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Review

Biosorption: Fabrication and interactions of polymeric membrane with lignin for effective removal of residual solvents – A review

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ABSTRACT

The scarcity of clean water is currently a global challenge. This situation is exacerbated by increasing levels of various volatile organic compounds in surface waters limiting their drinkability, as well as posing a major health risk to aquatic and human life. Biosorption is one extensively researched method with a great potential to remove a variety of toxic pollutants from contaminated wastewaters. This biotechnology has been tried, tested and reported to be more reliable for the removal of pollutants in industrial wastewaters owing to the availability of the biomaterials for the technology and renewability, eco-friendliness and its cost effectiveness. This review focuses on membrane technologies and the incorporation of lignin. Lignin is a biopolymer and by-product of organosolv and alkali pre-treatments in the pulp industry. The abundant availability of pure lignin has improved the performance of membranes for water treatment. The idea of fabricating or modifying lignin with composite materials capitalising on the maximum possible performance of the membranes without affecting its selectivity has attracted lots of research interest in recent times. This paper explores the bulk of literature and discusses the details of hydrogen bonding responsible for the interactions between the lignin and composite during the membrane fabrication process. This review found that valuable knowledge is available and still untapped for particular research and application interests.

KEYWORDS: residual solvents, biosorption, lignin, composite membranes, fabrication.

Introduction

Environmental pollution caused by a wide variety of pollutants discharged from pharmaceutical and chemical industries is increasingly recognized as a threat to ecosystem and human health across the globe. Residual solvents, often referred to as volatile organic compounds (VOCs), are often produced mostly in pharmaceutical and other chemical industries [1]. The ubiquitousness of this class of chemicals results from their continuous usage during manufacturing of active pharmaceutical ingredients (APIs), drug excipients, and other drug products [1-3]. Some of these residual solvents are known to be very toxic to both humans and aquatic life if they exceed the maximum permissible limits (MPLs) [4]. Residual solvents have been classified by the International Conference of Harmonization (ICH) into three classes based on their level of toxicity [5]. Class 1 solvents are known to be carcinogenic and their

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use is prohibited unless in cases where their use could be justifiable. Class 2 solvents can be toxic if their MPLs are exceeded, while class 3 solvents are regarded as low toxic and pose very little risk to human health [1, 6, 7]. It is noteworthy that there are currently no known reported practical methods for complete removal of these residual solvents from pharmaceutical products; therefore, their presence in finished products and subsequently in general pharmaceutical wastes is inevitable.

Rapid increase in industrialization in urban areas has recently been a driving factor in the increased levels of residual solvents in surface waters and underground water [8]. Wastewater Treatment Plants (WWTPs) are at a centre of this mammoth challenge as they continue to receive huge volumes of pharmaceutical waste from industrial waste effluents, domestic sewage, and hospital waste effluents [9]. Apart from infrastructural deterioration, most of these WWTPs, particularly in developing countries, are not adequately equipped to effectively remove these residual solvents [10]. As a result, they escape into the surface waters, thereby, posing a greater risk to both aquatic life and the humans [10]. According to Pereira, Calisto, and Santos [11], and Pal and Thakura, [9] only certain amounts of toxic organic compounds are partially removed, while a substantial amount is not removed at all by the standard treatment process in WWTPs.

Bio-based technologies have been identified as the most perfect replacement for the costly and declining fossil-based fuels. Amongst these technologies is the biosorption process which has been tried, tested and reported as reliable for the removal of a variety of toxic pollutants owing to its cost effectiveness, eco-friendliness, availability of the bio-materials, and renewability [12, 13]. Although biosorption of toxic pollutants, mainly heavy metals have been fairly explored, there is still limited literature on biosorption of residual solvents and VOCs in general in environmental matrices like aqueous systems. To provide an update in the knowledge pool in this area, this review has surveyed and discusses knowledgeable information on the topic with focus on the biosorption of residual solvents using lignin-fabricated membranes.

Fundamentals of biosorption

Biosorption is a physico-chemical technology which involves the use of living or dead organisms for removal of toxic pollutants from aqueous medium [12, 13]. This biotechnology is based on the interactions between sorbate (ions, atoms or molecules) and the active sites of the biomaterial’s surface in which the targeted ions, atoms, or molecules occurs as a passive mechanism based on the chemical properties of the surface’s biomaterial [14, 15]. This interaction results in the sorption and the accumulation in the sorbate-biosorbent interface, thereby, reducing the concentration of the sorbate [16]. Based on the literature, it is clear that several mechanisms are involved during a biosorption process. Some of the common mechanisms reported in the literature include: complexion [17], chelation [18], and ion exchange [19] which are involved mainly in the biosorption of heavy metals. From the literature, it is also clear that ion exchange and surface adsorption are the main mechanism that governs biosorption of a variety of pollutants [20-22]. More common biosorption mechanisms that govern cationic and anionic pollutants are illustrated in Figure 1. Hydrogen bonding and π-π dispersion interactions with anionic pollutants such as organic compounds were reported by Liu, Li and Campos, [23]. Biosorption process is reported to be highly dependent on the pH of the solution, and it also governs by the availability of binding sites [24, 25]. Other parameters that influence the process includes: temperature (^{o}C), concentration, contact time, as well as the nature and surface area of the biomaterial.

Lignin and its extraction methods

A quest for cost-effective, reliable, and sustainable alternative absorbents with less environmental impact has attracted strong interest in recent years due to growing environmental awareness and shortage of fossil-based fuels [26, 27]. With continuous research focused on new materials and technologies for the removal of organic pollutants and heavy metals in aqueous media, particularly from wastewaters, lignin has been found to be an ideal biosorbent due to its high adsorption capacity (effective adsorption sites in macropores), abundance, environmental

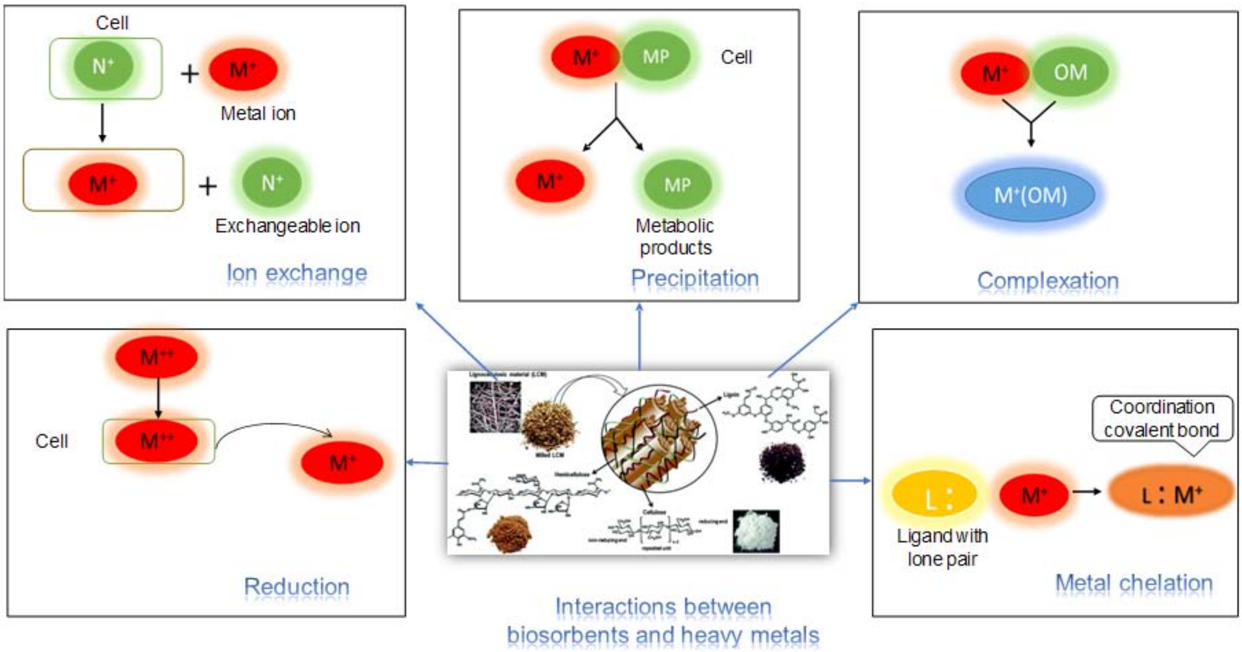

Figure 1. Common mechanisms involved in the biosorption of heavy metals (modified from Ramirez Calderon, Abdeldayem, Pugazhendhi, and Rene [16]).

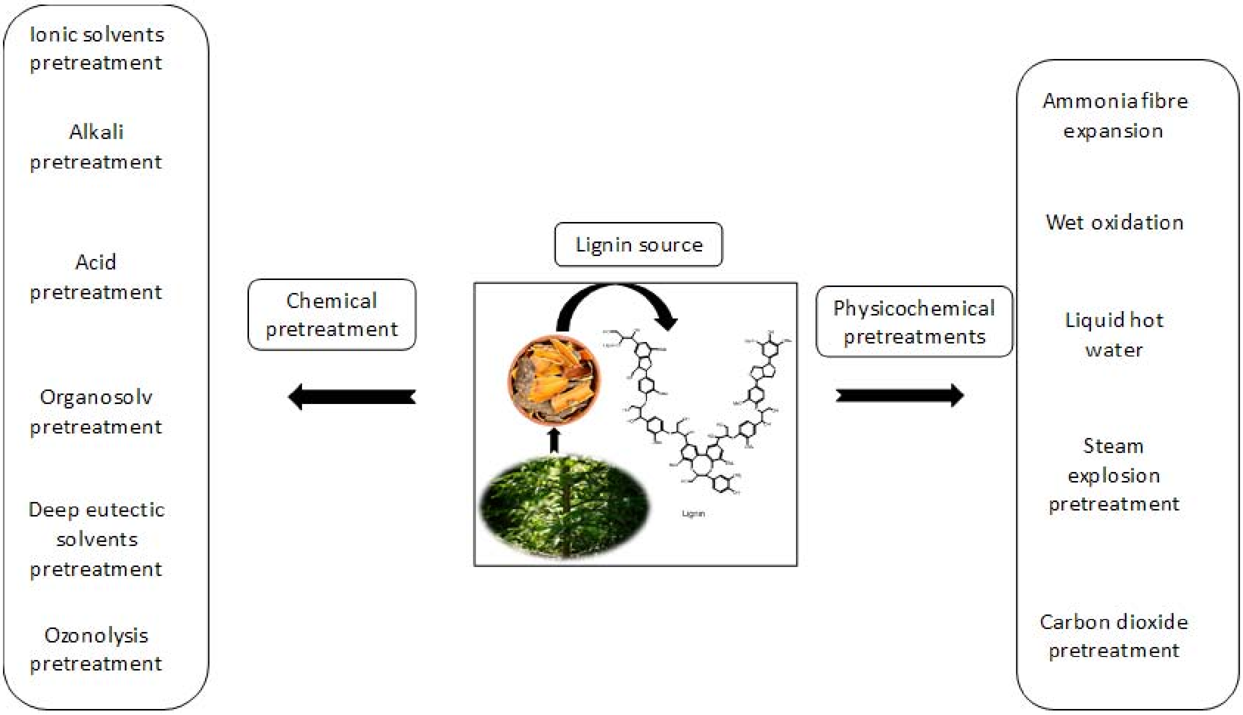

Figure 2. A summary of some common pre-treatment methods for the extraction of lignin (information collated from Aftab, Iqbal, Riaz, Karadag and Tabatabaei [39], and Collins, Nechifor, Tanasă, Zănoagă, McLoughlin, Stróżyk, Culebras, and Teacă, [43]).

friendliness and biodegradability [28, 29]. Lignin, which is known as a main component of lignocellulosic biomass, is a polyphenolic polymer consisting of approximately 15-30% by dry weight of lignocellulosic biomass [30, 31]. Being the most abundant natural polymer, lignin can serve as a potential alternative renewable resource to fulfil the current demand of biosorbents as it contains about 60% of carbon (C), higher than that in cellulose and hemicellulose [32, 33]. The fractionation of the lignocellulosic biomass into its major components (hemicellulose, cellulose and lignin) has drawn strong interest across the research community since these major components exhibit unique chemical properties which can be modified into different products [34]. Therefore, extraction of biopolymers is essential to overcome, amongst other crisis, the contamination by VOCs and heavy metals. According to recent literature, lignin can be used in a variety of value-added applications; however, its effective separation from lignocellulosic biomass is still an ongoing challenge due to the complex structure [32, 35]. It is important to note that the type of the source of lignin and its pre-treatment method will have a direct influence on the composition and chemical properties of the lignin [31]. Some of the common pre-treatment methods reported in the literature include: ionic liquid [34], deep eutectic solvent [36], organosolv [37] and alkali pre-treatments [31, 38]. However, many drawbacks such as waste management and high cost amongst others have resulted in the limited use of some of these methods such as ionic liquid and acid pre-treatment [39]. In their research, Brodeur [40] and co-authors found that many ionic liquids solvents do not alter the structure of lignin and hemicellulose. Hence, pretreatments methods such as organosolv and alkali pretreatments have gained attraction due to their simplicity, environmental friendliness, economic feasibility and also due to the large production amount of pure lignin [31, 32, 41, 42]. Figure 2 presents a summary of chemical and physicochemical pre-treatment methods for the extraction of lignin.

Structural characterization of lignin

The chemical structure of lignin and the functional groups on it will differ based on the source and extraction of the lignin. Literature reports that lignin has a high molecular weight and a surface of approximately 180 m^2/g, with a three-dimensional, and highly cross-linked macromolecule [44]. Lignin consists of three primary phenyl propane monomers namely; 4-hydroxy-3-5 dimethoxycinnamyl (sinapyl, S) alcohol, 4-hydroxycinnamyl (p-coumary, H) alcohol and 4-hydroxy-3-methoxy cynnamyl (conifenyl, G) alcohol, (Figure 3), that are connected *via* carbon-carbon and ether linkages [45, 46].

The monolignols resulting from the above dominant precursors are known as syringyl (S),

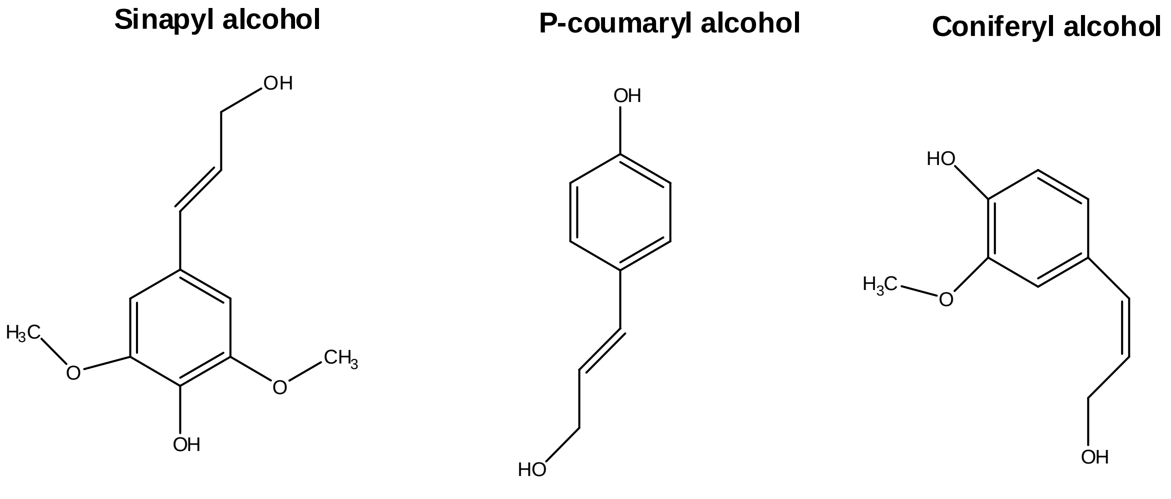

Figure 3. Three phenylpropanoid units in lignin structure (information obtained from Wang, and Chen, [45]).

p-hydroxypheyl (H) and Guaiacyl (G) when introduced in the lignin polymer and varies greatly owing to the different source, and extraction method of the lignin [47]. According to Yang and Lu [48], lignin is divided into three different types namely; softwood (gymnosperm), hardwood (angiosperm dicots) lignin and grass (angiosperm monocots). The G unit is dominant in softwood, whereas hardwood consists of an equal ratio of S and G units. The β-O-4$'$ ether linkages are responsible for the bonds between monomers in lignin and are crucial target for degradation mechanisms of lignin. The presence of reactive functional groups has been found to play a vitally important role in the modification of the lignin [49].

Functional groups endowed on lignin structure

Functional groups present on the surface of a biosorbent play a vital role during biosorption process. The surface structure of lignin is endowed with a variety of special and important functional groups such as phenolic hydroxyls (-OH), methoxyl ($O\text{-}CH_3$), carbonyl (C=O) and carboxyl functional groups (C=O) which interact with a variety of contaminants during a biosorption process [50]. These functional groups and their distribution relate to the type of lignin in a plant [51]. The monolignols further contains more functional groups such as hydroxyl and methoxyl which also play a role during biosorption process. However, it is the hydroxyl, carbonyl and carboxyl groups that are at the centre of biosorption and dictate which adsorption mechanism takes place. The content of syringyl (S) and guaiacyl (G) units in both softwood and hardwood has been extensively studied by solid-state ^{13}C NMR, FTIR, ^{31}P NMR and Py-GC/MS spectrometry [51-53]. Figure 4 illustrates the regions of the main functional groups present in the lignin including the syringyl and guaiacyl units.

Lignin carbon materials and their modification for effective adsorption of VOCs

Over the years, endless efforts have been made into the use of lignin as a high-performance adsorbent, with more studies focusing more on increasing the surface area and subsequently its adsorption efficiency [54]. Due to a growing interest demand for high capacity, regenerability, and sustainable energy storage, lignin carbons have been explored as an alternative. Carbon materials derived from lignin such as carbon fibers, carbon catalyst, carbon electrode and

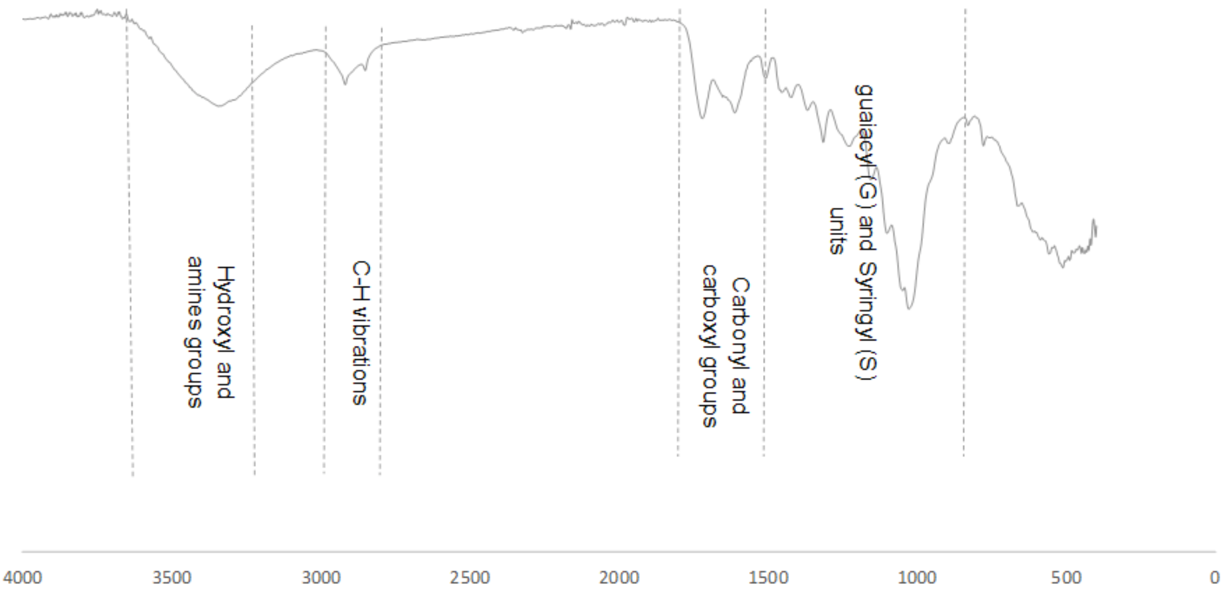

Figure 4. FTIR spectrum of organosolv lignin (information obtained from De, Mishra, Poonguzhali, Rajesh, and Tamilarasan, [31]).

carbon adsorbents can be modified by various methods to achieve improved mechanical and thermal stability, pore diameter and surface area [55]. Lignin-derived activated carbons, which are mostly common in adsorption applications are obtained by activation followed by carbonization, and are regarded as one of the most potential uses of lignin [56]. With the ongoing research on modification of lignin carbon adsorbents, different modification processes such as esterification [57], and dispersion of carbon nanotubes (CNTs) [58] have been tried and tested to increase adsorption capabilities which include thermal stability, pore diameter, etc. During esterification, functional groups such as hydroxyl groups present in the lignin reacts with the dicarboxylic acid anhydrides, thus, rendering the surface of the lignin carbons more hydrophobic [57]. This is because during esterification treatment, the interaction of the hydroxyl group with the anhydrides results in reduced hydroxyl groups and increased carbonyl and carboxyl groups [59]. In a study by Figueiredo, Lintinen, Hirvonen, Kostiainen, and Santos, [58], dispersion of carbon nanotubes (CNTs) onto carbon fibers resulted in the increase in pore diameters and thermal stability of the carbon fibers. Some methods reported in the literature include combining polymers of thermoplastic elastomer polyurethane, polyethylene terephthalate and polylactic acid or introducing a template agent to fabricate porous carbon [43]. However, this review focuses mainly on the fabrication using native lignin with composite membrane to increase adsorption efficiency of the lignin.

Lignin-based composite membranes

Agricultural residue-based composites are materials in combination with an agricultural residue acting as a reinforcement [60]. An excessive and uncontrollable environmental pollution has progressively led to the use of biodegradable-based resources as the central focus of renewable resources [60]. As much as lignin extensively exists in nature as part of the plant wood, it is also plentiful and rich in reserves. Hence, burning it as cheap fuel does not only waste resources, but also creates unwanted pollution to the environment [61, 62]. In order to reduce this wastage, lignin can be extracted and used as a biosorbent, stabilizer, an antioxidant, an antimicrobial agent etc. [34] – its abundance in nature may counterattack the challenges of rapid exhaustion of fossil resources. This would mean using lignin primary properties like, thermal stability, high carbon content, biodegradability, good stiffness and antioxidant nature is very beneficial [63]. More so, these lignin properties have been successfully examined in various biodegradable products, i.e., fuels, agricultural membranes, water treatment and food packaging [64].

There is handful literature regarding the advancement of fabrication of membranes with lignin in different fields of science where the focus is particularly on its potential applications in adsorption of anionic and cationic pollutants [65]. Based on their pore size and pore distribution, these lignin-based composites can be utilized in ultrafiltration and microfiltration. The already prepared membranes or membranes that currently exist in the market have been proven to exhibit poor environmental absorbability. The structural leaching and aging are amongst the major setbacks associated with these polymeric membranes. Therefore, in order to mitigate this issue of increasingly serious environmental pollution and the shortage of fossil-based polymers, it is vitally important to consider a renewable natural plant material such as lignin for the preparation of membrane materials [66]. The fabrication or modification of membranes by native lignin is slowly becoming a central focus in bettering the performance of membranes. Using natural additives, such as lignin, has advantages such as renewability, availability (because they are natural), and cost-effectiveness. The cost effectiveness is attributed to the biodegradability of the lignin and the reduction of membrane fabrication costs as compared to the synthetic additives [67]. Moreover, research on the manufacturing of composite membranes by blending lignin with starch, cellulose, polypropylene (PP), polyvinyl alcohol (PVA), chitosan, and other polymeric materials have also been reported in the literature [68, 69].

Polyether sulfone (PES) polymer has been widely preferred or used, and it is said to be one of the most favourable polymeric materials in the fabrication of ultrafiltration membrane [70].

This is because of its outstanding chemical and thermal stability, appropriate mechanical strength, and film-forming properties [71].

Interactions between the biopolymer and membrane materials

The extraction of biopolymer such as lignin from lignocellulosic biomass helps to improve the fiber-matrix interactions during fabrication process [72]. During incorporation of lignin into poly (vinyl alcohol) PVA, Posoknustakul and co-authors [73], reported that the hydroxyl ion adsorption on the particle surface in the lignin dispersion resulted in the negative charge. Furthermore, since the surface of lignin consists mainly of hydroxyl groups, which are hydrophilic, these result in the formation of hydrogen bond between lignin and membrane hydroxyl groups (Figure 5). These findings were confirmed by different studies such as that conducted by Boija and Johansson [74], as well as that of Esmaeili, Anugwom, Mänttäri,and Kallioinen, [75]. In their study [75], the FTIR results revealed that the main interactions between deep eutectic solvents lignin (DES-lignin) and polyethersulfone (PES) membrane were due to the hydrogen bonding between the hydroxyl groups in DES-Lignin and oxygen atoms of sulfone in PES. The surface charge on the lignin-modified membrane is negative, which increases with increasing pH of the solution.

Fabrication and subsequent production of lignin-composite membranes should aim to overcome challenges or setbacks such as particle dispersion and interfacial morphology. According to a study by Murawski, Diaz, Inglesby, Delabar, and Quirino [72], the lack of uniformity in fiber length and most importantly, the orientation in polymer-modified membranes often results in variation in

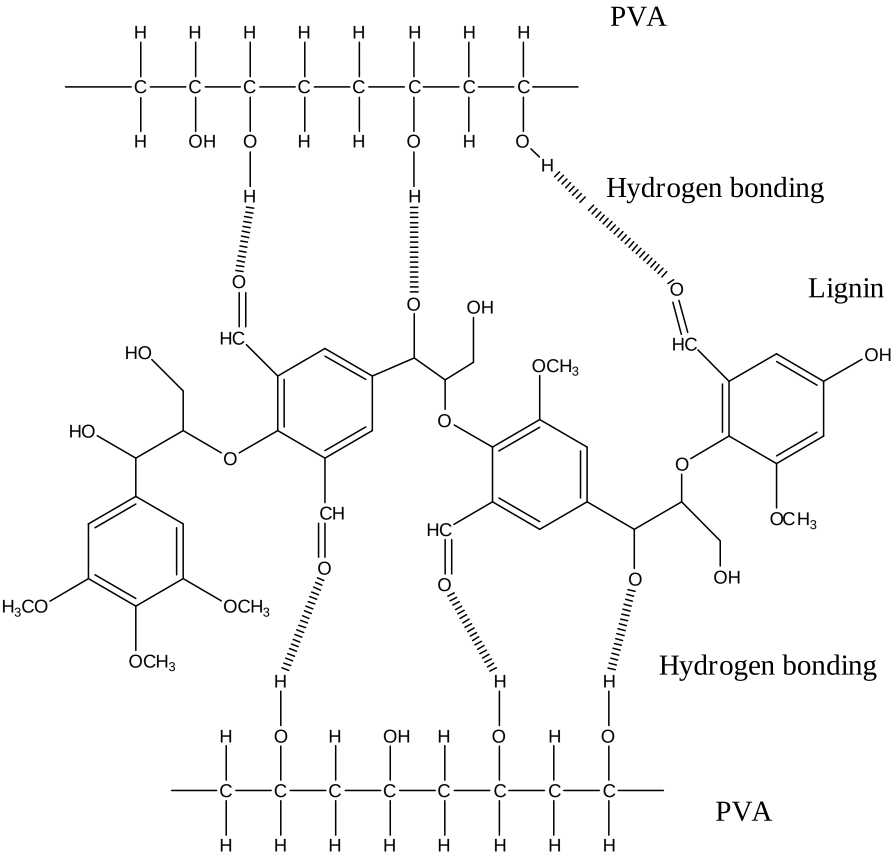

Figure 5. Interaction mechanism between the lignin and a PVA membrane (modified from Yong, Zhang, Sun, and Liu, [54]).

physical properties such as thermal and mechanical. In order to overcome these setbacks, Ghalia and Abdelrasoul [76] reported that choosing homogeneous and ultrafine particles can reduce sedimentation rate, while enhancing gas separation performance resulting in improved interfacial morphology.

Effect of DES-Lignin on the antioxidant activity of fabricated membranes

It is apparent from the study conducted by Esmaeili, Anugwom, Mänttäri, and Kallioinen [75] that, membranes with less negative charge and better hydrophilicity were obtained as the DES-lignin content in the polymer solution was uniformly added. With the highest dosage, the incorporation of DES-lignin in the membrane matrix improved the membrane permeability by 29.4% compared to a bare PES membrane. Moreover, no leakage of DES-lignin from the membrane structure was observed. This showed a good incorporation between DES-lignin and the PES polymer scaffold [77]. It was also found that the improvement of both rejection and pure water flux could be achieved by using a small dosage of DES-lignin (0.25 wt%) in membrane fabrication. Table 1 presents the result obtained by Esmaeili, Anugwom, Mänttäri, and Kallioinen [75] in their studies.

Conclusion and future recommendations

In this review, the fabrication of lignin with a polymeric membrane for efficient biosorption of residual solvents was discussed. Findings from the review indicate that the extraction of lignin including its wide applications as a natural binder, dispersant, emulsifier and as precursor in water treatment has been extensively investigated in recent years. However, literature on its modification with polymeric membranes is still limited. This allows a call in this paper for researchers to intensify work in this direction to fill in the gap with literature knowledge on fabrication of polymeric membranes reinforced with lignin for biosorptive applications in the removal of residual solvents. From some of the outstanding literature reviewed, it is now published knowledge that interactions between the lignin and polymeric membrane were found to be governed by hydrogen bonding between the lignin's hydroxyl groups and mostly membrane's oxygen atoms. Since lignin is endowed with positive and negative functional groups, this makes it an ideal precursor for uptake of both heavy metals and volatile organic compounds (VOCs). This study asserts that lignin could be utilized to improve polymeric membranes for effective removal of VOCs.

The review found that organosolv is well-known as the most preferred pretreatment method for extraction of lignin due to its ability to produce relatively pure lignin. However, organic acids used as a mixture in some instances during extraction are relatively expensive and require energy to recover; therefore, this could in some instances affect its large-scale commercialization. The usage of organic solvents such as ethanol can help in reducing the cost, as well as health hazards. Compared to the widely available literature on the extraction of lignin from the biomass, the literature on the modification of lignin materials and composites is still limited which leaves a gap that still needs to be further explored.

Table 1. The effect of DES-lignin on the bulk porosity, DPPH and ABTS antioxidant activity of fabricated membranes [75].

Membrane	PES (%)	Lignin (%)	Bulk porosity (%)	Antioxidant, DPPH (%)	Capacities, ABTS (%)
#1	20	-	69.3	19.3 ± 0.03	33.5 ± 0.1
#2	20	0.25	71.5	32.4 ± 0.06	42.5 ± 0.03
#3	20	0.50	72.5	43.1 ± 0.1	47.9 ± 0.06
#4	20	1.00	79.9	70.6 ± 0.2	71.7 ± 0.5

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CONFLICT OF INTEREST STATEMENT

The authors also declare that there are no conflicts of interest regarding the publication of this paper.

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