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unctionalized Alkaline Lignin for Lead Removal in Aqueous Solution

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Abstract

Lignin, the second most abundant natural polymeric globally, is considered the source of the renewable aromatic compound. It serves as an alternative feedstock for the elaboration of chemicals and polymers. However, even until now, it is still primarily used as a low-value fuel for boilers. In the current research, alkaline lignin was modified and used as an adsorbent for removing lead (Pb) in an aqueous solution. The functionalized alkaline lignin (FAL) was prepared by a Mannich reaction with formaldehyde and dimethylamine, followed by esterification of carbon disulfide. The FAL was characterized using CHN elemental analysis, X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared (FT-IR) to observe the changes in composition, morphology, and chemical structure. The analysis revealed that alkaline lignin was successfully modified using amine and carbon disulfide. The adsorption study shows that the lead concentration reduced to 93.7% after 2 hours in contact with FAL. The FAL adsorption capacity could obtain 0.44 mmol/g of lead.

1. Introduction

Indonesia is an archipelagic country whose most of the territory is water. With more sea than land, environmental impacts become a problem due to increasing industrialism and human activities. For instance, discharging industrial waste to the environment will pollute the water ecosystem, especially for heavy metals. These types of environmental issues are challenging to degrade since they accumulate quickly.

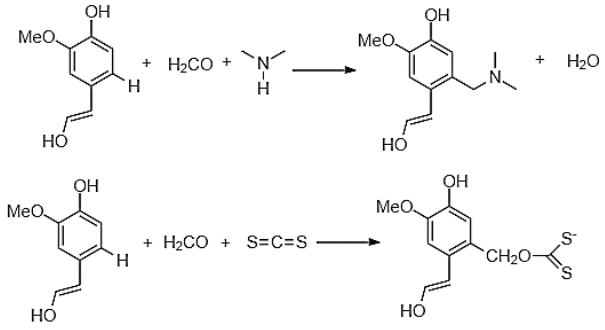
Lead, a natural constituent of the earth's crust, is one of the heavy metal contaminants in the ecosystem. In recent years, the demand for lead has increased along with its application in battery production, paint, gasoline, and textile industries [1, 2]. A study on the lead content test conducted in the coastal waters of Parepare, South Sulawesi, Indonesia, reveals that the lead content was high, exceeding the environmental health quality standards set by the government through the regulation of the Minister of Health No. 32 of 2017. The highest lead concentration was 0.7 mg/L, while the water threshold for sanitation hygiene was 0.05 mg/L [3, 4]. This lead waste pollution was considered from port activities, household waste, and agricultural waste. The same thing was also found in the coastal waters of Sidoarjo, East Java, Indonesia, where some people had brackishwater aquaculture activities. The lead concentration obtained was as high as 0.835 mg/L [5].

The existence of lead in ecosystems raises considerable toxicological concerns, particularly since the heavy metal cannot be degraded. Lead can accumulate in organisms, resulting in lead contaminating the food chain. High lead contamination in the human body will trigger health problems in the respiratory, nervous, digestive, cardiovascular, and kidney systems [6]. Appropriate remediation and water treatment must be developed and explored to address the problems.

Lignin, the main component of lignocellulosic biomass, is the second-largest natural polymer. In plants, lignin is located in the secondary cell walls of vascular plants and acts as water transport [7]. They also provide physical strength and protection from interference by some microbes and insects [8, 9]. Lignin has a complex structure constructed by aromatic compound, hydroxyl, methoxyl, and ethers groups. Unlike cellulose and hemicellulose, which are used to produce ethanol, pulp in papermaking, and more in biorefinery industries, lignin

is considered a low-value material. Its utilization is still prominent as the feeding material of the boiler to generate heat and electricity [10]. Lignin can be isolated by different extraction processes such as mechanical, physical, chemical, and enzymatic [11]. One type of lignin obtained by pulping process extraction is alkaline lignin.

We tried to functionalize alkaline lignin using dimethylamine and carbon disulfide in this current work. The functional groups found in lignin could improve their physical properties and create opportunities to produce new materials. The functionalized alkaline lignin (FAL) was used as an adsorbent to reduce lead (Pb) in an aqueous solution. The material is insoluble in water which makes it easier to recycle.



Scheme 1. Synthesis of FAL from alkaline lignin

2. Experiments

2.1. Materials

The solutions of 10 ppm $Pb(NO_3)_2$ were prepared by diluting 1000 mg/L stock solutions with distilled water. All chemicals used in this study were of analytical grade, commercially available, and were used without further purification. Alkaline lignin was purchased from Sigma-Aldrich. A 37% formaldehyde solution, 40% dimethylamine solution, and carbon disulfide were obtained from Merck.

2.2. Lignin Functionalized Dimethyl Amine and Carbon Disulfide

Functionalized Alkaline Lignin (FAL) was prepared through a Mannich reaction followed by amination of dimethylamine and sulphuration of carbon disulfide [12]. At first, 2 g of alkaline lignin, 10 g dimethylamine, and 150 g distilled water were added to a 250 mL Schott bottle. The mixture was closed and stirred for 30 minutes at room temperature. Then, 8 mL of formaldehyde was added to the mixture. The reaction proceeded at 90℃ for 5 hours. After that, the mixture was cooled to 40℃. The 10 mL of carbon disulfide was added dropwise to the mixture and kept for 3 hours at 40℃. Finally, the mixture was separated using a centrifuge and washed several times with distilled water and hexane. The filtrate was dried in a vacuum at 50℃ for 48 hours. The isolated lignin was denoted as FAL.

2.3. Adsorption studies

The adsorption capability of FAL towards lead was investigated. A total of 0.1 g of FAL was added into 100 mL of $Pb(NO_3)_2$ 10 ppm solution under stirring at 100 rpm at room temperature (25℃) for 12 hours. The lead concentration was monitored every three, six, nine, and twelve hours by taking each 10 mL of solution mixture and measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

2.4. Characterization

Scanning Electron Microscopy (SEM) was accomplished using a field-emission scanning electron microscope (Jeol JSM IT-200). The infrared spectra were recorded by Shimadzu IR Prestige-21. The CHN analysis was measured by Leco CHN 628, while the XRF analysis was performed using S2–PUMA, Bruker. The lead concentration was measured using ICP-OES (Agilent Technologies 5100).

3. Results and Discussion

The FAL was synthesized by reacting alkaline lignin with formaldehyde, dimethylamine, and carbon disulfide. As seen as in Scheme 1, alkaline lignin was modified through two reactions: amination and sulphuration. The alkaline lignin was well dissolved in water, formaldehyde, and dimethylamine. The dark brown color was observed for 5 hours. The addition of carbon disulfide made a solution mixture turbid and changed into bright brown color. The solid precipitation was formed, separated, and dried in the oven. The properties of alkaline lignin were changed from soluble to insoluble in water after being modified.

3.1. Characterization of FAL

Figure 1 shows the morphology of alkaline lignin before (a) and after (b) reaction. The SEM image clearly indicates the morphology changing before and after functionalization. Alkaline lignin seems fragile, rough, and round-shaped, with some hollows on the surface (Figure 1a,c). However, the FAL appears aggregated and has a smooth surface after reacting with dimethylamine and carbon disulfide.

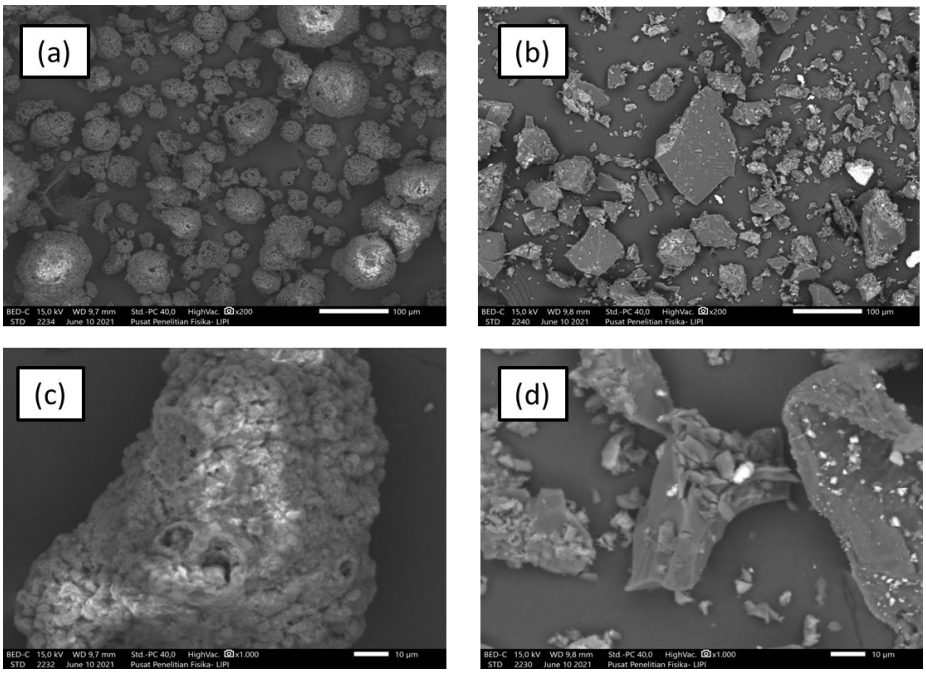


Figure 1. SEM image of (a,c) alkaline lignin and (b,d) FAL with 200× and 1000× magnification

Jin *et al.* [13] reported the changes in the morphology of lignin after it was modified with 5-sulfosalicylic. The modified lignin showed several cavities and cracks due to the clogging of 5-sulfosalicylic molecules on lignin surfaces. In addition, Li *et al.* [14] also discovered changing morphology of lignin from an irregular shape to a rough and obscure surface after it was modified with polyethyleneimine (PEI). They found morphological changes due to the PEI polymer coating on the lignin surface. Thus, we expected some chemical properties of alkaline lignin to change due to their morphological changes.

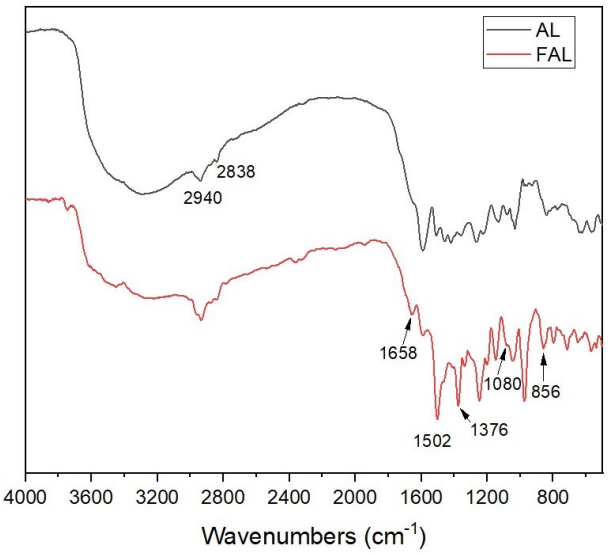


Figure 2. FT-IR spectra of alkaline lignin and FAL

The FT-IR spectra of alkaline lignin and FAL are shown in Figure 2. The large broadband between 3600 cm^{-1} and 3200 cm^{-1} is attributed to O-H stretching mode. The bands at 2940 cm^{-1} and 2838 cm^{-1} are attributed to the C-H stretching of methylene and methyl groups. The new band at 1658 cm^{-1} contributes to the vibration of the benzene ring skeleton stretching vibration [15]. The three new peaks at 1376, 1080, and 856 cm^{-1} stretching on the FAL compared to alkaline lignin, assigned to the C-N [16], C=S [17], and C-S [18], respectively. The FT-IR spectra changes suggest that dimethylamine and carbon disulfide were successfully anchored into the lignin.

Table 1. Elemental analysis of alkaline lignin and FAL

Materials	Elements contents (wt%)			
	C	H	N	S[a]
Alkaline lignin	45.09	4.86	0.21	12.60
FAL	46.84	6.33	4.68	37.80

[a] Obtained by XRF analysis

The elemental analysis was used to quantify the nitrogen and sulfur content in the FAL. As shown in Table 1, the weight percentage of nitrogen and sulfur distinctly increased. The incorporation of dimethylamine and carbon disulfide resulted in the higher contents of N (4.68%) and S (37.80%) of FAL than that of alkaline lignin (0.21% N and 12.60% S). It confirms that the amine and carbon disulfide successfully had introduced into alkaline lignin.

The FAL adsorption activity was investigated by adding FAL in the 10 ppm $Pb(NO_3)_2$ solution at room temperature. The adsorption capacity was measured as a function of contact time to determine an optimum contact time between FAL and lead. In Figure 3(a), FAL shows its adsorption capability for decreasing lead concentration in the solution. After an hour of contact, the FAL could remove 89% of lead content, which means only 1.12 ppm of lead remained in the solution. Lead concentration continuously decreased to 0.63 ppm in 2 hours of contact time but slightly increased to 0.80 ppm after 3 hours. We concluded that the optimum contact time was 2 hours in which the FAL could remove 93.7% of the lead from the solution.

3.2. Adsorption performance

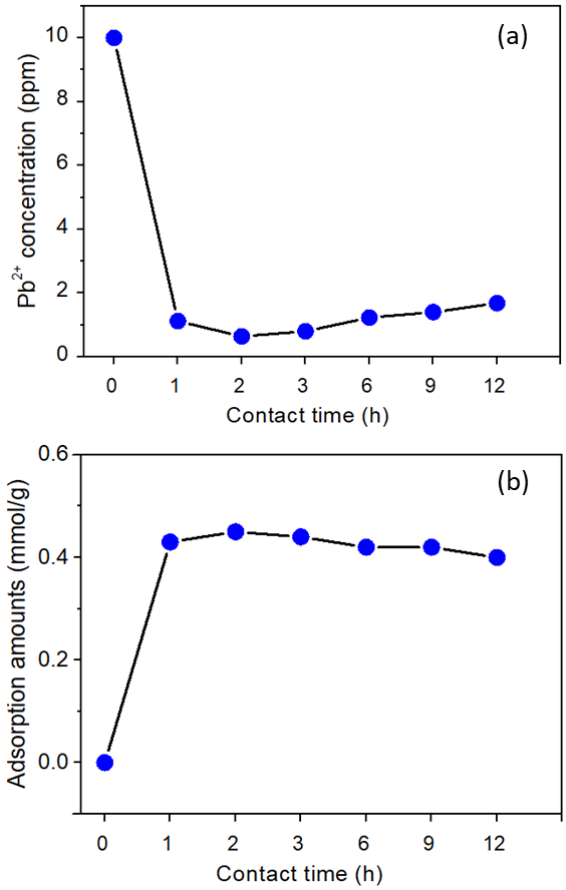


Figure 3. Effectivity test of FAL for lead removal

Extending contact time to more than 3 hours showed an increase in the lead concentration, and it increased gradually to 1.68 ppm in the solution after 12 hours of contact with FAL. During the experiment, the FAL was rigid and insoluble in the lead solution if it was in a short contact time (1 to 3 hours). However, some FAL dissolved in the lead solution in a long contact time. The lead solution colors changed to turbid because some parts of the FAL were soluble. The soluble FAL made adsorbed lead remixed to the solution. The researchers concluded that FAL was unstable when employed as an adsorbent for a long time. Nevertheless, the FAL only degraded slightly after 12 hours of contact time, and it continued maintaining its activity to adsorb lead from the solution.

Figure 3(b) shows the adsorption capacity of FAL for lead in the solution. The highest adsorption capacity of 0.44 mmol/g can be attained after 3 hours of contact time. The FAL appears to have a better adsorption capacity than the original lignin. As shown in Table 1, the adsorption performance of raw lignin is not as good as FAL. Šćiban *et al.* [19] reported that kraft lignin possessed adsorption of heavy metals such as Cu, Zn, Cd, and Cr. However, the maximum adsorption was relatively low, ranging from 0.02 to 0.2 mmol/g. Although the adsorption performance of kraft lignin was low and took several hours, it was able to remove lead from the solution [20]. In addition, another lignin source isolated from softwood could adsorb 0.02–0.03 mmol/g of Cu and Cd for 80 minutes of contact time [21].

Table 1. Adsorption performance of lignin for heavy metals removal

No.	Adsorbents	Metals	Maximum adsorption (mmol/g)	Contact time	Ref
1	Kraft lignin (pulping process)	Cu Zn Cd Cr	0.053 0.027 0.073 0.213	3 hours	[19]
2	Kraft lignin (paper industry)	Pb	0.005	75 hours	[20]
3	Softwood organosolv lignin	Cu	0.022	80 min	[21]
4	Softwood kraft lignin	Cd	0.029	80 min	[21]

Introducing the new functional group into lignin was reported to contribute to removing heavy metals in the solution. 5-sulfosalicylic acid-modified lignin exhibited a high adsorption ability for lead. The maximum adsorption capacity of the adsorbent approached 0.48 mmol/g for the lead after 12 hours of contact time [13]. The main functional groups that existed on the surface of modified lignin (carboxyl, hydroxyl, and sulfonic group) improved the removal efficiency and the adsorption capacity of lead compared to original lignin. In addition, the new functional groups were also successfully attached to lignin by using a high-branched structure of polyethyleneimine and carbon disulfide [22]. The active sites of new functional groups, C-N, N- H/O- H, C-S, and C=S, acted as the binding site by making a coordinate bond between lignin and lead. Similar to the modified lignin that has been reported, FAL has new functional groups, namely C-N, N-H/O-H, C-S, and C=S, and also can reduce lead concentration in solution. Therefore, it can be concluded that FAL can be a promising candidate as an adsorbent.

4. Conclusion

The result indicated that the alkaline lignin was successfully functionalized and could serve as an adsorbent for lead. The alkaline lignin had changed its morphology after being functionalized with dimethylamine and carbon disulfide. The FT-IR analysis showed that the new functional group, C-N, N-H/O-H, C=S, and C-S, was attached to FAL. Elemental analysis and XRF showed the higher contents of N (4.68%) and S (37.80%) of FAL than that of alkaline lignin (0.21% N and 12.60% S). FAL showed its adsorption capability for decreasing lead concentration to 93.7% after 2 hours of contact time. The FAL adsorption capacity could obtain 0.44 mmol/g of lead.

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References

[1] Geoffrey J. May, Alistair Davidson, Boris Monahov, Lead batteries for utility energy storage: A review, *Journal of Energy Storage*, 15, (2018), 145-157 https://doi.org/10.1016/j.est.2017.11.008

[2] David O'Connor, Deyi Hou, Jing Ye, Yunhui Zhang, Yong Sik Ok, Yinan Song, Frederic Coulon, Tianyue Peng, Li Tian, Lead-based paint remains a major public health concern: A critical review of global production, trade, use, exposure, health risk, and implications, *Environment International*, 121, 1, (2018), 85-101 https://doi.org/10.1016/j.envint.2018.08.052

[3] Ramlia Ramlia, Abidin Djalla, Uji Kandungan Logam Berat Timbal (Pb) di Perairan Wilayah Pesisir Parepare, *Jurnal Ilmiah Manusia Dan Kesehatan*, 1, 3, (2018), 255-264 https://doi.org/10.31850/makes.v1i3.111

[4] Kementerian Kesehatan, *Peraturan Menteri Kesehatan tentang Standar Baku Mutu Kesehatan Lingkungan dan Persyaratan Kesehatan Air Untuk Keperluan Higiene Sanitasi, Kolam Renang, Solus Per Aqua, dan Pemandian Umum*, 2017

[5] Akhmad Mustafa, Hasnawi Hasnawi, Tarunamulia Tarunamulia, Muhammad Banda Selamat, Muhammad Farid Samawi, Distribusi polutan logam berat di perairan pantai yang digunakan untuk memasok tambak udang terdekat dan mitigasinya di Kecamatan Jabon Provinsi Jawa Timur, *Jurnal Riset Akuakultur*, 14, 2, (2019), 127-138

[6] Marzie Boskabady, Narges Marefati, Tahereh Farkhondeh, Farzaneh Shakeri, Alieh Farshbaf, Mohammad Hossein Boskabady, The effect of environmental lead exposure on human health and the contribution of inflammatory mechanisms, a review, *Environment International*, 120, (2018), 404-420 https://doi.org/10.1016/j.envint.2018.08.013

[7] Qiao Zhao, Richard A. Dixon, Transcriptional networks for lignin biosynthesis: more complex than we thought?, *Trends in Plant Science*, 16, 4, (2011), 227-233 https://doi.org/10.1016/j.tplants.2010.12.005

[8] Ruben Vanholme, Kris Morreel, John Ralph, Wout Boerjan, Lignin engineering, *Current Opinion in Plant Biology*, 11, 3, (2008), 278-285 https://doi.org/10.1016/j.pbi.2008.03.005

[9] Scott E. Sattler, Deanna L. Funnell-Harris, Modifying lignin to improve bioenergy feedstocks: strengthening the barrier against pathogens?, *Frontiers in Plant Science*, 4, 70, (2013), 1-8 https://doi.org/10.3389/fpls.2013.00070s

[10] Maxim V. Galkin, Supaporn Sawadjoon, Volker Rohde, Monali Dawange, Joseph S.M. Samec, Mild heterogeneous palladium-catalyzed cleavage of β-O-4′-ether linkages of lignin model compounds and native lignin in air, *ChemCatChem*, 6, 1, (2014), 179-184 https://doi.org/10.1002/cctc.201300540

[11] Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, Bert M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, *Chemical Reviews*, 110, 6, (2010), 3552-3599 https://doi.org/10.1021/cr900354u

[12] Ding Wang, Sahng Ha Lee, Jinhyun Kim, Chan Beum Park, "Waste to wealth": lignin as a renewable building block for energy harvesting/storage and environmental remediation, *ChemSusChem*, 13, 11, (2020), 2807-2827 https://doi.org/10.1002/cssc.202000394

[13] Yanqiao Jin, Chaomin Zeng, Qiu-Feng Lü, Yan Yu, Efficient adsorption of methylene blue and lead ions in aqueous solutions by 5-sulfosalicylic acid modified lignin, *International Journal of Biological Macromolecules*, 123, (2019), 50-58 https://doi.org/10.1016/j.ijbiomac.2018.10.213

[14] Tiantian Li, Zhaohui Tong, Qingzhu Zheng, Hanxi Bao, Arianna Partow, Shanyu Meng, Lixia Li, Yuncong C. Li, Fabrication of a Lignin-Based Magnetic Nanocomposite Adsorbent to Recover Phosphorus in Water for Agricultural Reuse, *ACS Sustainable Chemistry & Engineering*, 9, 31, (2021), 10468-10478 https://doi.org/10.1021/acssuschemeng.1c01492

[15] Yang Liu, Tianjue Hu, Zhengping Wu, Guangming Zeng, Danlian Huang, Ying Shen, Xiaoxiao He, Mingyong Lai, Yibin He, Study on biodegradation process of lignin by FTIR and DSC, *Environmental Science and Pollution Research*, 21, 24, (2014), 14004-14013 https://doi.org/10.1007/s11356-014-3342-5

[16] Chao Liu, Ru-Na Jin, Xiao-kun Ouyang, Yang-Guang Wang, Adsorption behavior of carboxylated cellulose nanocrystal—polyethyleneimine composite for removal of Cr(VI) ions, *Applied Surface Science*, 408, (2017), 77-87 https://doi.org/10.1016/j.apsusc.2017.02.265

[17] H. O. Desseyn, A. C. Fabretti, F. Forghieri, C. Preti, Isotopic infrared study of some nickel(II) and copper(II) complexes containing heterocyclic dithiocarbamate ligands, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 41, 9, (1985), 1105-1108 https://doi.org/10.1016/0584-8539(85)80012-X

[18] Matthew M. Matlock, Brock S. Howerton, Kevin R. Henke, David A. Atwood, A pyridine-thiol ligand with multiple bonding sites for heavy metal precipitation, *Journal of Hazardous Materials*, 82, 1, (2001), 55-63 https://doi.org/10.1016/S0304-3894(00)00353-8

[19] Marina B. Šćiban, Mile T. Klašnja, Mirjana G. Antov, Study of the biosorption of different heavy metal ions onto Kraft lignin, *Ecological Engineering*, 37, 12, (2011), 2092-2095 https://doi.org/10.1016/j.ecoleng.2011.08.006

[20] S. B. Lalvani, T. S. Wiltowski, D. Murphy, L. S. Lalvani, Metal removal from process water by lignin, *Environmental Technology*, 18, 11, (1997), 1163-1168 https://doi.org/10.1080/09593331808616636

[21] Hengky Harmita, K. G. Karthikeyan, XueJun Pan, Copper and cadmium sorption onto kraft and organosolv lignins, *Bioresource Technology*, 100, 24, (2009), 6183-6191 https://doi.org/10.1016/j.biortech.2009.06.093

[22] Qiaorui Wang, Chunli Zheng, Zhenxing Shen, Qiang Lu, Chi He, Tian C. Zhang, Jianhui Liu, Polyethyleneimine and carbon disulfide co-modified alkaline lignin for removal of Pb^{2+} ions from water, *Chemical Engineering Journal*, 359, (2019), 265-274 https://doi.org/10.1016/j.cej.2018.11.130