

Lignin Nano Material from Waste Biomass as Emulsification Stabilization Agent for Enhanced Oil Recovery

Thi Lieu Nguyen*, Thi Thu Thuy Bui, Thi Viet Ha Luu

Faculty of Chemical Engineering, Industrial University of Ho Chi Minh City, 12 Nguyen Van Bao, Hanh Thong ward, Ho Chi Minh City, Vietnam
nguyenthilieu@iuh.edu.vn

Emulsification plays a key role in enhanced oil recovery (EOR) by facilitating the mobilization of residual oil. In this study, lignin nanoparticles (LNPs) were rapidly and environmentally synthesized from rice straw via acidification combined with ultrasonication, yielding spherical particles with sizes of 80–200 nm and a zeta potential of approximately -40 mV. FTIR analysis confirmed that the lignin structure was preserved after nanoization, while surface activity and dispersibility were enhanced. SEM, DLS, and zeta-potential results demonstrated that the obtained LNPs possessed suitable physicochemical properties for stabilizing oil-in-water emulsions. At low concentrations, LNPs acted as effective Pickering stabilizers, producing emulsions with high stability and nearly constant viscosity for up to 31 days. Compared with cellulose nanoparticles, biosurfactants, and alkali-based LNPs, the proposed green and scalable method achieved superior emulsion stability, highlighting the potential of lignin nanomaterials as environmentally friendly emulsifier stabilizers for EOR and promoting the valorization of agricultural residues.

1. Introduction

For most oil fields in the world, after the primary and secondary exploitation stages, about two-thirds of the original crude oil remains trapped in the reservoir due to capillary forces within the pore spaces of the rock. Meanwhile, the discovery of new oil fields is becoming increasingly difficult and expensive, as they are often located in offshore regions or in areas with complex geological conditions, high temperatures, and high salinity. (Nguyen *et al.*, 2023). Enhanced Oil Recovery (EOR) is defined as a group of advanced recovery techniques implemented after primary and secondary production to mobilize the remaining oil trapped in reservoir pore spaces. Current methods for increasing oil production are encountering serious challenges, and the development of new technologies or materials to enhance efficient EOR in the future is an essential task.

In EOR methods, chemical injection is widely used to improve oil transfer efficiency by injecting polymers or surfactants into the reservoir to adjust water mobility (Marchetti and Stoller, 2019). However, polymers are susceptible to degradation under harsh conditions (e.g., high temperature and high salinity), whereas the application of surfactants is restricted by their high cost (Gbadamosi *et al.*, 2019). Therefore, there is an urgent need to find new emulsifying stabilizers that are resistant to salinity and temperature, cost-effective, and environmentally friendly (Stoller *et al.*, 2019). Emulsification is considered as one of the most important mechanisms in chemical injection. Previous studies have demonstrated that emulsification can significantly increase the amount of oil recovered from the reservoir. The key principle of this approach is the formation of a stable emulsion between the injected fluid and crude oil (Wojtowicz *et al.*, 2025). In recent years, bio-based emulsifiers have attracted increasing attention due to their low cost, biodegradability, and environmental friendliness, and they show promising potential for EOR (Wojtowicz *et al.*, 2025). However, most studies have focused on cellulose and hemicellulose, while lignin—the second most abundant natural polymer—remains underutilized. Although lignin is abundantly generated from agricultural residues and the pulp and paper industry, it is still largely burned for energy recovery, resulting in significant resource waste (Zhao *et al.*, 2025). Lignin contains both hydrophilic and hydrophobic molecular components and has been shown to have potential for the preparation of surfactants. Lignin-based polymeric surfactants have been applied in many fields as

efficient emulsifiers. However, in EOR, the application of lignin remains limited, being primarily used as an additive in drilling fluids owing to its antioxidant properties. Recently, advances in nanotechnology have enabled the conversion of lignin into lignin nanoparticles (LNPs), with advantages such as large surface area, high surface activity, good dispersibility, and potential for Pickering emulsions. (Shorey *et al.*, 2024). Various methods for synthesizing lignin nanoparticles (LNPs) have been reported, including both physical (e.g., ultrasonication) and chemical approaches. However, many existing methods still rely on organic solvents or harsh reaction conditions, which limit their scalability and raise environmental concerns (Wang *et al.*, 2023). In addition, although lignin-based materials have shown promise as emulsifiers, their application in EOR remains limited, and systematic studies on lignin-derived Pickering emulsions, particularly those prepared from agricultural residues, are still scarce. In this study, we report a green, simple, and scalable route for synthesizing lignin nanoparticles from rice straw, an abundant agricultural by-product, and demonstrate their application as Pickering emulsion stabilizers for enhanced oil recovery. Unlike most previous studies that focus on cellulose-based or chemically modified lignin systems, the present work utilizes unmodified lignin nanoparticles prepared under mild conditions and systematically evaluates their physicochemical properties, emulsion stability, and long-term performance relevant to EOR conditions. To the best of our knowledge, this is the first report on rice straw-derived lignin nanoparticles used as Pickering stabilizers for EOR, providing a low-cost, environmentally friendly alternative to conventional polymers and surfactants and contributing to the valorization of lignin toward sustainable oil recovery technologies.

2. Materials and Methods

2.1. Materials and Raw Material Preparation

Sulfuric acid (H₂SO₄, 98%), sodium hydroxide (NaOH, 99.5%), ethanol (99%), acetone (99%), Span 80, Tween 80, and kerosene were purchased from China and used as received. Bagasse, straw, and corn stalks were collected from households in Vietnam after harvest. The raw biomass was washed to remove dust and impurities, dried at 60 °C for 24 h, and then crushed and sieved through a 60-mesh screen to obtain uniform powders for lignin extraction.

2.2. Lignin extraction

Lignin was extracted from straw, bagasse, and corn stalks by alkali hydrolysis. 100 g of biomass was treated with 5% NaOH (1,000 mL) at room temperature for 48 h, followed by filtration. The filtrate was acidified with 5% H₂SO₄ to pH ≈ 2 to precipitate lignin, which was washed to neutrality and either dried at 100 °C for 4 h to determine yield (Xu *et al.*, 2013) or adjusted to 100 mL for LNP synthesis.

2.3. Nanolignin synthesis

The standardized crude lignin solution was divided into 20 mL aliquots and gently stirred for 5 min at room temperature to ensure homogeneity (Agustin *et al.*, 2019). The samples were then ultrasonicated at 30 kHz for 5 min, followed by magnetic stirring for 30 min, yielding lignin nanoparticles (LNPs) stably dispersed in water. The final volume was adjusted to 100 mL to obtain a 20% (w/v) LNP solution for subsequent experiments.

2.4. Preparation of LNP emulsions

The LNP emulsion was prepared at room temperature as an oil-in-water system. The aqueous phase contained distilled water, LNPs at the ratios listed in Table 1, and Tween 80, while the oil phase consisted of base oil and kerosene (1:2, w/w) with Span 80.

Table 1: Composition of emulsion samples with 10 wt% LNP.

No	1	2	3	4	5	6	7	8	9	10
Water (g)	90	80	70	60	50	40	30	20	10	0
LNPs 10%(g)	10	20	30	40	50	60	70	80	90	100
Concentration	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1

The oil phase was prepared by dissolving 0.84 g of Span 80 in 35 g of the oil mixture at 60 °C, and the aqueous phase by dissolving 2.16 g of Tween 80 in 100 g of LNP dispersion at 60 °C. The aqueous phase was then added to the oil phase under stirring, followed by ultrasonication and magnetic stirring for 10 min to obtain the LNP emulsion (Zhao *et al.*, 2025).

2.5. Physicochemical Characterization and Potential Application of Materials for Enhanced Oil Recovery

The chemical structure of LNPs was characterized by FT-IR (Equinox 55, Bruker, Germany) in the range of

4000–400 cm^{-1} . Surface morphology was examined by SEM (Hitachi S-4800, Japan). Emulsion droplet morphology was observed within 1 h after preparation using an optical microscope (Olympus BX53M, Japan). The hydrodynamic size and zeta potential of LNPs were measured by DLS (Horiba SZ-100, Japan) using a 2 $\text{mg}\cdot\text{mL}^{-1}$ dispersion prepared from a 20% (w/v) stock solution. Zeta potential was determined at 25 °C and 40 V. The long-term stability of LNPs and LNP-based emulsions was evaluated after 31 days of static storage through viscosity and zeta-potential measurements.

3. Results and discussion

3.1. Lignin recovery efficiency

The efficiency of lignin recovery from the raw materials was investigated. The amounts of lignin obtained from 100 g of raw materials (straw, bagasse, and corn stalks) are summarized in Table 2:

Table 2: Lignin recovery yield from three agricultural residues (bagasse, straw, and corn stalks)

Raw material	Run 1 (g)	Run 2 (g)	Run 3 (g)	Average (g)
Bagasse	12.16	13.2	11.6	12.32
straw	13.24	14.25	13.60	13.70
Corn stalks	9.60	10	9.20	9.45

Lignin recovery from the three agricultural residues followed the order rice straw > bagasse > corn stalks across all three replicates. Rice straw exhibited the highest recovery yield (13.2–14.3%), indicating a lignin-rich and promising feedstock for recovery studies. Moreover, in Vietnam, large amounts of rice straw generated from paddy production are often openly burned, leading to resource waste and environmental pollution. Bagasse showed intermediate yields (11.6–13.2%), whereas corn stalks gave the lowest (9.2–10.0%), likely due to their higher cellulose-to-lignin ratio. These results are consistent with previous reports (Zhao *et al.*, 2025). In addition, the variation among replicates was negligible, indicating good repeatability of the extraction process.

3.2. FT-IR spectra

FT-IR spectra of lignin isolated from bagasse, rice straw, and corn husk all exhibited the characteristic absorption bands of lignin (Figure 1). The broad band at $\sim 3425 \text{ cm}^{-1}$ is assigned to the stretching vibrations of phenolic and aliphatic hydroxyl (–OH) groups, whereas the band at $\sim 2900 \text{ cm}^{-1}$ corresponds to asymmetric aliphatic C–H stretching in methyl and methylene groups (Blindheim and Ruwoldt, 2023). The sharp band at $\sim 1600 \text{ cm}^{-1}$, characteristic of aromatic C=C stretching, is consistent with the aromatic ring structure of lignin. Additionally, the band at $1110\text{--}1114 \text{ cm}^{-1}$ is attributed to C–O stretching vibrations C–O (Zhao *et al.*, 2025). Comparison of the spectra showed that lignin from rice straw exhibited stronger band intensities—indicative of a higher lignin content and a greater proportion of syringyl (S) units—whereas lignin from sugarcane bagasse showed intermediate intensities with a clear contribution from guaiacyl (G) units, and lignin from corn displayed the lowest intensities, consistent with the lignin quantification reported in Section 3.1; these observations are also in line with previous reports, in which lignin from grass-derived residues typically shows higher S/G contributions, while lignin from corn stover tends to be lower. (Zhao *et al.*, 2025).

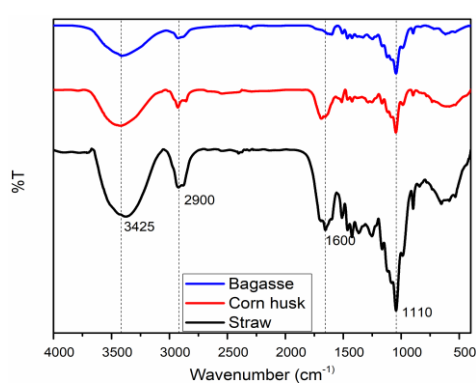


Figure 1: FT-IR spectra of lignin from straw, corn husk, and bagasse

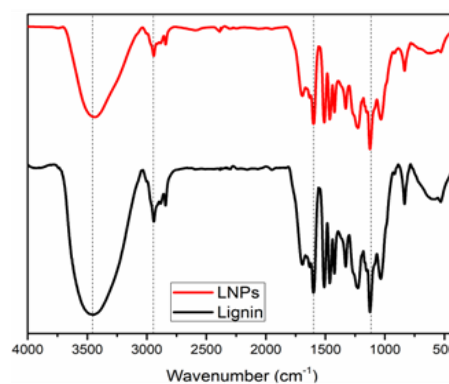


Figure 2: FT-IR spectra of lignin from straw and lignin nanoparticles (LNPs)

The FT-IR spectra of lignin and rice-straw-derived LNPs (Figure 2) showed similar characteristic lignin bands, with only slight blue shifts and minor intensity changes after ultrasonication, indicating that the overall chemical structure was preserved. Ultrasonication mainly modified surface properties and structural ordering without inducing oxidative changes, consistent with previous reports (Sun *et al.*, 2025). Based on these results and the extraction yields (Section 3.1), rice straw was selected for subsequent applications.

3.3. Scanning electron microscope (SEM) results

SEM images (Fig.3) show that bulk lignin exhibits a rough, irregular morphology with severe agglomeration and poor dispersion, whereas LNPs display near-spherical particles with a narrower size distribution in the nanometric range (~80–200 nm). The reduced particle size significantly increases the specific surface area, leading to improved dispersion and surface activity. (Ruffini *et al.*, 2025).

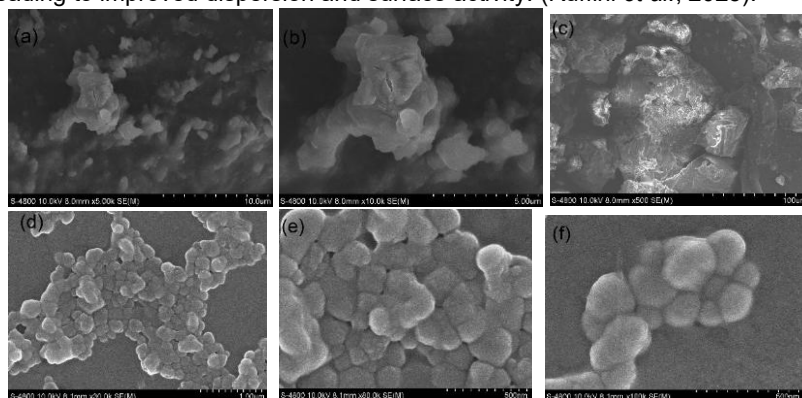


Figure 3: SEM images of lignin (a–c) and lignin nanoparticles (LNPs) (d–f).

3.4. DLS results and zeta potential of LNPs

The average hydrodynamic diameter of the LNPs, measured by dynamic light scattering (DLS), was ~206 nm with a polydispersity index (PDI) of 0.343 (Figure 4). This PDI indicates a moderately polydisperse system with a reasonably narrow size distribution, consistent with the SEM observations. Compared with the particle sizes observed in the SEM images (80–200 nm), the larger DLS-derived hydrodynamic diameter is expected owing to the solvated shell surrounding the particles and the intensity-weighted nature of DLS, which is more sensitive to larger particles. These results confirm that the nanoparticle-formation process converted bulk lignin into nanoparticles that disperse well in suspension (Perera, Foo and Chew, 2023).

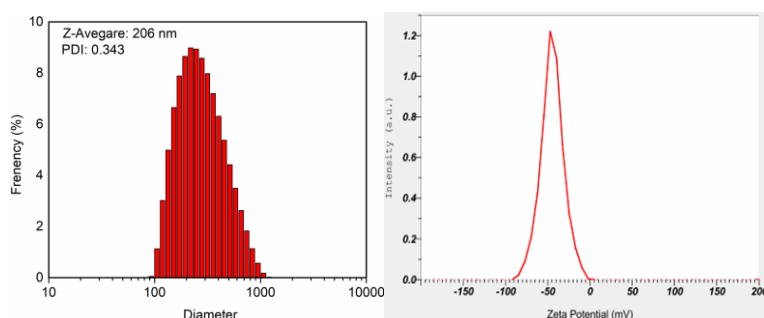


Figure 4: DLS results and zeta potential of LNPs

The zeta potential (ζ) of the LNP suspension was -40 mV, indicating a negatively charged surface arising from the ionization of phenolic and carboxylate groups in the lignin structure. The high absolute ζ -potential ($|\zeta| > 30$ mV) implies strong electrostatic repulsion between particles, conferring kinetic colloidal stability and consistent with the observed PDI value (Tian *et al.*, 2017). Taken together, the DLS and ζ -potential results confirm that the obtained LNPs form a stable, well-dispersed colloidal suspension of nanoscale particles.

Compared with previous reports on cellulose nanocrystals and biosurfactants (Dai *et al.*, 2021), the ζ -potential of our LNPs is markedly higher in absolute value, which contributes to superior electrostatic repulsion and dispersion stability. This indicates that LNPs can overcome the limitations of polymer- or surfactant-based

stabilizers that often suffer from aggregation or high production cost. Moreover, (Gao *et al.*, 2022) demonstrated that LNPs synthesized from alkali lignin maintained emulsion stability for only about 7–14 days. Stable emulsions were maintained for up to 31 days at optimized concentrations, demonstrating the effectiveness of the acid precipitation–ultrasonication route in producing well-dispersed LNPs. The enhanced stability is attributed to the uniform spherical morphology and abundant ionizable surface groups, which promote strong interfacial adsorption and steric stabilization. The superior emulsifying performance of rice-straw LNPs is further related to their higher syringyl-to-guaiacyl (S/G) ratio, leading to increased hydrophilicity and surface activity. Overall, these results highlight rice-straw-derived LNPs as promising green Pickering stabilizers for EOR, offering a sustainable alternative to conventional chemical additives.

3.5. Viscosity and microscopy characterization of lignin nanoemulsions

The viscosities of the oil-in-water (O/W) emulsions at different LNP concentrations at day 0 and day 31 are summarized in Table 3.

Table 3: Viscosity of O/W emulsions at different LNP concentrations at day 0 and day 31

Sample	1	2	3	4	5	6	7	8	9	10
Conc. (%)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
Viscosity(cP)	2.75	3.10	3.53	3.79	4.01	4.25	4.68	4.97	5.73	5.75
Viscosity after 31 days (cP)	2.73	3.05	3.49	3.70	4.01	4.05	4.56	4.8	5.70	5.71

Result shows that the viscosities of the LNP emulsions at different concentrations after 31 days changed little relative to the initial values. This indicates that the emulsions remained stable over a relatively long storage period.

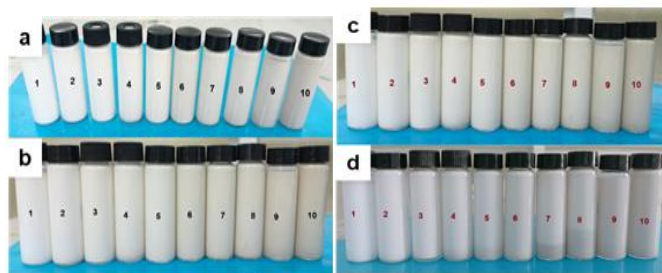


Figure 5: Appearance of the nanoemulsion at 0 (a), 7 (b), 21 (c), and 31 days (d).

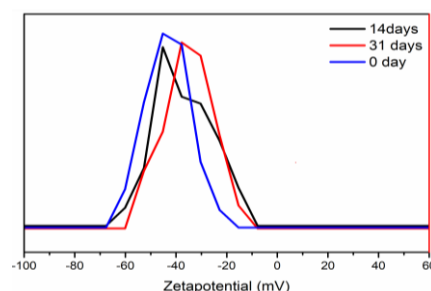


Figure 6: Zeta potential (ζ) of LNPs at 0, 15 and 31 days

Figure 5 shows the stability of oil–water emulsions stabilized by LNPs over 0, 7, 14, and 31 days. The emulsions remained homogeneous through day 14. By day 31, phase separation was observed, although some samples still retained partial stability. These results indicate that nanolignin can effectively stabilize oil–water emulsions over short to medium time scales (up to 14 days), while long-term stability (31 days) depends strongly on LNP concentration and interfacial particle distribution. This provides supporting evidence for the potential use of nanolignin as a natural Pickering stabilizer for EOR applications.

As shown in Figure 6, the ζ -potential remained strongly negative (-43 to -38.7 mV) over 31 days, confirming sustained electrostatic repulsion and good colloidal stability. Figure 7 presents optical micrographs of the oil-in-water LNP emulsions at different mass-percent concentrations at day 0 and day 31. The images show that increasing the LNP concentration leads to smaller droplet sizes and more uniform droplet populations. This trend is consistent with the strongly negative ζ -potentials observed in Figure 6, which promote electrostatic stabilization and limit coalescence. The emulsions retain relatively uniform droplet sizes and remain well dispersed across the field of view. After 31 days, the droplets are still stable with only minor changes, indicating excellent storage stability. These findings support further investigation of LNP-stabilized emulsions as natural Pickering stabilizers for EOR, for example in polymer flooding applications.

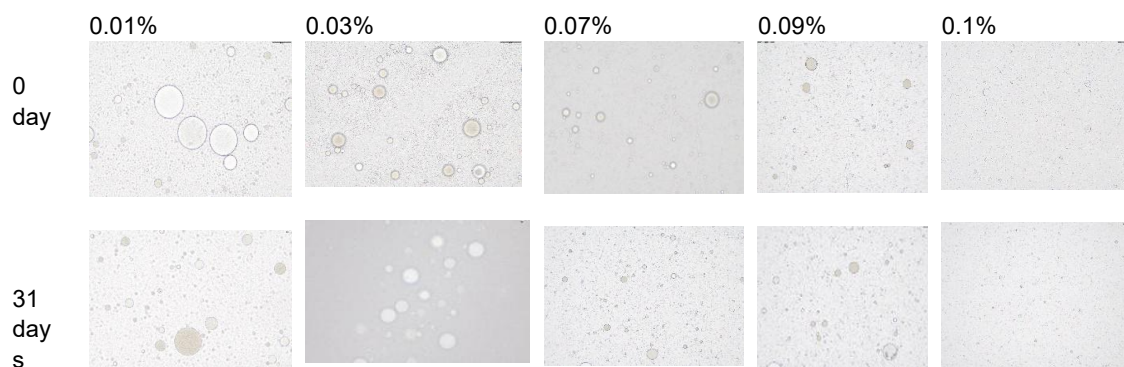


Figure 7: Spectroscopic micrographs of LNPs emulsion

4. Conclusion

This study presents a green, simple, and scalable method to produce lignin nanoparticles (LNPs) from agricultural by-products via acid precipitation coupled with ultrasonication. Rice straw afforded the highest lignin recovery yield 6.85%. The synthesized LNPs are spherical, with diameters of ~80–200 nm and exhibit good colloidal stability ($\zeta \approx -40$ mV). At low concentrations, LNPs act as Pickering stabilizers, forming oil-in-water emulsions that remain stable for up to 31 days. Over this period, the emulsions show nearly unchanged viscosity, strongly negative ζ -potentials, and relatively uniform droplet-size distributions. These findings support the potential application of LNPs as eco-friendly, low-cost, and effective emulsifier–stabilizers for EOR, while simultaneously promoting the valorization of agricultural by-products. Future work will evaluate the performance of LNPs in core-flooding experiments to validate their effectiveness under realistic reservoir conditions.

References

- Blindheim F.H., Ruwoldt J., 2023, The effect of sample preparation techniques on lignin Fourier Transform Infrared Spectroscopy, *Polymers*, 15(13), 2901.
- Dai H., Zhang H., Chen Y., Ma L., Wu J., Zhang Y., 2021, Co-stabilization and properties regulation of Pickering emulsions by cellulose nanocrystals and nanofibrils from lemon seeds, *Food Hydrocolloids*, 120, 106884.
- Gao K., Liu J., Li X., Gojzewski H., Sui X., Vancso G.J., 2022, Lignin nanoparticles as highly efficient, recyclable emulsifiers for enhanced oil recovery, *ACS Sustainable Chemistry and Engineering*, 10(29), 9334–9344.
- Gbadamosi A.O., Junin R., Manan M.A., Agi A., Yusuff., 2019, An overview of chemical enhanced oil recovery: recent advances and prospects, *International Nano Letters*, 9, 171–202.
- Marchetti a., Stoller M., 2019, On the micromixing behavior of a spinning disk reactor for metallic Cu nanoparticles production', *Applied Sciences*, 9(16).
- Perera U.P., Foo M.L., Chew M.L., 2023, Synthesis and characterization of lignin nanoparticles isolated from oil palm empty fruit bunch and application in biocomposites, *Sustainable Chemistry for Climate Action*, 2, 1.
- Ruffini E., Bellineto E., Turri S., Griffini G., 2025, Nanolignin by ultrasonication: Tuning the process for tailored materials characteristics, *ACS Omega*, 10(25), 27585–27597.
- Shorey R., Salaghi A., Fatehi P., Mekonnen T.H., 2024, Valorization of lignin for advanced material applications: a review, *RSC Sustainability*, 2, 804–831.
- Stoller M., Cheng K., Traore M., Marchetti A., Kanaev A., Chiavola A., 2019, Design of Novel Equipment Capable to Quickly Produce Efficient Nanomaterials for Use in Environmental and Sanitary Emergencies, *Chemical Engineering Transactions*, 173, 187-192.
- Sun Z., Liu Q., Li Y., Mazarji M., Feng L., Pan J., 2025, Deciphering the impact of lignin on anaerobic digestion: Focus on inhibition mechanisms and methods for alleviating inhibition, *ACS Omega*, 9, 44033-44041.
- Tian D., Hu J., Bao J., Chandra R.P., Saddler J.N., Lu C., 2017, Lignin valorization: Lignin nanoparticles as high-value bio-additive for multifunctional nanocomposites, *Biotechnology for Biofuels*, 10(1), 192.
- Wang L., Kang Y., Zhang W., Yang J., Li H., Niu M., Guo Y., Wang Z., 2023, Preparation of lignin-based nanoparticles with excellent acidic tolerance as stabilizer for Pickering emulsion, *Polymers*, 15(24), 4643.
- Wojtowicz K., Steliga T., Skalski T., Kapusta P., 2025, Influence of biosurfactants on the efficiency of petroleum hydrocarbons biodegradation in soil, *Sustainability*, 17(14), 6520.
- Zhao J., Zhu M., Jin W., Zhang J., Fan G., Feng Y., Li Z., Wang S., Lee J.S., Luan G., Dong Z., Li Y., 2025, A comprehensive review of unlocking the potential of lignin-derived biomaterials: From lignin structure to biomedical application, *Journal of Nanobiotechnology*, 23, 123.