

Supplementary Materials

Experimental thermal conductivity studies of agar-based aqueous suspensions with lignin magnetic nanocomposites

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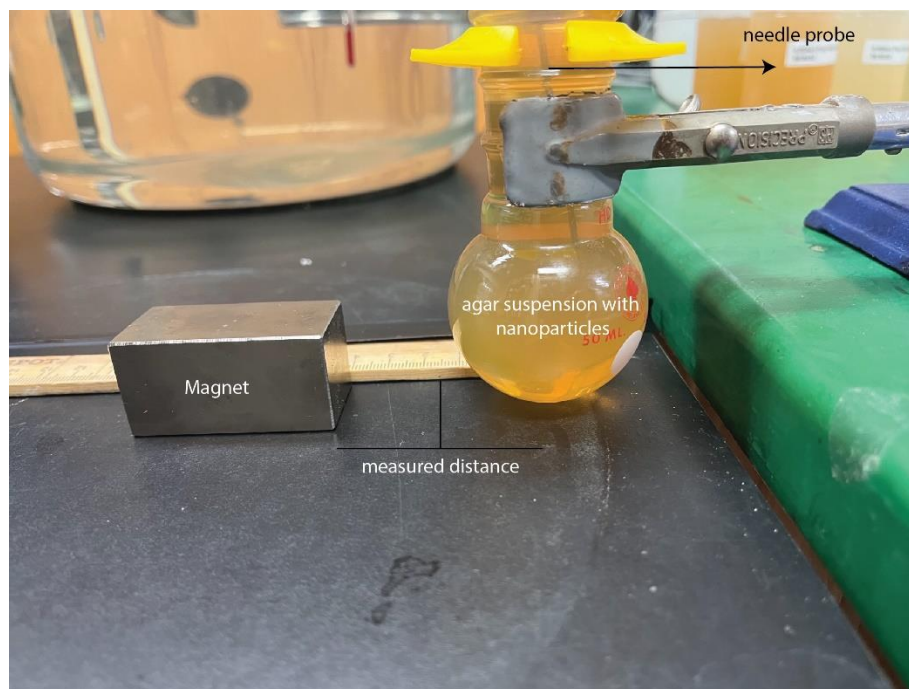


Figure S1. Thermal conductivity measurements of lignin@Fe₃O₄ agar-based aqueous suspensions at room temperature using a permanent magnet.

Table S1. Magnetic field strengths were measured at different distances from the top edge of the Neodymium magnet (1 inch x 1 inch x 2 inch) to the nearest outside vessel wall of the volumetric flask. The magnetic probe was always located on the outside vessel wall for all of the other distances measured. For example, a 0 cm distance means the magnetic probe was located precisely between the magnet and the outside vessel wall.

Distance from the top edge of the magnet to the closest vessel wall (cm)	Measured magnetic field (mT)
0	561
1.0	210
2.0	97
3.0	50
3.4	40
4.0	30
4.8	20
5.0	18
6.5	10

Section S1. Detailed procedure for the synthesis of lignin@Fe₃O₄ nanoparticles

Apparatus. The equipment utilized to synthesize the lignin@Fe₃O₄ nanoparticles is shown in Figure S2. The apparatus included a heating mantle, a 4-necked reaction kettle lid, an IKA RW 20 digital stirrer, and a clamp. The reaction was conducted under a continuous nitrogen flow, and rubber septa with stainless steel needles were used to generate an inert atmosphere within the 1000 mL 4-necked reaction vessel. The SS needles were also used to insert to or remove reactants from the reactor vessel. The vessel with initial reactants (i.e., iron salts) was sealed using a clamp and an O-ring, followed by positioning inside a heating mantle, which allowed it to control the temperature. An adapter was used to insert the mixing rod to the apparatus and to provide constant agitation.

Lignin@Fe₃O₄ nanoparticle synthesis. First, 21.0165 g of iron (III) chloride was measured in a 120 mL small plastic container and 12.88 g of iron (II) chloride was measured inside a glovebox so air would not react with the iron (II) chloride. In a separate container, lignin was dissolved in a 1 wt% sodium hydroxide solution, as described in Gautam's thesis [1]. Briefly, a 50 wt % stock solution of sodium hydroxide, with a density of 1.5253 g/mL, was obtained from Sigma Aldrich and used to prepare the 1 wt% NaOH solution. A total of 6.608 mL of NaOH stock solution was measured, and water was added until it reached a final volume of 500 mL. The lignin solution was prepared by measuring 45 g of lignin in a large container and adding NaOH 1 wt.% until a total of 450 g was obtained. A small mixing blade was used to mix overnight at a speed of 340 rpm to dissolve the lignin fully.

Once the apparatus setup was assembled and sealed, 500 mL of water was added and mixed with iron (III) chloride and iron (II) chloride salts under constant nitrogen flow. Each sample was poured inside the reactor using a syringe. The temperature of the solution was measured and heated until

a 60 °C set temperature was reached. A mixing blade was used to continuously stir and dissolve the chemicals inside the chamber, with mixing speeds varying from 600 to 1000 rpm.



Figure S2. Experimental apparatus for the synthesis of Lignin@Fe₃O₄ nanoparticles.

An ammonium hydroxide solution was prepared once the iron salts were fully dissolved in water and 100 mL of stock solution (90 g) was mixed with 160 mL of water. Two large syringes (200 mL) were filled with 130 mL each of the prepared ammonium hydroxide solution (Fig S2). A stainless-steel needle was connected to each syringe. Both syringes were mounted into a multi-syringe pump system, and the needles were passed through the rubber septa caps and used to pour the ammonium hydroxide inside the flask, as shown in Fig. S2. The multi-syringe pump system was set up at 100 μ L/min, with a total injection time of 2 hours. Three washing cycles were performed using clean water. A permanent magnet induced the magnetic separation of the freshly prepared magnetic nanoparticles. Once the particles settled, the syringes connected to the multi-syringe system removed the supernatant. To wash the magnetically separated nanoparticles, 140 mL of water was used, and the sample was stirred for 15 minutes to mix the nanoparticles thoroughly with clean water and remove any remaining salts (e.g., ammonium chloride). After

three washing cycles, the lignin solution was added to the reaction flask using the multi-syringe pump system. This injection process was done rapidly, at a 15 mL/min flow rate. The mixing blade was running simultaneously while adding lignin into the reactor flask. After adding lignin, a mixing blade was used for another 25 minutes to coat lignin on the surface of the Fe_3O_4 nanoparticles. The product was separated using a permanent neodymium magnet (2" x 2" x 1") with a maximum magnetic strength of 550 mT (measured using a PCF 300 magnetometer). The magnet was placed at the bottom of the reactor, and the nanoparticles were allowed to sit for 48 hours to separate them from the suspension (Note: the lignin@magnetic nanoparticles were colloidally stable, which is why a long separation time was needed). After 48 hours, all septum, rubber clamp, nitrogen purge, and supernatant (without particles) were removed. Then, 200 mL of water was added to the sedimented nanoparticles to disperse the nanoparticles with the aid of a sonicator bath (Branson 5800) for 15 minutes. The neodymium magnet was used again to induce separation of the particles, and the supernatant was removed using a syringe with a large stainless-steel needle. After a third wash cycle, the nanoparticles were dispersed in 50 mL of water and dried inside a vacuum oven overnight at 50 °C. Once the particles dried, a mortar and pestle (VWR 89037-486) was used to homogenize the powder samples. All the suspension that remained during the 1st, 2nd, and 3rd wash cycle was centrifuged and a few more particles were recovered. This method allowed the preparation of lignin magnetic nanocomposites with superparamagnetic properties that were encapsulated within lignin.

Section S2. FT-IR Analysis

The nanoparticles' chemical structure and morphological properties are crucial during thermal conductivity measurements. FT-IR data (Figure S3) indicated that the fingerprint IR spectrum region between 800 cm^{-1} to 1600 cm^{-1} of neat kraft lignin and lignin@ Fe_3O_4 showed similar peaks confirming the coating of kraft lignin in Fe_3O_4 [2]. Additionally, two peaks at 3380 cm^{-1} and 1636

cm^{-1} represented -OH stretching and -OH scissoring, respectively, while 1636 cm^{-1} was indicative of water interacting with the oxide group at the surface. This analysis indicates potential interactions between water molecules, forming hydrogen bonds to Fe_3O_4 . Additional peaks detected at 1040 cm^{-1} and 1120 cm^{-1} were associated with C-O and C-H deformation, respectively. The peak at 1120 cm^{-1} was associated with C-C, C-O or C=O stretching.

The peaks found at 1450 cm^{-1} , 1510 cm^{-1} , and 1590 cm^{-1} represent C=C stretching of aromatic bonds, C-C stretching of aromatic bonds, and aromatic vibrations, respectively [2] [3]. The peak at 1650 cm^{-1} is the indication of a conjugated carboxyl group. The peak at 2950 cm^{-1} indicates stretching vibrations of CH bonds [2]. FT-IR spectra of both lignin@ Fe_3O_4 and kraft lignin represented many similar peaks, confirming the lignin encapsulation at the surface of Fe_3O_4 nanoparticles.

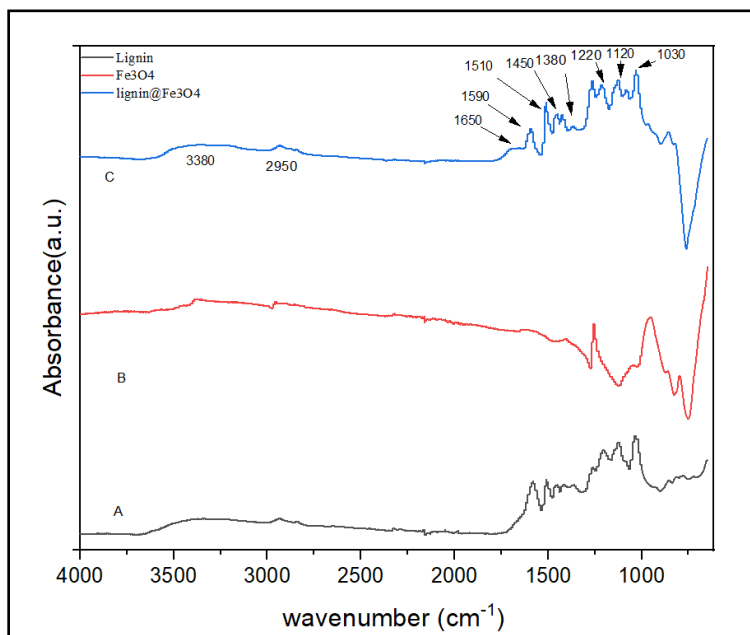


Figure S3. FT-IR spectra of lignin, Fe_3O_4 , and lignin@ Fe_3O_4 . A comparison between lignin and lignin@ Fe_3O_4 confirms coating on the surface of Fe_3O_4 nanoparticles.

Section S3. X-ray diffraction (XRD) analysis

The size of nanoparticles was described and calculated manually using the Scherrer equation, which is given by

$$\tau = \frac{\kappa\lambda}{\beta \cos \theta}$$

where τ = crystalline size of the particles.

κ = dimensionless shape factor (0.90).

β = width of the maximum intensity.

λ = wavelength (0.15418nm).

After the synthesis of lignin@Fe₃O₄ nanoparticles, XRD analysis was used to determine the crystalline structure of the lignin@Fe₃O₄ nanoparticles. Lignin@Fe₃O₄ and pure Fe₃O₄ showed the highest peak intensity at a 35° (Figure S4). At this peak, the crystal size was calculated manually using the Scherrer equation and was found to be 18.693 nm.

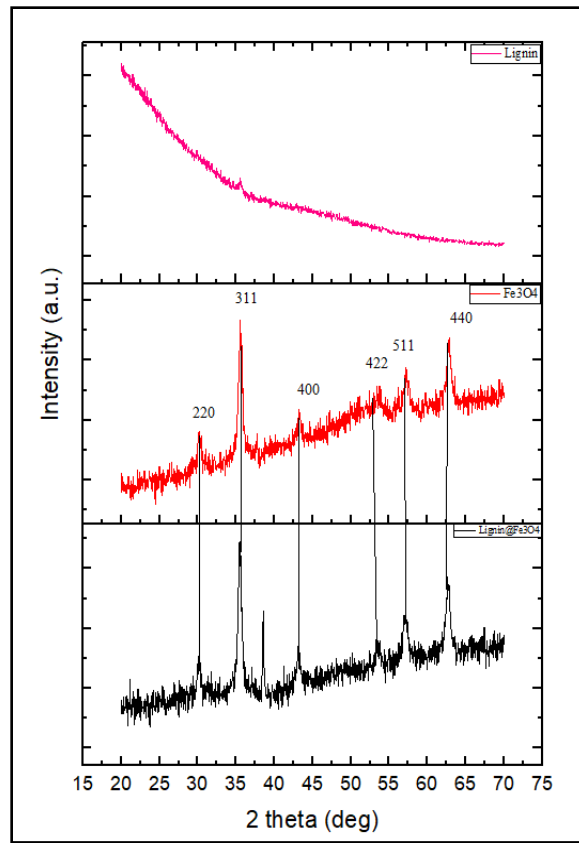


Figure S4: XRD spectra of neat lignin, pure Fe_3O_4 , and 3:1 ratio of lignin@ Fe_3O_4 nanoparticles. Six spectra at 30° , 35° , 43° , 53° , 57° , and 63° correspond to the miller indices of 220, 311, 400, 422, 511, and 440, respectively, indicating that the particles have a face-center cubic lattice structure [3] [4] [5] [6].

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