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## РЕАКЦИИ ЭЛЕКТРОФИЛЬНОГО И НУКЛЕОФИЛЬНОГО ЗАМЕЩЕНИЯ ЛИГНОСУЛЬФОНАТОВ КАК ОСНОВА ПЕРСПЕКТИВНЫХ НАПРАВЛЕНИЙ ПЕРЕРАБОТКИ ДРЕВЕСИНЫ

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*Несмотря на то, что lignosulfonates являются предметом исследования технологии производства целлюлозы, которая утрачивает свое ведущее место в общем списке производств волокнистой массы, достижения, связанные с использованием lignosulfonates, позволяют полностью вовлечь этот продукт в переработку.*

*Цель работы — анализ современных направлений модифицирования lignosulfonates с учетом их реакционной способности, обобщение перспектив расширения областей применения lignosulfonates и их производных.*

*Маркетинговый прогноз по промышленному использованию lignosulfonates показывает непрерывно увеличивающийся интерес к этому продукту. Некоторый спад публикаций с исследованиями, связанными с lignosulfonates, завершился примерно десять лет назад. Так как в основе lignosulfonates лежит фенилпропановая единица, то наиболее часто в способах модифицирования рассматриваются реакции замещения атомов водорода в ароматическом кольце. Сульфогруппа в lignosulfonates является достаточно прочно связанной с пропановой цепью и поэтому работ в этом направлении проводится значительно меньше. Еще одним реакционноспособным центром в молекуле lignosulfonates является фенольный гидроксил, водород которого способен вступать в реакции нуклеофильного замещения. В статье рассмотрена реакционная способность lignosulfonates в реакциях электрофильного и нуклеофильного замещения: нитрования, нитрозирования, сульфирования, галогенирования, ацилирования, меркурирования, окисиметилирования, азосочетания, карбоксиметилирования, оксипропилирования. Обсуждены экологические последствия применения lignosulfonates. Приведены многочисленные примеры применения lignosulfonates по новым направлениям в фармацевтике, производстве ионных жидкостей, суперконденсаторов, синтезе сополимеров, антикоррозионных присадок, пищевой упаковки, антипригаров.*

**Ключевые слова:** lignosulfonates, электрофильное и нуклеофильное замещение, нитрование, нитрозирование, сульфирование, галогенирование, ацилирование, меркурирование, окисиметилирование, азосочетание, карбоксиметилирование, оксипропилирование, производные lignosulfonates и их свойства.

## ELECTROPHILIC AND NUCLEOPHILIC SUBSTITUTION REACTIONS OF LIGNOSULFONATES AS THE BASIS FOR PROMISING DIRECTIONS FOR WOOD PROCESSING

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*Despite the fact that lignosulfonates are the subject of research in pulp production technology, which is*

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*losing its leading place in the general list of pulp production, advances associated with the use of lignosulfonates make it possible to fully involve this product in processing.*

*The aim of the work is the analysis of modern directions of lignosulfonates modification taking into account their reactivity, generalisation of perspectives of expansion of application areas of lignosulfonates and their derivatives.*

*The marketing forecast for the industrial use of lignosulfonates shows a continuously increasing interest in this product. The decline in lignosulfonate-related research publications ended approximately ten years ago. Since lignosulfonates are based on a phenylpropane unit, the modification methods most often involve substitution reactions of hydrogen atoms in the aromatic ring. The sulfonic group in lignosulfonates is quite tightly bound to the propane chain and therefore much less work is being done in this direction. Another reactive center in the lignosulfonate molecule is the phenolic hydroxyl hydrogen, which is capable of undergoing nucleophilic substitution reactions. The article examines the reactivity of lignosulfonates in reactions of electrophilic and nucleophilic substitution: nitration, nitrosation, sulfonation, halogenation, acylation, mercuration, oxymethylation, azo coupling, carboxymethylation, oxypropylation. The environmental consequences of the use of lignosulfonates are discussed. Numerous examples of the use of lignosulfonates in new areas in pharmacy, the production of ionic liquids, supercapacitors, the synthesis of copolymers, anti-corrosion additives, food packaging, and fire retardants are given.*

**Keywords:** lignosulfonates, electrophilic and nucleophilic substitution, nitration, nitrosation, sulfation, halogenation, acylation, mercuration, oxymethylation, azo-coupling, carboxymethylation, oxypropylation, lignosulfonate derivatives and their properties.

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#### Литература

- ИТС 1-2015. Информационно-технический справочник по наилучшим доступным технологиям. Производство целлюлозы, древесной массы, бумаги, картона. Введ. 2016-07-01. М. : Бюро НДТ, 2015. 479 с.
- Шорыгина Н. Н., Резников В. М., Елкин В. В. Реакционная способность лигнина. М. : Наука, 1976. 368 с.
- Hornof V., Homrek R. Surface-Active Agents Based on Propoxylated Lignosulfonate // Journal of Applied Polymer Science, 1990, vol. 41, pp. 2392–2398. doi: 10.1002/app.1990.070410939
- Wu L. C. F., Glasser W. G. Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin // Journal of Applied Polymer Science, 1984, vol. 29, is. 4, pp. 1111–1123. doi: 10.1002/app.1984.070290408

5. Alonso M. V., Rodriguez J. J., Oliet M., Rodriguez F., Garcia J., Gilarranz M. A. Characterization and Structural Modification of Ammonic Lignosulfonate by Methylolation // Journal of Applied Polymer Science, 2001, vol. 82, is. 11, pp. 2661–2668. doi: 10.1002/app.2119
6. Дудынов С. В. Теоретические принципы создания разжигителей для цементных систем // RuCEM. RU : интернет-журнал о цементе. 2020 [Электронный ресурс]. URL: <http://www.rucem.ru/staty/bgtu11.php> (дата обращения: 01.08.2020).
7. Базарнова Н. Г. Химические превращения древесины в реакциях О-алкилирования и этерификации : автореф. дис. док. хим. наук : 05.21.03. Красноярск, 1999. 40 с.
8. Chursin V. I. Synthesis and Use of Carboxymethylated Lignosulfonates // Russian Journal of Applied Chemistry, 2010, vol. 83, no. 2, pp. 312–315. doi: 10.1134/S1070427210020242
9. Ye D., Jiang X., Xia C., Liu L., Zhang X. Graft polymers of eucalyptus lignosulfonate calcium with acrylic acid: Synthesis and characterization // Carbohydrate Polymers, 2012, vol. 89, is. 3, pp. 876–882. doi: 10.1016/j.carbpol.2012.04.024
10. Patent US 4249606, IPC C09K8/90. Lignosulfonates carboxylated with carbon dioxide as additives in oil recovery processes involving. / G. Kalfoglou. N 91,427; Appl. 05.11.1979; Publ. 10.02.1981.
11. Гоготов А. Ф. Лужанская И. М. Азопроизводные лигнина. Применение реакции с солями диазония для исследования лигнина (обзор) // Химия растительного сырья. 2005. № 4. С. 5–24.
12. Галактионова Ю. А. Применение скрытых диазосоединений для крашения бумажной массы : дис. канд. техн. наук : 05.21.03. Красноярск, 2003. 101 с.
13. Li C., Pan Q., Zhang J., Qin X., Wang Z., Liu L. The Modification of Calcium Lignosulfonate and Its Applications in Cementitious Materials // Journal of Dispersion Science and Technology, 2007, vol. 28, is. 8, pp. 1205–1208. doi: 10.1080/01932690701669573
14. Mansouri N., Farriol X., Salvadó J. Structural Modification and Characterization of Lignosulfonate by a Reaction in an Alkaline Medium for Its Incorporation into Phenolic Resins // Journal of Applied Polymer Science, 2006, vol. 102, is. 4, pp. 3286–3292. doi: 10.1002/app.24744
15. Хабаров Ю. Г., Вешняков В. А., Кузяков Н. Ю. Получение и применение комплексов лигносульфоновых кислот с катионами железа // Известия высших учебных заведений. Лесной журнал. 2019. № 5. С. 167–187. doi: 10.17238/issn0536-1036.2019.5.167
16. Patent US 4488907, IPC C23F11/00. Process for the preparation of lignosulfonate-based mixtures used in particular as additives of concrete / V. Sarkkinen. N 538,909; Appl. 04.10.1983; Publ. 18.12.1984.
17. Khabarov Yu. G., Veshnyakov V. A., Komarova G., Kuzyakov N. Yu., Chukhchin D. Using Nitrated Lignosulfonates for the Synthesis of a Water-Based Magnetic Fluid // International Journal of Nanoscience, 2019, vol. 18, no. 2. doi: 10.1142/S0219581X18500187
18. Khabarov Yu. G., Veshnyakov V. A., Kuzyakov N. Yu., Onokhina N. A. Bioactive Properties of Iron-Nitrolignosulfonate Complexes with a Low Content of Ballast Ions // IOP Conference Series: Earth and Environmental Science, 2019, vol. 263. doi: /10.1088/1755-1315/263/1/012012
19. Patent US 5049661, IPC C08H6/00. Sulfonation of lignins / P. Dilling. N 298,677; Appl. 19.01.1989; Publ. 17.09.1991.
20. Кистер Э. Г. Химическая обработка буровых растворов. М. : Недра, 1972. 372 с.
21. Esterka F., Boríšek R. Vplyv ligninsulfonového komplexu na koloidné a reologické vlastnosti bentonitickej suspenzie // Chemické zvesti, 1956, vol. 10, no. 10, pp. 604–610.
22. Макарова Л. Г., Несмайнов А. Н. Методы элементоорганической химии. Ртуть. М. : Наука, 1965. 439 с.
23. Karbowska B., Rebiś T., Milczarek G. Mercury-modified Lignosulfonate-stabilized Gold Nanoparticles as an Alternative Material for Anodic Stripping Voltammetry of Thallium // Electroanalysis, 2017, vol. 29, is. 9. doi: 10.1002/elan.201700090
24. Chakrabarty K., Saha P., Ghoshal A. K. Simultaneous separation of mercury and lignosulfonate from aqueous solution using supported liquid membrane // Journal of Membrane Science, 2010, vol. 346, is. 1, pp. 37–44. doi: 10.1016/j.memsci.2009.09.010
25. Aro T., Fatehi P. Production and Application of Lignosulfonates and Sulfonated Lignin // ChemSusChem, 2017, vol. 10, is. 9, pp. 1861–1877. doi: 10.1002/cssc.201700082
26. Dailian Zhu, Cunqi Qin, Shanshi Ao, Mei Wang, Minghua Wu, Yaohong lü, Kemei Pei, Huagang Ni, Peng Ye. Hypercrosslinked functionalized lignosulfonates prepared via Friedel–Crafts alkylation reaction for enhancing Pb(II) removal from aqueous // Separation Science and Technology, 2019, vol. 54, is. 17, pp. 2830–2839. doi: 10.1080/01496395.2018.1554686
27. Li L., Hu Y. Preparation and characterization of acetylated lignosulfonate // Polymeric Materials Science and Engineering, 2015, vol. 31, is. 1, pp. 164–169.
28. Yanhua J., Weihong Q., Zongshi L., Lubai C. A Study on the Modified Lignosulfonate from Lignin // Energy Sources, 2004, vol. 26, is. 4, pp. 409–414. doi: 10.1080/00908310490281528
29. Wang Y., Zhu L., Wang X., Zheng W., Hao C., Jiang C., Wu J. Synthesis of aminated calcium lignosulfonate and its adsorption properties for azo dyes // Journal of Industrial and Engineering Chemistry, 2017, vol. 61, pp. 321–330. doi: 10.1016/j.jiec.2017.12.030
30. Сярки М. Т., Калинкина Н. М. Оценка влияния лигносульфоната натрия на состояние природных и лабораторных популяций ветвистоусых ракообразных // Биология внутренних вод. 2010. № 4. С. 80–86.
31. Du Plessis J. J. L., Janse van Rensburg L., Jansen van Rensburg L. P. Effectiveness of applying dust suppression palliatives on haul roads // Journal of the Mine Ventilation Society of South Africa, 2016, vol. 69, no. 2, pp. 15–19.
32. Adams J. W. Environmental effects of applying lignosulfonate to roads. 1988 [Электронный ресурс]. URL: <https://www.dustex.com.au/wp-content/uploads/2016/09/Environmental-Effects-of-Applying-Lignosulphonate-to-Roads.pdf> (дата обращения: 23.12.2022).
33. Gast R., Early J. Phytotoxicity of solvents and emulsifiers used in insecticide formulations // Agricultural Chemicals, 1956, vol. 11, is. 4, pp. 42–45, 136–137, 139.
34. Stapanian M., Shea D. Lignosulfonates: Effects on Plant Growth and Survival and Migration Through the Soil Profile // International Journal of Environmental Studies, 1986, vol. 27, is. 1–2, pp. 45–56. doi: 10.1080/00207238608710276
35. Хисматулина З. Н. Сущность, направление и роль окислительно-восстановительных реакций в биологии и медицине // Вестник Казанского технологического университета. 2011. № 19. С. 35–41.
36. Боголицын К. Г., Резников В. М. Химия сульфитных методов делигнификации древесины. М. : Экология, 1994. 288 с.
37. Patent WO 2012094838, IPC A61K31/185. Use and pharmaceutical composition of lignosulfonates / Z. Wu, Y. Chu, M. Qiu, Q. Wang, H. Song, Y. Sun, H. Jiang. N PCT/CN2011/070730; Appl. 28.01.2011; Publ. 19.07.2012.
38. Andrei G., Lisco A., Vanpouille C., Introini A., Balestra E., Oord J., Cihlar T., Perno C.-F., Snoeck R., Margolis L., Balzarini J. Topical tenofovir, a microbicide effective against HIV, inhibits herpes simplex virus-2 replication // Cell Host Microbe, 2011, vol. 10, is. 4, pp. 379–389. doi: 10.1016/j.chom.2011.08.015
39. Gordts S. C., Férim G., Dhuy T., I. Petrova M., Lebeer S., Snoeck R., Andrei G., Schols D. The Low-Cost Compound Lignosulfonic Acid (LA) Exhibits Broad-Spectrum Anti-HIV and Anti-HSV Activity and Has Potential for Microbicidal Applications // PLoS ONE, 2015, vol. 10, is. 7. doi: 10.1371/journal.pone.0131219
40. Qiu M., Wang Q., Chu Y., Yuan Z., Song H., Chen Z., Wu Z. Lignosulfonic acid exhibits broadly anti-HIV-1 activity-potential as a microbicide candidate for the prevention of HIV-1 sexual transmission // PLoS ONE, 2012, vol. 7, is. 4. doi: 10.1371/journal.pone.0035906
41. Raghuraman A., Tiwari V., Zhao Q., Shukla D., Debnath A. K., Desai U. R. Viral inhibition studies on sulfated lignin, a chemically

- modified biopolymer and a potential mimic of heparan sulfate // *Biomacromolecules*, 2007, vol. 8, no. 5, pp. 1759–1763. doi: 10.1021/bm0701651
42. Hasegawa Y., Kadota Y., Hasegawa C., Kawaminami S. Lignosulfonic acid-induced inhibition of intestinal glucose absorption // *Journal of Nutritional Science and Vitaminology*, 2015, vol. 61, is. 6, pp. 449–454. doi: 10.3177/jnsv.61.449
  43. Hasegawa Y., Nakagawa E., Kadota Y., Kawaminami S. Lignosulfonic acid promotes hypertrophy in 3T3-L1 cells without increasing lipid content and increases their 2-deoxyglucose uptake // *Asian-Australasian Journal of Animal Sciences*, 2017, vol. 30, is. 1, pp. 111–118. doi: 10.5713/ajas.16.0253
  44. Patent WO 024208. Compositions comprising lignin and methods of making and using the same / H. Alimi. Publ. date 28.03.2002.
  45. Ciesielczyk F., Żółtowska-Aksamitowska S., Jankowska K., Zembrzuska J., Zdarta J., Jesionowski T. The role of novel lignosulfonate based sorbent in a sorption mechanism of active pharmaceutical ingredient: batch adsorption tests and interaction study // *Adsorption*, 2019, vol. 25, is. 3, pp. 865–880. doi: 10.1007/s10450-019-00099-1
  46. Guterman R., Molinari V., Josef E. Ionic Liquid Lignosulfonate as a Dispersant and Binder for the Preparation of Biocomposite Materials // *Angewandte Chemie International Edition*, 2019, vol. 58, is. 37, pp. 13044–13050. doi: 10.1002/anie.2019073850
  47. Babkin I., Brovko O., Iakovlev M., Khabarov Y. Ferrofluid Synthesis Using Nitrosated Lignosulfonates // *Industrial & Engineering Chemistry Research*, 2013, vol. 52, is. 23, pp. 7746–7751. doi: 10.1021/ie400531f
  48. Fu F., Yang D., Zhang W., Wang H., Qiu X. Green self-assembly synthesis of porous lignin-derived carbon quasi-nanosheets for high-performance supercapacitors // *Chemical Engineering Journal*, 2020, vol. 392. doi: 10.1016/j.cej.2019.123721
  49. Pang J., Zhang W., Zhang J., Cao G., Han M., Yang Y. Facile and sustainable synthesis of sodium lignosulfonate derived hierarchical porous carbons for supercapacitors with high volumetric energy densities // *Green Chemistry*, 2017, vol. 19, is. 16, pp. 3916–3926. doi: 10.1039/C7GC01434A
  50. Lota G., Milczarek G. The effect of lignosulfonates as electrolyte additives on the electrochemical performance of supercapacitors // *Electrochemistry Communications*, 2011, vol. 13, is. 5, pp. 470–473. doi: 10.1016/j.elecom.2011.02.023
  51. Angelini S., Barrio A., Cerruti P., Scarinzi G., Garcia-Jaca J., Savy D., Piccolo A., Malinconico M. Lignosulfonates as Fire Retardants in Wood Flour-Based Particleboards // *International Journal of Polymer Science*, 2019, vol. 4. doi: 10.1155/2019/6178163
  52. Mandlikar N., Cayla A., Rault F., Giraud S., Salaün F., Guan J. Valorization of Industrial Lignin as Biobased Carbon Source in Fire Retardant System for Polyamide 11 Blends // *Polymers*, 2019, vol. 11, is. 1. doi: 10.3390/polym11010180
  53. Lu W., Li Q., Zhang Y., Yu H., Hirose Sh., Hatakeyama H., Matsumoto Y., Jin Zh. Lignosulfonate / APP IFR and its flame retardancy in lignosulfonate-based rigid polyurethane foams // *Journal of Wood Science*, 2018, vol. 64, is. 3, pp. 287–293. doi: 10.1007/s10086-018-1701-4
  54. Li P., Liu Ch., Xu Y.-J., Jiang Z.-M., Liu Y., Zhu P. Novel and eco-friendly flame-retardant cotton fabrics with lignosulfonate and chitosan through LbL: Flame retardancy, smoke suppression and flame-retardant mechanism // *Polymer Degradation and Stability*, 2020, vol. 181. doi: 10.1016/j.polymdegradstab.2020.109302
  55. Fu S., Li H., Liu H., Li X.-Y., Zhan H.-Y. Hydrophobic modification of pulp fiber surface via layer-by-layer self-assembly of lignosulfonates // *Journal of South China University of Technology*, 2010, vol. 38, is. 4, pp. 1–5. doi: 10.3969/j.issn.1000-565X.2010.04.001
  56. Komissarenkov A. A., Lukanina T. L. Use of lignosulfonates in newsprint paper production // *Russian Journal of General Chemistry*, 2012, vol. 82, no. 5, pp. 985–990. doi: 10.1134/s1070363212050325
  57. Ojagh S. M., Núñez-Flores R., López-Caballero M. E., Montero P., Gómez-Guillén M. C. Lessening of high-pressure-induced changes in Atlantic salmon muscle by the combined use of a fish gelatin-lignin film // *Food Chemistry*, 2011, vol. 125, is. 2, pp. 595–606. doi: 10.1016/j.foodchem.2010.08.072
  58. Núñez-Flores R., Giménez B., Fernández-Martín F., López-Caballero M. E., Montero P., Gómez-Guillén M. C. Role of lignosulphonate in properties of fish gelatin films // *Food Hydrocolloids*, 2012, vol. 27, is. 1, pp. 60–71. doi: 10.1016/j.foodhyd.2011.08.015
  59. Johansson K., Wineström S., Johansson C., Järnström L., Jönsson L. J. Oxygen-scavenging coatings and films based on lignosulfonates and laccase // *Journal of Biotechnology*, 2012, vol. 161, is. 1, pp. 14–18. doi: 10.1016/j.biote.2012.06.004
  60. Xia K., Ouyang Q., Chen Y., Wang X., Qian X., Wang L. Preparation and Characterization of Lignosulfonate-Acrylonitrile Copolymer as a Novel Carbon Fiber Precursor // *ACS Sustainable Chemistry & Engineering*, 2016, vol. 4, is. 1, pp. 159–168. doi: 10.1021/acssuschemeng.5b01442
  61. Brovko O., Palamarchuk I., Bogolitsyn K., Chukhchin D., Ivakhnov A., Valchuk N. Morphological features of aerogels and carbogels based on lignosulfonates // *Holzforschung*, 2017, vol. 71, is. 7–8, pp. 583–590. doi: 10.1515/hf-2016-0142
  62. Altwaiq A., Abdel-Rahem R., AlShamaileh E., Al-Juaibi S., Khouri S. Sodium lignosulfonate as a friendly-environment corrosion inhibitor for zinc metal in acidic media // *Eurasian Journal of Analytical Chemistry*, 2015, vol. 10, pp. 10–18.
  63. Ouyang X., Qiu X., Lou H., Yang D. Corrosion and Scale Inhibition Properties of Sodium Lignosulfonate and Its Potential Application in Recirculating Cooling Water System // *Industrial & Engineering Chemistry Research*, 2006, vol. 45, is. 16, pp. 5716–5721. doi: 10.1021/ie0513189
  64. Lin B., Zuo Y. Inhibition of Q235 Carbon Steel by Calcium Lignosulfonate and Sodium Molybdate in Carbonated Concrete Pore Solution // *Molecules*, 2019, vol. 24, is. 3. doi: 10.3390/molecules24030518

## References

1. ITS 1-2015. ITS 1-2015. Informatsionno-tehnicheskiy spravochnik po nailuchshim dostupnym tekhnologiyam. Proizvodstvo tsellyulozy, drevesnoy massy, bumagi, kartona [ITG 1-2015. Information and technical guide to the best available technologies. Production of pulp, wood pulp, paper, cardboard]. Moscow : Byuro NDT Publ., 2015. 479 p.
2. Shorygina N. N., Reznikov V. M., Elkin V. V. *Reaktsionnaya sposobnost' lignina* [Reactivity of lignin]. Moscow : Nauka Publ., 1976. 368 p.
3. Hornof V., Hombek R. Surface-Active Agents Based on Propoxylated Lignosulfonate. *Journal of Applied Polymer Science*, 1990, vol. 41, pp. 2392–2398. doi: 10.1002/app.1990.070410939
4. Wu L. C. F., Glasser W. G. Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin. *Journal of Applied Polymer Science*, 1984, vol. 29, is. 4, pp. 1111–1123. doi: 10.1002/app.1984.070290408
5. Alonso M. V., Rodríguez J. J., Oliet M., Rodríguez F., García J., Gilarranz M. A. Characterization and Structural Modification of Ammonic Lignosulfonate by Methylation. *Journal of Applied Polymer Science*, 2001, vol. 82, is. 11, pp. 2661–2668. doi: 10.1002/app.2119
6. Dudynov S. V. Teoreticheskie printsipy sozdaniya razzhizhiteley dlya tsementnykh sistem [Theoretical principles for the creation of thinners for cement systems] (2020). Available at: <http://www.rucem.ru/statyi/bgtu11.php> (accessed 01.08.2020).
7. Bazarnova N. G. Khimicheskie prevrashcheniya drevesiny v reaktsiyakh O-alkilirovaniya i eterifikatsii. Avtoref. diss. dokt. him. nauk [Chemical transformations of wood in the reactions of O-alkylation and esterification. Dr. chem. sci. diss. abstract]. Krasnoyarsk, 1999. 40

- P.
8. Chursin V. I. Synthesis and Use of Carboxymethylated Lignosulfonates. *Russian Journal of Applied Chemistry*, 2010, vol. 83, no. 2, pp. 312–315. doi: 10.1134/S1070427210020242
  9. Ye D., Jiang X., Xia C., Liu L., Zhang X. Graft polymers of eucalyptus lignosulfonate calcium with acrylic acid: Synthesis and characterization. *Carbohydrate Polymers*, 2012, vol. 89, is. 3, pp. 876–882. doi: 10.1016/j.carbpol.2012.04.024
  10. Kalfoglou G. Lignosulfonates carboxylated with carbon dioxide as additives in oil recovery processes involving. Patent US, no. 4249606, 1981.
  11. Gogotov A. F. Luzhanskaya I. M. Azoproizvodnye lignina. Primenenie reaktsii s solyami diazoniya dlya issledovaniya lignina (obzor) [Azo derivatives of lignin. Application of the reaction with diazonium salts to study lignin (Review)]. *Khimiya rastitel'nogo syr'ya* [Chemistry of plant raw materials], 2005, no. 4, pp. 5–24.
  12. Galaktionova Yu. A. Primenenie skrytykh diazosoderineniy dlya krasheniya bumazhnoy massy. Diss. kand. tehn. nauk [Application of Latent Diazo Compounds for Paper Pulp Dyeing. PhD eng. sci. diss.]. Krasnoyarsk, 2003. 101 p.
  13. Li C., Pan Q., Zhang J., Qin X., Wang Z., Liu L. The Modification of Calcium Lignosulfonate and Its Applications in Cementitious Materials. *Journal of Dispersion Science and Technology*, 2007, vol. 28, is. 8, pp. 1205–1208. doi: 10.1080/01932690701669573
  14. Mansouri N., Farriol X., Salvadó J. Structural Modification and Characterization of Lignosulfonate by a Reaction in an Alkaline Medium for Its Incorporation into Phenolic Resins. *Journal of Applied Polymer Science*, 2006, vol. 102, is. 4, pp. 3286–3292. doi: 10.1002/app.24744
  15. Khabarov Yu. G., Veshnyakov V. A., Kuzyakov N. Yu. Poluchenie i primenenie kompleksov lignosulfonovykh kislot s kationami zheleza [Preparation and application of complexes of lignosulfonic acids with iron cations]. *Izvestiya vysshikh uchebnykh zavedeniy. Lesnoy zhurnal* [News of higher educational institutions. Russian forestry journal], 2019, no. 5, pp. 167–187. doi: 10.17238/issn0536-1036.2019.5.167
  16. Sarkkinen V. Process for the preparation of lignosulfonate-based mixtures used in particular as additives of concrete. Patent US, no. 4488907, 1984.
  17. Khabarov Yu. G., Veshnyakov V. A., Komarova G., Kuzyakov N. Yu., Chukhchin D. Using Nitrated Lignosulfonates for the Synthesis of a Water-Based Magnetic Fluid. *International Journal of Nanoscience*, 2019, vol. 18, no. 2. doi: 10.1142/S0219581X18500187
  18. Khabarov Yu. G., Veshnyakov V. A., Kuzyakov N. Yu., Onokhina N. A. Bioactive Properties of Iron-Nitrolignosulfonate Complexes with a Low Content of Ballast Ions. *IOP Conference Series: Earth and Environmental Science*, 2019, vol. 263. doi: /10.1088/1755-1315/263/1/012012
  19. Dilling P. Sulfonation of lignins. Patent US, no. 5049661, 1991.
  20. Kister E. G. *Khimicheskaya obrabotka burovykh rastvorov* [Chemical treatment of drilling fluids]. Moscow : Nedra Publ., 1972. 372 p.
  21. Esterka F., Boríšek R. Vplyv lignínsulfónového komplexu na koloidné a reologické vlastnosti bentonitickej suspenzie. *Chemické zvesti*, 1956, vol. 10, no. 10, pp. 604–610.
  22. Makarova L. G., Nesmeyanov A. N. *Metody elementoorganicheskoy khimii. Rtut'* [Methods of organoelement chemistry. Mercury]. Moscow : Nauka Publ., 1965. 439 p.
  23. Karbowska B., Rębiś T., Milczarek G. Mercury-modified Lignosulfonate-stabilized Gold Nanoparticles as an Alternative Material for Anodic Stripping Voltammetry of Thallium. *Electroanalysis*, 2017, vol. 29, is. 9. doi: 10.1002/elan.201700090
  24. Chakrabarty K., Saha P., Ghoshal A. K. Simultaneous separation of mercury and lignosulfonate from aqueous solution using supported liquid membrane. *Journal of Membrane Science*, 2010, vol. 346, is. 1, pp. 37–44. doi: 10.1016/j.memsci.2009.09.010
  25. Aro T., Fatehi P. Production and Application of Lignosulfonates and Sulfonated Lignin. *ChemSusChem*, 2017, vol. 10, is. 9, pp. 1861–1877. doi: 10.1002/cssc.201700082
  26. Dailian Zhu, Cunqi Qin, Shanshi Ao, Mei Wang, Minghua Wu, Yaohong lü, Kemei Pei, Huagang Ni, Peng Ye. Hypercrosslinked functionalized lignosulfonates prepared via Friedel–Crafts alkylation reaction for enhancing Pb(II) removal from aqueous. *Separation Science and Technology*, 2019, vol. 54, is. 17, pp. 2830–2839. doi: 10.1080/01496395.2018.1554686
  27. Li L., Hu Y. Preparation and characterization of acetylated lignosulfonate. *Polymeric Materials Science and Engineering*, 2015, vol. 31, is. 1, pp. 164–169.
  28. Yanhua J., Weihong Q., Zongshi L., Lubai C. A Study on the Modified Lignosulfonate from Lignin. *Energy Sources*, 2004, vol. 26, is. 4, pp. 409–414. doi: 10.1080/00908310490281528
  29. Wang Y., Zhu L., Wang X., Zheng W., Hao C., Jiang C., Wu J. Synthesis of aminated calcium lignosulfonate and its adsorption properties for azo dyes. *Journal of Industrial and Engineering Chemistry*, 2017, vol. 61, pp. 321–330. doi: 10.1016/j.jiec.2017.12.030
  30. Syarki M. T., Kalinkina N. M. Otsenka vliyanija lignosulfonatov natriya na sostoyanie prirodnykh i laboratornykh populyatsiy vetyvistousykh rakoobraznykh [Evaluation of the effect of sodium lignosulfonates on the state of natural and laboratory populations of crustaceans]. *Biologiya vnutrennikh vod* [Biology of inland waters], 2010, no. 4, pp. 80–86.
  31. Du Plessis J. J. L., Janse van Rensburg L., Jansen van Rensburg L. P. Effectiveness of applying dust suppression palliatives on haul roads. *Journal of the Mine Ventilation Society of South Africa*, 2016, vol. 69, no. 2, pp. 15–19.
  32. Adams J. W. Environmental effects of applying lignosulfonate to roads (1988). Available at: <https://www.dustex.com.au/wp-content/uploads/2016/09/Environmental-Effects-of-Applying-Lignosulphonate-to-Roads.pdf> (accessed 23.12.2022).
  33. Gast R., Early J. Phytotoxicity of solvents and emulsifiers used in insecticide formulations. *Agricultural Chemicals*, 1956, vol. 11, is. 4, pp. 42–45, 136–137, 139.
  34. Stapanian M., Shea D. Lignosulfonates: Effects on Plant Growth and Survival and Migration Through the Soil Profile. *International Journal of Environmental Studies*, 1986, vol. 27, is. 1-2, pp. 45–56. doi: 10.1080/00207238608710276
  35. Khismatullina Z. N. Sushchnost', napravlenie i rol' okislitel'no-vosstanovitel'nykh reaktsiy v biologii i meditsine [Essence, direction and role of redox reactions in biology and medicine]. *Vestnik Kazanskogo tekhnologicheskogo universiteta* [Bulletin of Kazan Technological University], 2011, no. 19, pp. 35–41.
  36. Bogolitsyn K. G., Reznikov V. M. *Khimiya sul'fitnykh metodov delignifikatsii drevesiny* [Chemistry of sulfite methods of wood delignification]. Moscow : Ekologiya Publ., 1994. 288 p.
  37. Wu Z., Chu Y., Qiu M., Wang Q., Song H., Sun Y., Jiang H. Use and pharmaceutical composition of lignosulfonates. Patent WO, no. 2012094838, 2012.
  38. Andrei G., Lisco A., Vanpouille C., Introini A., Balestra E., Oord J., Cihlar T., Perno C.-F., Snoeck R., Margolis L., Balzarini J. Topical tenofovir, a microbicide effective against HIV, inhibits herpes simplex virus-2 replication. *Cell Host Microbe*, 2011, vol. 10, is. 4, pp. 379–389. doi: 10.1016/j.chom.2011.08.015
  39. Gordts S. C., Féris G., D'huys T., I. Petrova M., Lebeer S., Snoeck R., Andrei G., Schols D. The Low-Cost Compound Lignosulfonic Acid (LA) Exhibits Broad-Spectrum Anti-HIV and Anti-HSV Activity and Has Potential for Microbicidal Applications. *PLoS ONE*, 2015, vol. 10, is. 7. doi: 10.1371/journal.pone.0131219
  40. Qiu M., Wang Q., Chu Y., Yuan Z., Song H., Chen Z., Wu Z. Lignosulfonic acid exhibits broadly anti-HIV-1 activity-potential as a microbicide candidate for the prevention of HIV-1 sexual transmission. *PLoS ONE*, 2012, vol. 7, is. 4. doi: 10.1371/journal.pone.0035906
  41. Raghuraman A., Tiwari V., Zhao Q., Shukla D., Debnath A. K., Desai U. R. Viral inhibition studies on sulfated lignin, a chemically modi-

- fied biopolymer and a potential mimic of heparan sulfate. *Biomacromolecules*, 2007, vol. 8, no. 5, pp. 1759–1763. doi: 10.1021/bm0701651
42. Hasegawa Y., Kadota Y., Hasegawa C., Kawaminami S. Lignosulfonic acid-induced inhibition of intestinal glucose absorption. *Journal of Nutritional Science and Vitaminology*, 2015, vol. 61, is. 6, pp. 449–454. doi: 10.3177/jnsv.61.449
  43. Hasegawa Y., Nakagawa E., Kadota Y., Kawaminami S. Lignosulfonic acid promotes hypertrophy in 3T3-L1 cells without increasing lipid content and increases their 2-deoxyglucose uptake. *Asian-Australasian Journal of Animal Sciences*, 2017, vol. 30, is. 1, pp. 111–118. doi: 10.5713/ajas.16.0253
  44. Alimi H. Compositions comprising lignin and methods of making and using the same. Patent WO, no. 024208, 2002.
  45. Ciesielczyk F., Źółtowska-Aksamitowska S., Jankowska K., Zembrzuska J., Zdarta J., Jesionowski T. The role of novel lignosulfonate based sorbent in a sorption mechanism of active pharmaceutical ingredient: batch adsorption tests and interaction study. *Adsorption*, 2019, vol. 25, is. 3, pp. 865–880. doi: 10.1007/s10450-019-00099-1
  46. Guterman R., Molinari V., Josef E. Ionic Liquid Lignosulfonate as a Dispersant and Binder for the Preparation of Biocomposite Materials. *Angewandte Chemie International Edition*, 2019, vol. 58, is. 37, pp. 13044–13050. doi: 10.1002/anie.2019073850
  47. Babkin I., Brovko O., Iakovlev M., Khabarov Y. Ferrofluid Synthesis Using Nitrosated Lignosulfonates. *Industrial & Engineering Chemistry Research*, 2013, vol. 52, is. 23, pp. 7746–7751. doi: 10.1021/ie400531f
  48. Fu F., Yang D., Zhang W., Wang H., Qiu X. Green self-assembly synthesis of porous lignin-derived carbon quasi-nanosheets for high-performance supercapacitors. *Chemical Engineering Journal*, 2020, vol. 392. doi: 10.1016/j.cej.2019.123721
  49. Pang J., Zhang W., Zhang J., Cao G., Han M., Yang Y. Facile and sustainable synthesis of sodium lignosulfonate derived hierarchical porous carbons for supercapacitors with high volumetric energy densities. *Green Chemistry*, 2017, vol. 19, is. 16, pp. 3916–3926. doi: 10.1039/C7GC01434A
  50. Lota G., Milczarek G. The effect of lignosulfonates as electrolyte additives on the electrochemical performance of supercapacitors. *Electrochemistry Communications*, 2011, vol. 13, is. 5, pp. 470–473. doi: 10.1016/j.elecom.2011.02.023
  51. Angelini S., Barrio A., Cerruti P., Scarinzi G., Garcia-Jaca J., Savy D., Piccolo A., Malinconico M. Lignosulfonates as Fire Retardants in Wood Flour-Based Particleboards. *International Journal of Polymer Science*, 2019, vol. 4. doi: 10.1155/2019/6178163
  52. Mandlikar N., Cayla A., Rault F., Giraud S., Salaün F., Guan J. Valorization of Industrial Lignin as Biobased Carbon Source in Fire Retardant System for Polyamide 11 Blends. *Polymers*, 2019, vol. 11, is. 1. doi: 10.3390/polym11010180
  53. Lu W., Li Q., Zhang Y., Yu H., Hirose Sh., Hatakeyama H., Matsumoto Y., Jin Zh. Lignosulfonate / APP IFR and its flame retardancy in lignosulfonate-based rigid polyurethane foams. *Journal of Wood Science*, 2018, vol. 64, is. 3, pp. 287–293. doi: 10.1007/s10086-018-1701-4
  54. Li P., Liu Ch., Xu Y.-J., Jiang Z.-M., Liu Y., Zhu P. Novel and eco-friendly flame-retardant cotton fabrics with lignosulfonate and chitosan through Lbl: Flame retardancy, smoke suppression and flame-retardant mechanism. *Polymer Degradation and Stability*, 2020, vol. 181. doi: 10.1016/j.polymdegradstab.2020.109302
  55. Fu S., Li H., Liu H., Li X.-Y., Zhan H.-Y. Hydrophobic modification of pulp fiber surface via layer-by-layer self-assembly of lignosulfonates. *Journal of South China University of Technology*, 2010, vol. 38, is. 4, pp. 1–5. doi: 10.3969/j.issn.1000-565X.2010.04.001
  56. Komissarenkov A. A., Lukina T. L. Use of lignosulfonates in newsprint paper production. *Russian Journal of General Chemistry*, 2012, vol. 82, no. 5, pp. 985–990. doi: 10.1134/s1070363212050325
  57. Ojagh S. M., Núñez-Flores R., López-Caballero M. E., Montero P., Gómez-Guillén M. C. Lessening of high-pressure-induced changes in Atlantic salmon muscle by the combined use of a fish gelatin-lignin film. *Food Chemistry*, 2011, vol. 125, is. 2, pp. 595–606. doi: 10.1016/j.foodchem.2010.08.072
  58. Núñez-Flores R., Giménez B., Fernández-Martín F., López-Caballero M. E., Montero P., Gómez-Guillén M. C. Role of lignosulphonate in properties of fish gelatin films. *Food Hydrocolloids*, 2012, vol. 27, is. 1, pp. 60–71. doi: 10.1016/j.foodhyd.2011.08.015
  59. Johansson K., Winstrand S., Johansson C., Järnström L., Jönsson L. J. Oxygen-scavenging coatings and films based on lignosulfonates and laccase. *Journal of Biotechnology*, 2012, vol. 161, is. 1, pp. 14–18. doi: 10.1016/j.biote.2012.06.004
  60. Xia K., Ouyang Q., Chen Y., Wang X., Qian X., Wang L. Preparation and Characterization of Lignosulfonate-Acrylonitrile Copolymer as a Novel Carbon Fiber Precursor. *ACS Sustainable Chemistry & Engineering*, 2016, vol. 4, is. 1, pp. 159–168. doi: 10.1021/acssuschemeng.5b01442
  61. Brovko O., Palamarchuk I., Bogolitsyn K., Chukhchin D., Ivakhnov A., Valchuk N. Morphological features of aerogels and carbogels based on lignosulfonates. *Holzforschung*, 2017, vol. 71, is. 7–8, pp. 583–590. doi: 10.1515/hf-2016-0142
  62. Altwaiq A., Abdel-Rahem R., AlShamaileh E., Al-luaibi S., Khouri S. Sodium lignosulfonate as a friendly-environment corrosion inhibitor for zinc metal in acidic media. *Eurasian Journal of Analytical Chemistry*, 2015, vol. 10, pp. 10–18.
  63. Ouyang X., Qiu X., Lou H., Yang D. Corrosion and Scale Inhibition Properties of Sodium Lignosulfonate and Its Potential Application in Recirculating Cooling Water System. *Industrial & Engineering Chemistry Research*, 2006, vol. 45, is. 16, pp. 5716–5721. doi: 10.1021/ie0513189
  64. Lin B., Zuo Y. Inhibition of Q235 Carbon Steel by Calcium Lignosulfonate and Sodium Molybdate in Carbonated Concrete Pore Solution. *Molecules*, 2019, vol. 24, is. 3. doi: 10.3390/molecules24030518