Chemical Modification of Lignin and Its Environmental Application

Zhili Li, Yuanyuan Ge, Jiubing Zhang, Duo Xiao and Zijun Wu

1 Introduction

Lignin constitutes one of the main component of lignocellulosic biomass (15–30% by weight), which is second only to cellulose in mass on the earth. Lignin acts as the essential glue that gives plants their structural integrity and resistance against microbial, chemical attack and prevents other outside stresses from destroying the structure of plant cell walls [1]. Lignin is a complex and recalcitrant phenolic macromolecule composed of three phenylpropane units: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), cross-linked by β-o-4, α-o-4, β-β, and 5-5′ bonds etc. (as depicted in Fig. 1). Among them, the main linkage is the β-o-4 bond, about 40–60% of all inter-unit linkages in lignin belong to this bond [2]. The component and structural characterizations of lignin are quite different even it is separated from the same plant. It is to say, the lignin obtained from a plant is a mixture of different lignin polymers which is dependent on the source plant, species, and growing ages of the plant, such as softwood, hardwood, and grass [3].

A large quantity of technical lignin was produced as a main component in black liquor by the pulp and papering industry, which is a big threat to the environment [4]. It is estimated that the global annual production of technical lignin in pulp making is *ca.* 70 million tons, much of which is consumed as a low-value fuel. Although there are some other applications, such as a binder or dispersing agent, no large-scale application has so far been found [4]. Lignin has significant potential as a source for the production of the bio-renewable polymer [5, 6]. The main active sites of lignin are comprised of phenolic or alcoholic hydroxyl groups, which accounts for its

---

Z. Li (✉) · Y. Ge (✉) · J. Zhang · D. Xiao · Z. Wu
School of Chemistry and Chemical Engineering, Guangxi University,
100 Daxuedong Road, Nanning 530004, China
e-mail: lizhili@gxu.edu.cn

Y. Ge
e-mail: geyy@gxu.edu.cn

Inamuddin et al. (eds.), *Sustainable Polymer Composites and Nanocomposites*,
https://doi.org/10.1007/978-3-030-05399-4_45

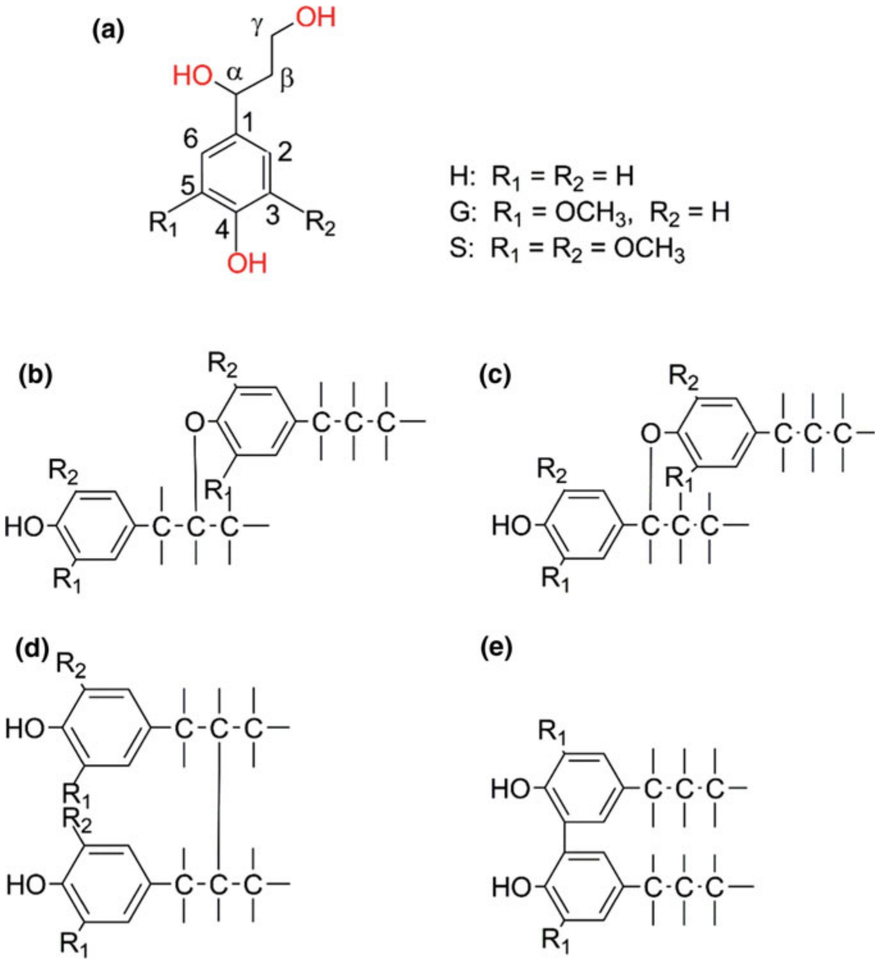

Fig. 1 **a** The phenylpropane type units: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S); and **b** β-o-4, **c** α-o-4, **d** β-β, and **e** 5-5′ linkages in lignin

reactivity, hydrophilicity as well as other chemical and physical attributes of lignin [2]. Recently, due to the unique polyphenol structure, chemical stability and wide availability, different kinds of adsorbents, particularly for dyes and heavy metals removal from wastewater are potentially obtainable from lignin [7].

Water pollution by different kinds of contaminants is currently serious concerned [8–13]. A large amount of organic, inorganic, and biological compounds have been reported as water contaminants. For example, the dyes, particularly azo dyes are recalcitrant molecules and resistant to aerobic digestion and are also stable to oxidizing agents that makes them being hard to treat [14]. The heavy metals, lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As), etc., are notorious with high toxicity and carcinogenicity. These toxic pollutants, even with a trace amount in water, can pollute water resources and transfer throughout the food chain to accumulate in animals and mankind, causing various diseases and disorders [15]. Therefore, the pollutants should be removed before its discharge into the environment.

Several physical and chemical treatment techniques have been reported for the removal of pollutants from wastewater, including precipitation, oxidation, biodegradation, ion exchange, adsorption [16], membrane separation [17–19], coagulation and flocculation, flotation, electrochemical methods. These methods still suffer from the limitations of low effectiveness and high cost.

Adsorption using cost-effective adsorbents is now considered as an efficient, convenient and economical method for wastewater treatment, due to the feasibility in design and operation, effectiveness in treating and the recyclability of the adsorbents [20, 21]. Activated carbon (AC) is being recognized as one of the most popular adsorbents used in the removal of contaminants from water. However, AC is of high capital cost due to the prolong production process [22]. In recent years, the development of various environmentally friendly adsorbents from biomass, biopolymers, especially the natural-occurring polymers, including cellulose, lignin, and chitosan, etc., has been intensified [23–25]. It could be seen from the literature that the adsorption of dyes and heavy metals using lignin is one of the most reported methods for the removal of contaminants from water [26–28].

Unfortunately, original lignin is less competitive in adsorption applications due to the low adsorption capability, and lignin does not own specific selectivity for a certain kind of pollutant from complex polluted water [29, 30]. The goal for the lignin modification for pollutants adsorption is to promote the adsorption capability, including adsorption capacity, stability, selectivity and recyclability [15]. The ease of separation from wastewater after the operation and the cost-effectiveness of the adsorbents should also be considered. The modification of lignin could be achieved by various methods including crosslinking, hybridization, hydrogen bonding formation, condensation, grafting and copolymerization [31]. Therefore, the main objective of this article is to collect and compile the most recent reported literature regarding the modified lignin for adsorption applications and to discuss the advantageous and disadvantageous issues of the resulting lignin as an adsorbent to remove o different environmental pollutants from the aqueous phase.

2 Modified Lignin for Dyes Adsorption

Dyes contaminated wastewater is hard to treat because of their inert properties and the residual trace amount of dyes in water. Recently, adsorption techniques using modified lignin have been widely reported in removing dyes as a promising wastewater treatment process. The dyes adsorption capacities of the modified lignin-based adsorbents are tabulated in Table 1. And the modified lignin-based materials for removing dyes will be fully discussed in the following section.

Table 1 Reported modified lignin for adsorption of dyes in water

Modified lignin	Dye	T (°C)/pH	Q_m (mg/g)	Reference
Chitosan-alkali lignin	RBBR	27/5.9	111.11	[32]
ALiCE	MB	20/7.0	36.25	[33]
Chitin/lignin hybrid	DB71	20–50/2.4–8.4	40.0	[28]
CAML	C-3R	RT/4.0–10	99.3%	[34]
	MO		67.0%	
LBF	RB	–/2.0–10	93%	[34]
MLS	MB	40/–	31.23	[35]
	RB		17.62	
Oxidized lignin	EV	30/7.0	70–80 wt%	[36]
	BB		80–95 wt%	
ALR	CV	25/3.0–12	150.4	[37]
Lignin-g-p(AM-co-NIPAM)/MMT	MB	25/1.0–11.0	9646.9	[38]
LS-g-AA	MB	30/3.0–8.0	2013	[39]
LPUF	MG	25–65/2.0–9.0	80	[40]
AAL	MB	30/5.0	63.3	[41]
Lignin sulfonate polymer	MG	30/7.0	60.2	[42]
LSMMs	MG	24/3.0–7.0	150.3	[43]
The hydrogel of acylated hemicelluloses, acrylic acid and lignosulfonate	MB	30–70/7.0–10	2691	[44]
Hydrogel of kraft lignin-*N*-isopropyl acrylamide	MB	15–45/1.0–11	–	[45]
CML-Al	PB	25/2.0	73.52	[46]
CML-Mn			55.16	
CML-Fe	BR-2	25/2.0	73.6	[47]

Nair et al. [32] reported a novel chitosan-alkali lignin composite prepared from chitosan and alkali lignin (as shown in Fig. 2). The weak interactions between β-1,4-glycosidic linkage, amide and hydroxyl groups of chitosan, and ether, an aromatic ring and hydroxyl groups of alkali lignin, impart enhanced surface and chemical properties to the composite than chitosan and alkali lignin. The composite with 50:50 chitosan: alkali lignin exhibited maximum adsorption (111.11 mg/g) of Remazol Brilliant Blue R (RBBR) compared to chitosan (76.92 mg/g), which showed that the composite exhibits 33% improvement in the maximum adsorption amount. Batch adsorption of RBBR on the composite followed the Langmuir equation, while the dynamic adsorption followed the pseudo-second-order equation. A lignin-chitosan pellet (ALiCE) was prepared for adsorption of methylene blue (MB) [33]. The results indicated the ALiCE had a maximum adsorption capacity of 36.25 mg/g for MB according to the fitting of the Langmuir equation ($R^2 = 0.997$), yielding. The adsorption kinetic data could be fitted well by the pseudo-second-order-model [33]. A chitin/lignin hybrid biosorbent was prepared

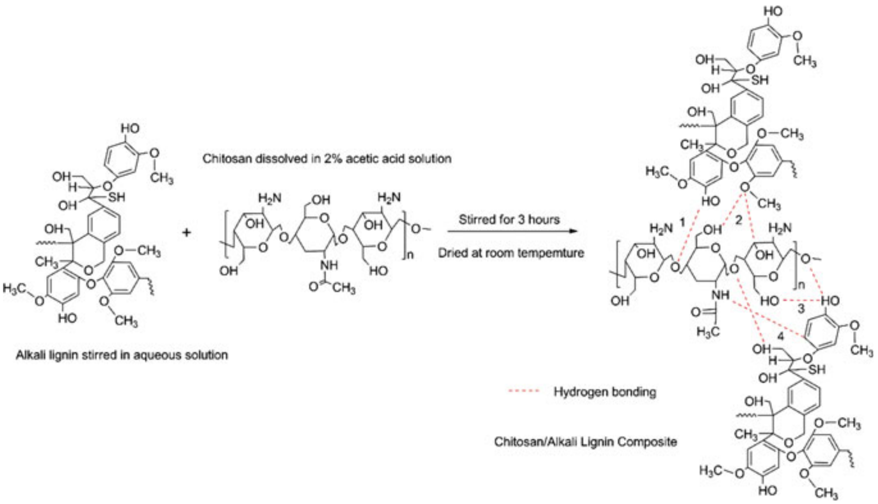

Fig. 2 An illustrative diagram of chitosan-alkali lignin composite. Reprinted with permission [32]. Copyright 2014 Elsevier

and used to adsorb C.I. Direct Blue 71 (DB71) from water [28]. The adsorption capacities of DB71 by the chitin and chitin/lignin hybrid biosorbent were 30.7 and 40 mg/g, respectively, which indicated that the hybrid chitin/lignin material has a stronger adsorptive affinity for DB 71 than the chitin. The adsorption of DB 71 onto the hybrid could be described by the Freundlich equation and the pseudo-second-order equation, respectively. The optimum solution pH for dye removal was in the range 2.4–8.4. The adsorption of DB 71 by the chitin/lignin hybrid was spontaneous and endothermic in nature [28].

Lou et al. [34] developed a ternary graft copolymer based on chitosan, acrylamide, and lignin (CAML) by a microwave-assisted method (as shown in Fig. 3). The copolymer was loosely aggregated powder with a particle size range of 1–3 μm. Adsorption experiment showed that the CAML (chitosan:acrylamide:lignin = 1:1:1) exhibited maximum removal efficiency of 99.3 and 67.0% for reactive orange C-3R and methyl orange, respectively. The CAML had a wide suitable pH range, although the removal efficiency was slightly higher under lower pH values. The removal mechanism was combined charge neutralization and bridging effects [34]. Guo et al. [48] prepared a lignin-based flocculant (LBF) via grafting

$$\text{Chitosan} + \text{Acrylamide} + \text{Lignin} \xrightarrow[K_2S_2O_8\ +\ Na_2S_2O_3]{\text{Microwave irradiation}} \text{CAML polymer solution}$$

$$\xrightarrow[\text{filtration}]{\text{ethanol}} \text{CAML cake} \xrightarrow{\text{freeze drying}} \text{CAML powder}$$

Fig. 3 Synthetic process of CAML. Reprinted with permission [34]. Copyright 2018 Elsevier dimethyldiallylammonium chloride and acrylamide onto lignin. Adsorption results demonstrated that a high removal efficiency of 93% was achieved for the reactive dye by LBF with the addition of PAC. The high removal efficiency of dye by LBF was because of the electrostatic attraction effect and bridging action [48].

Li et al. [35] prepared magnetic lignin spheres (MLS) from different organosolv lignins with maleic anhydride and Fe_3O_4 nanoparticles. The adsorption amounts of methylene blue and Rhodamine B by the MLS from larch lignin (31.23, and 17.62 mg/g, respectively) were higher than that from poplar lignin (25.95 and 15.79 mg/g, respectively). The adsorption kinetics and isotherm were could be described by the pseudo-second-order equation and Langmuir equation, respectively. Moreover, the MLS from larch and poplar lignin had a good recyclability, after three cycles of adsorption-desorption, the removal efficiencies for the dyes still remained at 98 and 96%, respectively [35].

Couch et al. obtained [36] oxidized lignin products from softwood lignin by using HNO_3 (as shown in Fig. 4). The products were used to remove ethyl violet (EV) and basic blue (BB) dyes from simulated water. The results showed that the dyes removal efficiency was 70–80 wt% for EV and 80–95 wt% for BB within the dyes concentrations of 50 and 400 mg/L. The dye removal was pH and ionic strength dependent. Feng et al. [41] prepared a methylene blue (MB) adsorbent from acetic acid lignin (AAL) via deacetylation in NaOH aqueous solution followed by fractionation in methanol. The maximum adsorption capacity of MB reached to 63.3 mg/g by the AAL. In addition, the adsorption of MB was pH and dosage dependent.

Xu et al. [37] developed an acrylic-lignosulfonate resin (ALR) from calcium lignosulfonate and acrylic acid. The resin had a high surface area of 190.55 m^2/g with a porous structure in an average pore diameter of 11.34 nm. The maximum adsorption capacity of crystal violet (CV) by the ALR was 150.40 ± 4.80 mg/g at 25 °C. The kinetic and equilibrium data could be fitted by the pseudo-second-order equation and Freundlich equation, respectively. In addition, the calculation of thermodynamic parameters demonstrated the adsorption of CV on ALR was exothermic and spontaneous in nature.

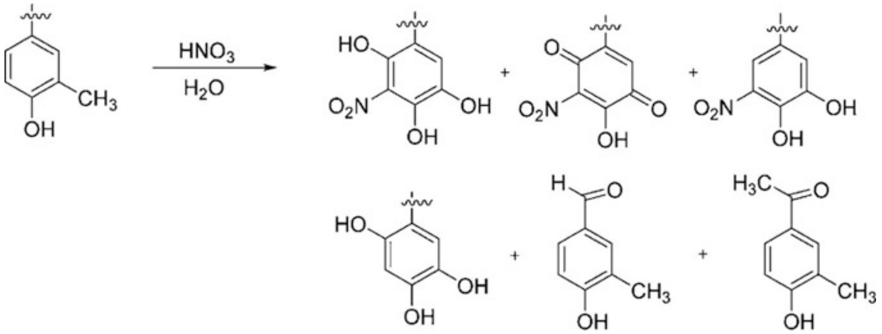

Fig. 4 Scheme of oxidized softwood lignin products. Reprinted with permission [36]. Copyright 2016 American Chemical Society

Wang et al. [38] prepared a hybrid hydrogel from lignin grafted with acrylamide and N-isopropyl acrylamide as well as montmorillonite (lignin-g-p(AM-co-NIPAM)/MMT, as shown in Fig. 5). The prepared hydrogel presented thinner pore walls, good thermal stability and strong mechanical strength due to the existence of montmorillonite. The hydrogel showed an excellent removal efficiency for methylene blue in water, as indicated by the maximum adsorption capacity of 9646.92 mg/g. The adsorption was dependent on the pH and temperature. Dynamic adsorption could be described by the pseudo-second-order equation, while both of the Langmuir and Freundlich equations could describe the equilibrium adsorption. Furthermore, the hydrogel showed an excellent reusability within five adsorption-desorption cycles.

Yu et al. [39] also prepared an LS-g-AA hydrogel by grafting of acrylic acid on lignosulfonate backbone using *N*,*N′*-methylene-bis-acrylamide and laccase/t-BHP (tert-butyl hydroperoxide) as cross linker and initiator respectively (Fig. 6). The successful grafting of the monomer was confirmed using FTIR. The prepared hydrogel showed a high adsorption capacity of 2013 mg/g for methylene blue (MB) dye in water. Besides, excellent reusability was shown by the LS-g-AA hydrogel with adsorption capacity of 1757 and 1681 mg/g for 3 and 4 cycles, respectively.

Kumari et al. [40] reported a pine needle lignin-based polyurethane foam (LPUF) as an adsorbent of dyes removal from water. The experiment results showed that the LPUF was effective in removing a cationic dye, malachite green (MG) with a maximum adsorption capacity of 80 mg/g, other than an anionic dye, methyl orange (MO), from the water. The adsorption kinetics and isotherms could

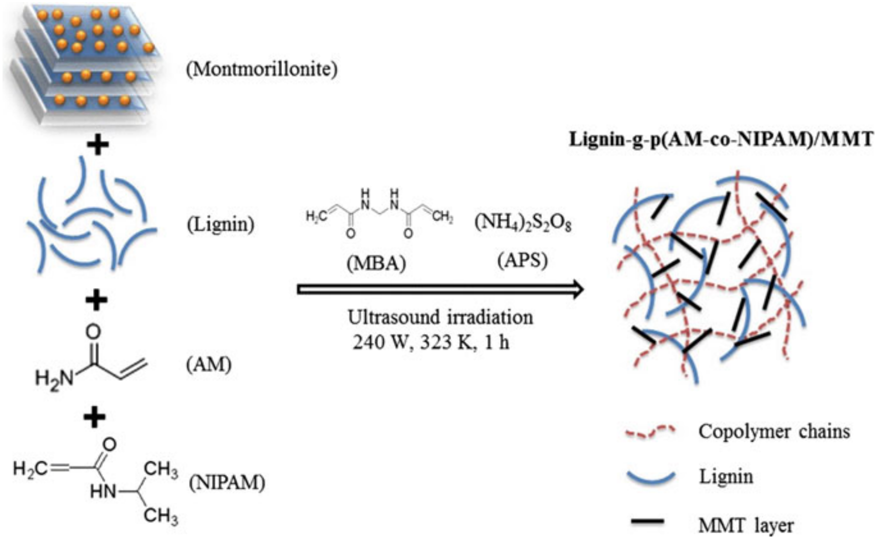

Fig. 5 Diagram of synthesis of lignin-g-p(AM-co-NIPAM)/MMT. Reprinted with permission [38]. Copyright 2017 Elsevier

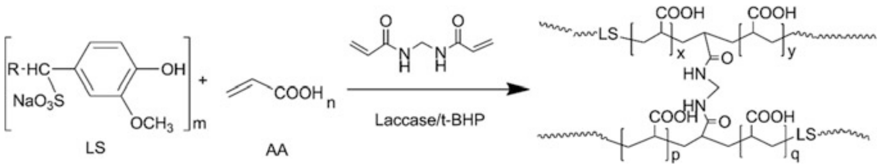

Fig. 6 Synthesis of LS-g-AA hydrogel from lignosulfonate and acrylamide catalyzed by laccase. Reprinted with permission [39]. Copyright 2016 Elsevier

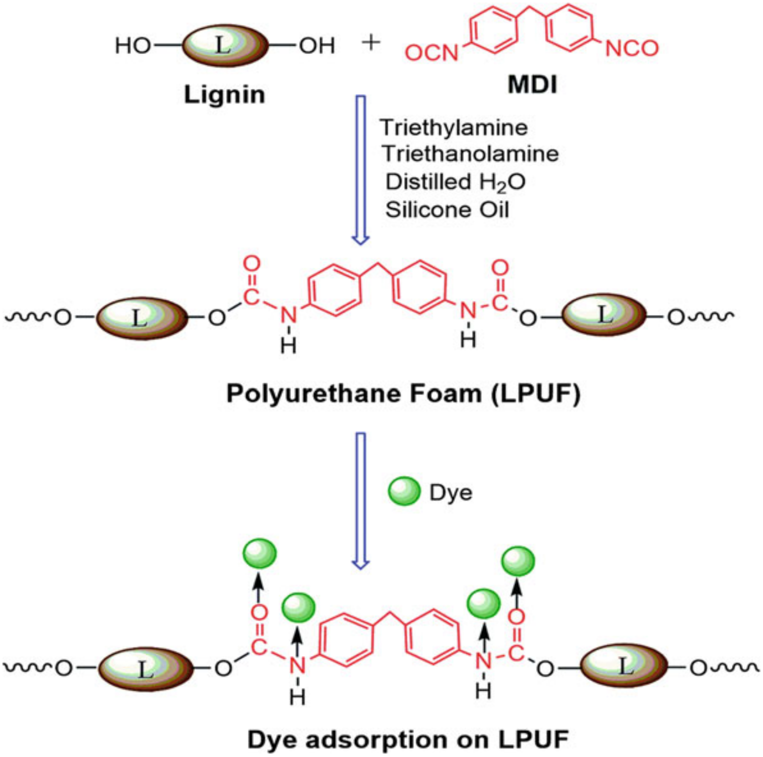

Fig. 7 Schematics of LPUF synthesis and application. Reprinted with permission [40]. Copyright 2016 Royal Society of Chemistry

be described well by the pseudo-second-order equation and Langmuir equation, respectively. Moreover, the LPUF could be used for 20 regeneration cycles with a cumulative adsorption capacity of 1.33 g/g to MG (Fig. 7).

Tang et al. [42] have reported their studies on the preparation of a lignin sulfonate polymer by a simple emulsion polymerization method and the adsorption properties of the lignin sulfonate polymer towards malachite green (MG) dyes (as shown in Fig. 8). The obtained lignin sulfonate polymer showed an effective

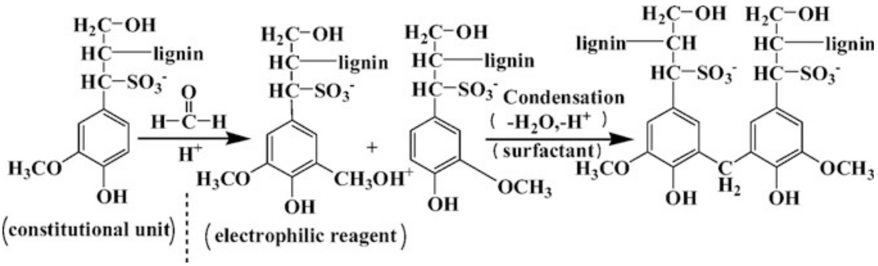

Fig. 8 Schematic diagram of the lignin sulfonate polymer. Reprinted with permission [43]. Copyright 2016 Royal Society of Chemistry

adsorption of MG with a maximum adsorption capacity of 60.2 mg/g for MG according to the Langmuir equation. A Lignosulfonate-based mesoporous material was further prepared by grafting of acrylic acid and acrylamide onto the backbone of lignosulfonate for adsorbing MG from the water. This synthesized material was mesoporous confirmed by using N_2 adsorption/desorption curve. The BET surface area was 118 m^2/g and the mesopores are in an average diameter of 3.8 nm. Due to the presence of pores in the mesoporous material, it showed an enhanced adsorption capacity, 150.376 mg/g for MG.

Song et al. [44] prepared a hydrogel consisted of acylated hemicelluloses, acrylic acid, and sodium lignosulfonate by using initiator ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine. The honeycomb-like morphology was observed in the prepared hydrogel. The adsorption kinetics of methylene blue (MB) by the hydrogel was fitted well with pseudo-second-order kinetics and the isotherm was fitted well with the Langmuir isotherm model, respectively. The adsorption capacity of MG by the hydrogel could reach to 2691 mg/g. Even after a further cycle, the hydrogel exhibited an approximately 80% adsorption efficiency for MG, and accordingly, it was proposed to be a promising material for dye removal from wastewater [44].

Adebayo et al. prepared carboxyl-methyl lignin CML from the acid hydrolysis lignin from sugarcane bagasse (as shown in Fig. 9) [46]. The CMLs was further bound with Al(III) (CML-Al) and Mn(II) (CML-Mn) for the removal of Procion Blue MX-R (PB) in aqueous solutions. The experiment optimum pH and contact time were 2.0 and 5 h, respectively. The CML-Al and CML-Mn showed a

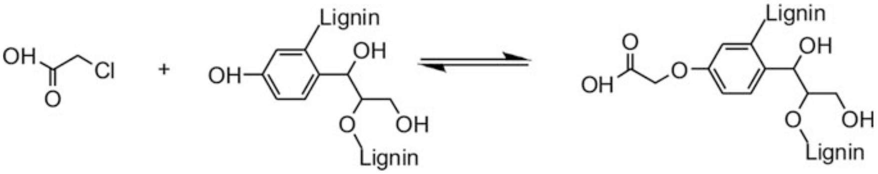

Fig. 9 Schematic of Carboxyl-methyl lignin (CML) from lignin and monochloroacetic acid. Reprinted with permission [46]. Copyright 2014 Elsevier

maximum adsorption capacity of 73.52 and 55.16 mg/g for PB at 25 °C, respectively. 98.33% of CML-Al and 98.08% of CML-Mn could be regenerated from dye-loaded adsorbents by using 50% acetone + 50% of 0.05 mol L^{-1} NaOH. After four adsorption-desorption cycles, the removal efficiency of the dyes still remained *ca.* 93.97% and *ca.* 75.91% by the CML-Al and CML-Mn, respectively. Silva et al. [47] also reported a carboxy-methylated lignin complexed with Fe^{3+} (CML-Fe) for the adsorption of Brilliant Red 2BE (BR-2) textile dye from aqueous solutions. The maximum adsorption capacity of BR-2 was 73.6 mg/g by the CML-Fe adsorbent. Besides, the dye-loaded adsorbent could be recycled with 0.050 mol/L NaOH.

3 Modified Lignin for Heavy Metals Adsorption

Heavy metal ions are more toxic than dyes and cover a wider region of pollutants during the past decades. Modification of lignin by introducing the desired properties in physical, chemical and mechanic properties is a key issue to achieve proper characters of lignin including the hydrophilicity, hydrophobicity and adsorption ability. The most common strategies in the modification of lignin for heavy metal ion adsorption include amination, methylolation, alkylation, carboxylation, acylation, sulfonation/sulfomethylation, phosphorylation, and copolymerization etc.

Ge et al. [49] prepared an aminated lignin-based adsorbent from alkaline lignin grafted by methylamine and formaldehyde, as shown in Fig. 10. Kinetic adsorption suggested the aminated lignin could adsorb Pb(II) in water quickly and the adsorption process could be described well by a second-order model. The obtained adsorbent presented a maximum adsorption amount of 60.5 mg/g for Pb(II) that was 4.2 fold of the original alkaline lignin. Ge et al. [50] further investigated the influence of numbers of the carbon in an alkyl, from C2 (ethyl) to C18 (octadecyl), on the adsorption capacity of lignin for the lead ion. The results indicated that the carbon number had a strong influence on the adsorption of Pb(II). A suitable carbon number of alkyl (C4) helped the adsorption of Pb(II), due to the electron donating ability of the alkyl groups. Recently, Huang et al. [51] reported a modified enzymatic hydrolysis lignin-containing nitrogen and sulfur moieties, which showed a high adsorption capacity of 180 mg/g for Hg(II) at 25 °C. The adsorption kinetics

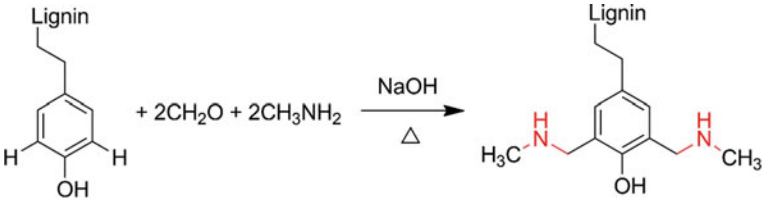

Fig. 10 Synthetic diagram of a Mannich base from lignin. Reprinted with permission [49]. Copyright 2015 Elsevier

could be fitted well with the pseudo-second-order equation, while the adsorption isotherms could be fitted well with the Freundlich equation. Besides, the increasing value of the constant (*n*) with temperature indicated the adsorption became more favourable at a higher temperature.

Carboxyl is a common component of lignin. The frequency of the group can be adjusted by chemical modifications as well as the hydrophilicity and polyelectrolyte characters. Quintana et al. [52] investigated the oxidized lignins from sulfuric acid pretreated cane bagasse, soda pulping bagasse, eucalypt Kraft lignin and commercial Kraft lignin. The results indicated the oxidized lignins showed higher adsorption capacities than the original lignins, due to the higher contents of carboxyl groups in the oxidized lignins. Peternele et al. [53] reported a functionalized formic lignin from sugarcane bagasse for the adsorption of Pb(II) and Cd(II). Batch adsorption equilibrium could be described well by the Langmuir equation. The oxidative modification of a wheat straw organosolv lignin has been investigated by Dizhbite et al. [54] to introducing –COOH and –OH groups. The oxidation was conducted under a polyoxometalate $H_3[PMo_{12}O_{40}]$ and O_2 or H_2O_2. The oxidative modification did not damage the lignin skeleton, while the carboxyl and hydroxyl group's contents in lignin increased distinctly. As expected, the oxidized lignin showed high adsorption amounts of 35.9 and 155.4 mg/g toward Cd(II) and Pb(II), respectively, at pH 5, 20 °C.

Sulfonate functional groups can be introduced into lignin via sulfomethylation and sulfonation, which has been reported as an effective way to improve the hydrophilicity of lignin [55, 56]. Li et al. [29] prepared a modified lignin-containing both amino and sulfonic groups (as shown in Fig. 11). It was found that the modified lignin could adsorb heavy metals effectively even at low pH values. The dynamic adsorption and equilibrium adsorption could be fitted well by the pseudo-second-order equation and D–R equation, respectively. Xu et al. [57] developed a mesoporous lignin-based biosorbent (MLBB) from rice straw. The MLBB had an excellent adsorption performance for Pb(II) with a maximum capacity of 952 ± 31 mg/g at 20 °C, which was due to the large surface area (186 m^2/g), plenty of mesopores (d_p = 5.5 nm) and high content of sulfonic groups (S: 2.51 ± 0.01%)].

Dithiocarbamated lignin is the most reported modified lignin due to its good adsorption ability toward heavy metal ions. Ge et al. [58] developed a lignin-based

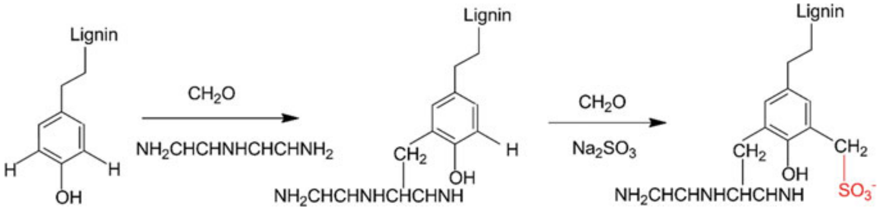

Fig. 11 Synthetic diagram of a modified lignin-containing amino and sulfonic groups. Reprinted with permission [29]. Copyright 2014 Elsevier

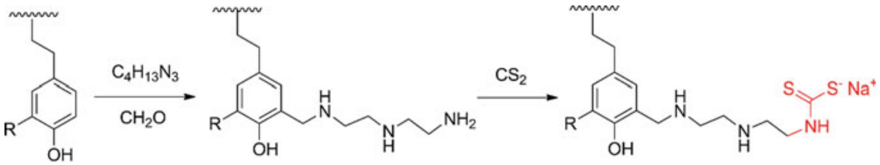

Fig. 12 Synthetic diagram of dithiocarbamated lignin. Reprinted with permission [58]. Copyright 2016 Royal Society of Chemistry

dithiocarbamate (LDTC), as shown in Fig. 12. The developed LDTC showed a high adsorption amount of 175.9 and 103.4 mg/g toward copper and lead ions, respectively. Li et al. [15] developed a porous lignin-containing a large number of mesopores and functional groups. The surface area of the modified lignin increase 11 fold of lignin to 22.3 m^2/g. Accordingly, the modified lignin had a high adsorption capacity of 188 mg/g to Pb(II), 13 fold of the lignin and 7 fold of activated carbon. Ge et al. [27] further prepared a dithiocarbamate modified lignin from organosolv lignin. The modified lignin showed a high adsorption amount of 210 mg/g to Hg(II). The adsorption kinetics could be fitted well by a pseudo-second-order equation, and the adsorption equilibrium could be fitted well by the Freundlich equation. Li et al. [59] prepared a lignin xanthate resin (LXR) with xanthate functional groups ($-CSS^-$) (as shown in Fig. 13). The adsorption capacity of Pb(II) was 64.9 mg/g at pH 5.0, 30 °C.

Ge et al. [26] prepared a new kind of lignin microspheres (LMS) through an inverse suspension copolymerization method. The LMS was in diameter of 348 μm with plenty of amine groups (total N: 7.5 mmol/g). LMS showed an adsorption capacity of 33.9 mg/g for lead ions at pH 6.0, 25 °C, and the adsorption kinetics could be fitted well by the pseudo-second-order equation. Liang et al. [60] prepared a lignin-based resin (LBR) from sodium lignosulfonate and glucose. The maximum adsorption capacity of Cr(VI) by the LBR was 57.68 mg/g. The adsorption equilibrium could be fitted well by the Freundlich equation. The calculated thermodynamic parameters of the adsorption (ΔG, ΔH and ΔS) indicated that the adsorption of Cr(VI) by the LBR is a spontaneous and endothermic process. Parajuli et al. [61] developed a crosslinked lignocatechol gel from catechol and

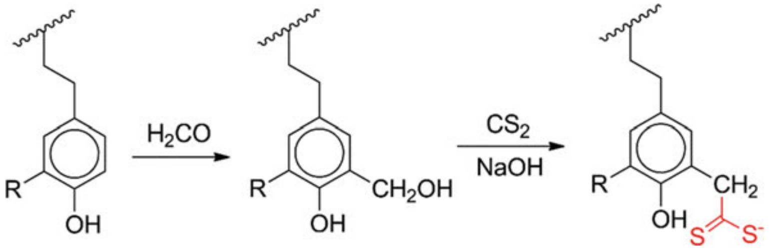

Fig. 13 Synthetic diagram of the lignin xanthate resin (LXR). Reprinted with permission [59]. Copyright 2015 Elsevier

wood lignin. The gel showed a saturated adsorption amount of 37.05 mg/g toward Pb(II) at pH 5.2. The adsorption process was mainly due to the cation exchange mechanism.

Lignin composites are now considered as a talented candidate to traditional adsorbents for cleanup of heavy metal ions in water. Qin et al. [62] synthesized a composite from poly (ethylene imine) and lignin. The composite presented a high adsorption amount of 98.0 mg/g to Cu(II), 78.0 mg/g to Zn(II) and 67.0 mg/g to Ni(II) at pH 6.0, 25 °C. In addition, the composite had good recyclability stability within 5 adsorption-desorption cycles. Klapiszewskia et al. [63] prepared new TiO_2/lignin and TiO_2-SiO_2/lignin hybrids. The adsorption capacity of Pb(II) by the TiO_2/lignin and TiO_2-SiO_2/lignin was 35.7 and 59.9 mg/g, respectively, at pH 5.0, 20 °C. Kinetic analysis revealed that the adsorption followed by the pseudo-second-order equation that meant a chemical interaction occurred during the adsorption process. Equilibrium adsorption was well described well by the Langmuir equation that meant a monolayer coverage of the adsorbates on the homogeneous surface of the adsorbents. Li et al. [64] prepared a composite lignin sphere from sodium alginate and epichlorohydrin. The obtained sphere showed an excellent removal efficiency ($95.6 \pm 3.5\%$, $C_0 = 25.0$ mg/L) to Pb(II). Li et al. [65] reported a new nano-composite composed of lignin and carbon nanotubes (L-CNTs). The as-prepared nano-composite not only showed a good water-dispersibility and environmentally friendliness but also presented an excellent adsorption ability to Pb(II) with a maximum adsorption amount of 235 mg/g. The nano-composite with a lignin layer has advanced adsorption ability, low in cost and environmentally friendliness, and therefore is a talented alternative for wastewater treatment. Klapiszewski et al. [66] synthesized a ‘green’ adsorbent with a high surface area of 223 m^2/g from the commercial silica Syloid®244 and Kraft lignin for the removal of nickel(II) and cadmium(II). The results indicated the adsorbents had maximum sorption capacities of 77.11 mg/g for Ni(II) and 84.66 mg/g for Cd(II), respectively. The kinetics adsorption data could be described well by a pseudo-second-order equation while the adsorption isotherms fitted well with Langmuir equation. Yao et al. [67] synthesized a composite composed of bentonite/ sodium lignosulfonate with acrylamide and maleic anhydride (BLPAMA). Results showed that the adsorption of Pb(II) by the BLPAMA was correlated with pH values but not with the temperatures. It showed a maximum adsorption capacity of 314.8 mg/g for Pb(II) at pH 5.0, 25 °C.

The above mentioned modified lignin adsorbents for adsorption of heavy metals are tabulated in Table 2, from which it can be seen that the adsorption capacity was much dependent on the chemical methods for lignin modification and heavy metals species as well as the temperature and pH values. According to the analysis of the published literature, the research on the development of advanced lignin-based adsorbents, especially lignin-based nano-composites, is greatly needed in the coming decades.

Table 2 Comparison of adsorption capacity of heavy metals with modified lignins

Modified lignin	Heavy metal	*T* (°C)/pH	Q_m (mg/g)	Reference
Mannich base from lignin	Pb(II)	25 ± 1/ 6.0	60.5	[49]
EHL-NS	Hg(II)	25/6.0	180	[51]
CMLSCB	Pb(II)	30/6.0	122.9	[68]
BL	Pb(II) Cd(II)	20/5.0	35.9 155.4	[54]
ASL	Cu(II) Pb(II)	25 ± 0.5/ 6.0	6.3 49.6	[29]
MLBB	Pb(II)	20/7.0	952 ± 31	[57]
LDTC	Cu(II) Pb(II)	25 ± 0.5/ 6.0	175.9 103.4	[58]
SFPL	Pb(II)	25 ± 0.5/ 5.0	188	[15]
Dithiocarbamate functionalized organosolv lignin	Hg(II)	25 ± 0.5/ 5.0	210	[27]
LMS	Pb(II)	25/6.0	33.9	[26]
LBR	Cr(VI)	50/2.0	57.68	[60]
Crosslinked lignocatechol gel	Pb(II)	25/5.2	37.05	[61]
Poly (ethylene imine) anchored lignin	Cu(II) Zn(II) Ni(II)	25/6.0	98.0 78.0 67.0	[62]
TiO_2/lignin TiO_2-SiO_2/lignin	Pb(II)	20/5.0	35.7 59.9	[63]
PLS	Pb(II)	30.2/5.0	31.8	[64]
Siliceous lignin	Pb(II)	70/2.0	–	[69]
L-CNT	Pb(II)	25/6.3	235	[65]
Silica/lignin	Ni(II) Cd(II)	25/3.0 9.0/–	77.11 84.66	[66]
BLPAMA	Pb(II)	25/5.5	314.8	[67]

4 Modified Lignin for Other Pollutants Adsorption

Except for the above discussed main pollutants (dyes and heavy metals), some other pollutants by lignin-based adsorbents are also reported in literature during the past decades. Although there are few papers on the topic, the removal of some other toxic and hazardous pollutants is also very important. Saad et al. [70] investigated two lignins, including alkaline lignin and organosolv lignin, for the adsorption of 2,4-dinitroanisole (DNAN) from the water. The adsorption of DNAN on both lignins could be described well with pseudo-second-order equation. The organosolv lignin showed a maximum adsorption amount of 7.5 mg/g to DNAN while the alkaline lignin showed a maximum adsorption amount of 8.5 mg/g to DNAN. The adsorption equilibrium for either alkali or organosolv lignin could be described well by the Freundlich model.

Chen et al. [71] reported spherical lignin beads as an adsorbent to adsorb L-lysine in water. The results indicated the beads showed a maximum adsorption capacity of 67.11 mg/g to L-lysine. Dynamic adsorption was fitted well by the pseudo-first-order equation, and the adsorption of L-lysine on the beads was initially determined by film diffusion, and then by intra-particle diffusion. Adsorption equilibrium was described well with the Langmuir equation.

Żółtowska-Aksamitowska et al. [72] firstly investigated the use of chitin modified Kraft lignin as an effective sorbent of ibuprofen and acetaminophen. Batch adsorption results indicated the modified lignin showed an adsorption capacity of 400.39 μg/g to ibuprofen and 267.07 μg/g to acetaminophen, respectively. Adsorption isotherms data could be described with the Langmuir equation for ibuprofen, and with the Freundlich equation for acetaminophen, while the adsorption kinetics followed well to the pseudo-second-order equation for both pollutants ($R^2 = 0.999$). These results indicated that the adsorption belonged to a chemisorption. Furthermore, the used adsorbents could be easily regenerated with ethanol (yield 82.2%) in the case of ibuprofen and methanol (yield 80.8%) in the case of acetaminophen.

Application of the oxidative modification of sulfate kraft lignin with sodium periodate under mild conditions is suggested in order to obtain a sorbent for detoxication of spillage places of rocket fuels based on 1,1-dimethylhydrazine and to purify wastewaters containing this compound [73]. It was found that processing with sodium periodate at 55 °C for 20 h resulted in a more than two-fold increase in the content of carbonyl and quinone groups in lignin and a three-fold increase in the adsorption capacity for 1,1-dimethylhydrazine. The adsorbent can bind 6.7% of 1,1-dimethylhydrazine and substantially surpasses in this parameter other lignin-based adsorbents.

Table 3 listed all these reported modified lignin-based adsorbents for adsorption of some other pollutants in water. As could be seen, the adsorption capability of lignin-based adsorbents for other species is much lower than those for dyes and heavy metals. Therefore, it is in a great need of developing new lignin-based adsorbents with enhanced adsorption capability toward the emerging pollutants in the future.

Table 3 Adsorption capacity of modified lignin for other pollutants in water

Modified lignin	Species	*T* (°C)/pH	Q_m (mg/g)	Reference
Alkali and organosolv lignin	DNAN	25/5.7	7.5	[70]
Spherical lignin beads	L-lysine	25/9.0	67.11	[71]
Kraft lignin	Ibuprofen acetaminophen	25/6.0	0.40 0.27	[72]
Periodate oxidation of lignin	UDMH	55/5.0	67 ± 1	[73]

5 Outlook and Conclusions

With the depletion of fossil-based resources and increasing environmental concerns, the research and development of new low-cost adsorbents derived from renewable resources have received more and more attention. The utilization of aromatic lignin in replace of the fossil-based carbon will help to the establishment of the sustainable society. In this content, the adsorption of dyes, heavy metals and some other pollutants by various modified lignin materials have been collected and discussed in this study. Based on the above discussions, adsorption performance of these modified lignin materials for dyes, heavy metals, and other pollutants is expected to be amplified in the near future. It should be noted that the cost-effectiveness is firstly important because low manufacturing cost and high adsorption capability of an adsorbent is desired in practical large-scale applications. Lignin is an abundant polymer derived from plant kingdom that can provide CO_2 neutral, cost-effective, environmentally friendly and therefore can be used as building blocks to create "green" adsorbents. Secondly, although modified lignin is efficient to capture different kinds of pollutants through physical or chemical interactions, regeneration by feasible methods should be studied carefully as it is very important for the improvement of economics. The regeneration of lignin-based materials could be carried out by the most common solvent extraction method with EDTA, HCl, HNO–, NaCl, and NaOH solutions et al. Thirdly, experiments should not only stay in the lab. As all known, the industrial wastewater always contains many kinds of contaminants. Although different kinds of modified lignin adsorbents can be obtained with good adsorption capacity and selectivity for the target contaminants, such as methylene blue (MB), toxic metals (Hg), and (Pb, Cu) et al., it is desirable in developing a multipurpose adsorbent from lignin that can be used to adsorb different kinds of contaminants simultaneously. Therefore, specific attention should be focused on the modification of lignin matrix, via hybriding, cross-linking and grafting to develop lignin-based advanced composite, and accordingly broadening the kinds of pollutants for efficient removal and improving the reusability of the modified lignin-based composites.

Acknowledgements Financial support from the National Natural Science Foundation of China (No. 21264002, 21464002), and Guangxi Natural Science Foundation (No. 2015GXNSFBA139215, 2016GXNSFAA380329) is gratefully acknowledged.

References

1. Abe A, Dusek K, Kobayashi S (2010) Biopolymers: lignin, proteins, bioactive nanocomposites. Springer, Berlin
2. Upton BM, Kasko AM (2016) Strategies for the conversion of lignin to high-value polymeric materials: review and perspective. Chem Rev 116:2275–2306

3. Holladay JE, White JF, Bozell JJ, Johnson D (2007) Top value-added chemicals from biomass—volume II—results of screening for potential candidates from biorefinery lignin. In: Pacific Northwest National Laboratory (PNNL), Richland, WA (US), 2007, Medium: ED; Size: PDFN
4. Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM (2010) The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev 110:3552–3599
5. Li Z, Zhang J, Qin L, Ge Y (2018) Enhancing antioxidant performance of lignin by enzymatic treatment with laccase. ACS Sustain Chem Eng 6:2591–2595
6. Calvo-Flores FG, Dobado JA (2010) Lignin as renewable raw material. Chemsuschem 3:1227–1235
7. Thakur VK, Thakur MK, Raghavan P, Kessler MR (2014) Progress in green polymer composites from lignin for multifunctional applications: a review. ACS Sustain Chem Eng 2:1072–1092
8. Rezakazemi M, Maghami M, Mohammadi T (2018) High loaded synthetic hazardous wastewater treatment using lab-scale submerged ceramic membrane bioreactor. Periodica Polytechnica Chem Eng 62:299–304
9. Rezakazemi M, Khajeh A, Mesbah M (2018) Membrane filtration of wastewater from gas and oil production. Environ Chem Lett 16:367–388
10. Rezakazemi M, Dashti A, Riasat Harami H, Hajilari N (2018) Fouling-resistant membranes for water reuse. Environ Chem Lett 1–49
11. Azimi A, Azari A, Rezakazemi M, Ansarpour M (2017) Removal of heavy metals from industrial wastewaters: a review. Chem Bio Eng Rev 4:37–59
12. Shirazian S, Rezakazemi M, Marjani A, Moradi S (2012) Hydrodynamics and mass transfer simulation of wastewater treatment in membrane reactors. Desalination 286:290–295
13. Rezakazemi M, Shirazian S, Ashrafizadeh SN (2012) Simulation of ammonia removal from industrial wastewater streams by means of a hollow-fiber membrane contactor. Desalination 285:383–392
14. Gupta VK (2009) Application of low-cost adsorbents for dye removal—a review. J Environ Manage 90:2313–2342
15. Li Z, Xiao D, Ge Y, Koehler S (2015) Surface-functionalized porous lignin for fast and efficient lead removal from aqueous solution. ACS Appl Mater Interfaces 7:15000–15009
16. Rezakazemi M, Zhang Z (2018) 2.29 desulfurization materials A2. In: Dincer I (ed) Comprehensive energy systems. Elsevier, Oxford, pp 944–979
17. Rezakazemi M, Sadrzadeh M, Matsuura T (2018) Thermally stable polymers for advanced high-performance gas separation membranes. Progr Energy Combust Sci 66:1–41
18. Rezakazemi M, Marjani A, Shirazian S (2018) Organic solvent removal by pervaporation membrane technology: experimental and simulation. Environ Sci Poll Res
19. Rezakazemi M, Ebadi Amooghin A, Montazer-Rahmati MM, Ismail AF, Matsuura T (2014) State-of-the-art membrane based CO_2 separation using mixed matrix membranes (MMMs): an overview on current status and future directions. Prog Polym Sci 39:817–861
20. Foroutan R, Esmaeili H, Abbasi M, Rezakazemi M, Mesbah M (2017) Adsorption behavior of Cu(II) and Co(II) using chemically modified marine algae. Environ Technol 1–9
21. Ge YY, Cui XM, Liao CL, Li ZL (2017) Facile fabrication of green geopolymer/alginate hybrid spheres for efficient removal of Cu(II) in water: batch and column studies. Chem Eng J 311:126–134
22. Saleh TA, Gupta VK (2014) Processing methods, characteristics and adsorption behavior of tire derived carbons: a review. Adv Colloid Interfac 211:93–101
23. Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: a review. J Hazard Mater 177:70–80
24. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource Technol 98:2243–2257
25. Deng S, Ting Y-P (2005) Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II). Water Res 39:2167–2177

26. Ge YY, Qin L, Li ZL (2016) Lignin microspheres: an effective and recyclable natural polymer-based adsorbent for lead ion removal. Mater Des 95:141–147
27. Ge Y, Wu S, Qin L, Li Z (2016) Conversion of organosolv lignin into an efficient mercury ion adsorbent by a microwave-assisted method. J Taiwan Inst Chem Eng 63:500–505
28. Wawrzkiewicz M, Bartczak P, Jesionowski T (2017) Enhanced removal of hazardous dye form aqueous solutions and real textile wastewater using bifunctional chitin/lignin biosorbent. Int J Biol Macromol 99:754–764
29. Ge Y, Li Z, Kong Y, Song Q, Wang K (2014) Heavy metal ions retention by bi-functionalized lignin: synthesis, applications, and adsorption mechanisms. J Ind Eng Chem 20:4429–4436
30. Ge Y, Li Z (2018) Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. ACS Sustain Chem Eng 6:7181–7192
31. Laurichesse S, Avérous L (2014) Chemical modification of lignins: towards biobased polymers. Prog Polym Sci 39:1266–1290
32. Nair V, Panigrahy A, Vinu R (2014) Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater. Chem Eng J 254:491–502
33. Albadarin AB, Collins MN, Naushad M, Shirazian S, Walker G, Mangwandi C (2017) Activated lignin-chitosan extruded blends for efficient adsorption of methylene blue. Chem Eng J 307:264–272
34. Lou T, Cui G, Xun J, Wang X, Feng N, Zhang J (2018) Synthesis of a terpolymer based on chitosan and lignin as an effective flocculant for dye removal. Coll Surf A 537:149–154
35. Li YL, Wu M, Wang B, Wu YY, Ma MG, Zhang XM (2016) Synthesis of magnetic lignin-based hollow microspheres: a highly adsorptive and reusable adsorbent derived from renewable resources. ACS Sustain Chem Eng 4:5523–5532
36. Couch RL, Price JT, Fatehi P (2016) Production of flocculant from thermomechanical pulping lignin via nitric acid treatment. ACS Sustain Chem Eng 4:1954–1962
37. Xu WJ, Zhang WS, Li Y, Li W (2016) Synthesis of acrylic-lignosulfonate resin for crystal violet removal from aqueous solution. Korean J Chem Eng 33:2659–2667
38. Wang Y, Xiong Y, Wang J, Zhang X (2017) Ultrasonic-assisted fabrication of montmorillonite-lignin hybrid hydrogel: highly efficient swelling behaviors and super-sorbent for dye removal from wastewater. Coll Surf A 520:903–913
39. Yu C, Wang F, Zhang C, Fu S, Lucia LA (2016) The synthesis and absorption dynamics of a lignin-based hydrogel for remediation of cationic dye-contaminated effluent. React Funct Polym 106:137–142
40. Kumari S, Chauhan GS, Monga S, Kaushik A, Ahn J-H (2016) New lignin-based polyurethane foam for wastewater treatment. RSC Adv 6:77768–77776
41. Feng Q, Cheng H, Chen F, Zhou X, Wang P, Xie Y (2016) Investigation of cationic dye adsorption from water onto acetic acid lignin. J Wood Chem Technol 36:173–181
42. Tang Y, Hu T, Zeng Y, Zhou Q, Peng Y (2015) Effective adsorption of cationic dyes by lignin sulfonate polymer based on simple emulsion polymerization: isotherm and kinetic studies. RSC Adv 5:3757–3766
43. Tang Y, Zeng Y, Hu T, Zhou Q, Peng Y (2016) Preparation of lignin sulfonate-based mesoporous materials for adsorbing malachite green from aqueous solution. J Environ Chem Eng 4:2900–2910
44. Song X, Chen F, Liu S (2016) A lignin-containing hemicellulose-based hydrogel and its adsorption behavior. BioResources 11:6378–6392
45. Luo H, Ren S, Ma Y, Fang G, Jiang G (2015) Preparation and properties of kraft lignin-N-isopropyl acrylamide hydrogel. BioResources 10:3507–3519
46. Adebayo MA, Prola LDT, Lima EC, Puchana-Rosero MJ, Cataluña R, Saucier C, Umpierres CS, Vaghetti JCP, da Silva LG, Ruggiero R (2014) Adsorption of Procion Blue MX-R dye from aqueous solutions by lignin chemically modified with aluminium and manganese. J Haz Mater 268:43–50
47. da Silva LG, Ruggiero R, Gontijo PdM, Pinto RB, Royer B, Lima EC, Fernandes THM, Calvete T (2011) Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin. Chem Eng J 168:620–628

48. Guo K, Gao B, Li R, Wang W, Yue Q, Wang Y (2018) Flocculation performance of lignin-based flocculant during reactive blue dye removal: comparison with commercial flocculants. Environ Sci Pollut R 25:2083–2095
49. Ge Y, Song Q, Li Z (2015) A Mannich base biosorbent derived from alkaline lignin for lead removal from aqueous solution. J Ind Eng Chem 23:228–234
50. Li Z, Xiao D, Kong Y, Ge Y (2015) Enhancing lead adsorption capacity by controlling the chain length of alkyl amine grafted lignin. BioResources 10:2425–2432
51. Huang W-X, Zhang Y-H, Ge Y-Y, Qin L, Li Z-L (2017) Soft nitrogen and sulfur incorporated into enzymatic hydrolysis lignin as an environmentally friendly antioxidant and mercury adsorbent. BioResources 12:7341–7348
52. Quintana GC, Rocha GJM, Goncalves AR, Velasquez JA (2008) Evaluation of heavy metal removal by oxidised lignins in acid media from various sources. BioResources 3:1092–1102
53. Peternele WS, Winkler-Hechenleitner AA, Pineda EAG (1999) Adsorption of Cd(II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse. Bioresource Technol 68:95–100
54. Dizhbite T, Jashina L, Dobele G, Andersone A, Evtuguin D, Bikovens O, Telysheva G (2013) Polyoxometalate (POM)-aided modification of lignin from wheat straw biorefinery. Holzforschung 67:539–547
55. Li Z, Pang Y, Ge Y, Qiu X (2011) Evaluation of steric repulsive force in the aqueous dispersion system of dimethomorph powder with lignosulfonates via X-ray photoelectron spectroscopy. J Phys Chem C 115:24865–24870
56. Li Z, Ge Y (2011) Extraction of lignin from sugar cane bagasse and its modification into a high performance dispersant for pesticide formulations. J Brazil Chem Soc 22:1866–1871
57. Xu F, Zhu TT, Rao QQ, Shui SW, Li WW, He HB, Yao RS (2017) Fabrication of mesoporous lignin-based biosorbent from rice straw and its application for heavy-metal-ion removal. J Environ Sci 53:132–140
58. Ge Y, Xiao D, Li Z, Cui X (2014) Dithiocarbamate functionalized lignin for efficient removal of metallic ions and the usage of the metal-loaded bio-sorbents as potential free radical scavengers. J Mater Chem A 2:2136–2145
59. Li Z, Kong Y, Ge Y (2015) Synthesis of porous lignin xanthate resin for Pb2 + removal from aqueous solution. Chem Eng J 270:229–234
60. Liang F-B, Song Y-L, Huang C-P, Zhang J, Chen B-H (2013) Adsorption of hexavalent chromium on a lignin-based resin: equilibrium, thermodynamics, and kinetics. J Environ Chem Eng 1:1301–1308
61. Parajuli D, Inoue K, Ohto K, Oshima T, Murota A, Funaoka M, Makino K (2005) Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel. React Funct Polym 62:129–139
62. Qin L, Ge Y, Deng B, Li Z (2017) Poly(ethylene imine) anchored lignin composite for heavy metals capturing in water. J Taiwan Inst Chem Eng 71:84–90
63. Klapiszewski L, Siwinska-Stefanska K, Kolodynska D (2017) Preparation and characterization of novel TiO2/lignin and TiO2-SiO2/lignin hybrids and their use as functional biosorbents for Pb(II). Chem Eng J 314:169–181
64. Li Z, Ge Y, Wan L (2015) Fabrication of a green porous lignin-based sphere for the removal of lead ions from aqueous media. J Haz Mater 285:77–83
65. Li Z, Chen J, Ge Y (2017) Removal of lead ion and oil droplet from aqueous solution by lignin-grafted carbon nanotubes. Chem Eng J 308:809–817
66. Klapiszewski L, Bartczak P, Wysokowski M, Jankowska M, Kabat K, Jesionowski T (2015) Silica conjugated with kraft lignin and its use as a novel ‘green’ sorbent for hazardous metal ions removal. Chem Eng J 260:684–693
67. Yao Q, Xie J, Liu J, Kang H, Liu Y (2014) Adsorption of lead ions using a modified lignin hydrogel. J Polym Res 21:465
68. Peternele WS, Winkler-Hechenleitner AA, Gómez Pineda EA (1999) Adsorption of Cd(II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse. Bioresour Technol 68:95–100

69. Cui J, Sun H, Wang X, Sun J, Niu M, Wen Z (2015) Preparation of siliceous lignin microparticles from wheat husks with a facile method. Ind Crop Prod 74:689–696
70. Saad R, Radovic-Hrapovic Z, Ahvazi B, Thiboutot S, Ampleman G, Hawari J (2012) Sorption of 2,4-dinitroanisole (DNAN) on lignin. J Environ Sci 24:808–813
71. Chen GF, Liu MH (2012) Adsorption of L-lysine from aqueous solution by spherical lignin beads: kinetics and equilibrium studies. BioResources 7:298–314
72. Żółtowska-Aksamitowska S, Bartczak P, Zembrzuska J, Jesionowski T (2018) Removal of hazardous non-steroidal anti-inflammatory drugs from aqueous solutions by biosorbent based on chitin and lignin. Sci Total Environ 612:1223–1233
73. Kozhevnikov AY, Ul'yanovskaya SL, Semushina MP, Pokryshkin SA, Ladesov AV, Pikovskoi II, Kosyakov DS (2017) Modification of sulfate lignin with sodium periodate to obtain sorbent of 1,1-dimethylhydrazine. Russ J Appl Chem + 90:516–521