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Chapter 8

BIOSORBENTS BASED ON LIGNIN USED IN BIOSORPTION PROCESSES FROM WASTEWATER TREATMENT: A REVIEW

Daniela Suteu,^{1} Carmen Zaharia² and Teodor Malutan³*

¹'Gheorghe Asachi' Technical University of Iasi,
Faculty of Chemical Engineering and Environment Protection,
Department of Organic and Biochemical Engineering,
71A Prof.dr.docent D. Mangeron Blvd, 700050, Iasi, Romania

²'Gheorghe Asachi' Technical University of Iasi,
Faculty of Chemical Engineering and Environment Protection,
Department of Environmental Engineering and Management,
71A Prof. dr.docent D. Mangeron Blvd, 700050, Iasi, Romania

³'Gheorghe Asachi' Technical University of Iasi,
Faculty of Chemical Engineering and Environment Protection,
Department of Natural and Synthetic Polymers,
71A Prof. dr.docent D. Mangeron Blvd, 700050, Iasi, Romania

ABSTRACT

Taking into consideration the advantages of using natural materials as biosorbents in the cleaning and/or clearing wastewater technologies, the specialists' attention has been turned to the development of some new treatment methods, as a part of the environmental biotechnologies. These include, among others, biosorption. A special attention is focused on lignocellulosic materials, due to their fundamental characteristics, such as accessibility and low prices, mechanical resistance, high porosity and specific surface area, hydrophilic character that ensures a rapid sorption rate, tolerance to biological adsorbed solid layers, easy functionalization, the possibility of be used in different forms (particles of different dimensions, fibbers, filters, textile materials for cloths) and regimes (discontinuous and continuous processes).

* Email corresponding author: danasuteu67@yahoo.com.

The paper is a review about our researches and comparisons with literature regarding different types of industrial wasted lignocellulose and lignin materials with sorptive properties that were used into biosorption processes of wastewater treatment.

Keywords: lignocellulosic materials, biosorption, dyes, batch experiments, modeling and optimization sorption process.

INTRODUCTION

All industries discharge potential contaminants into public sewerage systems or different emissaries and have the obligation to report to the local water authority each exceeding of the maximum admissible concentration or hourly load. To avoid the pollution of water resources it is necessary the individual or combined industrial wastewater treatment with municipal wastewater.

The viable procedures of the '*production water*' management into each company take into consideration the following possible options: (1) minimization of water use; (2) the development of new processes for different industrial effluents or final wastewater treatment, and the optimization of existing or new ones with the aim of saving water, materials and energy, and (3) the reuse and recycling of industrial wastewater [1-5].

An industrial effluent treatment can be applied into decentralized treatment systems with or without reuse or central wastewater treatment. For a high wastewater flow rate and a high COD concentration, an estimation of the treatment costs lets us know whether it is better to treat it in an end-of-pipe system or in a decentralized effluent treatment system.

The interest towards an entire production process respecting the requirements of environment protection must direct all efforts to develop new production processes with reduced consumption levels of water and raw materials (i.e. dry processes or other electrochemical, physical ones), with reduced production of wastewater and to treat efficiently the individual or final effluents [3].

By large volume and composition of wastewaters from dyeing processes, the textile industry has a great polluting impact. Within this industry, the industrial processing of textile materials is a complex process, and the chemical textile finishing involves a high water consumption (ca 100 m³/tone of product) used mainly as transportation media of dyes, auxiliaries and thermal energy. Because of the effluents' volume but also of the fact that ca 90% from the consumption water is used for pretreatment operations, dyeing, printing and finishing, the produced wastewaters of textile industry have a high pollution level so that this industry represents one of the most pollutant economic sectors [6-8]. During the dyeing and finishing operations, 10-15% of the dye is lost in the wastewaters [8, 9].

Concerning the elimination of pollutants from wastewaters produced into textile industry, because of their presence in mixture and extremely various quantities into the polluted environment, it is very difficult to establish or design some general treatment technologies, being proposed technological scheme dependent of the pollutants composition and structure, and also of the origin media. The characteristics of wastewaters produced from the processes of chemical textile finishing depend on both type of the production process (i.e. glueing together, whitening, dyeing, hot alkaline treatment, etc.) and also the nature of textile material

for chemical finishing (cotton, proteic fibers, polyamides fibers, etc.). Even in the same textile enterprise can appear important modifications of wastewater composition, determined by the changes interfering in the production structure or restructuring of the technological process [2]. The textile effluents resulted in tinctorial processes contain many types of dangerous chemical organic and inorganic compounds that influence the quality of wastewaters and need to be treated before their disposal in municipal pipe network or other receiving basins [10].

An important category of organic compounds into textile effluents is represented by the *textile dyes* - synthetic compounds with aromatic molecular structures, resistant to light, heat and oxidizing agents and other non-biodegradable materials. It has been suggested that the presence of coloured compounds in aqueous environments can reduce light penetration, thus affecting the photosynthesis process of aquatic plants. In addition to their visual effect (aesthetic impact on receiving waters), many synthetic dyes are toxic, mutagenic and carcinogenic. Due to their aromatic structures these compounds are more stable, no biodegradable and difficult to remove from the industrial effluents before their discharges into the urban wastewater sewage system or different emissaries [15]. One of the most important group of dyes are represented by the *reactive dyes* as industrial compounds for dyeing the cellulose fibres, and can be characterized by low absorbability on a wide range of adsorbent, and limited biodegradability in an aerobic environment [11]. However, many reactive dyes contain in their molecules some azo compounds that transform these dyes into important organic pollutants for aquatic ecosystems because of their potential to form dangerous aromatic amines, other carcinogenic and mutagenic compounds [10].

The methods used for colour removal from industrial effluents (decolourization) are based on [3, 6, 7, 12, 13]:

- Biological processes – that achieve dyes decolourization and decomposition/mineralization in aerobic or anaerobic conditions, under the influence of some bacteria (*pseudomonas*) or fungi.
- Physical processes – that suppose the dyes elimination by filtration (inverse osmosis, micro-filtration, ultra-filtration, nano-filtration), separation through membrane, flotation and adsorption.
- Chemical processes – that suppose the dyes elimination and mineralization/decomposition by chemical precipitation and complexation, coagulation-flocculation, electro-coagulation, chemical reduction, chemical oxidation, and homogenous or heterogeneous photochemical oxidation. The advanced oxidation processes (AOPs) are based on the action of some oxidants as ozone (O_3), H_2O_2 , UV, O_3/UV , H_2O_2/UV , $O_3/UV/H_2O_2$, Fe^{2+}/H_2O_2 (Fenton), $UV/H_2O_2/Fe^{2+}$ (foto-Fenton) or photocatalytic oxidation – UV/TiO_2 , UV/ZnO , $UV/Ti-MCM-41$, $UV/Ti-Sn-MCM-41$.
- Mixed processes: physical-chemical, biochemical, electrochemical processes.

As a function of their specificity, the non-biological processes present both advantages (i.e. do not produce residual sludge in high quantities, perform decolourization both of soluble and insoluble dyes, a part of secondary products are not dangerous) but also disadvantages (i.e. some methods produce concentrated sludge or secondary products that must be eliminated, applicability only for aminic aromatic compounds, some of them involve high

costs or are not efficient for all types of dyes) [2, 3, 7, 12]. Many of these processes are often complicated and time consuming, generate sludge or other toxic wastes and may be ineffective or expensive for diluted dye solutions [15].

Sorption is one of the methods very useful in the treatment of coloured wastewaters because of their design simplicity, inexpensiveness, specific physic-chemical interactions between dyes and the solid sorbent, and low matrix effects [6, 12, 16, 17]. Dye removal by sorption in batch conditions is a relatively simple method which can be carried out without sophisticated equipments. Decolourisation by adsorption is mainly determined in equal extent on the dyes's properties and structure and on the surface chemistry of the sorbent. Interaction of the functional group of the dyes (one or more groups of -OH, -COOH, -SO₃H, -N=N-, etc.) with the sorbent surface could be result anywhere from covalent, coulombic, hydrogen bonding or weak van der Waals forces [18]. Several research studies indicate that adsorbents which contain high concentrations of cellulose irreversibly adsorb basic dyes through coulombic attraction and ion exchange processes. Acid dyes are mostly adsorbed in a reversible process involving physical adsorption (combination of van der Waals attraction, hydrogen bonding and coulombic attraction that generates a negative surface charge of the adsorbent in contact with water) [4, 5].

One of the main advantages of sorption process is the possibility to use as sorbents many classes of materials: synthetic to natural low-cost materials (natural as well as wasted materials from different industries and agriculture) as suitable sorbents for decolourization of industrial effluents [6].

Selection of new sorbents is determined by the high efficiency of the sorption process (high affinity and dye binding capacity, sorption kinetics, regeneration properties and cost), cost effectiveness, availability and adsorptive properties. Most sorbents discussed into the scientific literature are synthetic and engineered materials, such as synthetic resins, ion exchange celluloses, chemically modified fibers, activated charcoal and ashes.

The high costs of sorbent preparation, the necessity to avoid some disadvantages of conventional sorbents based on synthetic polymers (high prices, difficulties in obtaining, pollution produced during their synthesis), and the actual tendency of replacing chemically synthesized compounds with others of natural origin [10] reoriented the researches to the testing of low cost materials and easily obtainable, included into the category of 'non-conventional' or 'low cost', having a synthetic (such industrial wastes) and/or natural (such cellulosic and/or lignocellulosic agricultural wastes) structure, such as:

- i. industrial/ agricultural/ domestic wastes or industrial/agricultural by-products (ash, sludge, sawdust, textile fibbers, mud, bark, straw, etc.)
- ii. natural materials (peat, seashell, algae, lignite, wood, etc.).

that assure large specific surface areas, high sorption rates, the possibility to be functionalized with organic ligands for increasing their sorption capacity [16].

Recently, one of the most important subjects is to investigate new materials with sorptive potential and to implicate them into wastewater treatment process. Sorption onto activated charcoal is a very useful technique, but the high cost implied to obtain this sorbent stimulated the search of cheaper alternatives. In this context, the overall attention was moved to the non-conventional and low-cost materials which include some agriculture and industrial by-

products and wastes, industrial wasted biomass and natural materials to retain and accumulate the textile dyes [3, 16, 19].

The sorption capacities of dyes onto non-biological wastes or by-products as activated carbon, coal ash, fly ash, physicochemical modified coal ashes depend on the surface charge of the adsorbent on contact with water. For activated carbon, the surface charge will be neutral, the physical adsorption will predominate and a high adsorption capacity for both acid and basic dyes will be achieved [20, 21].

A special attention was focused on *lignocellulosic materials*, due to their fundamental characteristics, such as accessibility and low prices, mechanical resistance, high porosity and specific surface area, hydrophilic character that ensures a rapid sorption kinetic, tolerance to biological structures, easy functionalization, the possibility to be used in different forms (particles of different dimensions, fibbers, filters, cloths) and in continuous or discontinuous processes [22]. The removal of some pollutant species by sorbents based on lignin, modified lignin and/or lignocellulosic materials has been intensively studied (Table 1) [23]; the results suggested that sorption on lignin is ‘a progression towards a perspective method’.

Table 1. Applicability of lignocellulosic sorbents in the removal of pollutants from aqueous systems

Sorbent	Retained pollutants	Adsorption capacity	Ref.
Modified lignin	Pb (II) Cd (II)	q= (8.2-9.0) mg Pb/ g q= (6.7 – 7.5) mg Cd/g	24
Modified corncob: -with nitric acid - with citric acid	Cd(II) Cd(II)	q= 19.3 mg Cd (II)/ g q= 55.2 mg Cd (II)/g	25
Pine fruit	Cu (II) Fe (II)	q= 4.8 mg Fe(II)/ g q= 14.1 mg Cu (II)/g	26
Wood apple carbon	Methylene Blue	q = 36.9 mg/g	27
Kraft lignin	Cu (II) Cd (II)	q = 87.05 mg Cu (II) /g q = 137.14 mg Cd (II) /g	28
Sawdust	Brilliant Red HE-3B Methylene Blue Rhodamine B Crystal Violet	q = 11.61 mg/g q = 7.215 mg/g q = 7.309 mg/g q= 12.594 mg/g	29
Peat	Brilliant Red HE-3B Methylene Blue Rhodamine B	q = 16.286 mg/g q = 38.314 mg/g q = 16.722 mg/g	30
Rice bran Bagase fly ash of sugarcane <i>Moninga oleifera</i> pods Rice husk	Methyl parathion pesticide	q = 0.9 mmol/g q = 1 mmol/g q = 1 mmol/g q = 0.9 mmol/g	31
Corncoobs	Cu (II)	q = 26 mg/g	32
Pre-boiled sunflower stem	Cr (VI)	q = 5.34 mg/g	33
Formaldehyde-treated sunflower stem	Cr (VI)	q = 4.81 mg/g	
Black tea waste	Cu (II) Pb(II)	q = 48 mg/g q = 65 mg/g	34

This paper reviews our researches in comparison with scientific literature regarding different types of industrial wasted lignocellulosic and lignin materials with sorptive properties which were used into biosorption processes of wastewater treatment. In the same time, we want to present an overview about effects of various parameters (factors) that influence the biosorption of textile dyes onto industrial wasted lignocellulosic and lignin materials, and also the equilibrium, kinetic and thermodynamic models studied in order to understand the biosorption mechanism.

2. GENERALITIES

2.1. Working Methodology

Biosorption is a process of chemical species sorption on biological or natural materials as sorbents [35]. This process is characterized mainly by: low cost, elimination of ecological risk of the toxic compounds recovery, the possibility to treat large volumes of effluents with low concentrations of pollutants [36]. Biosorption is a process achieved through extracellular and intracellular bonding, interactions that depend of the nature of pollutants, of the structure of biosorptive materials into the microbial metabolism and into the transport process. Similar as the biodegradation of organic compounds, biosorption implies the breaking and creating new chemical bonds that can change the molecular structure of the pollutant.

The biosorption experiments were usually performed using 'batch technique' - a simple and ease to operate methodology (easily control and adjustment of the operating parameters) in the case of small and medium size processes from laboratory practice in order to obtain the preliminary information about parameters or variables (factors) that affect the biosorption process, and that are necessary for the modelling of process and for future simulation of real case study [38].

The main factors influencing the sorption equilibrium can be classified in two groups:

- 1) process variables such as pH, temperature, sorbent dose, initial dye concentration, sorption time, and
- 2) variables depending on sorbent and sorbet such as structure of dyes and sorbent, and the particle size of sorbent [1, 38-43].

It was worked with suspending samples of sorbent into volumes of aqueous solution containing knowing dye concentrations placed into 100 mL Erlenmeyer flasks, under an intermittent agitation, at different temperatures (2° - 45°C). The pH of aqueous solutions was adjusted to a desired value by addition of HCl 1M solution and measuring the pH value with a HACH One Laboratory pH meter. After an established sorption time, the concentration of the dyes in supernatant was determined by absorbance measurement with a VIS Spectrophotometer, model SP 830 Plus, Metertech Inc. Version 1.06 (i.e. a digital microprocessor controlled instrument providing photometric absorbance, transmittance and concentration measurements with a wavelength range of studied dyes).

For the evaluation of the potential sorptive capacity of different materials the laboratory experiments, in static conditions, applied for aqueous systems or synthetic wastewaters that

contain textile dyes were studied the influence of some operational parameters (temperature, pH, quantity of sorbent, time of equilibrium and initial dye concentration) against the dyes removal.

The biosorption capacity of the sorbents was expressed by:

- the amount of dye sorbed: $q = (C_0 - C) \cdot V \cdot 10^{-3} / G$ (mg of dye/g of sorbent),
- percentage of dye removal (R), $R = [(C_0 - C) / C_0] \cdot 100$ (%)

where: C_0 and C are the initial and equilibrium concentration of dye in solution (mg/L), G is the amount of sorbent (g) and V is the volume of solution (mL).

The relationship between the amount of sorbate at constant temperature and its concentration in the solution equilibrium is named *sorption isotherm*. For the interpretation of sorption equilibrium and calculation of the characteristic constants were used the usual models of isotherms (linear, Freundlich, Langmuir, Dubinin-Radushkevich, Temkin) [37].

The calculation of thermodynamic parameters (ΔG , ΔH and ΔS) [37] and the study of dye sorption kinetic (based on the main models from literature: pseudo-first order (Lagergreen model), pseudo-second order (Ho model) and intraparticle diffusion (Webber and Morris) models [37]) were contributed to the elucidation of sorption mechanism.

2.2. Selected Textile Dyes

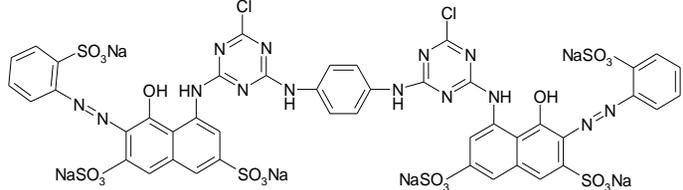
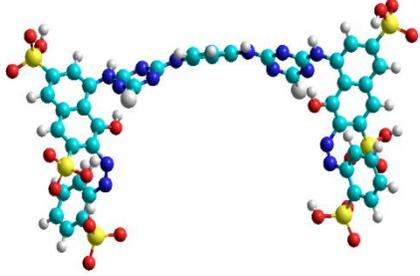
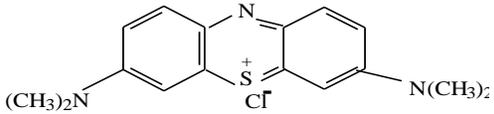
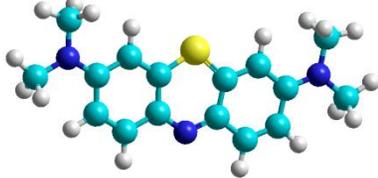
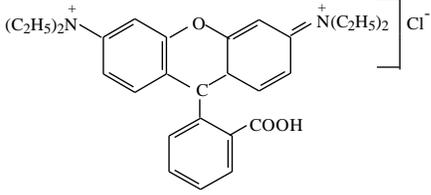
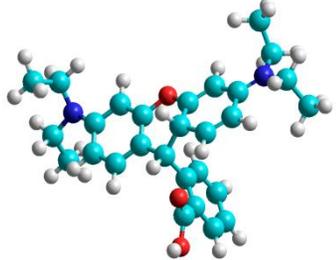
The textile dyes represent a category of organic compounds, generally considered as pollutants, presented into wastewaters resulting mainly from processes of chemical textile finishing.

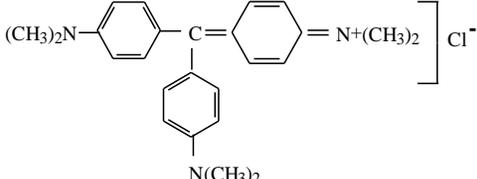
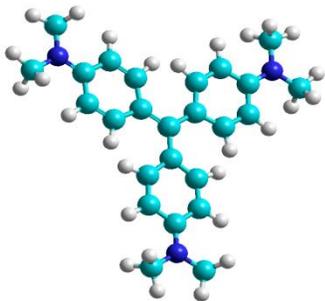
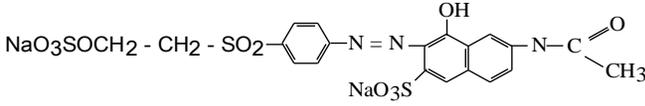
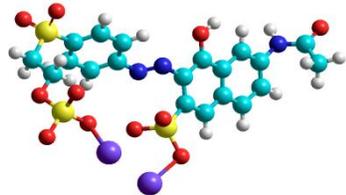
These are aromatic compounds produced by chemical synthesis, and having into their structure aromatic rings that contain electrons delocated and also different functional groups. Their color is due to the chromogene-chromophore structure (acceptor of electrons) and the dyeing capacity is due to auxochrome groups (donor of electrons). The chromogene is constituted from an aromatic structure normally based on rings of benzene, naphthaline or anthracene, from which are binding chromofores that contain double conjugated links with delocated electrons. The chromofore configurations are represented by the azo group (-N=N-), ethylene group (=C=C=), methin group (-CH=), carbonylic group (=C=O), carbon-nitrogen (=C=NH; -CH=N-), carbon-sulphur (=C=S; $\equiv C-S-S-C\equiv$), nitro (-NO₂; -NO-OH), nitroso (-N=O; =N-OH) or chinoide groups. The auxochrome groups are ionizable groups, that confer to the dyes the binding capacity onto the dyeing textile material. The usual auxochrome groups are: -NH₂ (amino), -COOH (carboxyl), -HSO₃ (sulphonate) and -OH (hydroxil).

The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several azo (-N=N-) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable; they exhibit a high resistance to microbial degradation and are highly persistent in natural environment.

The *selected dyes* by authors that are used as commercial salts are characterized in Table 2.

Table 2. Structure and characteristics of the studied dyes

 <p>Brilliant Red HE-3B (Reactive Red 120) C.I. 25810 Anionic, bifunctional reactive dye; MW = 1463 g.mol⁻¹; λ_{\max} = 530 nm; Concentration of the stock solution – 500 mg.L⁻¹</p>	
 <p>Methylene Blue (Basic Blue 9); C.I. 52015 Cationic, phenothiazine dye; MW = 319.85 g.mol⁻¹; λ_{\max} = 660 nm; Concentration of the stock solution – 320 mg.L⁻¹</p>	
 <p>Rhodamine B (Basic Violet 10) ; C.I. 45170 Xanthenic dye; MW = 479.2 g.mol⁻¹; λ_{\max} = 550 nm; Concentration of the stock solution – 479 mg.L⁻¹</p>	

 <p>Crystal Violet (Basic Violet 3); C.I. 42555; Cationic triphenylmethane dye; MW = 407.99 g.mol⁻¹; λ_{max} = 590 nm; Concentration of the stock solution – 408 mg.L⁻¹</p>	
 <p>Reactive Orange 16 C.I.18097; anionic reactive dye; MW = 617.54 g.mol⁻¹; λ_{max} = 495 nm ; Concentration of the stock solution – 500 mg L⁻¹</p>	

Abbreviations: BRed - Brilliant Red HE-3B; MB – Methylene Blue; RB – Rhodamine B; CV - Crystal Violet; RO – Reactive Orange.

2.3. Biosorbents Based on Lignin, Modified Lignin and/or Lignocellulose

The following materials can be used for their properties as biosorbents:

- biomass (natural support, generated by plants, mushrooms, seaweed, microorganisms from soil or water is biodegradable and can be integrated in carbon cycles being also compatible with self control environmental processes) which includes: phytomass agriculturally produced such as lignin – cellulose biomass of wooden plants [22,44] ; the aquatic biomass [45]; biomass obtained as agriculture waste; domestic biomass used in technologies for biogas production; microbial biomass from pharmaceutical and food industry [46-48] ; microorganisms easily available in large amounts in nature or especially cultivated or propagated for these process.
- abundant natural materials as peat, charcoal, moss, sawdust, hemp fibers [35, 49-51];
- biosorbents – resulting from the biomass transforming in a form much easier to use that finally leads to high efficiency of the separation process of biomass containing metals from solution. Also, they are effective and sustainable in repeated long-term applications. Different types of support can be used for retaining biomass with various forms and porosity. Biosorbents can be used as filling material for chromatographic columns used for purifying wastewaters. They are efficient in metal-ions and organic compounds removing from aqueous medium and have the sorption feature superior in comparison with conventional materials from final treatment of effluents.

Table 3. Intrinsic properties of lignocellulosic components of wasted sorptive material [53]

Component	Properties
Cellulose	<ul style="list-style-type: none"> - linear homo polysaccharide with repeating β-D-glucopyranose units - the degree of polymerization is 10000-15000 - high crystallinity and hydrophilicity - capacity to form intra- and intermolecular hydrogen bonds - insoluble in water and common organic solvents - presents three hydroxyls with differ reactivity in the elementary structure - good chelating properties - the presence of interfibrillar interstices, voids and capillaries - negative charge on the macromolecular chains - non toxic - potential enzymatic degradation
Lignin	<ul style="list-style-type: none"> - cross-linked aromatic polymer (phenyl propane units) - hydrophobic and amorphous component of biomass - various reactive groups for chemical activation - insoluble in water (except lignosulphonates) - potential degradation made by micro-organisms like fungi and bacteria
Hemicelluloses	<ul style="list-style-type: none"> - hetero polysaccharide with various sugar units - the degree of polymerization is low (100-200) - amorphous matrix component of vegetal materials - partly or even totally water soluble; soluble in diluted alkali; - low chemical and thermal stability - chelating properties - non toxic - potential enzymatic degradation

A new wasted material, characterized by low cost and huge availability is that with lignocellulosic composition (table 3).

An important constituent of *lignocellulosic materials* is *lignin* (Figure 1) and represent 16% - 33% from composition of plant biomass after celluloses and hemicelluloses. Is an inexpensive natural material, available as a by-product from the paper and pulp industry (50 millions tones /years). Lignin is an aromatic, three-dimensional polymer, containing many oxygen functionalities (phenolic and alcoholic hydroxyl, carbonyl, carboxyl, methoxyl, ether) which can be responsible of the sorptive capacity [53, 54].

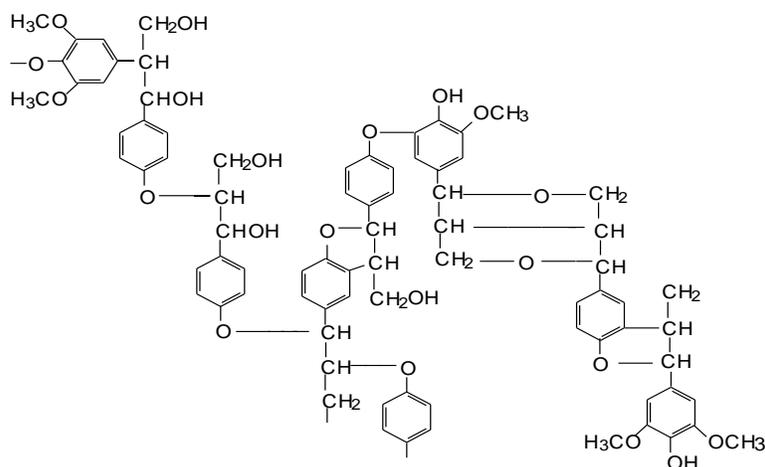


Figure 1. Chemical structure of a portion of a lignin macromolecule.

The wasted lignin is in a huge amount, but less than 10% of them were utilized and this fact is imposing as a serious environmental problem [53, 54].

As a function of the composition of residual vegetal material (table 4) these materials can be valorised by hydrolytic and/or fermentative procedures for obtaining of: etheric oils, furfural, proteic mass, bioethanol, different composts, adhesives, antimicrobial agents, antioxidants, sorptive material for wastewater treatment, alimentary additives, etc.

Table 4. Chemical composition of some vegetal lignocellulosic wastes

Type of agricultural waste	Cellulose	Hexosane	Pentosane	Polyuronic acids	Furfurol	SR obtained from total hydrolysis	Lignin
Creeping stalks of grape vine	29	38	17	9	13	66	35
Corncoobs	32	38	33	7.4	25	79	15
Sunflower seed shells	25	28	17	11	14	56	28
Rice straws	28	32	16	4	12	52	19
Hemp	36	-	25	8	15	61	19
Reed	37	39	20	5	15	67	21

The selected lignocellulosic materials for our works (Table 5) are characterized by high capacity for pollutants removal, employing and disposing, and also low cost, accessibility, high inner and outer surface, macro and micro-porous structure, rapid kinetics of the sorption process, the possibility to use some materials in different shapes (particles of different dimensions, fibres, filters, textures) [16].

Table 5. Characteristics of the employed sorbents

Lignocellulosic sorbent	Characteristics
Industrial lignin	It is the main by-product of the pulp industry and also represents a product obtained from renewable resources The characteristics had been: acid insoluble lignin, 90%; acid soluble lignin, 1 %; COOH, 3.8 mmole/g; aromatic OH, 1.7-1.8 mmole/g; OH/C9 groups chemical method = 1.02; Ash, 2.5 %; pH (10% dispersion) = 2.7; MW = 3510; T softening, 170 °C; Solubility in furfural alcohol, 88.5 %; Solubility in aqueous alkali, pH 12, 98.5%
Sphagnum moss peat	Collected from Poiana Stampei (Romania), sphagnum moss peat is a fibrous natural material. Having as main components: cellulose, lignin, humic and fulvic acids, the peat moss contain different polar functional groups such as carboxyl, carbonyl, phenolic and enolic hydroxide. The employed material has the following physical and chemical characteristics: colour - brown; organic carbon content - 49 w%; total proteins - 7.8 w%; ash 3.44 w%; pH - 3.5; specific surface area - 192 m ² /g.
Sawdust	It is a fibrous waste material produced during the mechanical manufacture of the conifer wood. Sawdust contains various organic compounds (hemicelluloses (10-16%), cellulose (48-57), lignin (27-33%) with polyphenolic groups and, also, ionisable carboxylic groups (uronic acids) which are the most important sorption sites. The humidity of tested material was of 4%.
Cellulignin	Represent a residual product obtained after treating the wood with dilute mineral acid at a temperature of 150-160°C, with following composition: (45-48) % cellulose, (32-35) % lignin, (4-8) % pentosane and (1-1.5) % ash.
Sun flower seed shells	These materials were obtained from local oil industry and used after air drying at room temperature for two days. The seed shells were grounded and sieved to obtain a particle size range of 0.8 mm and stored in plastic bottle for further use. No other chemical or physical treatments were performed. The major constituents of sunflower seed shells are cellulose, lignin and pentose.
Corn cob	The material represents an important by-product from local agro-industrial activities and can be included in the lignocellulosic groups of the sorptive materials. The crude material was dried at room temperature, granulated and sieved to obtain different fractions. We used the fractions with size < 800 µm.

3. PERFORMANCE EVALUATION OF LIGNOCELLULOSIC SORBENT

3.1. Influence of Lignocellulosic Sorbent Nature

The sorption capacity of lignocellulosic materials is closely dependent of their composition (especially the lignin percentage into the polymeric structure, that pretends the highest capacity of dye binding) as well of material graining (Table 4). It can be considered that the highest quantity of lignin can be found into the grape wine stalks close to sunflower

seed shells and reed. It must be mentioned the fact that the lignin is higher than 19% in almost all wasted sorptive materials, fact that give to the tested sorbents good sorptive capacity that is clearly presented into the following table (Table 7).

3.2. Influence of Operating Parameters

Biosorption of different dyes on lignocellulosic materials (natural, such as sphagnum moss peat, and by-products, such as sawdust, cellolignin, lignin, sunflower seed shells, and corncob) is strongly dependent on the solution pH. These sorbents are characterized by the pH of zero charge (pH_{pzc}), as neutral pH beyond which the material surface is either positively or negatively charged. The dyes sorption is dependent on both the ionic charge of the dyes and the ionic character of the sorbent. At pH lower than pH_{pzc} the sorbent has affinity for anionic dyes, but at pH higher than pH_{pzc} the sorbent is available to interaction with cationic dyes (Figure 2a, 2b) [43].

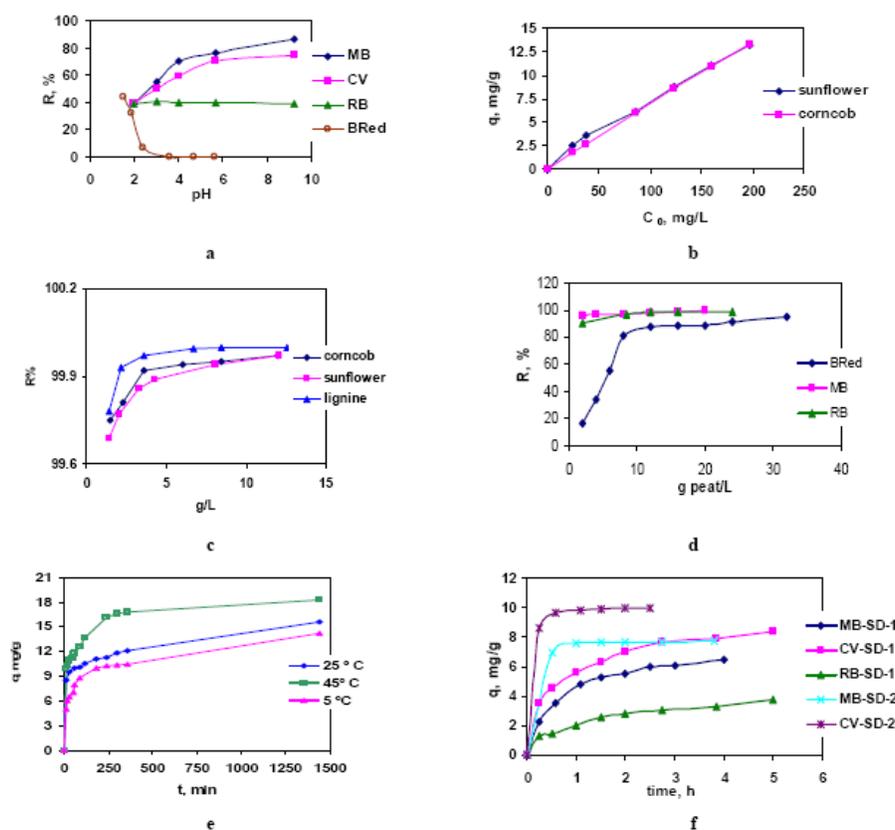


Figure 2. The influence of some operational parameters of the dye sorption onto different wasted materials at room temperature: a) influence of solution pH on the dye sorption on sawdust; b) influence of initial RO dye concentration on sorption onto sunflower shells and corncob; c) influence of dose of corncob, lignin and sunflower seed shell onto sorption the MB dye; d) effect of sphagnum peat dose on sorption the dyes; e) influence of contact time and temperature on the MB dye sorption onto cellolignin; f) influence of sawdust particles size and contact time on sorption of dyes (SD-1 - particle size 1-2 mm, SD-2 – powdered with particle size < 0.1 mm) [10, 43, 55, 56].

Studies about the influence of sorbent dose (Figure 2c) on the decolourization of aqueous dye solutions showed that the sorption of dyes increases with the amount of sorbent. This fact can be attributed to an increase of sorbent surface area availability for more sorption sites than a result of an increase of sorbent amount. In the same time, the amount of sorbed dye per mass unit of sorbent decreased with the increase of sorbent dose.

The results show that the amount of dyes retained increases with increases in initial dye concentration (Figure 2b). Also, the obtained results indicate that the amount of dyes sorbed onto employed sorbents increases with an increasing in temperature, suggesting an endothermic process and, also, the fact that the high temperatures favour the dye molecule diffusion in the internal porous structure of sorbent [10, 21, 43, 55-57]. The effect is more important at higher concentrations.

The influence of sorption time on the decolourization of aqueous solutions containing different textile dyes is different, depending on the sorbent structure (Figures 2e, 2f) [10]. For example, in the case of cellulignin (Figure 2e) the experimental data showed that the removal of dye is faster into initial stages of contact period and then, the amounts of sorbed dye slowly increases near the equilibrium: after 2 hours were removed more than 75 % from the total amount of MB dye corresponding to the dye amount removed after 24 h [58].

3.3. Modelling of the Biosorption Process

3.3.1. Equilibrium Isotherm Models

The equilibrium sorption data were adequately analyzed by the Freundlich, Langmuir, Dubinin-Radushkevich and Temkin sorption isotherm models, in order to calculate the values of sorption constants (Table 6). The best fit equilibrium model was established based on the linear regression correlation coefficients [37]. Figure 3 presents sorption isotherms for dyes removal onto different studied lignocellulosic materials.

Table 6. Mathematical equation forms, constants and parameters of the tested isotherm models [56]

Sorption isotherm model	Linear form of equation	Isotherms parameters, significance	Ref.
Freundlich	$\lg q = \lg K_F + 1/n \lg C$	K_F – adsorption capacity n – adsorption intensity	21
Langmuir	$\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}$	q_0 - saturation capacity K_L - binding (sorption) energy	21
Temkin	$q = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C$	b_T – heat of sorption K_T – intensity of sorption (maximum binding energy)	59
Dubinin-Radushkevich	$\ln q = \ln q_D - \beta_D \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C}\right)$ $E = \frac{1}{\sqrt{-2\beta_D}}$	q_D - the maximum amount sorbed β_D – sorption energy ε - Polanyi potential E – mean free energy of sorption	60

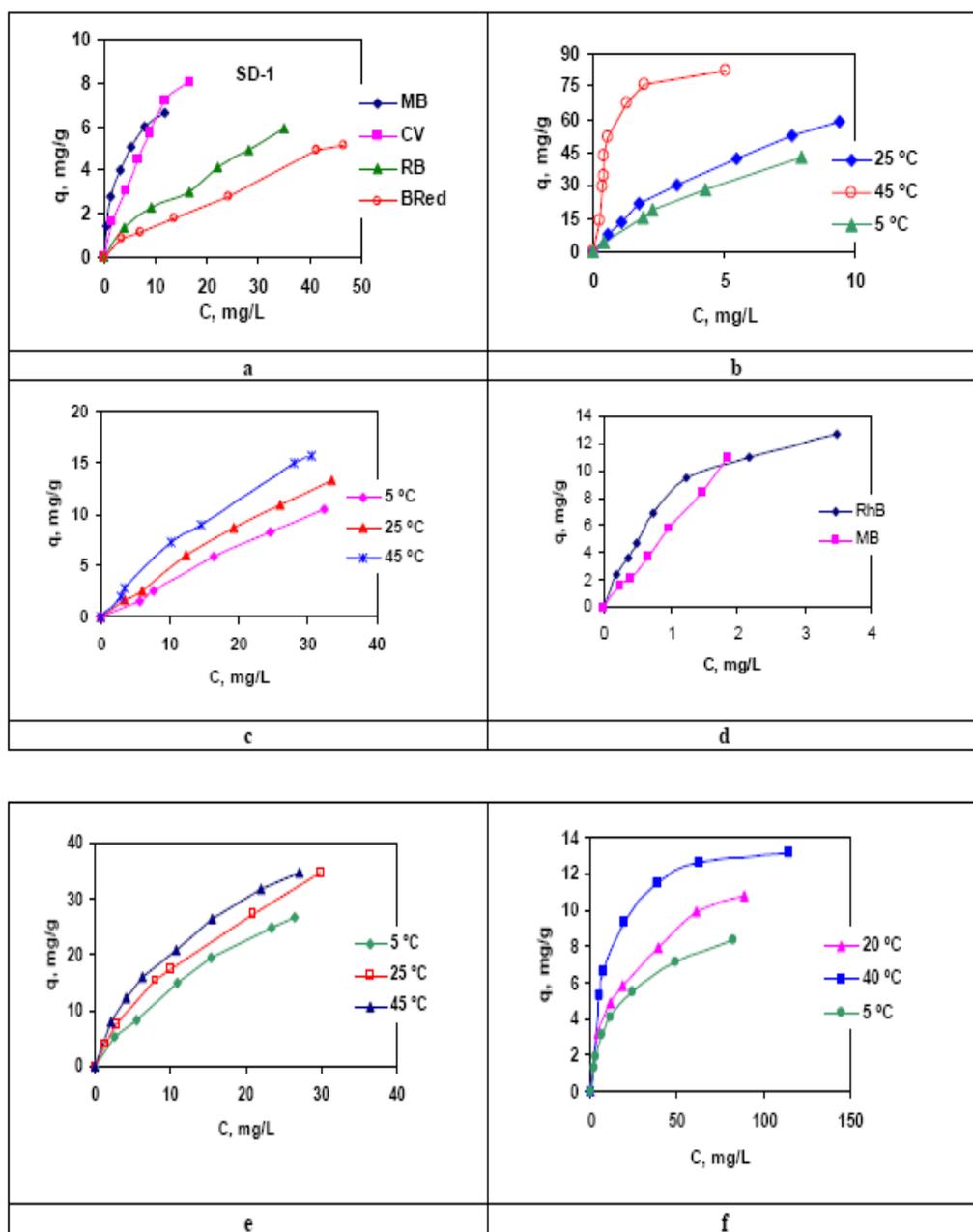


Figure 3. The isotherms of the sorption of some studied dyes onto: a) sawdust; b) MB dye sorption onto cellolignin; c) Orange 16 dye sorption onto corncob; d) peat; e) MB dye sorption onto sunflower seed shell; f) BRed dye sorption onto lignin.

Some of the most important parameters of sorption processes were presented in Table 7, together with the main experimental conditions.

Table 7. The isotherm constants for the biosorption of the studied textile dyes onto lignocellulosic materials

Sorbent	Experimental conditions and sorption constants determined at room temperature (K_L - Langmuir constant; q_0 - the maximum value of sorption capacity; K_F and n - Freundlich constants; C_0 - concentration of dye working solution; E (kJ/mol) - mean energy of sorption)	Ref
Sawdust	BRed: (pH = 2; sorbent dose -20 g/L; C_0 = (20-150) mg/L) q_0 = 11.61 mg/g; K_L = 0.0146 L/mg; K_F = 0.293; n = 1.36;	[41]
	MB:(pH = 5.7; sorbent dose - 4 g/L; C_0 = (6.4-38.4) mg/L) q_0 = 7.215 mg/g; K_L = 0.479 L/mg; K_F = 2.236; n = 1.99	
	CV: (pH= 5.7; sorbent dose - 4 g/L; C_0 = (8.16-48.96) mg/L) q_0 = 12.594 mg/g; K_L = 0.0899 L/mg; K_F = 1.151; n = 1.391	
	RB: (pH = 5.7; sorbent dose - 4 g/L; C_0 = (9.58-57.5) mg/L) q_0 = 7.309 mg/g; K_L = 0.056 L/mg; K_F = 1.95; n = 1.482	
	RO: (pH= 1; sorbent dose - 8 g/L; C_0 = (24.7- 159.25) mg/L) q_0 = 8.554 mg/g; K_L = 0.0175 L/mg; K_F = 0.307; n = 1.562	[10]
Lignin	BRed: (pH = 1.5; sorbent dose - 14 g/L; C_0 = (20-300) mg/L) q_0 = 10.173 mg/g; K_L = 10.19 L/mg; K_F = 1.9602; n = 2.621; E = 13.13 kJ/mol	[23, 42]
	MB: (pH= 6; sorbent dose - 4 g/L; C_0 = (25.6 - 281.6) mg/L) q_0 =28.01 mg/g; K_L = 0.309 L/mg; K_F = 6.179; n = 1.9; E = 11.47 kJ/mol	[61]
	RO: (pH = 1.5; sorbent dose - 12 g/L; C_0 = (30-200) mg/L) q = 6.45-90.46 mg/g; K_L =21.38 L/mg; K_F =3.304; n = 2.964; E =16.18 kJ/mol	this paper
Sunflower seed shell	RO: (pH= 1; sorbent dose - 8 g/L; C_0 = (24.7- 159.25) mg/L) q_0 = 8.554 mg/g; K_L = 0.0175 L/mg; K_F = 0.307; n = 1.562; E = 8.276 kJ/mol	[10]
	MB: (pH= 6; sorbent dose - 4g/L; C_0 = (25.6 - 281.6) mg/L) q_0 = 43.29 mg/g; K_L = 0.0748 L/mg; K_F = 3.49; n = 1.457; E = 9.806 kJ/mol	[55]
Corncob	RO: (pH= 1; sorbent dose - 8 g/L; C_0 = (24.7-159.25) mg/L) q_0 = 8.554 mg/g; K_L = 0.0175 L/mg; K_F = 0.307; n = 1.562; E = 8.28 kJ/mol	[56, 65]
	MB: (pH= 6; sorbent dose - 4 g/L; C_0 = (25.6 - 281.6) mg/L) q_0 = 28.11 mg/g; K_L = 0.4002 L/mg; K_F = 6.725; n = 1.632; E = 10.66 kJ/mol	
Cellolignin	MB: (pH= 6; sorbent dose - 4 g/L; C_0 = (25.6 - 281.6) mg/L) q_0 = 92.59 mg/g; K_L = 0.164 L/mg; K_F = 12.963; n = 1.428; E = 10 kJ/mol	[58]

Abbreviations: BRed - Brilliant Red HE-3B; MB - Methylene Blue; RB - Rhodamine B; CV - Crystal Violet; RO - Reactive Orange.

3.3.2. Kinetic Studies

Effect of contact time on the biosorption of dyes onto lignocellulosic materials was determined by the 'limited bath' technique, when sample of biosorbent was added under stirring to volume of solution of dye with necessary pH and knowing initial concentration. The temperature of solutions was maintained constant, in general at room value. After different contact times, volumes of supernatant were taken for spectrophotometric measurements of dye content. The extent of sorption was expressed by the fractional attainment of equilibrium: $F = \frac{q_t}{q}$, where q_t and q (mg/g) are the amounts of dye sorbed at

time t and at equilibrium (24 h), respectively.

In order to analyse the sorption of dyes onto the lignocellulosic sorbents and also to understand the dynamic of the sorption process in terms of the order of the rate:

- pseudo-first order model (Lagergreen 1898), applied when the sorption is preceded by diffusion through a boundary,
- pseudo-second order kinetic model (Ho model 1999) which assumes that the sorption follows a second order mechanism and the rate limiting step may be chemical sorption involving valence forces or covalent forces between sorbent and sorbate,
- intraparticle diffusion kinetic model (Webber and Morris 1963) which assumes that adsorption is a multi-step process involving transport of sorbate from aqueous solution to the sorption sites of the sorbent and the diffusion into pores is the slow rate determining process.

were applied to the data (Table 8) [23].

Table 8. Mathematical equation forms and constants of the tested kinetic models

Kinetic model	Equation	Kinetic parameters	Ref.
Pseudo-first order (Lagergreen model)	$\lg(q_0 - q) = -\frac{k_1}{2.303}t + \lg q_0$	k_1 – rate constant of pseudo-first order model sorption	[24]
Pseudo-second order (Ho model)	$\frac{t}{q} = \frac{1}{k_2 q_0^2} + \frac{1}{q_0} \cdot t$	k_2 – rate constant of pseudo-second order model sorption $k_2 q_0^2 = h$ – initial sorption rate	[25]
Intraparticle diffusion (Webber and Morris model)	$q = k_p t^{0.5} + c$	k_p is the rate constant for intra-particle diffusion ($\text{mg/g} \cdot \text{min}^{0.5}$) C - constant	[37]

Some of the most important results of kinetic studies about biosorption processes of studied dyes onto selected lignocellulosic sorbents were presented in Table 9, together with the main experimental conditions.

3.3.3. Thermodynamic Studies

The evolution of biosorption vs. temperature modification, together with the calculation of thermodynamic parameters has an important role to determine spontaneity and heat change for the biosorption process.

In order to evaluate the effect of temperature on the dyes biosorption onto lignocellulose sorbents, the apparent thermodynamic parameters (free energy change - ΔG , enthalpy change - ΔH and entropy change - ΔS) were determined using the values of binding Langmuir constant, K_L (L/mol) at temperatures desired, previously determined, and also by the following two equations [37]:

$$\text{Gibbs equation: } \Delta G = -RT \ln K_L \quad (4)$$

$$\text{van't Hoff equation: } \ln K_L = -\frac{\Delta H}{R \cdot T} + \frac{\Delta S}{R} \quad (5)$$

where R is the universal gas constant and T is the absolute temperature.

Table 9. The kinetic evaluation and thermodynamic nature of the biosorption of the studied textile dyes onto lignocellulosic materials

Sorbent	Experimental conditions, kinetic evaluation and thermodynamic nature of biosorption process	Ref
Sawdust	RO: (pH= 1; sorbent dose – 8 g/L; $C_0 = (24.7- 159.25)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.431 \times 10^{-4}$ g/ mg · min); $\Delta G = (-23.352 \div - 20.725$ kJ/mol) - thermodynamic spontaneous sorption process; $\Delta H = -4.8115$ kJ/mol shows the exothermic nature of the sorption process; $\Delta S < 0$	[15]
Lignin	BRed: (pH = 1.5; sorbent dose – 14 g/L; $C_0 = (20-300)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.00547$ g/ mg · min); $\Delta G = (-31.516 \div - 27.468$ kJ/mol) - thermodynamic spontaneous sorption process; $\Delta H = 4.589$ kJ/mol shows the endothermic nature of the sorption process; $\Delta S > 0$	[56]
	MB: (pH= 6; sorbent dose – 4 g/L; $C_0 = (25.6 - 281.6)$ mg/L) $\Delta G = (-31.390 \div - 26.998$ kJ/mol) - thermodynamic spontaneous sorption process; $\Delta H = 3.7587$ kJ/mol shows the endothermic nature of the sorption process; $\Delta S > 0$	[61]
Sunflower seed shell	RO: (pH= 1; sorbent dose – 8 g/L; $C_0 = (24.7- 159.25)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.0105$ g/ mg · min); $\Delta G = (-27.707 \div -21.564$ kJ/mol) - thermodynamic spontaneous sorption process; $\Delta H = 20.952$ kJ/mol shows the endothermic nature of the sorption process; $\Delta S > 0$	[55]
	MB: (pH= 6; sorbent dose – 4 g/L; $C_0 = (25.6 - 281.6)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.00485$ g/ mg · min); $\Delta G < 0$ - thermodynamic spontaneous sorption process	this paper
Corncob	RO: (pH= 1; sorbent dose – 8 g/L; $C_0 = (24.7-159.25)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.045$ g/ mg · min); $\Delta G = (-23.835 \div -22.343$ kJ/mol) - thermodynamic spontaneous sorption process; $\Delta H = -14.324$ kJ/mol shows the exothermic nature of the sorption process; $\Delta S > 0$	[56]
	MB: (pH= 6; sorbent dose – 4 g/L; $C_0 = (25.6 - 281.6)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.00626$ g/ mg · min); $\Delta G < 0$ - thermodynamic spontaneous sorption process	this paper
Cellulignin	MB: (pH= 6; sorbent dose – 4 g/L; $C_0 = (25.6 - 281.6)$ mg/L) sorption process followed the pseudo-second order kinetic model ($k_2 = 0.0062$ g/ mg · min); $\Delta G < 0$ - thermodynamic spontaneous sorption process	this paper

Abbreviations: BRed - Brilliant Red HE-3B; MB – Methylene Blue; RB – Rhodamine B; CV - Crystal Violet; RO – Reactive Orange.

Analysis of thermodynamic parameters must offer supplementary information about the nature of sorption process. Literature data underline that there are two main types of sorption [62, 63]:

- physical, determined by weak forces and characterized by ΔH value no more higher than 4.2 kJ/mol and ΔG values lower than -16 kJ/mol
- chemical, determined by forces much stronger than those implicated in physical process, and characterized by ΔH value higher than 21 kJ/mol and ΔG higher than 20 kJ/mol.

The appreciation of the thermodynamic nature of biosorption processes of studied dyes onto lignocellulosic sorbents were presented in Table 9, together with the main experimental conditions.

In all the studied cases, the negative values of apparent free energy change (ΔG) indicate that the dyes biosorption onto studied materials is spontaneous and feasible thermodynamically on the studied temperature range. The positive values of enthalpy change (ΔH) confirmed the endothermic nature of biosorption process (the case of Orange 16 reactive dye biosorption onto sunflower seed shells and Brilliant Re HE-3B reactive dye sorption onto lignin), and the negative values of enthalpy change (ΔH) underline the exothermic nature of biosorption process (the other cases) (Table 9). The positive value of entropy change (ΔS) suggests the increased randomness at the solid-liquid interface during the biosorption of dyes and some structural changes in the sorbate and the sorbent [55]. It can be suggested that the driving force of biosorption is an entropy effect.

4. AN OVERVIEW OF RECENT LITERATURE ON THE SORPTION OF TEXTILE DYES ONTO LIGNOCELLULOSIC SORBENTS

The importance of introduction of new materials with sorptive properties, preferably ease to be procured, cheap and ease to be conditioned and operated, that will give a high efficiency to the sorption process into favourable economic conditions, is illustrated by the numerous studies from scientific literature [16, 25, 32, 35-37]. It must be underlined especially the natural materials, agro-industrial and industrial by-products, wastes from agro-industrial processing, that have a complex composition, are biodegradable, composed by a complex of lignocellulosic substances. These materials, named also 'biosorbents' were used for removal of pollutants with inorganic origin but also organic (such as dyes) one from different aqueous systems.

The studies were extended also in the field of dyeing effluent treatment. Thus, in Table 10 are selected a series of recent results on sorption/biosorption of some textile dyes onto different lignocellulosic biosorbents.

Table 10. Literature data selection of ‘batch biosorption’ of different types of dyes onto lignocellulosic biosorbents

Lignocellulosic materials	Dye	Adsorption capacity, mg/g	Ref
Modified spherical sulphonic lignin provided by a bamboo pulp mill	Cationic Red GTL Cationic turquoise GB Cationic Yellow X-5GL	576.0 582.4 640.8	62
Rice husk	Methylene Blue	321.26	63
Rice straw thermochemically modified (with carbonyl groups)	Basic Blue 9 Basic green 4 (malachite green)	256.4 238.1	64
Rice straw Rice straw thermochemically modified with citric acid as esterifying agent	Basic green 4 (malachite green) Basic green 4 (malachite green)	94.34 256.41	65
Rice husk	Methylene Blue	40.5833	66
Rice straw – derived char	Basic green 4 (malachite green)	148.74	67
Rice straw modified with phosphoric acid	Methylene Blue	208.33	68
Cedar sawdust	Methylene Blue	142.36	69
Beech wood sawdust	Direct Brown Direct Brown 2 Basic Blue 86	526.3 416.7 136.9	70
Beech sawdust Prehydrolysed beech sawdust	Methylene Blue Red Basic 22 Methylene Blue Red Basic 22	9.78 20.16 30.5 24.10	71
Salts treated beech sawdust CaCl ₂ ZnCl ₂ MgCl ₂ NaCl	Methylene Blue	12.3 11.7 14.2 9.2	72
Poplar sawdust	Metanil Yellow Methylene Blue	1.996 0.3744	73
Tree fern	Basic Red 13	408	74
Wood shavings Treated wood shavings: - with HCl 0.5 mol/L - with Na ₂ CO ₃ -with Na ₂ HPO ₄	Methylene Blue Methylene Blue Methylene Blue Methylene Blue	17.92 1.248 268.8 6.08	75
Pumpkin seed hull	Methylene Blue	141.92	76
Coffee husks	Methylene Blue	90.1	77
Peanut hull	Methylene Blue	68.03	78
Dehydrated peanut hull	Methylene Blue	108.6	79
Cereal chaff	Methylene Blue	20.3	80
Palm shell powder	Methylene Blue Rhodamine 6G	121.5 105.0	81
Hazelnut shells	Congo Red	13.75	82
Hazelnut shells	Methylene Blue Acid Blue 25	76.9 60.2	83
Wood sawdust - walnut	Methylene Blue Acid Blue 25	59.17 36.98	
- cherry	Methylene Blue Acid Blue 25	39.84 31.98	
- oak	Methylene Blue Acid Blue 25	29.94 27.85	

Lignocellulosic materials	Dye	Adsorption capacity, mg/g	Ref
- Pitch-pine	Methylene Blue Acid Blue 25	27.78 26.19	
Sunflower seed shells	Reactive Black 5	0.875	84
Husk of mango seed	Acid Blue 80 Acid Blue 324 Acid green 25 Acid green 27 Acid Orange 7 Acid Orange 8 Acid Orange 10 Acid Red 1	9.2 12.8 8.6 12.3 17.3 15.2 8.3 11.2	85
Waste sugar beet pulp	Gemazol turquoise blue-G	234.8	86
Cashew nut shell	Congo Red	5.184	87
Banana stalk waste	Methylene Blue	243.90	88
Castor seed shell	Methylene Blue	158	89
Wheat straw modified with citric acid	Methylene Blue Crystal Violet	321.50 227.27	90

CONCLUSIONS

The lignocellulosic materials (i.e. lignin, sawdust, sunflower seed shells, corncobs) can be used as good and resistant sorbents for removal of different potential pollutants from wastewaters (e.g., heavy metals, dyes, other organic compounds), due to their fundamental characteristics, such as mechanical resistance, high porosity and specific surface area, hydrophilic character, tolerance to biological adsorbed solid layers, easy functionalization, the possibility of being used in different forms and regimes.

The influence of some operational parameters or factors (i.e. pH, initial pollutant concentration, temperature, contact time, sorbent concentration etc.) is studied in order to find the best operational condition for high sorption efficiency. These are dependent on the pollutant types, characteristics, chemical structure, initial concentration, and also the initial wastewater flow, working regime, the manner of phase contact (L/S) etc.

There were analyzed some kinetic models, determined the forms of different sorption isotherms, calculated the main sorption constants, sorption kinetic and thermodynamic parameters in order to find the nature of sorption interaction between pollutants and aquatic environment and the optimal conditions in order to apply these laboratory scale results into a real case of a textile chemical finishing effluent.

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