

University of Dayton

eCommons

Chemical and Materials Engineering Faculty
Publications

Department of Chemical and Materials
Engineering

6-30-2021

Facile fabrication and characterization of kraft lignin@Fe₃O₄ nanocomposites using pH driven precipitation: Effects on increasing lignin content

Frankie A. Petrie
University of Dayton

Justin M. Gorham
National Institute of Standards and Technology


Robert T. Busch
University of Dayton

Serhiy O. Leontsev
UES Inc.

Esteban E. Ureña-Benavides
University of Texas at San Antonio

Follow this and additional works at: https://ecommons.udayton.edu/cme_fac_pub

See next page for additional authors

 Part of the [Other Chemical Engineering Commons](#), and the [Other Materials Science and Engineering Commons](#)

eCommons Citation

Frankie A. Petrie, Justin M. Gorham, Robert T. Busch, Serhiy O. Leontsev, Esteban E. Ureña-Benavides, Erick S. Vasquez, "Facile fabrication and characterization of kraft lignin@Fe₃O₄ nanocomposites using pH driven precipitation: Effects on increasing lignin content," *International Journal of Biological Macromolecules*, Volume 181, 2021, Pages 313-321.

This Article is brought to you for free and open access by the Department of Chemical and Materials Engineering at eCommons. It has been accepted for inclusion in Chemical and Materials Engineering Faculty Publications by an authorized administrator of eCommons. For more information, please contact mschlengen1@udayton.edu, ecommons@udayton.edu.

Author(s)

Frankie A. Petrie, Justin M. Gorham, Robert T. Busch, Serhiy O. Leontsev, Esteban E. Ureña-Benavides, and Erick S. Vasquez

Facile fabrication and characterization of kraft lignin@Fe₃O₄ nanocomposites using pH driven precipitation: effects on increasing lignin content

Frankie A. Petrie[†], Justin M. Gorham[‡], Robert T. Busch[†], Serhiy O. Leontsev^{}, Esteban E. Ureña-Benavides⁺, Erick S. Vasquez^{†,‡,*}*

[†]Department of Chemical and Materials Engineering, University of Dayton, 300 College Park, Dayton, OH, 45469-0256, USA

[‡] Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD, 20899, USA

^{*} UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH, 45432, USA

⁺ Department of Biomedical Engineering and Chemical Engineering, The University of Texas at San Antonio, One UTSA Circle, San Antonio, 78249, TX, USA

[‡] Integrative Science and Engineering Center, University of Dayton, 300 College Park, Dayton, OH, 45469, USA

*Corresponding author: Erick S. Vasquez, Ph.D.

Tel: +1 937-229-2627

Email: evasquez1@udayton.edu

Fax: +1 937-229-4006

Department of Chemical and Materials Engineering

University of Dayton

300 College Park, Dayton, OH, 45469-0256, USA

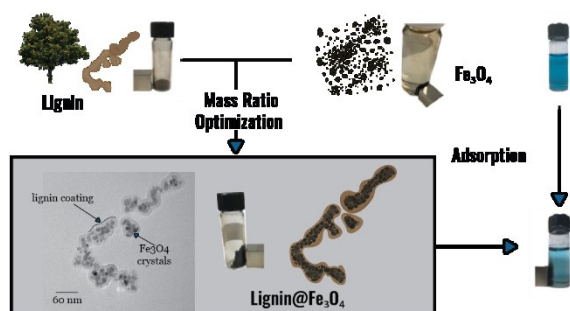
Abstract

This work offers a facile fabrication method for lignin nanocomposites through the assembly of kraft lignin onto magnetic nanoparticles (Fe₃O₄) based on pH-driven precipitation, without needing organic solvents or lignin functionalization. Kraft lignin@Fe₃O₄ multicore nanocomposites fabrication proceeded using a simple pH-driven precipitation technique. An alkaline solution for kraft lignin (pH 12) was rapidly injected into an aqueous-based Fe₃O₄ nanoparticle colloidal suspension (pH 7) under constant mixing conditions, allowing the fabrication of lignin magnetic nanocomposites. The effects of increasing lignin to initial Fe₃O₄ mass content (g/g), increasing in ratio from 1:1 to 20:1, are discussed with a complete chemical, structural, and morphological characterization. Results showed that nanocomposites fabricated above 5:1 lignin:Fe₃O₄ had the highest lignin coverage and content (>20%), possessed

superparamagnetic properties ($M_s \approx 45,000 \text{ A}\cdot\text{m}^2/\text{kg}^2$); had a negative surface charge (-30 mV), and formed multicore nanostructures ($D_H \approx 150 \text{ nm}$). The multicore lignin@ Fe_3O_4 nanocomposites allowed rapid magnetically induced separations from suspension. After 5 min exposure to a rare-earth neodymium magnet ($1.27 \text{ mm} \times 1.27 \text{ mm} \times 5.08 \text{ mm}$), lignin@ Fe_3O_4 nanocomposites exhibited a maximum methylene blue removal efficiency of $74.1\% \pm 7.1\%$. These nanocomposites have potential in magnetically induced separations to remove organic dyes, heavy metals, or other lignin adsorbates.

KEYWORDS: Fe_3O_4 , kraft lignin, lignin@ Fe_3O_4 nanocomposites

GRAPHICAL ABSTRACT



1. Introduction

Lignin is a high-value, underutilized macromolecule with unique properties, making it an attractive material for multifunctional structures ranging from the nano- to the macroscopic scale [1–3]. This biomacromolecule has been used to prepare antioxidant and UV adsorbent materials, antimicrobial agents, polymer-metal nanocomposites, and reinforced polymer blends [4–6]; however, only $\approx 2\%$ of lignin is recovered and used in value-added products or applications [7]. An increase in lignin valorization could result from efficient methods to prepare lignin nanoparticles or nanocomposites. These have proven potential as protein vehicles for biomedical

applications, templates to prepare hollow particles, and coatings to prevent degradation, oxidation, or dehydration of polymeric- and metal oxide particles [8–10].

Traditional synthetic routes for lignin nanoparticles include solvent evaporation, sonication and mechanical shearing, and crosslinking reactions [11–13]. Recent efforts demonstrated antisolvent driven techniques as efficient, economical, and simple methods to prepare lignin nanoparticles [9,14,15]. The antisolvent induced nanomaterial formation proceeds by merely adding a lignin solution in a good solvent into a poor solvent, or vice versa [14,16–20]. Nanoparticle properties are often controlled by adjusting experimental conditions such as the injection rate of the poor solvent,[9] the total concentration of the initial lignin solution,[15] or solution pH [21]. Once lignin nanoparticles are prepared, the preparation of nanocomposites proceeds by including other types of materials such as polymers or metallic nanoparticles.

The addition of magnetic nanoparticles to lignin imparts additional features allowing its manipulation in suspension by an external magnetic field. Magnetite, Fe_3O_4 , is commonly used in nanocomposites due to its biocompatibility, stability in different physiological conditions, high magnetic saturation, superparamagnetic properties, and tunability in shape and dimensions [22–25]. Using lignin as a coating of Fe_3O_4 results in a highly adsorptive nanocomposite with magnetic properties that can ultimately be used for many separation processes, from environmental to biological applications [26–35]. Unfortunately, the current fabrication methods for the preparation of lignin-magnetic nanocomposites require lignin chemical functionalization protocols,[29,36,37] or numerous solvents and purification steps [33,38]. To the authors' knowledge, only a few reports have analyzed the chemical, morphological, and magnetic properties of lignin magnetic nanocomposites based on the fabrication method. Understanding

these properties as a function of preparation conditions could lead to an optimized synthesis that can facilitate large scale-up production.

This work provides a facile fabrication technique to prepare lignin magnetic nanocomposites, based on the rapid injection of a kraft lignin aqueous solution—initially dissolved at a pH 12—into a colloidal suspension of Fe₃O₄ magnetic nanoparticles dispersed in water (pH 7) under constant mixing conditions. Kraft lignin was chosen due to its proven dissolution in alkaline solutions above pH 10[39,40], and large availability[7]. The precipitation and assembly of lignin onto the as-prepared magnetic nanoparticles suspended in water occur by merely adjusting the pH, from alkaline to neutral conditions, eliminating the need for organic solvents such as ethanol or tetrahydrofuran (THF) found in antisolvent induced precipitation. This procedure results in the assembly of kraft lignin coated magnetic nanocomposites (lignin@Fe₃O₄), which possess a unique multicore structure where multiple Fe₃O₄ crystals are encapsulated within the kraft lignin shell. This multicore, heterogenous lignin structures are attractive due to improved magnetically driven separation with low magnetic fields[41].

The study also examines the effects of increasing kraft lignin content on the assembly of lignin@Fe₃O₄ nanocomposites at five different mass ratios of lignin to Fe₃O₄: 1:1, 5:1, 10:1, 12.5:1 and 20:1. Lignin@Fe₃O₄ nanocomposites assembly through the pH-driven precipitation technique is confirmed through the following: 1) the chemical characterization using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS); 2) the lignin coating content using thermogravimetric analysis (TGA); 3) the morphological features using transmission electron microscopy (TEM) imaging and stability in suspension with dynamic light scattering (DLS) and ζ-potential measurements; and 4) the magnetic properties using superconducting quantum interference device (SQUID)

measurements, and demonstrated separation of methylene blue by using only a rare-earth magnet and the lignin@Fe₃O₄ nanocomposites.

2. Experimental Section¹

Note: Additional details for the synthesis and characterization of the lignin@Fe₃O₄ nanocomposites (Sections 2.2 – 2.7) can be found in the supporting information (SI).

2.1. Materials

Iron (II) chloride (98%), iron (III) chloride (97%), ammonium hydroxide solution (28.0 % to 30.0 %), and kraft lignin ($M_w \approx 10,000$ u), the lignin type used throughout this study, were supplied by Sigma-Aldrich (St. Louis, MO, USA). Methylene blue (pure, certified) was supplied by Acros Organics (Fair Lawn, NJ). Ultrapure water with 18.2 M Ω -cm resistivity was obtained from an Elga PURELAB (UK) system and used in all experiments. All chemicals were used as received without further purification.

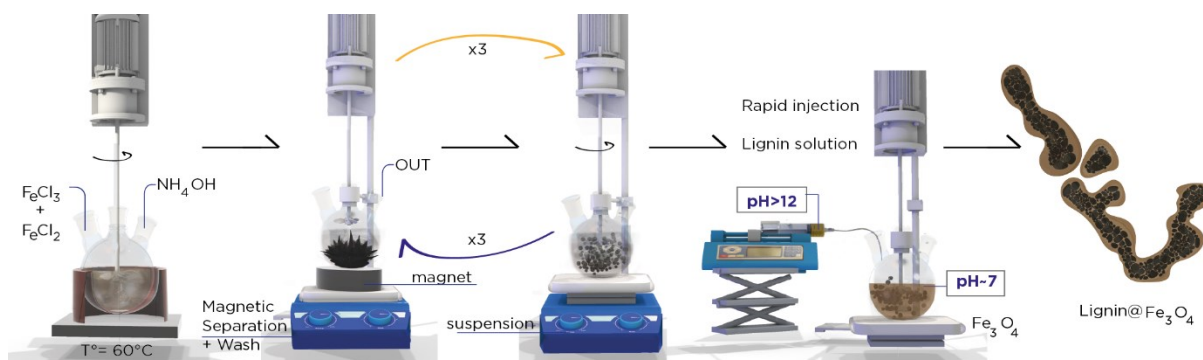
2.2. Synthesis of Fe₃O₄ magnetic nanoparticles

The synthesis of Fe₃O₄ magnetic nanoparticles was based on Massart's method with slight modifications[42], which can be found in the SI. In brief, iron (II) chloride solution was mixed with iron (III) chloride solution in a nitrogen-purged vessel at room temperature and then heated to 60°C for 30 min. Magnetic nanoparticles were formed using 1 mol/L ammonium hydroxide solution added by syringe pump and separation of the black precipitate formed was achieved using an external magnet. The precipitate was washed in triplicate with water and stored at a final pH of 7.2 ± 0.2 .

¹Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.

2.3. Fabrication and assembly of lignin@Fe₃O₄ nanocomposites

Kraft lignin was dissolved in an aqueous ammonium hydroxide solution (volume fraction of 5 % or $\phi_{\text{NH}_4\text{OH}} = 5 \%$) at a concentration of 0.1 g/mL (pH = 12.3). The assembly of kraft lignin onto Fe₃O₄ nanoparticles proceeded by rapidly injecting the lignin solution into the Fe₃O₄ colloidal suspension at injection rates of 15 - 30 mL/min using a syringe pump, as shown in **Scheme 1**. Five conditions were studied at the following theoretical lignin to Fe₃O₄ mass ratios: 1:1, 5:1, 10:1, 12.5:1, 20:1 [SI, please refer to **Table S1** for specific details]. After the rapid lignin solution injection, each colloidal suspension was mixed for 30 min at ≈ 17 Hz using an overhead stirrer followed by a centrifugation step at ≈ 417 Hz for 15 min. The supernatant was removed, and the solid precipitate was washed with water and sonicated in an ultrasonic bath for 20 min. This washing process was repeated three times, followed by the re-dispersion of the lignin@Fe₃O₄ in water. The final pH of the lignin@Fe₃O₄ suspension was 7.2 ± 0.2 .



Scheme 1. Fabrication scheme for the facile preparation of lignin@Fe₃O₄ nanocomposites using a pH-induced precipitation of kraft lignin (pH > 12) injected into a colloidal iron oxide suspension (pH ≈ 7), at a high injection rate and mixing speed.

2.4. Chemical characterization of lignin@Fe₃O₄ nanocomposites

A Nicolet iS50 FTIR spectrophotometer (Madison, WI) with an iS50 MCT-A liquid nitrogen cooled detector with a CdTe window, and a Smart Golden Gate ZnSe Attenuated total

reflectance (ATR) accessory was used for ATR-FTIR data collection. To ensure accuracy, each spectrum was taken three times, and all subsequent data presented is an average of the values for the three spectra plus or minus the standard error of the mean. The displayed FTIR spectra in graphics are a single instance representative of a typically acquired spectrum. Please see SI for more information on sample preparation and analysis details.

XRD data were collected using a Rigaku SmartLab XRD instrument (The Woodlands, TX) with Cu K-alpha radiation at 40 kV and a current setting of 44 mA (please see SI for more details). The Scherrer equation (1) was used to determine the crystallite size “ τ ” using the most intense XRD peak at 35 °, where K is the shape factor (0.9), λ is the wavelength (0.15418 nm), β is the full width at half maximum (FWHM), and θ is the Bragg diffraction angle.

$$\tau = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

XP spectra were acquired on an Axis Ultra DLD spectrometer from Kratos Analytical (Chestnut Ridge, NY) using monochromatic Al K α X-rays operating at 150 W (10 mA; 15 kV) under ultra-high vacuum system ($P_{\text{base}} \approx 6.6 \times 10^{-8}$ Pa) conditions. After surface neutralization, spectra were acquired using a pass of 40 eV with photoelectron intensity measured in 0.1 eV steps in elemental regions of interest. Unless otherwise mentioned, all spectra were (A) processed and analyzed using CasaXPS software (Teignmouth, UK), (B) fit with a Shirley background, and (C) charge referenced to 530.1 eV consistent with O 1s for iron oxide particles [61]. All elements were corrected using elemental relative sensitivity factors provided by the manufacturer. Unless otherwise stated, the semi-quantitative XPS values represent the average of four spatially unique measurements from one sample with the standard deviation representing the heterogeneity of that sample [Please see the SI for additional details on sample preparation, measurement conditions and analysis].

2.5. Lignin coating percentage and morphological characteristics of lignin@Fe₃O₄ nanocomposites

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q500 analyzer (New Castle, DE). The powdered nanoparticles (≈ 6 mg) were placed onto a platinum pan, and the tests were run under nitrogen flow at a flow rate of 10 mL/min and a temperature range of 25 °C to 900 °C. A constant heating rate of 10 °C/min was used. At each lignin:Fe₃O₄ mass ratio, measurements were obtained from unique reaction batches. The percent lignin content calculated is the average of at least three independent runs.

2.6. Morphology, dynamic light scattering, and zeta-potential measurements of lignin@Fe₃O₄ nanocomposites

A Hitachi H-7600 TEM was used to visualize the nanoparticle morphologies, and it was operated at an accelerating voltage of 100 kV. The size of the Fe₃O₄ nanoparticles was calculated with ImageJ processing. The average particle size is reported from fifteen separate TEM images of each lignin:Fe₃O₄ mass ratio discussed. A NanoBrook 90Plus (BIC, Holtsville, NY) with a 40 mW, 640 nm temperature-controlled diode laser was used for DLS data collection. ζ -potential measurements were collected using an Anton Paar Litesizer 500 instrument (Graz, Austria) that has a 40 mW, 658 nm laser. For both DLS and ζ -potential measurements, each trial was run at least in triplicate, collected at 25 °C, and the average results with a standard deviation is reported.

2.7. lignin@Fe₃O₄ nanocomposites: magnetic properties and magnetically-induced separation of methylene blue.

The magnetic moment of the lignin@Fe₃O₄ nanocomposites was measured at room temperature in the range of applied DC field of -3 T to 3 T using a Quantum Design XL superconducting quantum interference device (SQUID) magnetometer (San Diego, CA) (please

see SI, for instrumental capabilities and parameters). Lignin@Fe₃O₄ powder samples were placed in size four snap-fit gel capsules (TedPella, Inc, Redding, CA) for analysis in the instrument with a minimum powder amount of 50 mg. Measured saturation magnetic moment values normalized by sample mass were used to compare lignin mass fractions between the nanocomposite samples.

A Perkin-Elmer Lambda 900 UV-Vis/NIR spectrometer (Waltham, MA) was used to analyze methylene blue (MB) adsorption by the fabricated lignin@Fe₃O₄ nanocomposites at the different lignin to Fe₃O₄ mass ratios. A stock solution of 7.2×10^{-3} mg/mL MB was prepared, and a UV-Vis spectrum was collected. 3 mg of each lignin@Fe₃O₄ type were placed in a vial and combined with 3 mL of the stock MB solution, sonicated for 3 min. Next, the vial was placed beside a neodymium magnet (1.77 cm x 1.77 cm x 5.08 cm; Applied Magnets, Plano, TX) for 5 min to separate the lignin@Fe₃O₄ nanoparticles. The remaining solution was then removed via pipette and ran through UV-Vis to determine the amount of non-adsorbed MB. Each sample was run in triplicate, including the stock solution.

2.8. Statistical Analysis

Quantitative data are expressed as the mean \pm standard deviation/error of the mean and noted in figure captions for each experimental result. TGA and DLS data and methylene blue adsorption studies were analyzed using one-way analysis of variance (ANOVA) to confirm statistical difference. All data, and additional statistical tests, were processed using JMP Pro v.14 by the SAS Institute or OriginPro v.2020b by the OriginLab corporation.

3. Results and Discussion

3.1. Chemical characterization of lignin and lignin@Fe₃O₄ nanocomposites

The Fe₃O₄, kraft lignin, and the lignin@Fe₃O₄ nanocomposites were chemically characterized by ATR-FTIR, XRD, and XPS. For Fe₃O₄, the FTIR spectrum (**Figure 1A**) had two peaks, one at 3382 cm⁻¹ representative of -OH stretching and one at 1636 cm⁻¹, which indicated O-H scissoring. Compared to the original water spectra, the 3382 cm⁻¹ peak was red-shifted slightly while the 1636 cm⁻¹ was indicative of water interacting with a surface—generally an oxide group—and had been posited as water molecules forming hydrogen bonds to the Fe₃O₄.^[45,46] For the neat kraft lignin, the FTIR spectrum (**Figure 1A**) revealed several peaks in the 1750 cm⁻¹ to 1000 cm⁻¹ range. The peak identified at 1040 cm⁻¹ is associated with C-O deformation.^[47] The peak at 1120 cm⁻¹ was assigned to the aromatic C-H deformation. The peak at 1220 cm⁻¹ was identified as C-C, C-O, or C=O stretching.^[47] The peak at 1380 cm⁻¹ was attributed to C-C stretching.^[47,48] The peaks identified at 1450 cm⁻¹, 1510 cm⁻¹, 1590 cm⁻¹ corresponded to the C=C stretching of aromatic bonds, C-C stretching of aromatic bonds, and the aromatic vibrations, respectively.^[49] The peak at 1650 cm⁻¹ is representative of the conjugated carboxyl group, and the peak at 2950 cm⁻¹ is related to the stretching vibrations of C-H bonds.^[9,50]

The FTIR spectra of the lignin@Fe₃O₄ nanocomposites contained many of the same peaks as neat kraft lignin, confirming successful formation of the conjugate system. **Figure 1A** shows the lignin@Fe₃O₄ nanoparticles prepared at a 10:1 lignin:Fe₃O₄ mass ratio. As observed, there was a blueshift of ≈ 10 cm⁻¹ on the peak at 1650 cm⁻¹ for the lignin@Fe₃O₄. This shift was attributed to the hydrogen bonding between -OH groups on the Fe₃O₄ and the -OH groups on lignin.^[30,51] Due to the large number of interactions occurring within the lignin structure, this shift may be caused by structural changes within the lignin during the binding procedure, including π - π interactions.^[45,52] The peaks at 1120 cm⁻¹, 1380 cm⁻¹, and 1590 cm⁻¹ attributed

to the C-H deformation, C-C stretching, and aromatic vibrations, respectively, had a lower signal intensity for the lignin@Fe₃O₄. Note that few lignin peaks were found in the 1:1 mass ratio of lignin to Fe₃O₄ spectrum, which were in a closer agreement to the uncoated nanoparticle spectrum [Fig. S1A], consistent with the notion that less lignin coated the nanoparticles at this condition than at higher mass ratios. For all other samples, the IR peaks corresponding to lignin were observed. [SI; Fig. S1B and Table S2].

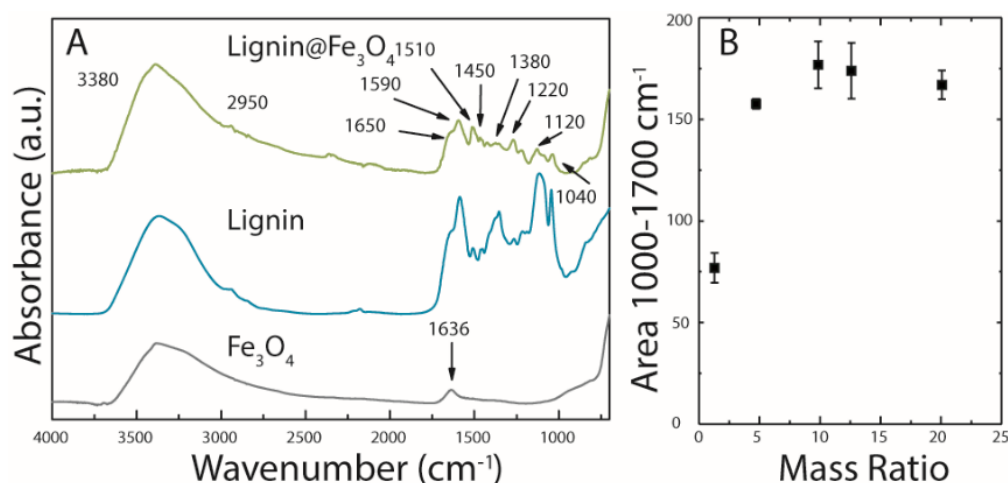


Figure 1. (A) ATR-FTIR spectra of Fe₃O₄, neat kraft lignin, and lignin@Fe₃O₄ nanocomposites prepared at a 10:1 lignin:Fe₃O₄ mass ratio. (B) Integrated absorbance in the 1000 cm⁻¹ to 1700 cm⁻¹ region for each lignin@Fe₃O₄ nanocomposites as a function of lignin to Fe₃O₄ mass ratio, normalized to the 3380 cm⁻¹ peak before integration. Results are the average +/- the standard error from triplicate measurements.

The signal intensity of the 1000 cm⁻¹ to 1700 cm⁻¹ region was integrated to represent the relative amount of lignin adsorption at the different mass ratios, as there are no reported contributions from the Fe₃O₄ surface in this region, and the results are shown in **Figure 1B**. The integrated absorbance exhibited logarithmic growth with increasing mass ratio, achieving saturation near the 5:1 mass ratio. The 10:1 had the highest absorbance ratio; however, no significant statistical differences were found for ratios greater than 5:1. Hence through FT-IR analysis, at or above this ratio, no differences were found on the highest achievable lignin content on the lignin@Fe₃O₄ nanocomposites.

XRD patterns for Fe₃O₄ were collected as a reference before adding any amount of the lignin. Primary Bragg reflections were identified at 2-theta of 30°, 35°, 43°, 53°, 57°, and 63°. The Miller indices were identified at these positions and are shown in **Figure 2**, (220), (311), (400), (422), (511), and (440), indicating that the structure is a face-centered cubic lattice. These results matched previous literature values on Fe₃O₄. [48,53–57] In addition, **Figure 2** shows XRD profiles for each of the lignin@Fe₃O₄ nanocomposites prepared at each mass ratio and compared to the uncoated Fe₃O₄ nanoparticles. These results showed no changes in composition of the Fe₃O₄ core upon the addition of the lignin coating. The average size of the neat Fe₃O₄ was 10.0 nm ± 1.9 nm, based on eqn. 1, for the Fe₃O₄, which is within range of reported crystallite sizes prepared using co-precipitation methods. [48,54,55,57] Note that the lignin@Fe₃O₄ nanocomposites had an initial increase in crystallite size at the 1:1 ratio of 16.2 nm ± 0.4 nm before converging near original crystallite size of 10.3 nm ± 0.8 nm by the 10:1 sample (**Fig. S2**). The increase of crystallite size at low lignin ratios (1:1 and 5:1) was likely due to lowered concentration of available kraft lignin capping agents during pH precipitation, resulting in a decreased ability to form a lignin coating, as previously discussed in the preparation of coated maghemite particles. [58]

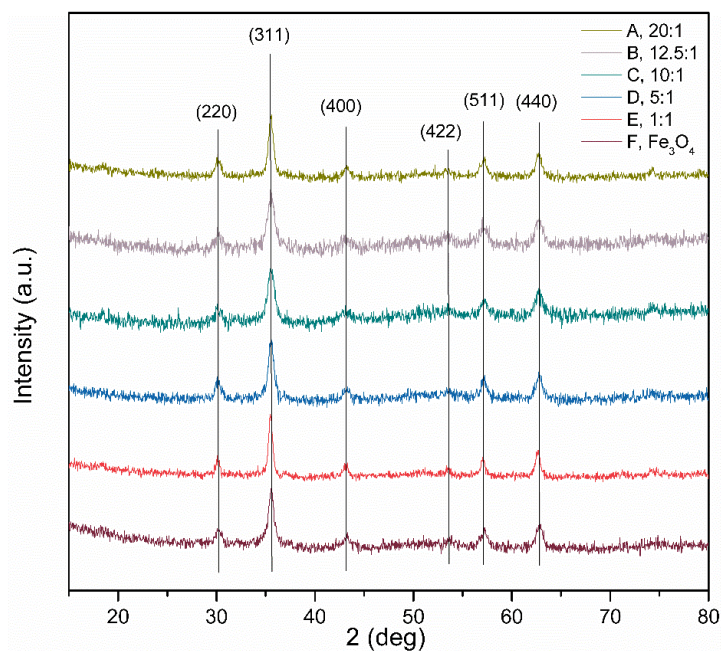


Figure 2. Normalized XRD spectra for the five mass ratios of lignin@Fe₃O₄ nanocomposites and neat Fe₃O₄, identifying the Miller indices and Bragg reflections. The lignin coating amount had a negligible impact on the Fe₃O₄ peaks. [Results are from one sample measurement]

XPS was employed to evaluate the relative elemental and chemical changes in the lignin@Fe₃O₄ nanocomposites as a function of mass ratio. **Figure 3** provides representative spectra from select lignin@Fe₃O₄ specimens (lignin:Fe₃O₄ = 0, 1, and 10; Fig. S3 for all mass ratios). The Fe 2p spectra had a peak maximum at 710.6 eV ± 0.2 eV (average and standard deviation of 24 Fe measurements) with an observable satellite feature between 718 eV and 719.5 eV. This line shape more closely resembled Fe₂O₃ than with Fe₃O₄, [59] suggesting that at least some oxidation of the nanoparticle occurred post-synthesis. Indeed, previous reports have shown that non-stoichiometric Fe₃O₄ also results in the appearance of the Fe³⁺ satellite due to the loss of the Fe²⁺ satellite from FeO. [44,60] The O 1s spectra were fit with three different oxygen features at 530.1 eV ± 0.0 eV (*O-1*: representative of the O-Fe peak), 531.2 eV ± 0.1 eV (*O-2*: attributed to both the nanoparticle and lignin), and 533.1 eV ± 0.1 eV (*O-3*: representative of O-C from lignin) (positions are the average and standard deviation of 5 lignin@Fe₃O₄ specimens; please see the SI for further analysis/fitting details). As is evident from **Figure 3**, *O-3* was

especially useful as it can be employed to monitor the adsorption of the lignin to the surface of the Fe₃O₄ nanoparticle surface. XPS results for the nanocomposites prepared in this work did not show evidence for a covalent bond between the kraft lignin and the Fe₃O₄ nanoparticles.

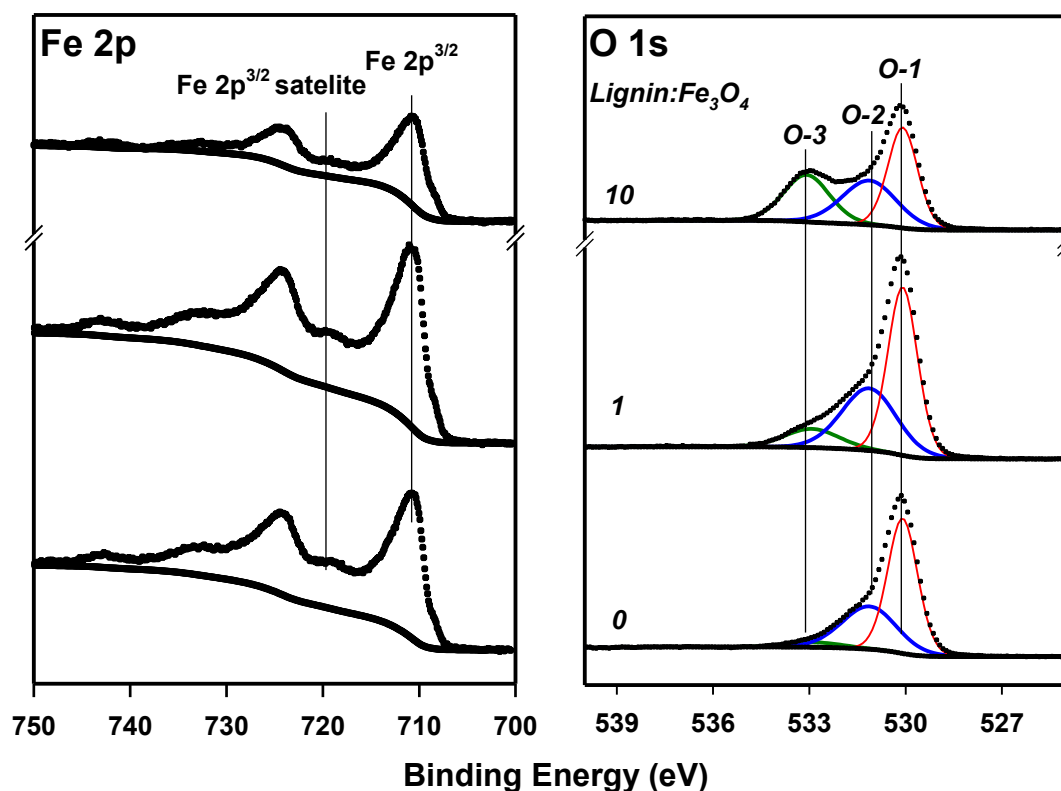


Figure 3. Representative stackplots for the Fe 2p region and the fitted O 1s region for the lignin@Fe₃O₄ at different lignin:Fe₃O₄ mass ratios. Number labels represent lignin:Fe₃O₄ ratios. (right) The spectra for O1s (black) is fitted with three curves: O-1 for Fe-O (red), O-2 for contributions from both Fe₃O₄ and lignin (blue), and O-3 for lignin contributions (green)

Figure 4A presents the surface elemental distribution as a function of lignin:Fe₃O₄ mass ratio. The Fe:O ratio decreased while the C:O ratio increased as a function of increased lignin:Fe₃O₄ mass ratio, confirming the lignin surface layer formation. At a lignin:Fe₃O₄ ratio of 5, the changes ceased and the carbon and iron levels reached a steady state. The distribution of surface oxygen functionality did change as initially shown in **Figure 3** and is plotted in **Figure**

4B. Consistent with the Fe and the C signals, the *O-1* (Fe) decreased and *O-3*- (lignin) increased with increasing lignin:Fe₃O₄ mass ratio, respectively. The *O-2* modifies only slightly with increasing mass ratio.

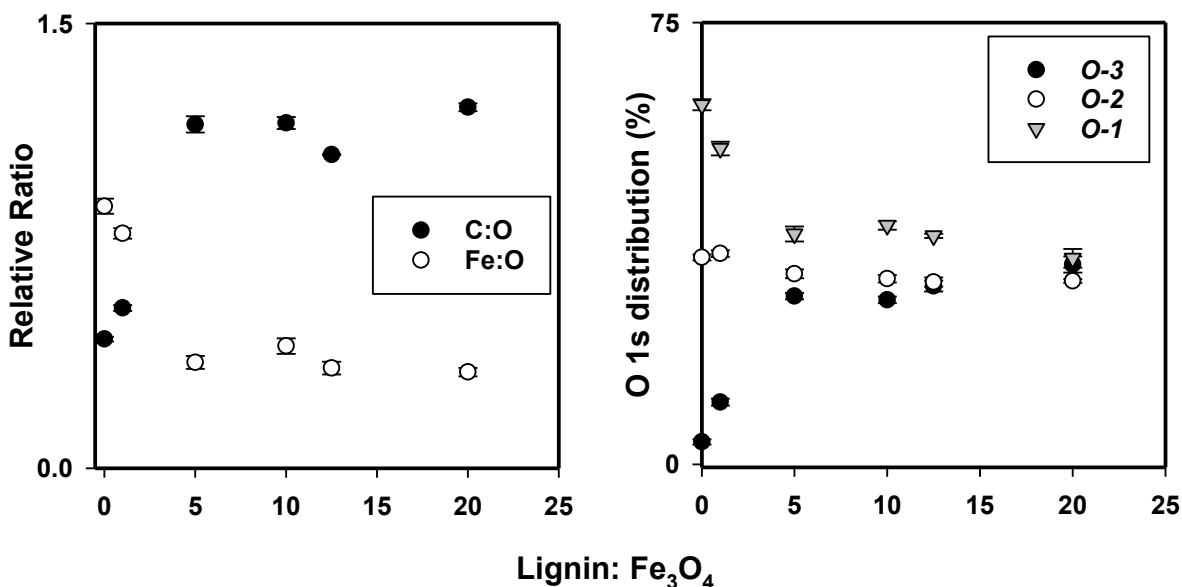


Figure 4. XPS relative ratios (semi-quantitative) (A), and distribution of O 1s functionality for O-Fe (*O-1*), O-C (*O-2*), and O-lignin (*O-3*) bonds observed in high-resolution scans (B). [Data is representative of the average ± 1 standard deviation of 4 spatially unique measurements of one sample]

3.2. Lignin content assessment in lignin@Fe₃O₄ nanocomposites

TGA analysis was utilized to determine bound lignin content and thermal stability of the lignin@Fe₃O₄ nanocomposites. **Figure 5A** shows the total percent weight loss for each of the nanocomposites prepared in this study. The lignin content on the fabricated nanocomposites was calculated using the weight percentage reported at 800 °C, as shown in **Equation S1**. **Figure 5A** displays the lignin content for each lignin:Fe₃O₄ mass ratio analyzed in this study, which varied between 5 % to 40 % [**Table S3** shows the calculated values]. An increase in the lignin content was observed as the lignin mass used in the preparation of the nanocomposites increased. In fact, at lignin:Fe₃O₄ mass ratios above 5:1, a one-way ANOVA fails at an $\alpha = 0.01$, suggesting that

differences above the 5:1 mass ratio are not statistically significant. The general trend of the average lignin content can be represented as a logarithmic function, which is a similar trend to the results obtained for the FTIR (**Fig. 1B**).

Figure 5B shows representative thermograms ran up to 850 °C. Moisture and residual solvent remained observed by the weight loss up to 120 °C. After this temperature, the mass losses were attributed exclusively to the lignin content. Fe₃O₄ was stable and shows negligible weight changes up to 850 °C. Lignin, however, had almost a 65 % weight loss at this temperature. Lignin@Fe₃O₄ nanocomposite had a lower weight loss with a similar trend compared to the neat lignin and Fe₃O₄ samples. For example, the 10:1 sample lost less than 30 % of the initial weight at 850 °C (**Figure 5B**), confirming improved thermal stability of the nanocomposites as compared to neat kraft lignin.

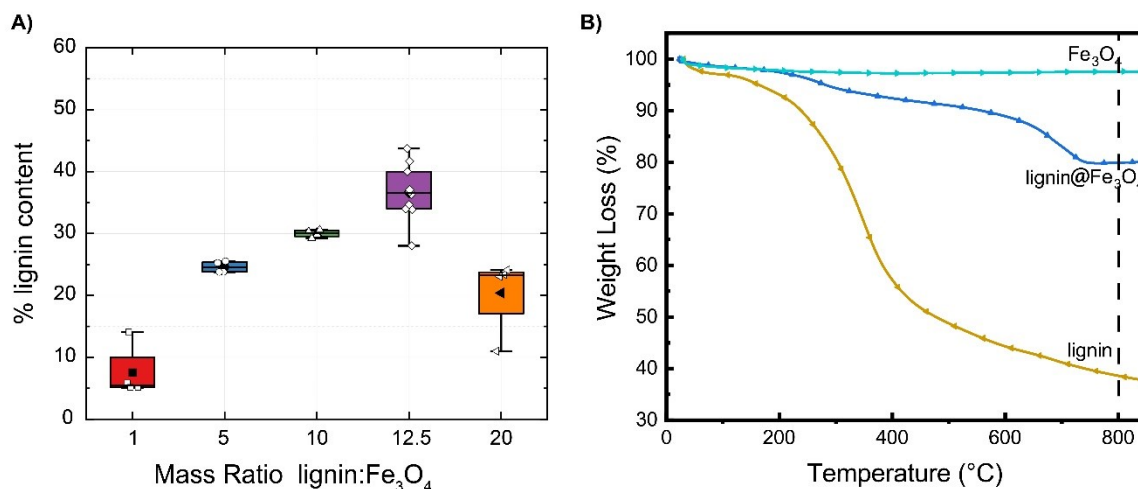


Figure 5. (A) lignin % content is shown for the various mass ratios of lignin@Fe₃O₄ nanocomposites. Average results of four samples are shown, each obtained in a different reaction (white dots), with the error bars representing one standard deviation. Figure B shows representative TGA data for Fe₃O₄, 10:1 lignin@Fe₃O₄, and as-received lignin, respectively.

3.3 Morphological properties and particle size of lignin@Fe₃O₄ nanocomposites

TEM aided in identifying the morphology of the lignin@Fe₃O₄ nanocomposites prepared at different mass ratios. **Figure 6** shows each prepared lignin@Fe₃O₄ nanocomposite and the bare Fe₃O₄ nanoparticles as a control. These micrographs indicated that the lignin encapsulated the Fe₃O₄ particles, and upon drying, formed aggregated clusters. Based on the TEM analysis, the average size of the magnetic nanoparticles was 18.0 nm ± 4.8 nm for all the lignin@Fe₃O₄ prepared at the different lignin:Fe₃O₄ mass ratios (**Fig. S4**), which is comparable to the obtained XRD results. Previous studies have shown that kraft lignin can cause agglomerates of lignin networks under alkaline conditions at low concentrations, resulting in fractal clusters,[11] consistent with this study. Aggregated structures were observed at low lignin concentrations for the 1:1 lignin:Fe₃O₄ nanocomposites (**Fig. 6B**). As the lignin:Fe₃O₄ ratio increased, less agglomerates and more evenly dispersed nanoparticles with multiple nanoparticles encapsulated within a lignin shell (light contrast in TEM images) were observed (**Figs. 6C-6E**). A thick coating of 7 nm to 14 nm was observed in the 10:1 and 12.5:1 samples (**Figs. 6D and 6E**) while a thin lignin corona layer (< 5 nm) was observed for the 20:1 sample, suggesting that a large presence of kraft lignin during the pH precipitation does not enhance the lignin coating thickness. These results confirmed the presence of lignin and indicated a unique heterogeneous, multicore structure for the lignin@Fe₃O₄ nanocomposites prepared in this work for samples prepared at a minimum of 5:1 ratio. [see **Figure S5** additional TEM images for each mass ratios].

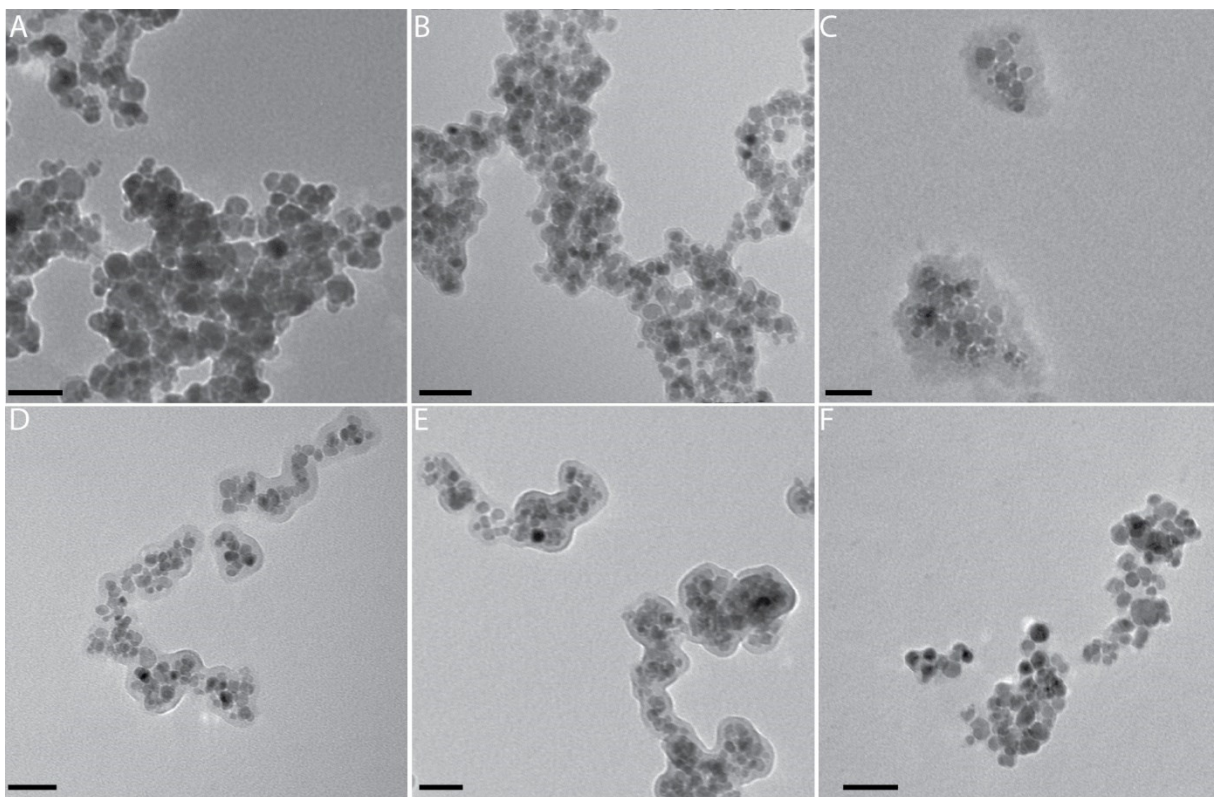


Figure 6. TEM images of lignin@Fe₃O₄ nanocomposites and Fe₃O₄ nanoparticles. A is pristine Fe₃O₄, B is 1:1, C is 5:1, D is 10:1, E is 12.5:1 and F is 20:1 mass ratio of lignin to Fe₃O₄, respectively. For all the lignin@Fe₃O₄ samples, a lignin coating (lighter structure) around multiple magnetic nanoparticles (darker spheres) is observed. [Scale bar represents 50 nm]

The average hydrodynamic diameter measured using DLS was obtained for each lignin@Fe₃O₄ nanocomposite suspended in water (**Figure S6A**). These results were used to determine if the reported particle size measured with DLS was affected from increasing the lignin:Fe₃O₄ mass ratios while suspended in water. Average hydrodynamic diameter was not consistent and varied from 129 nm to 182 nm. In addition, a multimodal intensity plot was obtained for the lignin@Fe₃O₄ nanocomposites hydrodynamic diameter measurements (**Fig S5B**). Possibly, this result could be due to the presence of heterogeneous nanostructures for the assembled nanoparticles. An additional comparison of the hydrodynamic diameter of the nanocomposites was performed using a Tukey test ($\alpha = 0.05$), revealing significant differences among the mean of most paired samples (**Fig. S7**). A one-way ANOVA test with an $\alpha = 0.05$

also confirmed that the means are significantly different. Despite these differences, the mean hydrodynamic diameter of each nanocomposite was stable, demonstrating that the lignin@Fe₃O₄ are suspended in water. TEM analysis revealed a multicore structure and the different diameters obtained through DLS for each nanocomposite can be attributed to the lignin content and assemblies in suspension, related to the fabrication and assembly process. ζ -potential measurements were performed to assess surface charge, showing a constant value for all lignin@Fe₃O₄ nanoparticles at *ca.* -30 mV (**Fig. S8**). This result was slightly higher to the ζ -potential of the neat Fe₃O₄ (-40 mV) and closer to the lignin ζ -potential (-30 mV).

3.4. Magnetic study and separation of Lignin@Fe₃O₄ nanocomposites from aqueous colloidal suspensions

Room temperature plots of the magnetic moment as a function of applied field M(H) measured with the SQUID instrument for neat Fe₃O₄ and various lignin:Fe₃O₄ mass ratios are shown in **Figure 7A**. Uncoated Fe₃O₄ exhibited typical magnetization curve similar to the results reported by other groups,[61] with low coercivity (<7958 A/m) and a saturation magnetization (M_s), of $\approx 64000 \text{ A}\cdot\text{m}^2/\text{kg}^2$ which is comparable to previous literature values between $50,000 \text{ A}\cdot\text{m}^2/\text{kg}^2$ to $72,000 \text{ A}\cdot\text{m}^2/\text{kg}^2$. [26,29,62] As the magnetic nanoparticles are coated with lignin, M_s decreases due to the polymer coating contributing to the mass of the sample. Based on the values of the saturation moment, the amount of lignin coating in the samples with different mass ratios can be compared. The 1:1 ratio of lignin@Fe₃O₄ nanocomposite had similar M(H) results to uncoated Fe₃O₄ indicating little to no coating on the Fe₃O₄ particles. The other lignin@Fe₃O₄ nanocomposites showed a decrease in M_s and are presumed to contain more lignin coating. Samples with mass ratios of 5:1, 10:1 and 20:1 have very similar magnetic saturation; (45300, 45200, and 46600) $\text{A}\cdot\text{m}^2/\text{kg}^2$ respectively, implying that the coating amounts are also similar

among these materials. These results showed a higher magnetization than other studies on lignin coated Fe₃O₄ that reported 15,000 A·m²/kg² to 40,000 A·m²/kg². [28,29] This magnetization study confirmed the lignin@Fe₃O₄ nanocomposites magnetic properties and further identified the lignin coating on the particles.

A preliminary adsorption test was performed using methylene blue (MB) and the prepared Lignin@Fe₃O₄ nanocomposites. UV-Vis absorbance was measured before and after the addition of the various ratios of lignin@Fe₃O₄ nanocomposites to determine the amount of MB adsorbed. [Table S4]. All lignin@Fe₃O₄ nanocomposites removed at least 55 % of the dye, demonstrating that these particles have the potential to be used as organic dye sorbents, which is consistent with the previous characterization results. For instance, the 1:1 lignin:Fe₃O₄ sample had a 55.6% ± 10.4 % adsorption efficiency. This removal efficiency increased, reaching values as high as 74.1% ± 7.1 % as the lignin:Fe₃O₄ content increased to 20:1. Variations in the adsorption efficiency also increased by increasing the mass ratio (**Figure 7B**).

The maximum MB amount removed was 12.53 mg/g, demonstrating the potential of lignin@Fe₃O₄ nanocomposites sorbents that can be separated under the presence of an external magnetic field. Average adsorption capacities for samples with a lignin content at 10:1 or higher do not show significant MB adsorption efficiency changes (<10%); but the difference between the 1:1 to 10:1 is greater than 10%. Under this preliminary adsorption test, a one-way ANOVA test fails at $\alpha = 0.05$, suggesting there is no conclusive evidence of an adsorption performance enhancement based on the means for the five analyzed lignin:Fe₃O₄ samples. Future efforts should focus on obtaining a complete understanding of the sorption kinetics and performance of the lignin@Fe₃O₄ magnetic nanocomposites prepared and characterized in this work for the removal of dyes or other compounds of interest.

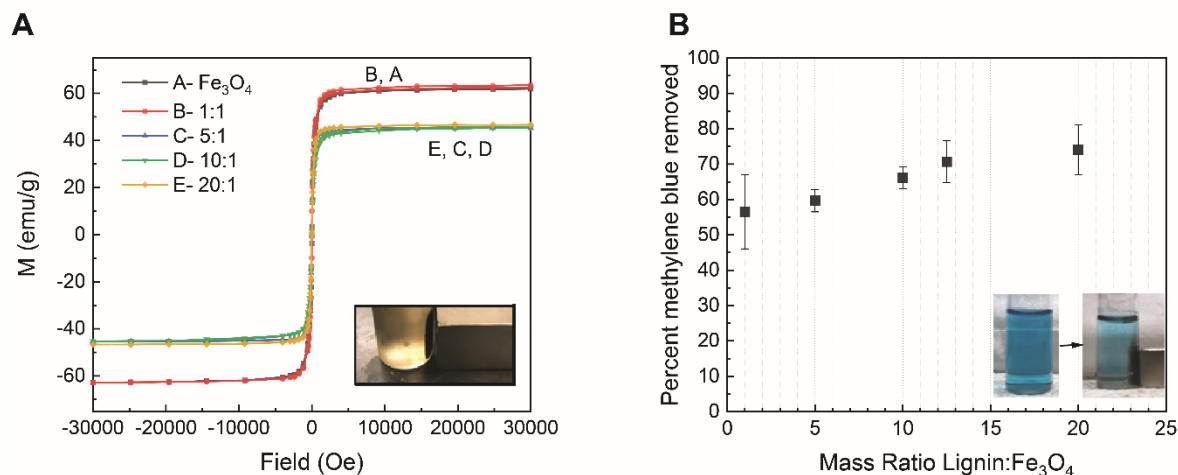


Figure 7. A) Magnetization measurements of lignin@Fe₃O₄ nanocomposites (lignin:Fe₃O₄) and neat Fe₃O₄ at 300K [inset shows the magnetic separation of 1:1 specimen in solution with the aid of an external magnet; results were obtained with a minimum of 50 mg for each sample]. B) Methylene Blue percent removed using lignin@Fe₃O₄ nanocomposites at the different lignin to Fe₃O₄ mass ratios [inset shows initial methylene blue solution and the 10:1 lignin:Fe₃O₄ sample added and separated with a strong magnet, demonstrating a visible color change in solution; reported values represent the average and standard deviation of three samples]

4. Conclusions

This work demonstrated a completely aqueous phase synthesis, based only on pH-driven precipitation, to prepare lignin@Fe₃O₄ nanocomposites using kraft lignin. We successfully demonstrated the formation of core-shell lignin@Fe₃O₄ nanostructures by TGA, FTIR, XPS, TEM, and SQUID for lignin:Fe₃O₄ mass ratios greater than 5. The nanocomposites possessed a well-defined heterogeneous, multicore magnetic structure where kraft lignin acts as a shell, and multiple Fe₃O₄ magnetic nanoparticles cluster together, forming the core. A thick lignin shell ranged between 7 nm to 14 nm based on the lignin to Fe₃O₄ mass ratio. At mass ratios of lignin to Fe₃O₄ greater than five, results showed a magnetic saturation value of approximately 45,000 A·m²/kg² and a maximum 74.1% ± 7.1% methylene blue adsorption efficiency. The inherent magnetic and adsorptive properties of lignin@Fe₃O₄ multicore nanostructures show potential in adsorption or chemical separation processes induced by low-strength, rare-earth magnets. Moreover, the demonstrated methodology eliminates the need to functionalize lignin or use

organic solvents to prepare nanocomposites. Ultimately, this pH-induced method can potentiate other nanomaterials encapsulation with a kraft lignin shell to fabricate numerous lignin-based nanocomposites.

Notes

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Authors' ORCID information

Erick S. Vasquez: 0000-0002-4811-6155

Justin M Gorham: 0000-0002-0569-297X

Esteban Ureña-Benavides: 0000-0002-5525-488X

CRedit authorship contribution statement

Frankie Petrie: Conceptualization, Investigation, Visualization, Formal analysis, Writing - Original Draft. **Justin Gorham:** Investigation, Formal analysis, Resources, Visualization, Writing - Review & Editing. **Robert Busch:** Investigation, Formal analysis, Data Curation, Visualization, Writing- Review & Editing. **Serhiy Leontsev:** Formal analysis, Writing-Review & Editing. **Esteban Ureña-Benavides:** Writing - Review & Editing, Funding acquisition. **Erick Vasquez:** Conceptualization, Formal analysis, Resources, Data Curation, Visualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Acknowledgment

The authors would like to acknowledge equipment access granted by the NEST center and the Chemistry Department at the University of Dayton, and access to the SQUID instrument in the Nanosystems Laboratory at The Ohio State University.

Funding Source

This research was funded by the National Science Foundation (CBET-1704897, CBET-1705331). Additional support for TEM access was provided by The School of Engineering at The University of Dayton.

Declaration of competing interest

None

Appendix A. Supplementary Information

Supplementary information to this article can be found online at XXXX.

REFERENCES

- [1] S. Gillet, M. Aguedo, L. Petitjean, A.R.C. Morais, A.M. Da Costa Lopes, R.M. Łukasik, P.T. Anastas, Lignin transformations for high value applications: Towards targeted modifications using green chemistry, *Green Chem.* 19 (2017) 4200–4233. <https://doi.org/10.1039/c7gc01479a>.
- [2] B. Wang, D. Sun, H.-M. Wang, T.-Q. Yuan, R.-C. Sun, Green and Facile Preparation of Regular Lignin Nanoparticles with High Yield and Their Natural Broad-Spectrum Sunscreens, (2018). <https://doi.org/10.1021/acssuschemeng.8b05735>.
- [3] S.M. Roopan, An overview of natural renewable bio-polymer lignin towards nano and biotechnological applications, *Int. J. Biol. Macromol.* 103 (2017) 508–514. <https://doi.org/10.1016/j.ijbiomac.2017.05.103>.
- [4] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, in: *Ind. Crops Prod.*, 2004. <https://doi.org/10.1016/j.indcrop.2004.04.016>.
- [5] G. Gellerstedt, Softwood kraft lignin: Raw material for the future, *Ind. Crops Prod.* 77 (2015) 845–854. <https://doi.org/10.1016/j.indcrop.2015.09.040>.
- [6] H. Wang, X. Qiu, W. Liu, F. Fu, D. Yang, A Novel Lignin/ZnO Hybrid Nanocomposite with Excellent UV-Absorption Ability and Its Application in Transparent Polyurethane Coating, *Ind. Eng. Chem. Res.* 56 (2017) 11133–11141. <https://doi.org/10.1021/acs.iecr.7b02425>.
- [7] A. Vishtal, A. Kraslawski, Challenges in industrial applications of technical lignins, *BioResources*. 6 (2011) 3547–3568. <https://doi.org/10.15376/biores.6.3.3547-3568>.
- [8] E.D. Bartzoka, H. Lange, K. Thiel, C. Crestini, Coordination Complexes and One-Step Assembly of Lignin for Versatile Nanocapsule Engineering, *ACS Sustain. Chem. Eng.* 4 (2016) 5194–5203. <https://doi.org/10.1021/acssuschemeng.6b00904>.
- [9] F. Xiong, Y. Han, S. Wang, G. Li, T. Qin, Y. Chen, F. Chu, Preparation and Formation Mechanism of Renewable Lignin Hollow Nanospheres with a Single Hole by Self-Assembly, *ACS Sustain. Chem. Eng.* 5 (2017) 2273–2281. <https://doi.org/10.1021/acssuschemeng.6b02585>.
- [10] T. Leskinen, J. Witos, J.J. Valle-Delgado, K. Lintinen, M. Kostianen, S.K. Wiedmer, M. Österberg, M.-L. Mattinen, Adsorption of Proteins on Colloidal Lignin Particles for

- Advanced Biomaterials, Biomacromolecules. 18 (2017) 2767–2776. <https://doi.org/10.1021/acs.biomac.7b00676>.
- [11] W. Zhao, B. Simmons, S. Singh, A. Ragauskas, G. Cheng, From lignin association to nano-/micro-particle preparation: extracting higher value of lignin, *Green Chem.* 18 (2016) 5693–5700. <https://doi.org/10.1039/C6GC01813K>.
- [12] M. Ago, B.L. Tardy, L. Wang, J. Guo, A. Khakalo, O.J. Rojas, Supramolecular assemblies of lignin into nano- and microparticles, *MRS Bull.* 42 (2017) 371–378. <https://doi.org/10.1557/mrs.2017.88>.
- [13] M.B. Agustin, P.A. Penttilä, M. Lahtinen, K.S. Mikkonen, Rapid and Direct Preparation of Lignin Nanoparticles from Alkaline Pulping Liquor by Mild Ultrasonication, *ACS Sustain. Chem. Eng.* 7 (2019) 19925–19934. <https://doi.org/10.1021/acssuschemeng.9b05445>.
- [14] Z.H. Liu, N. Hao, S. Shinde, M.L. Olson, S. Bhagia, J.R. Dunlap, K.C. Kao, X. Kang, A.J. Ragauskas, J.S. Yuan, Codesign of Combinatorial Organosolv Pretreatment (COP) and Lignin Nanoparticles (LNPs) in Biorefineries, *ACS Sustain. Chem. Eng.* 7 (2019) 2634–2647. <https://doi.org/10.1021/acssuschemeng.8b05715>.
- [15] H. Li, Y. Deng, B. Liu, Y. Ren, J. Liang, Y. Qian, X. Qiu, C. Li, D. Zheng, Preparation of Nanocapsules via the Self-Assembly of Kraft Lignin: A Totally Green Process with Renewable Resources, *ACS Sustain. Chem. Eng.* 4 (2016) 1946–1953. <https://doi.org/10.1021/acssuschemeng.5b01066>.
- [16] Supramolecular assemblies of lignin into nano- and microparticles, *MRS Bull.* 42 (2017) 371–378. <https://doi.org/10.1557/mrs.2017.88>.
- [17] Y. Pang, S. Wang, X. Qiu, Y. Luo, H. Lou, J. Huang, Preparation of Lignin/Sodium Dodecyl Sulfate Composite Nanoparticles and Their Application in Pickering Emulsion Template-Based Microencapsulation, *J. Agric. Food Chem.* 65 (2017) 11011–11019. <https://doi.org/10.1021/acs.jafc.7b03784>.
- [18] P.K. Mishra, A. Ekielski, A Simple Method to Synthesize Lignin Nanoparticles, *Colloids and Interfaces.* 3 (2019) 52. <https://doi.org/10.3390/colloids3020052>.
- [19] On the solution structure of kraft lignin in ethylene glycol and its implication for nanoparticle preparation, *Nanoscale Adv.* (2018). <https://doi.org/10.1039/C8NA00042E>.
- [20] F. Zikeli, V. Vinciguerra, S. Sennato, G. Scarascia Mugnozza, M. Romagnoli, Preparation of Lignin Nanoparticles with Entrapped Essential Oil as a Bio-Based Biocide Delivery System, *ACS Omega.* 5 (2020) 358–368. <https://doi.org/10.1021/acsomega.9b02793>.
- [21] Fabrication of Environmentally Biodegradable Lignin Nanoparticles, *ChemPhysChem.* 13 (2012) 4235–4243. <https://doi.org/10.1002/cphc.201200537>.
- [22] E.S. Vasquez, J.M. Feugang, S.T. Willard, P.L. Ryan, K.B. Walters, Bioluminescent magnetic nanoparticles as potential imaging agents for mammalian spermatozoa, *J. Nanobiotechnology.* 14 (2016) 1–9. <https://doi.org/10.1186/s12951-016-0168-y>.
- [23] A. Ali, H. Zafar, M. Zia, I. ul Haq, A.R. Phull, J.S. Ali, A. Hussain, Synthesis, characterization, applications, and challenges of iron oxide nanoparticles, *Nanotechnol. Sci. Appl.* Volume 9 (2016) 49–67. <https://doi.org/10.2147/NSA.S99986>.
- [24] W. Wu, Z. Wu, T. Yu, C. Jiang, W.-S. Kim, Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications., *Sci. Technol. Adv. Mater.* 16 (2015) 023501. <https://doi.org/10.1088/1468-6996/16/2/023501>.
- [25] R.J. Hickey, A.S. Haynes, J.M. Kikkawa, S.-J. Park, Controlling the Self-Assembly Structure of Magnetic Nanoparticles and Amphiphilic Block-Copolymers: From Micelles

- to Vesicles, *J. Am. Chem. Soc.* 133 (2011) 1517–1525. <https://doi.org/10.1021/ja1090113>.
- [26] J. Zdarta, K. Anteck, A. Jędrzak, K. Synoradzki, M. Łuczak, T. Jesionowski, Biopolymers conjugated with magnetite as support materials for trypsin immobilization and protein digestion, *Colloids Surfaces B Biointerfaces*. 169 (2018) 118–125. <https://doi.org/10.1016/J.COLSURFB.2018.05.018>.
- [27] Ł. Klapiszewski, K. Siwińska-Stefańska, D. Kołodyńska, Development of lignin based multifunctional hybrid materials for Cu(II) and Cd(II) removal from the aqueous system, *Chem. Eng. J.* 330 (2017) 518–530. <https://doi.org/10.1016/J.CEJ.2017.07.177>.
- [28] Y. Ma, D. Zheng, Z. Mo, R. Dong, X. Qiu, Magnetic lignin-based carbon nanoparticles and the adsorption for removal of methyl orange, *Colloids Surfaces A Physicochem. Eng. Asp.* 559 (2018) 226–234. <https://doi.org/10.1016/J.COLSURFA.2018.09.054>.
- [29] Ł. Klapiszewski, J. Zdarta, K. Anteck, K. Synoradzki, K. Siwińska-Stefańska, D. Moszyński, T. Jesionowski, Magnetite nanoparticles conjugated with lignin: A physicochemical and magnetic study, *Appl. Surf. Sci.* 422 (2017) 94–103. <https://doi.org/10.1016/J.APSUSC.2017.05.255>.
- [30] D. Kołodyńska, M. Gęca, I. V. Pylypchuk, Z. Hubicki, Development of New Effective Sorbents Based on Nanomagnetite, *Nanoscale Res. Lett.* 11 (2016) 152. <https://doi.org/10.1186/s11671-016-1371-3>.
- [31] B. Yu, A. Gele, L. Wang, Iron oxide/lignin-based hollow carbon nanofibers nanocomposite as an application electrode materials for supercapacitors, *Int. J. Biol. Macromol.* 118 (2018) 478–484. <https://doi.org/10.1016/J.IJBIOMAC.2018.06.088>.
- [32] A. Jędrzak, T. Rębiś, M. Kuznowicz, T. Jesionowski, Bio-inspired magnetite/lignin/polydopamine-glucose oxidase biosensing nanoplatfrom. From synthesis, via sensing assays to comparison with others glucose testing techniques, *Int. J. Biol. Macromol.* 127 (2019) 677–682. <https://doi.org/10.1016/j.ijbiomac.2019.02.008>.
- [33] T. Baran, I. Sargin, Green synthesis of a palladium nanocatalyst anchored on magnetic lignin-chitosan beads for synthesis of biaryls and aryl halide cyanation, *Int. J. Biol. Macromol.* 155 (2020) 814–822. <https://doi.org/10.1016/j.ijbiomac.2020.04.003>.
- [34] M. Nasrollahzadeh, N.S.S. Bidgoli, Z. Issaabadi, Z. Ghavamifar, T. Baran, R. Luque, Hibiscus Rosasinensis L. aqueous extract-assisted valorization of lignin: Preparation of magnetically reusable Pd NPs@Fe₃O₄-lignin for Cr(VI) reduction and Suzuki-Miyaura reaction in eco-friendly media, *Int. J. Biol. Macromol.* 148 (2020) 265–275. <https://doi.org/10.1016/j.ijbiomac.2020.01.107>.
- [35] X. Zhang, Y. Li, Y. Hou, Preparation of magnetic polyethylenimine lignin and its adsorption of Pb(II), *Int. J. Biol. Macromol.* 141 (2019) 1102–1110. <https://doi.org/10.1016/j.ijbiomac.2019.09.061>.
- [36] A. Hasan, P. Fatehi, Self-assembly of kraft lignin-acrylamide polymers, *Colloids Surfaces A Physicochem. Eng. Asp.* 572 (2019) 230–236. <https://doi.org/10.1016/j.colsurfa.2019.04.002>.
- [37] Development of New Effective Sorbents Based on Nanomagnetite, *Nanoscale Res. Lett.* 11 (2016) 152–161. <https://doi.org/10.1186/s11671-016-1371-3>.
- [38] X. Zhang, M. Yang, Q. Yuan, G. Cheng, Controlled Preparation of Corncob Lignin Nanoparticles and their Size-Dependent Antioxidant Properties: Toward High Value Utilization of Lignin, *ACS Sustain. Chem. Eng.* (2019). <https://doi.org/10.1021/acssuschemeng.9b03535>.

- [39] *,†,‡ Magnus Norgren, ‡ and Håkan Edlund, L. Wågberg‡, Aggregation of Lignin Derivatives under Alkaline Conditions. Kinetics and Aggregate Structure, (2002). <https://doi.org/10.1021/LA011627D>.
- [40] E. Melro, A. Filipe, D. Sousa, A.J.M. Valente, A. Romano, F.E. Antunes, B. Medronho, Dissolution of kraft lignin in alkaline solutions, *Int. J. Biol. Macromol.* 148 (2020) 688–695. <https://doi.org/10.1016/j.ijbiomac.2020.01.153>.
- [41] Multicore Assemblies Potentiate Magnetic Properties of Biomagnetic Nanoparticles, *Adv. Mater.* 23 (2011) 4793–4797. <https://doi.org/10.1002/adma.201102948>.
- [42] R. Massart, Preparation of aqueous magnetic liquids in alkaline and acidic media, *IEEE Trans. Magn.* 17 (1981) 1247–1248. <https://doi.org/10.1109/TMAG.1981.1061188>.
- [43] H. A. Al-Abadleh, V. H. Grassian, FT-IR Study of Water Adsorption on Aluminum Oxide Surfaces, *Langmuir.* 19 (2002) 341–347. <https://doi.org/10.1021/la026208a>.
- [44] T. Fujii, F.C. Voogt, T. Hibma, G.A. Sawatzky, *In situ* XPS Spectra of Nonstoichiometric Fe_{3-δ}O₄ (100) Films, *Surf. Sci. Spectra.* 6 (1999) 337–346. <https://doi.org/10.1116/1.1247938>.
- [45] M.S. Kent, J. Zeng, N. Rader, I.C. Avina, C.T. Simoes, C.K. Brenden, M.L. Busse, J. Watt, N.H. Giron, T.M. Alam, M.D. Allendorf, B.A. Simmons, N.S. Bell, K.L. Sale, Efficient conversion of lignin into a water-soluble polymer by a chelator-mediated Fenton reaction: optimization of H₂O₂ use and performance as a dispersant, *Green Chem.* 20 (2018) 3024–3037. <https://doi.org/10.1039/C7GC03459H>.
- [46] Q. Du, E. Freysz, Y.R. Shen, Surface Vibrational Spectroscopic Studies of Hydrogen Bonding and Hydrophobicity, *Science* (80-.). 264 (n.d.) 826–828. <https://doi.org/10.2307/2884027>.
- [47] W. Yang, E. Fortunati, D. Gao, G.M. Balestra, G. Giovanale, X. He, L. Torre, J.M. Kenny, D. Puglia, Valorization of Acid Isolated High Yield Lignin Nanoparticles as Innovative Antioxidant/Antimicrobial Organic Materials, *ACS Sustain. Chem. Eng.* 6 (2018) 3502–3514. <https://doi.org/10.1021/acssuschemeng.7b03782>.
- [48] M. Yamaura, R.. Camilo, L.. Sampaio, M.. Macêdo, M. Nakamura, H.. Toma, Preparation and characterization of (3-aminopropyl)triethoxysilane-coated magnetite nanoparticles, *J. Magn. Mater.* 279 (2004) 210–217. <https://doi.org/10.1016/J.JMMM.2004.01.094>.
- [49] Ł. Kłapiszewski, K. Siwińska-Stefańska, D. Kołodyńska, Preparation and characterization of novel TiO₂/lignin and TiO₂-SiO₂/lignin hybrids and their use as functional biosorbents for Pb(II), *Chem. Eng. J.* 314 (2017) 169–181. <https://doi.org/10.1016/J.CEJ.2016.12.114>.
- [50] M.I. Khalil, Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron(III) salts as precursors, *Arab. J. Chem.* 8 (2015) 279–284. <https://doi.org/10.1016/J.ARABJC.2015.02.008>.
- [51] C. Yuan, Z. Lou, W. Wang, L. Yang, Y. Li, Synthesis of Fe₃C@C from pyrolysis of Fe₃O₄-lignin clusters and its application for quick and sensitive detection of PrP^{Sc} through a sandwich SPR detection assay, *Int. J. Mol. Sci.* 20 (2019). <https://doi.org/10.3390/ijms20030741>.
- [52] P.K. Mishra, A. Ekielski, The Self-Assembly of Lignin and Its Application in Nanoparticle Synthesis: A Short Review, *Nanomaterials.* 9 (2019) 243. <https://doi.org/10.3390/nano9020243>.
- [53] J.M. Coey, *Magnetism and magnetic materials*, Cambridge University Press, 2010.
- [54] I. Martínez-Mera, M.E. Espinosa-Pesqueira, R. Pérez-Hernández, J. Arenas-Alatorre,

- Synthesis of magnetite (Fe₃O₄) nanoparticles without surfactants at room temperature, *Mater. Lett.* 61 (2007) 4447–4451. <https://doi.org/10.1016/J.MATLET.2007.02.018>.
- [55] M. Ma, Y. Zhang, W. Yu, H. Shen, H. Zhang, N. Gu, Preparation and characterization of magnetite nanoparticles coated by amino silane, *Colloids Surfaces A Physicochem. Eng. Asp.* 212 (2003) 219–226. [https://doi.org/10.1016/S0927-7757\(02\)00305-9](https://doi.org/10.1016/S0927-7757(02)00305-9).
- [56] Size-Controlled Synthesis of Magnetite Nanoparticles, *J. Am. Chem. Soc.* 124 (2002) 8204–8205. <https://doi.org/10.1021/ja026501x>.
- [57] H. Zhang, X. Zhong, J.-J. Xu, H.-Y. Chen, Fe₃O₄/Polypyrrole/Au Nanocomposites with Core/Shell/Shell Structure: Synthesis, Characterization, and Their Electrochemical Properties, *Langmuir.* 24 (2008) 13748–13752. <https://doi.org/10.1021/la8028935>.
- [58] A. Bee, R. Massart, S. Neveu, Synthesis of very fine maghemite particles, *J. Magn. Magn. Mater.* 149 (1995) 6–9. [https://doi.org/https://doi.org/10.1016/0304-8853\(95\)00317-7](https://doi.org/https://doi.org/10.1016/0304-8853(95)00317-7).
- [59] A.P. Grosvenor, B.A. Kobe, M.C. Biesinger, N.S. McIntyre, Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds, *Surf. Interface Anal.* 36 (2004) 1564–1574. <https://doi.org/10.1002/sia.1984>.
- [60] T. Fujii, F.M.F. de Groot, G.A. Sawatzky, F.C. Voogt, T. Hibma, K. Okada, *In situ* XPS analysis of various iron oxide films grown by NO₂-assisted molecular-beam epitaxy, *Phys. Rev. B.* 59 (1999) 3195–3202. <https://doi.org/10.1103/PhysRevB.59.3195>.
- [61] A. Gholizadeh, A comparative study of physical properties in Fe₃O₄ nanoparticles prepared by coprecipitation and citrate methods, *J. Am. Ceram. Soc.* 100 (2017) 3577–3588. <https://doi.org/10.1111/jace.14896>.
- [62] X. Li, Y. He, H. Sui, L. He, One-Step Fabrication of Dual Responsive Lignin Coated Fe₃O₄ Nanoparticles for Efficient Removal of Cationic and Anionic Dyes, *Nanomaterials.* 8 (2018) 162. <https://doi.org/10.3390/nano8030162>.