetic flocculant particles were then magnetically settled for 30 min as above, and the supernatant TiO₂ suspension separated by magnetic decantation for reuse in another flocculation cycle, following neutralization to pH 7 with NaOH. A control TiO₂ suspension, without addition of magnetic flocculant, was run alongside each experiment according to the same conditions, and relative TiO₂ concentrations in the flocculated samples were calculated in comparison to this control.

In one experiment, to study the effect of pH, the flocculation tests were performed in 10 mmol/L phosphate or carbonate buffer instead of DI water. In another experiment, to study recyclability of the system, the flocculation tests were performed in PTFE beakers instead of vials, and the same set of TiO_2 nanoparticles and magnetic flocculant nanoparticles were reused continuously throughout the experiment.

TiO₂ nanoparticle concentrations were determined by UV/Vis spectroscopy at 250 nm, comparing to calibration curves prepared from TiO₂ suspensions of known concentration (Figure S13 and Table S2). In the case that the measured absorbance at 250 nm was >1.5, the absorbance at 350 or 400 nm was used instead. In one experiment, to measure the nanoparticle residual after flocculation, TiO₂ concentrations were instead determined ICPMS of total Ti (EPA method 200.8, limit of detection 3 μ g/L Ti) by ALS Environmental (Waterloo, ON, Canada), comparing to a calibration curve prepared from TiO₂ suspensions of known concentration (Figure S14). This method was also used to measure TiO₂ concentrations in the recyclability study (Figure 9a).

Photocatalytic Treatment Experiments

The OSPW photocatalytic treatment experiment was performed in a custom photoreactor enclosure described previously,¹³ consisting of an array of UVA fluorescent bulbs (Philips F20T12/BL, peak emission ~350 nm) suspended above the samples. The UV intensity was measured to be ~45 W/m² with a UVA/B light meter (Sper Scientific, NIST certified calibration), which is similar to the UV content of the solar spectrum (ASTM G173-03 global tilt). TiO₂ nanoparticles were stirred into 80 mL of OSPW (0.1 g/L) in a borosilicate glass beaker (46 mm diameter) and dispersed by sonication. The beaker was sealed with polyethylene film (Glad, measured to be UV transparent by spectrophotometry) to prevent evaporation during the experiment, and its sides were wrapped with Al foil. The mixture was stirred in the dark for 1 h to attain adsorption-desorption equilibrium of organics with the TiO₂ surface, and then placed in the photoreactor and exposed to UV light while stirring, with 1 mL aliquots sampled periodically for measurement of NA concentration, which were subsequently returned to the beaker.

The FGDW photocatalytic treatment experiment was performed in a custom photoreactor enclosure consisting of an array of UVC fluorescent bulbs (Sani-Ray RRDHO36-4, peak emission ~254 nm) suspended above the samples. The UV intensity was measured to be ~16 W/m² with a UVC light meter (Sper Scientific, NIST certified calibration) at the surface of the water within the reaction chamber through the quartz window. TiO₂ nanoparticles were stirred into 350 mL of FGDW (0.2 g/L) in a polytetrafluoroethylene (PTFE) beaker (76 mm diameter) along with 300 ppm formic acid to act as an electron hole scavenger for the reduction reaction. The beaker was sealed in an air tight stainless steel vessel with a quartz window to prevent exposure to oxygen during the experiment, while N₂ gas was purged throughout the reaction to remove any H₂Se gas generation which was flowed through two subsequent liquid scrubbers of CuSO₄ and NaOH, respectively.^{14,15} The mixture was stirred in the dark for

1 h to attain adsorption-desorption equilibrium of inorganics with the TiO_2 surface, and then placed in the photoreactor and exposed to UV light while stirring, with 5 mL aliquots sampled periodically for measurement of Se concentration, which were centrifuged so the TiO_2 could be returned to the beaker at the end of the experiment.

For both the OSPW and FGDW experiments, following the UV treatment, the TiO_2 suspension was separated by magnetic flocculation and deflocculated as described above, using $Fe_3O_4@SiO_2@PDADMAC$ particles (at 0.316 g/L) as the MF, and stirring at 120 rpm and 15 rpm with a mechanical stirrer for the flash and slow mix periods respectively. The recovered TiO_2 was then dispersed into a fresh sample of either OSPW or FGDW for a subsequent cycle of photocatalytic treatment.

Naphthenic acid fraction extractable organics (NAs) concentrations were determined by UV/Vis spectroscopy at 220 nm,¹⁶ comparing to a calibration curve prepared from NAs extracted from the same OSPW sample. Briefly, OSPW was adjusted to pH 10.5 with NH₄OH, extracted thrice with DCM (in total 1:2 solvent to sample volumetric ratio), acidified to pH 7 with H₂SO₄, extracted thrice with DCM, and finally acidified to pH 2 with H₂SO₄, and extracted thrice with DCM. The acidic, neutral, and basic DCM extracts were then combined, and dried under N₂. While naphthenic acids are defined by the classic formula $C_nH_{2n+z}O_2$ (where z is a negative even integer related to the number of rings and double bonds), OSPW naphthenic acid fraction extractable organics (referred to as NAs herein) also contain a broad range of organics not conforming to this classic structure, including aromatic and heteroatom-containing acids, as well as basic and low polarity species.^{17–20}

Selenium concentrations were determined using a hydride generation set-up (CETAC, HGX-200 Advanced Membrane Cold-Vapor and Hydride Generation System) prior to quantification using inductively coupled plasma optical emission spectroscopy (ICP-OES, Teledyne Leeman Prodigy). The samples were acid digested in 6M hydrochloric acid (HCl) and 0.2M nitric acid (HNO₃) by adding 3.9 mL of HCl and 0.1 mL HNO₃ to a 4 mL aqueous sample. Samples were then boiled for 30 minutes prior to hydride generation and analysed using ICP-OES to pre-reduce all selenate to selenite. The LOD of the above Se detection technique is 2 μ g/L. The starting concentration of the FGDW, 300 ± 15 μ g/L, was reduced past the detection limit for the first 4 cycles.

Materials Characterization

Particle size and structure was analyzed by TEM (Philips CM-10, 60 keV). The hydrodynamic diameter of the particles in water was measured by DLS (Brookhaven 90Plus Particle Size Analyzer, lognormal volume-weighted median diameter). Crystal phase was assessed by powder XRD (Bruker D8-Advance, Våntec-1 detector, 1.5405 Å Cu-Kα radiation). The magnetic properties of the powders were measured at 300 K with SQUID VSM (Quantum Design MPMS). The surface area of the particles (pre-dried at 200 °C in N₂) was calculated from the Brunauer–Emmett–Teller (BET) equation using data from N₂ adsorption isotherms obtained at 77 K (Micrometrics Gemini VII 2390 Surface Area Analyser). Zeta potential measurements were taken with a Malvern Zetasizer Nano ZS. FTIR spectra were obtained for powder samples in KBr pellets (Bruker Tensor 27). XPS was performed at room temperature (VG Scientific ESCALab 250, Al Kα radiation), and the binding energy scale was corrected by referencing the C 1s peak to 285 eV. TGA was performed at 10 °C/min in air (TA Instruments Q500). Photomicrographs of flocs were obtained using an optical microscope (Zeiss Axioskop with AxioCam ERc 5s camera).



Figure S1. Zeta potential of aqueous TiO_2 nanoparticle suspensions as a function of pH, where pI is the isoelectric point.



Figure S2. Magnetic hysteresis curve of the Fe₃O₄@SiO₂@PDADMAC particles at 300 K.



Figure S3. TEM images of (a) $Fe_3O_4@SiO_2@PDADMAC$ particles, exhibiting strands as potential evidence of the polymeric coating, and (b) $Fe_3O_4@SiO_2@CS$ particles exhibiting ~1 µm aggregates.



Figure S4. FTIR spectra of the particle formulations, where the 1113 cm⁻¹ peak is characteristic of silica, and the 3425 cm⁻¹ peak is attributed to hydroxyl groups.



Figure S5. XPS (a) survey spectra of the $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@PDADMAC$ particles, as well as (b) N 1s and (c) S 2p narrow scan spectra of the $Fe_3O_4@SiO_2@PDADMAC$ particles.



Figure S6. TGA curves of the $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@PDADMAC$ particles, with the weight of each sample normalized at 200 °C (weight loss below this temperature taken as water evaporation).



Figure S7. TEM image of the TiO₂ nanoparticles used in this work (Evonik Aeroxide P25). The mean primary particle diameter was measured to be 24.0 ± 7.1 nm (n = 121), and is reported by the manufacturer to be ~21 nm.



Figure S8. Photos of CTAB stabilized Ag nanoparticle aqueous suspensions (a) before and (b) after separation by magnetic flocculation with the MF particles indicated (added at 0.316 g L^{-1}).



Figure S9. Relative TiO_2 concentration remaining in suspension after sequential magnetic flocculation passes of Fe₃O₄@SiO₂@PDADMAC particles (added at 316 mg L⁻¹). LOD refers to the ICPMS limit of detection.



Figure S10. Flocculation efficacy of free polymeric PDADMAC compared to PDADMAC bound on $Fe_3O_4@SiO_2@PDADMAC$ MFs, toward separation of TiO_2 nanoparticles (0.1 g L⁻¹). The concentration of PDADMAC in the MF sample was calculated from the mass fraction of the terminal PDADMAC layer, taken as one third of the total polymer coating mass measured by TGA, *i.e.*, 0.51 wt.%.



Figure S11. Optical micrographs of flocs formed in TiO_2 nanoparticle suspensions (0.1 g L⁻¹) following addition of $Fe_3O_4@SiO_2@PDADMAC$ particles at different concentrations: (a) & (b) 31.6 mg L⁻¹, (c) & (d) 100 mg L⁻¹, (e) & (f) 316 mg L⁻¹, and (g) & (h) 1 g L⁻¹.



Figure S12. Separation of TiO₂ nanoparticles from aqueous suspension (0.1 g L⁻¹) by magnetic flocculation and deflocculation recovery with $Fe_3O_4@SiO_2@PDADMAC$ particles, where the same TiO₂ and MF particles were recycled and used throughout each test.

Table S1. Water quality characteristics of OSPW. All parameters apart from NAs and AEO were measured according to standard methods by ALS Environmental (Waterloo, ON, Canada), a laboratory accredited by the Canadian Association for Laboratory Accreditation (CALA) according to international standards (ISO 17025).

| Parameter | Value |
|---|------------|
| NAs (mg/L) | 79.5 ± 2.3 |
| AEO (mg/L)ª | 40.9 ± 2.4 |
| TOC (mg/L) | 54 |
| COD (mg/L) | 153 |
| BOD (mg/L) | 3.0 |
| рН | 8.30 |
| Conductivity (mS/cm) | 1.630 |
| Anions | |
| Bromide (mg/L) | <0.50 |
| Chloride (mg/L) | 172 |
| Fluoride (mg/L) | 3.00 |
| Nitrate (mg/L) | <0.10 |
| Nitrite (mg/L) | <0.050 |
| Sulphate (mg/L) | 207 |
| Alkalinity (mg/L as CaCO ₃) | 400 |
| Dissolved Metals | |
| Aluminum (Al) (mg/L) | <0.050 |
| Antimony (Sb) (mg/L) | 0.0011 |
| Arsenic (As) (mg/L) | 0.0027 |
| Barium (Ba) (mg/L) | 0.0976 |
| Beryllium (Be) (mg/L) | <0.0010 |
| Bismuth (Bi) (mg/L) | <0.00050 |
| Boron (B) (mg/L) | 2.00 |
| Cadmium (Cd) (mg/L) | <0.00010 |
| Calcium (Ca) (mg/L) | 15.7 |
| Chromium (Cr) (mg/L) | <0.0050 |
| Cobalt (Co) (mg/L) | 0.0022 |
| Copper (Cu) (mg/L) | 0.0021 |
| Iron (Fe) (mg/L) | <0.10 |
| Lead (Pb) (mg/L) | <0.00050 |
| Lithium (Li) (mg/L) | 0.140 |
| Magnesium (Mg) (mg/L) | 14.4 |
| Manganese (Mn) (mg/L) | 0.0205 |
| Molybdenum (Mo) (mg/L) | 0.0613 |

| Nickel (Ni) (mg/L) | 0.0075 | |
|-----------------------|----------|--|
| Phosphorus (P) (mg/L) | <0.50 | |
| Potassium (K) (mg/L) | 15.6 | |
| Rubidium (Rb) (mg/L) | 0.0144 | |
| Selenium (Se) (mg/L) | 0.00056 | |
| Silicon (Si) (mg/L) | 2.81 | |
| Silver (Ag) (mg/L) | <0.00050 | |
| Sodium (Na) (mg/L) | 300 | |
| Strontium (Sr) (mg/L) | 0.468 | |
| Sulfur (S) (mg/L) | 71.0 | |
| Tellurium (Te) (mg/L) | <0.0020 | |
| Thallium (Tl) (mg/L) | <0.00010 | |
| Thorium (Th) (mg/L) | <0.0010 | |
| Tin (Sn) (mg/L) | <0.0010 | |
| Titanium (Ti) (mg/L) | <0.0030 | |
| Tungsten (W) (mg/L) | 0.0047 | |
| Uranium (U) (mg/L) | 0.00376 | |
| Vanadium (V) (mg/L) | <0.0050 | |
| Zinc (Zn) (mg/L) | <0.010 | |
| Zirconium (Zr) (mg/L) | <0.0030 | |

^aAEO = acid extractable organics, measured by FTIR and quantified using a calibration curve prepared from a commercial naphthenic acid mixture, described previously.¹³



Figure S13. (a) UV/Vis spectra of TiO_2 nanoparticle aqueous suspensions and (b) calibration curves prepared from the spectra in (a).

| | 250 nm | 350 nm | 400 nm |
|--------------------------------|--------------|--------------|--------------|
| Slope x 10 ³ (L/mg) | 37.94 ± 0.10 | 21.95 ± 0.21 | 12.02 ± 0.06 |
| Intercept x 10 ³ | 62.44 ± 2.08 | 54.63 ± 7.18 | 36.79 ± 2.02 |
| Limit of Detection (mg/L) | 0.16 | 0.98 | 0.50 |
| Limit of Quantification (mg/L) | 0.55 | 3.27 | 1.68 |

Table S2. Regression parameters of the UV/Vis calibration curves used to determine TiO₂ concentration.



Figure S14. Calibration curve relating TiO₂ nanoparticle concentration to total Ti measured by ICPMS.

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