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THE USE OF LIGNIN FOR ENVIRONMENTAL PROTECTION: AN OVERVIEW OF RECENT LITERATURE

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ABSTRACT

Reducing environmental pollution is a particularly important issue, intensively studied nationally and internationally, as evidenced by the large number of scientific papers published on this topic. Literature studies show that reducing environmental pollution means not only reducing the amount of air / water / soil pollutants but also finding ways to recover waste from industrial activities that will reduce the problems of environmental pollution due to their storage.

The materials resulting from the gasification processes of cellulose waste, as well as the materials obtained with the help of cellulose extracted from cellulose waste, were tested in the adsorption processes of some polluting species and the results demonstrated the efficiency of these materials for reducing the environmental pollution. The use of lignin as an adsorbent for the removal of pollutants (organic dyes or metal ions) from industrial wastewater can be considered a viable alternative, which can be a solution to both the problem of lignin recovery and the reduction of pollutant content in industrial wastewater.

KEYWORDS: lignin, heavy metals, dyes, cellulose waste, pollution

1. Introduction

In addition to environmental pollution caused by the development of anthropogenic activities, referred to in the literature as permanent pollution, in recent years, both worldwide and at European level, there has been an increase in the number of pollution phenomena caused by technological accidents, from various branches of industry, car and rail transport or the mismanagement and/or irrational management of liquid and solid waste from domestic activity [1, 2].

Legislation in many parts of the world severely penalizes environmental pollution. The mining industry, the metallurgical industry, and the textile industry (especially textile chemical finishing) have felt drastically the rigors of the new requirements of the legislation regarding environmental protection [1-3].

Due to their relatively high solubility, a wide variety of pollutants (metal ions, phenols, or organic dyes) easily reach industrial wastewater and their content in such effluents depends on the type of industrial activity and the nature of the technological process applied [5-9].

Numerous methods are presented in the literature for the removal of metal ions and dyes from industrial wastewater: physical processes (membrane filtration, flotation); simple chemical processes (chemical precipitation, coagulation, ion exchange, electrolysis, solvent extraction, adsorption); use of biologically active microorganisms [1, 2-9].

Studies in the literature on the reduction of environmental pollution have shown that a number of materials, which have a porous structure and a relatively large number of superficial functional groups, can be used effectively to remove pollutants from aqueous solutions. Thus, natural materials or various categories of agricultural or industrial waste, generically called low-cost adsorbents can be successfully used for the removal of heavy metal ions and organic substances from wastewater [3-5, 10-12]. Adsorption is an efficient method for removing dyes, heavy metals, and phenol derivatives [10-13].

The lignocellulosic materials can be used as efficient sorbents for the removal of different pollutants from wastewaters (heavy metal ions, dyes, and other organic compounds), due to their fundamental characteristics, such as high porosity and specific surface area, good mechanical resistance,

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tolerance to biological adsorbed solid layers [1, 2, 4-12].

Lignin constitutes one-third of biomass and this component is typically burned to produce heat and electricity within paper mills and biorefineries [3, 13]. For many years, lignin was considered just a waste material or a very low-grade by-product of the pulping process. The use of lignin as an adsorbent for the removal of pollutants (organic dyes or metal ions) from industrial wastewater can be considered a viable alternative, which can be a solution to both the problem of lignin recovery and the reduction of pollutant content in industrial wastewater. Lignin is a natural polymer, which is abundantly present in cell walls of terrestrial plants and acts as a binding agent [2, 13-16]. Infrared spectroscopy is the most suitable analysis method for identifying the presence of polar functional groups in the molecule structure of organic compounds. Lignin contains many functional groups: hydroxyl, carbonyl, methoxyl, carboxyl, and the Infrared spectrum clearly indicates their presence in the molecule (Table 1); the FTIR spectra of lignin include the most extensive set of stretching and bending vibration bands of them. These functional groups can interact with ionic species (organic or inorganic) present in wastewater, making this natural material useful in adsorption processes [1, 2, 14]. The removal of different pollutant species by adsorbents based on natural or modified lignin and/or lignocellulosic materials has been intensively studied (Tables 2, 3) [1, 2, 13-20]. The results suggested that the adsorption of inorganic and organic pollutants on lignin is a progression towards a perspective method.

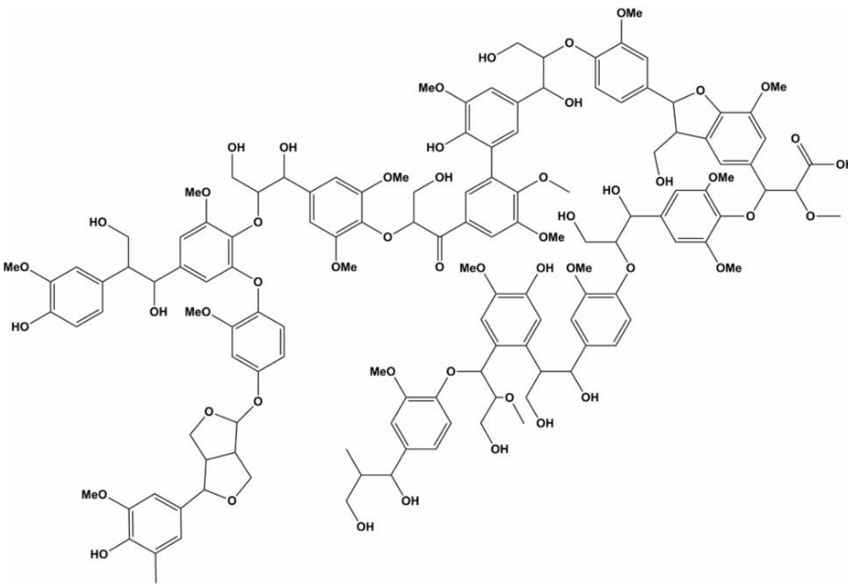

Fig. 1. *Lignin structure* [1, 3]

Table 1. *FTIR spectrum of lignin* [1-3, 13]

IR Absorption band (cm^{-1})	Type of vibration
3500-3400	Stretching vibration of alcoholic and phenolic –OH groups
2920-2840	Stretching vibration of C–H bonds in –CH_3 and –CH_2 groups
1715-1710	Stretching vibration of C=O bonds (in –COOH group)
1515-1500	Aromatic ring vibrations
1130-1035	Deformation vibrations of aromatic C–H bonds and C–O stretching for secondary alcohols

2. The use of lignin as an adsorbent for the removal of pollutants

From a chemical point of view, lignin is considered an amorphous crosslinked polymer, which has a three-dimensional aromatic structure and it contains many functional groups, such as hydroxyl, carbonyl, methoxyl, and carboxyl. These functional groups can interact with ionic species present in aqueous media, making this material useful in adsorption processes [1, 2, 13, 14].

The presence of these functional groups and the porous structure of lignin, demonstrated by microscopic studies, show that this material can be used as an adsorbent to retain pollutant species from aqueous solutions and can therefore be used in processes to reduce environmental pollution [2, 12-14].

There are numerous data from the literature attesting to the quantitative retention of organic dyes on lignin. Due to this behavior, lignin differs significantly from cellulose, on which dyes cannot be permanently fixed [1, 15].

Regardless of the nature of the dye used, their adsorption on lignin is a relatively complex process, the efficiency of which depends on a number of experimental parameters, such as: the pH of the solution, adsorbent dose, initial concentration of the dye in the solution, contact time and temperature [14, 16-21].

The reviewed literature demonstrated that non-hazardous materials can be used as inorganic and organic pollutants removers from industrial effluents to overcome water pollution [12, 14-21].

3. Lignin as an adsorbent for the removal of pollutants. Adsorption studies and mathematical modelling

Adsorption equilibrium data are important to provide physicochemical information to explain the mechanism of adsorption. The absorption capacity of an adsorbent can also be described by the equilibrium sorption isotherm, which is characterized by specific constants, whose values represent the surface properties and affinity of an adsorbent [12, 13-16].

Different mathematical models, generically called models of adsorption isotherms are used to interpret experimentally obtained adsorption isotherms. Langmuir and Freundlich models are most commonly used to establish equilibrium conditions in the case of adsorption processes and are considered classical models of adsorption isotherms [14-20]. The adsorbent material used in recent studies was residual lignin, obtained as waste from the pulp and paper industry, which from a macroscopic point of view is a dark brown powder [1, 2]. The wasted lignin is a huge amount, but less than 10% of this waste material was utilized and this fact is imposing as an important environmental problem [2].

There are numerous data from the literature attesting to the quantitative retention of organic dyes and heavy metals on lignin. Due to this behavior, lignin differs significantly from cellulose, on which dyes cannot be permanently fixed, regardless of whether they are acidic or basic [1, 2-5]. However, regardless of the nature of the dye used, their adsorption on lignin is a relatively complex process, the efficiency of which depends on a number of experimental parameters, such as: the pH of the aqueous solution, adsorbent dose, initial concentration of the dye in the solution, time contact, and temperature [1, 2].

Table 1. *Equilibrium adsorption data for some pollutants using lignin as adsorbent* [1, 2]

Pollutant	Langmuir Model	Freundlich Model
Brilliant Red	$R^2 = 0.9980$ $q_m = 12.05$ mg/g $K_L = 0.051$ L/mg	$R^2 = 0.9630$ $K_F = 1.77$ mg/g n = 2.44
Pb(II)	$R^2 = 0.9979$ $q_m = 32.36$ mg/g $K_L = 0.111$ L/mg	$R^2 = 0.9232$ $K_F = 7.26$ mg/g n = 2.61
Cu(II)	$R^2 = 0.9979$ $q_m = 32.36$ mg/g $K_L = 0.159$ L/mg	$R^2 = 0.9374$ $K_F = 7.55$ mg/g n = 2.56

In order to increase the adsorption performance of lignin in the processes of reducing environmental pollution, it is necessary to activate it and the activation treatments used in this case must be simple, so that the preparation costs of the adsorbent material remain low. One of the possibilities of lignin capitalization described in the literature is its use as fuel in order to obtain energy. Thus, the combustion of lignin can be considered an activation process because the material obtained can be used as an adsorbent for retaining polluting species from aqueous media. In addition, as a result of this activation process, significant amounts of heat are obtained, which in turn can be used for various purposes [1, 2, 20-22]. From the comparison of the experimental data presented in the literature, it can be said that thermally activated lignin has a much higher adsorption capacity for heavy metal ions and dyes in aqueous solutions compared to unburned lignin [1-3].

Table 2. *Adsorption capacities of different natural adsorbents for heavy metal ions and dyes* [14-21]

Adsorbent type	Pollutant	Uptake capacity (mg/g)
Activated carbon	Cr(VI)	39.54 mg/g
Lignin	Cr(VI)	17.96 mg/g
Modified lignin	Zn(II)	95.0 mg/g
Chitin/lignin adsorbent	Ni(II)	88.0 mg/g
Kraft lignin	Cd(II)	137.14 mg/g
Activated carbon from pomelo peels	Malachite green	178.43 mg/g
Yellow clay	Congo Red	22.0 mg/g
Activated carbon	Reactive Blue 171	71.94 mg/g
Peat	Rodamine B	16.72 mg/g
Wood sawdust (walnut)	Methylene Blue	59.17 mg/g
Cereal chaff	Methylene Blue	20.3 mg/g

4. Conclusions

The materials resulting from the gasification processes of cellulose waste, as well as the materials obtained with the help of cellulose extracted from cellulose waste, were tested in the adsorption processes of some polluting species and the results demonstrated the efficiency of these materials for reducing the environmental pollution.

The lignocellulosic materials can be used as efficient sorbents for the removal of different pollutants from wastewaters (heavy metal ions, dyes, and other organic compounds), due to their fundamental characteristics, such as high porosity and specific surface area, good mechanical resistance, tolerance to biological adsorbed solid layers.

The use of lignin as an adsorbent for the removal of pollutants (organic dyes or metal ions) from industrial wastewater can be considered a viable alternative, which can be a solution to both the problem of lignin recovery and the reduction of pollutant content in industrial wastewater.

Lignin offers some important advantages over synthetic materials such as: biodegradability, availability in various industrial waste, it is CO_2 neutral, environmentally friendly nature, and cost-effective.

The reviewed literature demonstrated that non-hazardous materials can be used as inorganic and organic pollutants removers from industrial effluents to overcome water pollution.

References

[1]. Crini G., *Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment*, Progress in Polymer Science, 30, p. 38-70, 2005.

[2]. Şuteu D., Maluţan T., Bîlbă D., *Removal of reactive dye Brilliant Red HE- 3B from aqueous solutions by industrial lignin: Equilibrium and kinetics modelling*, Desalination, 225 (1-3), p. 84-90, 2010.

[3]. Nandanwar R. A., Chaudhari A., Ekhe J., J. Chem. Bio. Phy. Sci. Sec. D, 6 (3), p. 501-513, 2016.

[4]. Auta M., Hameed B. H., Chem. Eng. J., 175, p. 233, 2011.

[5]. Suteu D., Zaharia C., Chemical Bulletin of "Politehnica" University of Timisoara, Romania, Series of Chemistry and Environmental Engineering, 56(70), p. 85, 2011.

[6]. Ata S., Hamid W., Rukh S., Hamid S., Syed A., Din I., Mohsin I., Turkish Journal of Biochemistry, 37 (3), p. 272, 2012.

[7]. Salazar-Rabago J., Ramos R., Utrilla J., Ocampo-Perez R., Cerino-Cordova F., Sustainable Environment Research, 27, p. 32, 2017.

[8]. Tran V., Ngo H., Guo W., Zhang J., Liang S., Ton-That C., Zhang X., Bioresource Technology, 182, p. 353, 2015.

[9]. Leroux-Berger M., Queguiner I., Maciel T., Ho A., Relaix F., Kempf H., Journal of Bone and Mineral Research, 26, p. 1543, 2011.

[10]. Sujitha R., Ravindhranath K., Der Pharma Chemica, 8(9), p. 63, 2016.

[11]. Jacob J. S., Roberto L.-R., Jose Rivera-Utrilla, Ocampo-Pere, R., Cerino-Cordova F., Sustainable Environment Research, 27, p. 32, 2017.

[12]. Bondarev A., *Application of the Natural Cellulosic Supports for the Treatment of the Industrial Effluents*, The Annals of "Dunarea de Jos" University of Galati, Fascicle IX. Metallurgy and Materials Science, vol. 3, p. 48-55, 2021.

[13]. Rodrigues P., Eduardo A., Dasilva B., Rodrigues A. E., *Insights into oxidative conversion of lignin to high added value phenolic aldehydes*, Ind. Eng. Che. Res., 50, p. 741-748, 2011.

[14]. Bondarev A., Gheorghe C., Gheorghe V., Bombos M., *Removal of dyes from textile wastewater using sawdust as low-cost biosorbent*, Rev. Chim., 71, no. 3, p. 387-396, 2020.

[15]. Auta M., Hameed B. H., Chem. Eng. J., 175, p. 233, 2011.

[16]. Hameed K. S., Muthirulan P., Meenakshi S. M., Arabian J. Chem, 10, p. 2225, 2017.

[17]. Malik R., Ramteke D. S., Wate S. R., Waste Management, 27, p. 1129, 2007.

[18]. Paul S. A., Chavan S. K., Oriental Jr. Chem., 27, p. 4, 2011.

[19]. Li P., Su Y., Wang Y., Liu B., Sun L. M., Journal of Hazardous Materials, 179, p. 43, 2010.

[20]. Singha B., Das S. K., Colloids and Surfaces B, 107, p. 97, 2013.

[21]. Shanavas S., Salahuddin Kunju A., Varghese H. T., Panicker C. Y., Orient. J. Chem., 27 (1), p. 245, 2011.