PETRU PONI INSTITUTE OF MACROMOLECULAR CHEMISTRY

MACRO Iași 2021

LIGNIN AS SOURCE OF NEW HYBRID MATERIALS

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Introduction

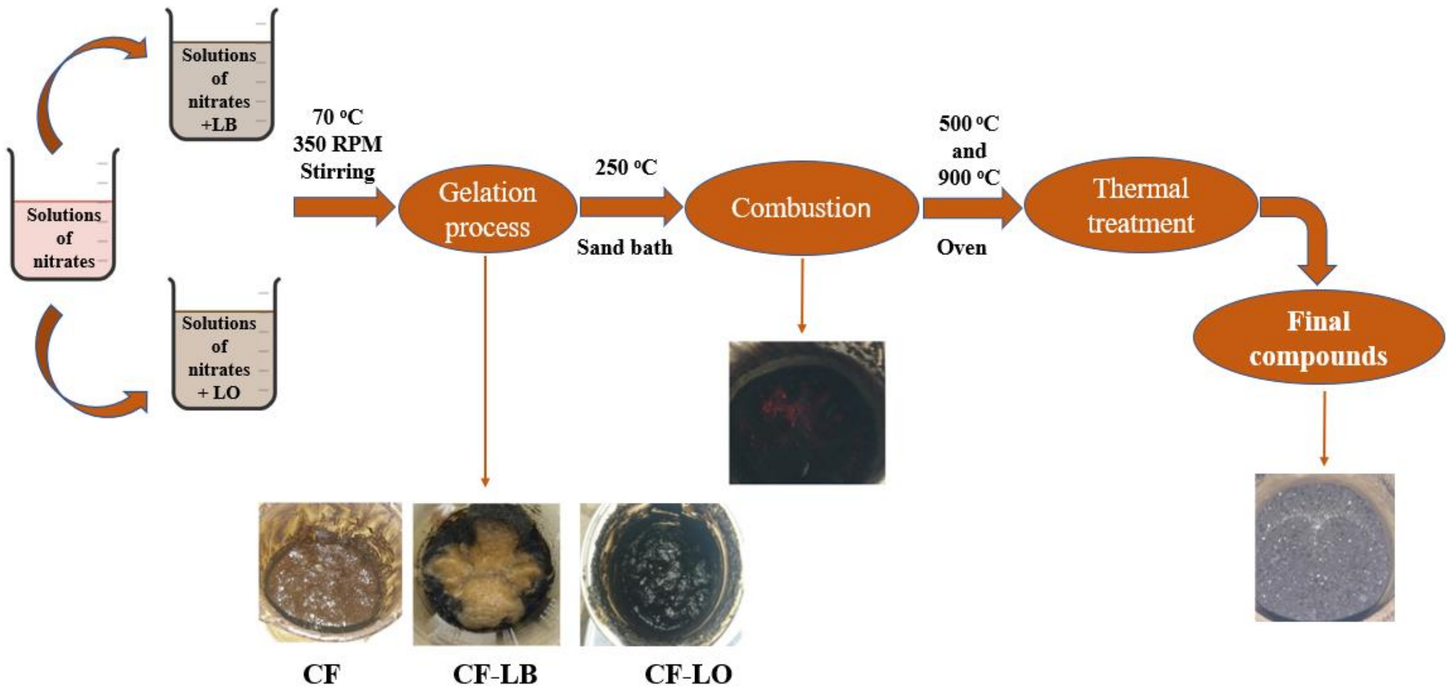
Lignin is a major constituent of lignocellulosic biomass. It mainly consists of three kind of phenylpropanoid units named p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), linked by different carbon-carbon and/or carbon-oxygen bonds[1]. The proportion of these monomers varies as a function of the biomass source[2]. The interest in lignin has increased due to the environmental needs to replace pollutant materials. Thus, lignin is already being used in different materials for biomedical applications[2], photocatalysis[3] or dye removal[4]. Cobalt ferrite ($CoFe_2O_4$) is one of the most studied spinel materials due to its properties (magnetism, chemical stability or electrical insulation) and it can be used to synthetize new hybrid/composite materials[5]. In this work, we have used Organosolv lignin (LO) and Lignoboost® lignin (LB) to prepare new cobalt ferrite-lignin hybrids.

Experimental

Synthesis: The hybrids materials were synthetized by sol-gel auto-combustion method. All the components of reaction system were dissolved in distilled water. The atomic ratio of the metal cation Co^{2+}: Fe^{3+} was 1:2 and the mass ratio for ferrite: lignin was 1:3, according to Scheme 1.

The samples were named according to the chelating/combustion agents used and the treatment temperatures, as follows: CF-LB500, CF-LB900, CF-LO500, and CF-LO900.

Characterization: The crystalline structure of synthesized hybrids was evaluated by XRD on a Rigaku Miniflex 600 diffractometer (Tokyo, Japan) in the angular range of 10–80° (2θ), using CuKα-emission. The phase assignment for each sample was verified using the whole-powder-pattern fitting calculation (Rietveld method) and the determined parameters were Rwp (weighted profile residual), S (structural parameter) and χ^2 (goodness of fit). XPS was performed on an Axis Nova device (Kratos Analytical, Manchester, UK),using AlKα radiation, with a 20 mA current and 15 kV voltage (300 W), and a base pressure of 10^{-8} to 10^{-9} Torr in the sample chamber. The measurements were performed to provide chemical state information on the materials.



Scheme 1. Schematic illustration of the $CoFe_2O_4$-lignin hybrids' obtainment

Results and discussion

XRD

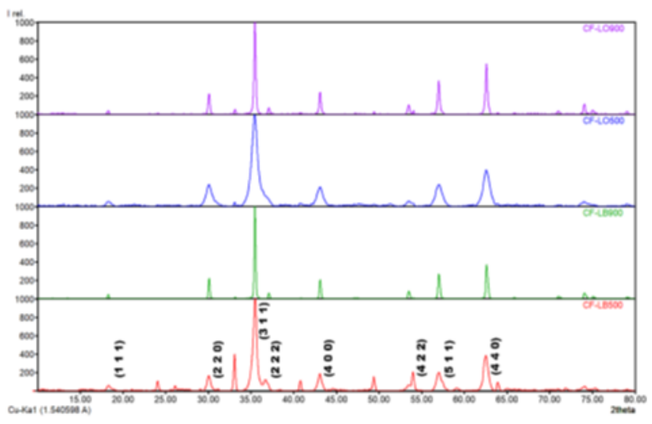


Figure 1. XRD spectra of lignin hybrids

The two-theta values confirm the hybrid formation with a spinel structure.

Crystallite size increased with the calcination temperature due to the variation in microstructure during thermal treatment.

The parameters indicative of the refinement effectiveness Rwp, S, and χ^2, were obtained for all the samples, showing a good fit between the measured and the calculated data.

Table 1. Statistical numeric indicators of the Rietveld method (Rwp, S and χ^2), the calculated lattice parameter (a) and unit cell volume (V)

Sample	Rwp (%)	S	χ^2	a (Å)	V (Å^3)	Crystallite size (Å)
CF-LB500	4.96	2.044	4.178	8.4104 ± 0.0018	594.914	119
CF-LB900	2.66	1.0920	1.1924	8.38490 ± 0.00017	589.514	615
CF-LO500	1.92	0.8064	0.6503	8.3816 ± 0.00010	588.827	76
CF-LO900	3.22	1.1147	1.2425	8.3858 ± 0.0003	589.708	332

Characterization

XPS

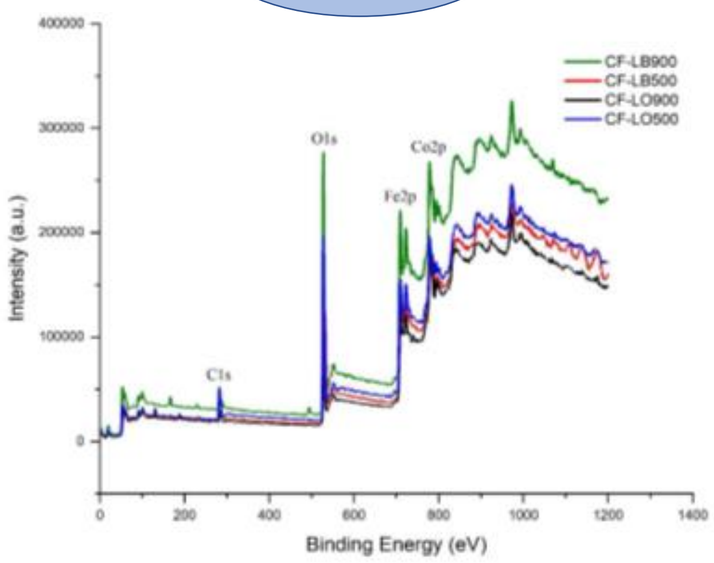


Figure 2. XPS spectra of $CoFe_2O_4$-lignin hybrids

The binding energies (780.1 eV, 710.7 eV, 529.8 eV, and 284.7 eV) are attributed to the core photoionization peaks of Co 2p, Fe 2p, O 1s, and C 1s, respectively, which represent a clear proof of successful synthesis of ferrite-lignin hybrids.

Peak at 284.7 eV is relative height and confirms that carbon is present in all materials.

Conclusions

New $CoFe_2O_4$ - lignin hybrids were synthetized by sol-gel combustion method, using lignin as chelating/combustion agent. The evaluation of the developed materials by XRD and XPS techniques evidenced the formation of hybrids with a spinel structure. The lignin needed for the designed hybrids is a by-product of the paper and pulp industry, which means that ferrite-lignin hybrids could be produced at a low cost, as compared with other synthesis routes.

References

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Acknowledgements

Irina Apostol thanks professor M.N. Palamaru, professor A.R. Iordan and PhD A.I. Borhan for the support provided during the process of obtaining $CoFe_2O_4$-lignin hybrids.