Electronic Supplementary Information (ESI)

Adsorptive properties and on-demand magnetic response of Lignin@Fe_3O_4 nanoparticles at castor oil-water interfaces

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ESI 1. Synthesis of Fe3O4 nanoparticles

Briefly, iron (II) chloride and iron (III) chloride were mixed with water in a 1-L nitrogen purged vessel at room temperature and stirred using an overhead at 600 RPM at 60 °C for 30 minutes. A concentrated ammonium hydroxide solution (260 mL, ~ 5.7 M) was added to the vessel using a syringe pump at a 2 ml/s flowrate, followed by mixing for another 30 minutes. The IONPs were then formed and separated from the liquid using the N42 permanent magnet. The precipitate was washed three times with clean water using the magnet, while keeping the vessel under nitrogen. The washed IONPs were then redispersed in water.

ESI 2. Synthesis of lignin@Fe_3O_4 nanocomposites

Using a 3:1 mass ratio of kraft lignin (KL) to magnetite, the desired amount of KL was added to 1 wt% sodium hydroxide solution at a 1:9 weight ratio and mixed overnight with the IKA RW20 stirrer until all the KL particles were dissolved into the solution. Then the alkaline KL solution was sonicated in a sonication bath (Branson CPX5800H) for two hours. Afterwards, the KL/sodium hydroxide solution was quickly added to the 1-L vessel at a volumetric rate of 15 mL/min using four syringes and a syringe pump (PHD 4X140 multi rack pump, Harvard Apparatus). After mixing the vessel contents for 25 minutes at 600 RPM, lignin@Fe_3O_4 nanoparticles were successfully synthesized. The 1 L vessel was opened to atmospheric conditions, and the N42 magnet sat underneath the system for 1-2 days to precipitate the nanoparticles from the supernatant. Once the supernatant started to clear up, the liquid was removed using a syringe, and any dispersed nanoparticles were washed three times using a centrifuge for 15 minutes at 20,000 RPM at 4 °C (Allegra 64R; Beckman Coulter). The bulk of the nanoparticles at the bottom of the vessel was washed three times using the same neodymium magnet and clean water. After the third wash, the lignin@Fe_3O_4 nanoparticles were redispersed in pure water and added to a 600 mL lyophilizer

flask to freeze dry overnight using a freeze drier (Labconco, Freezone, 6 L Benchtop). Once dried, the nanoparticles were ground into a fine powder using a mortar and pestle (VWR, 64 mm O.D.x 51 mm ID).

ESI 3. Characterization of Fe_3O_4 and lignin@Fe_3O_4 nanocomposites

A Nicolet iS50 FT-IR Spectrometer with an iS50 DLaTGS Detector and a KBr window (Thermo Fisher Scientific) was used for FT-IR data collection. Background spectrum was collected before the first sample and also collected after each individual sample, with a minimum of 64 runs and a resolution of 4 cm^{-1}, and a clean ZnSe crystal. Spectra of the lignin@Fe_3O_4 powder samples, neat Fe_3O_4, and kraft lignin were collected on the ZnSe ATR crystal using the OMNIC Spectra Nicolet iS50 software.

TGA data was collected using a TGA Q500 (TA Instrument) to determine the thermal stability of lignin@Fe_3O_4 nanoparticles, neat Fe_3O_4, and kraft lignin, as well as the percent lignin coating on the Fe_3O_4 nanoparticles. A balance nitrogen flow of 10 mL/min and a sample nitrogen flow rate of 90 mL/min was used for all samples, along with a temperature range from 25 – 900 °C with a constant ramp rate of 10 °C/min. At least 5 mg of the sample was placed on a platinum pan to provide accurate results. The amount of lignin coating on the magnetite was calculated using Eqn. (S1):

$$\%\ lignin\ content = \frac{Initial\ Weight - Final\ Weight}{0.6189 * Initial\ Weight} * 100\% \quad \text{(S1)}$$

The percent lignin content is the average of three independent runs.

A Rigaku SmartLab XRD instrument was used to collect the X-ray diffraction data with Cu K-alpha radiation set at 40 kV voltage and 44 mA current settings for the powder samples of lignin@Fe_3O_4 nanoparticles, neat Fe_3O_4, and kraft lignin. The samples were placed on a 5 x 0.2 mm well sample holder (Rigaku 906162), and a 2-theta range from 20° to 70° with a step size of 0.04°

and step time of 1 second was used for all samples. The crystalline size (τ) of the lignin@Fe_3O_4 nanoparticles was calculated using the Scherrer equation (S2)

$$\tau = \frac{\kappa\lambda}{\beta\cos(\theta)} \quad \text{(S2)}$$

where κ is the dimensionless shape factor (0.90), λ is the wavelength (0.15418 nm), β is the width at half the maximum intensity (FWHM), and θ is the Bragg diffraction angle. The crystallite size was calculated at the most intense XRD peak at 35°.

Zeta potential of the lignin@Fe_3O_4 nanoparticles was measured using an Anton Paar Litesizer 500 instrument with a 40 mW, 658 nm laser. The average zeta potential value was calculated on the Anton Paar Kalliope software using a Smoluchowski approximation. The target temperature was set at 77 °F, with a 3-minute equilibrium time, 1.5 Debye factor, and a maximum of 1,000 runs. A 0.05 wt% NP solution was diluted further with a 1 mL solution:3 mL water ratio and was placed in an Anton Paar Ω-shaped capillary cuvette. This cuvette has two gold electrodes on opposite sides where the voltage can be applied to the solution.

A DLS NanoBrook 90Plus (Brookhaven Instruments Corporation) instrument with a 40 mW, 640 nm temperature-controlled diode laser was used to measure hydrodynamic diameter data for the lignin@Fe_3O_4 nanoparticles. A diluted NP solution (<0.05 wt%) was added to a 4 mL plastic cuvette and analyzed on the NanoBrook software using Non-Negative Least Squares (NNLS) fitting for the size distribution so that any negative x-values were eliminated from the analysis. Hydrodynamic diameter, or effective diameter (D_{eff}), was measured on the software using the Stokes-Einstein equation (3):

$$d(H) = \frac{kT}{3\pi\eta D} \quad \text{(S3)}$$

where k is the Boltzmann's constant, T is the absolute temperature, η is viscosity, and D is the translational diffusion coefficient.[1] Diameter by number ($D_{\#}$) was also calculated using the Mie

theory, where the intensity distribution was transformed into a number distribution.[2] DLS ran five measurements on the lignin@Fe_3O_4 nanoparticles, which were averaged together for the results.

TEM (JEOL 2100, 200 kV) was utilized to capture images of the magnetite encapsulated by KL. A 5 mg NP/10 mL water colloidal suspension was prepared, and 1 mL of that solution was added to 3 mL of pure water, where 3 drops were placed on one Lacey Carbon 300 mesh copper TEM grid (concentrated) and 1 drop was placed on a second Lacey Carbon 300 mesh copper TEM grid (diluted). ImageJ software was used to measure the average diameter of 60 IONPs for each of the samples.

Lastly, a Quantum Design Physical Properties Measurement System (PPMS), specifically the vibrating sample magnetometer (VSM) option, measured the magnetization of lignin@Fe_3O_4 and neat Fe_3O_4 nanoparticles. Magnetic hysteresis loops were measured, along with a magnetization-temperature profile, of the samples in the powder state. A magnetization from -80 to 80 emu/g and a magnetic field from -4 to 4 T was used for the hysteresis loops, and a magnetization-temperature profile was obtained from the temperature 0 K to 300 K.

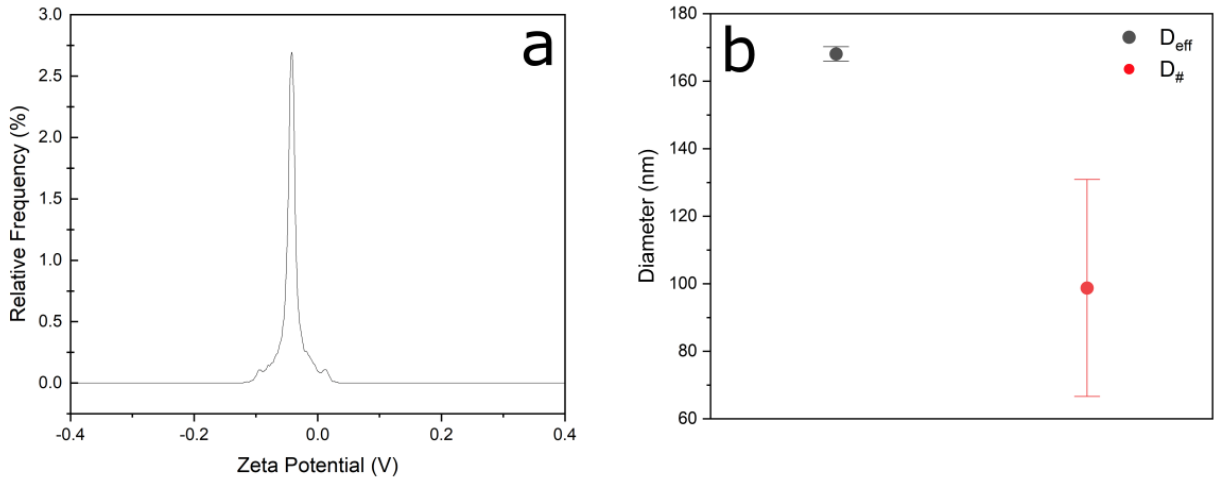

Figure S1: (a) Zeta potential of lignin@Fe_3O_4 nanoparticles, and (b) DLS plot comparing D_{eff} and $D_{\#}$ for lignin@Fe_3O_4 nanoparticles.

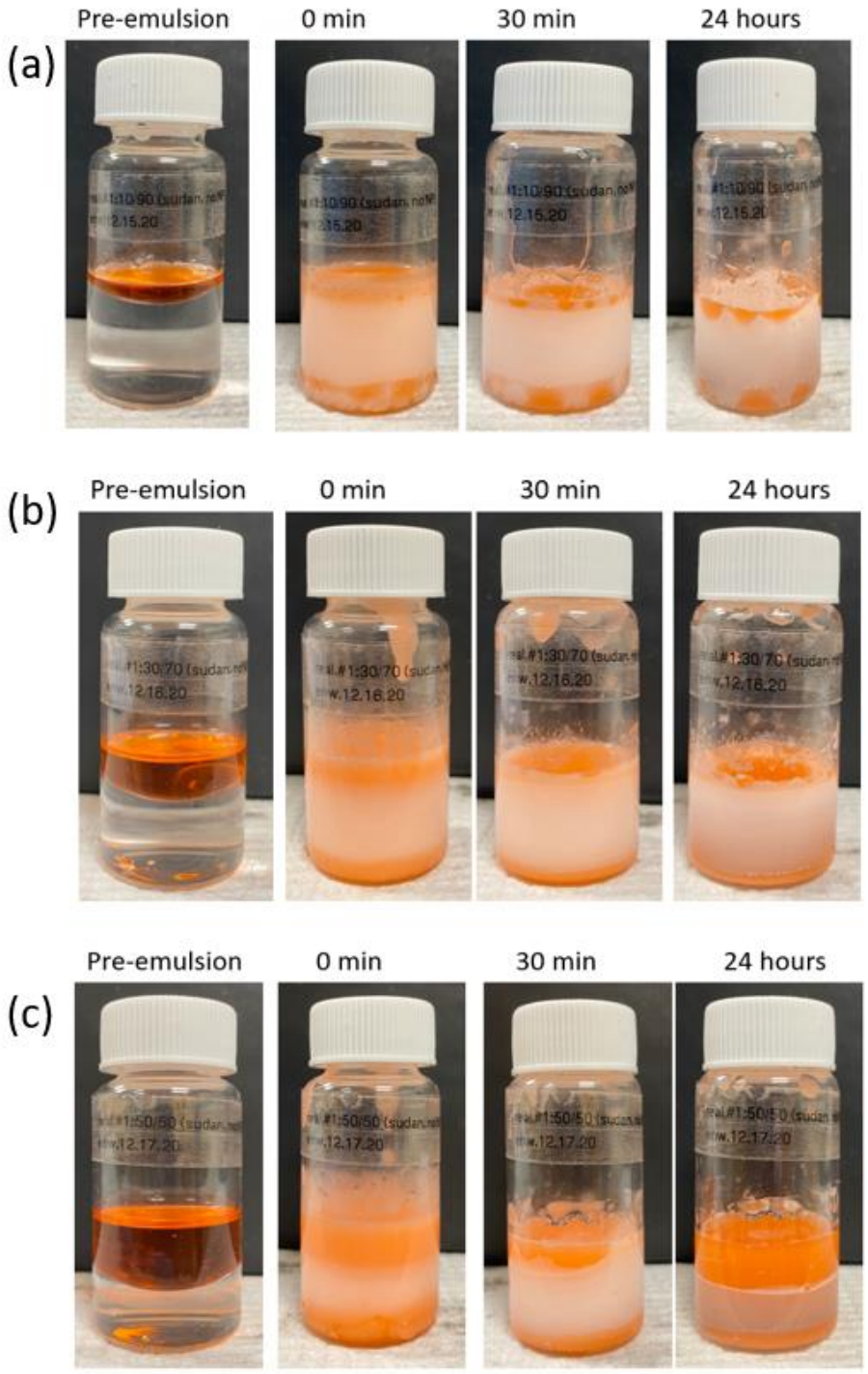

Figure S2: 3 Control emulsions (no particles) prepared at castor oil to water volume ratio of (a) 10/90; (b) 30/70; and (c) 50/50

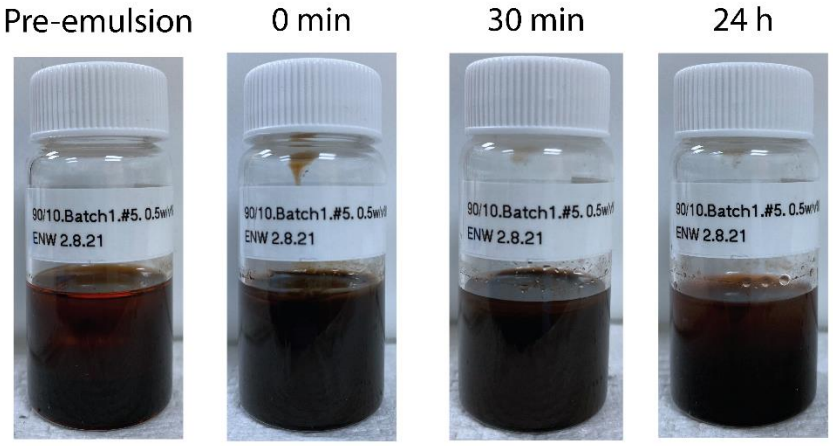

Figure S3: Control emulsions prepared with 0.5 wt% lignin@Fe3O4 nanoparticles prepared at castor oil to water volume ratio of 10/90 and no magnetic field.

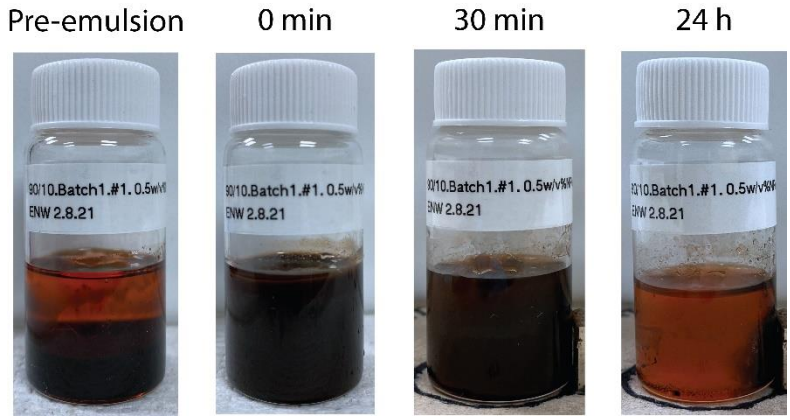

Figure S4: Magnetic demulsification prepared with 0.5 w/v % lignin@Fe3O4 nanoparticles prepared at castor oil to water volume ratio of 10/90 and a 540 mT magnetic field.

<u>Oil Herding Experiments</u>

(a) Oil herding using medium magnet – Video S1
(b) Oil Herding using large magnet – Video S2

References:

1. Mirzazadeh Ghanadi, A. Heydari Nasab, D. Bastani and A. A. Seife Kordi, *Chemical Engineering Communications*, 2015, **202**, 600–605.
2. Instruments, Malvern. "Intensity-volume-number: Which size is correct." *Technical Note MRK1357-01* (2014).