

Chapter

Phenolic Compounds in the Built Environment

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Abstract

This chapter examines source and application of phenolic compounds in the built environment as well as their environmental fate and treatment methods. We further describe the role of phenolic compounds in delaying aging and degradation of outdoor construction elements when exposed to intense solar radiation. In this chapter both plant-based and synthetic sources of phenolic compounds and their fate in the environment were examined. In addition, merits of select sources of phenolic compounds to resist ultraviolet radiation in composites as well as delaying degradation were studied. This chapter further provides insights pertaining to the underlying molecular interactions which afford phenol's role as an anti-aging additive for outdoor construction elements. This in turn provides a solution to promote bio-economy and enhance sustainability in the built environment.

Keywords: phenols, bio-mass, construction, aging, radiation, sustainability

1. Introduction to phenolic compounds

1.1 Structures and classification

There are more than ten thousand phenolic structures identified in nature, ranging from simple aromatic rings to complex polymerized compounds, making the phenolic compounds one of the main and largest groups of secondary metabolites of plants [1, 2].

The polyphenol structure (composed of several hydroxyl groups on aromatic rings) has been identified in higher plants in abundance, and to a lesser degree in edible plants [3]. Depending on the extent of their distribution in nature, phenolic compounds have been classified as being shortly distributed, widely distributed, or as polymers [4]. The types of phenolic compounds that are present or available in all plants are considered widely distributed. Examples include flavonoids and/or flavonoid derivatives, coumarins, and a wide range of phenolic acids including benzoic acid and cinnamic acid (**Figure 1**).

Phenolic compounds that are shortly or less widely distributed have limited presence in plants and include simple phenols, pyrocatechol, hydroquinone, and resorcinol (**Figure 2**).

The polymer class of phenolic compounds contains macromolecules such as tannin and lignin, illustrated in **Figure 3**.

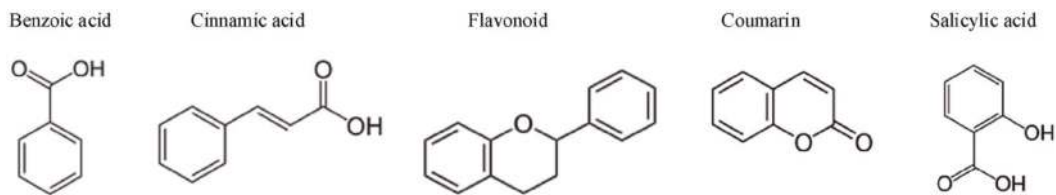


Figure 1.
Examples of widely distributed phenolics.

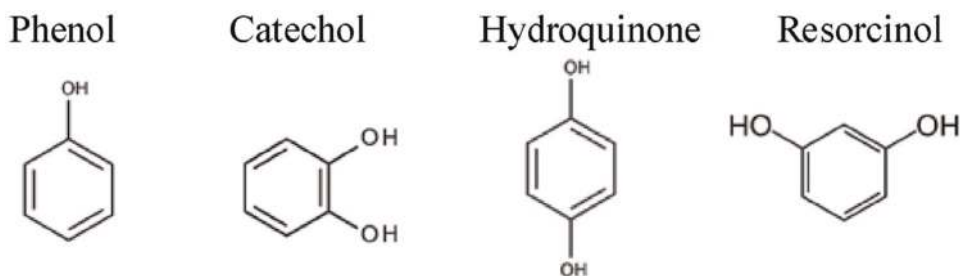


Figure 2.
Examples of shortly distributed phenolics.

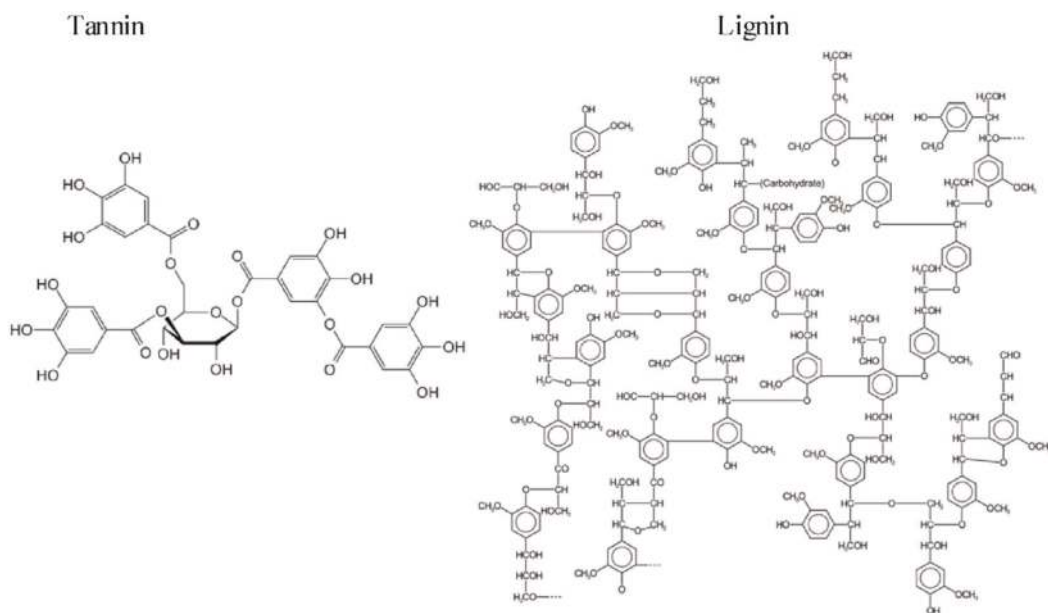


Figure 3.
Examples of polyphenolic compounds.

Another method of classification is according to the size of a phenolic compound's carbon chain, dividing the compounds into 16 major classes: simple phenols (C_6), benzoquinones (C_6), phenolic acids (C_6-C_1), acetophenones (C_6-C_2), phenylacetic acids (C_6-C_2), hydroxycinnamic acids (C_6-C_3), phenylpropenes (C_6-C_3), coumarins and isocoumarins (C_6-C_3), chromones (C_6-C_3), naphthoquinones (C_6-C_4), xanthenes ($C_6-C_1-C_6$), stilbenes ($C_6-C_2-C_6$), anthraquinones ($C_6-C_2-C_6$), flavonoids ($C_6-C_3-C_6$), lignins ($(C_6-C_3)_n$), lignans and neolignans ($(C_6-C_3)_2$) [5].

A broader designation into flavonoids and non-flavonoids has traditionally been used; it was brought on based on the plethora of natural flavonoids and the diversity

of C₆-C₃-C₆ structural offshoots [6]. The nonflavonoids group is classified according to the number of carbons that they have and comprises the following subgroups: phenolic acids, stilbenes, lignans, and others [5, 6]. **Figure 4** shows the main groups of plant phenolics.

1.2 Production and functions

The results of plants' photosynthesis can be classified as primary or secondary metabolites. Primary metabolites are usually described as substances that are essential chemical units of living plant cells. These fundamental substances are cellulose, hemicelluloses, polysaccharide, and lignin [7]. Plants synthesize a vast number of smaller molecules that are secondary metabolites. The secondary metabolites are formed by evolution to defend plants against harmful attacks by herbivores, pathogens, insects, and parasitic species [8].

Polyphenols, as secondary metabolites, are involved in functions related to reproduction, growth, defense, and pigmentation in plants, acting against pathogens, parasites, and predators. They also exhibit a great capacity to minimize the harmful effects of UV radiation, which may alter the regular metabolism in plants [2, 3]. Phenolic compounds are second only to cellulose in making up the bulk of organic matter, with phenolics (mainly lignin) accounting for about 40% of the organic carbon in the

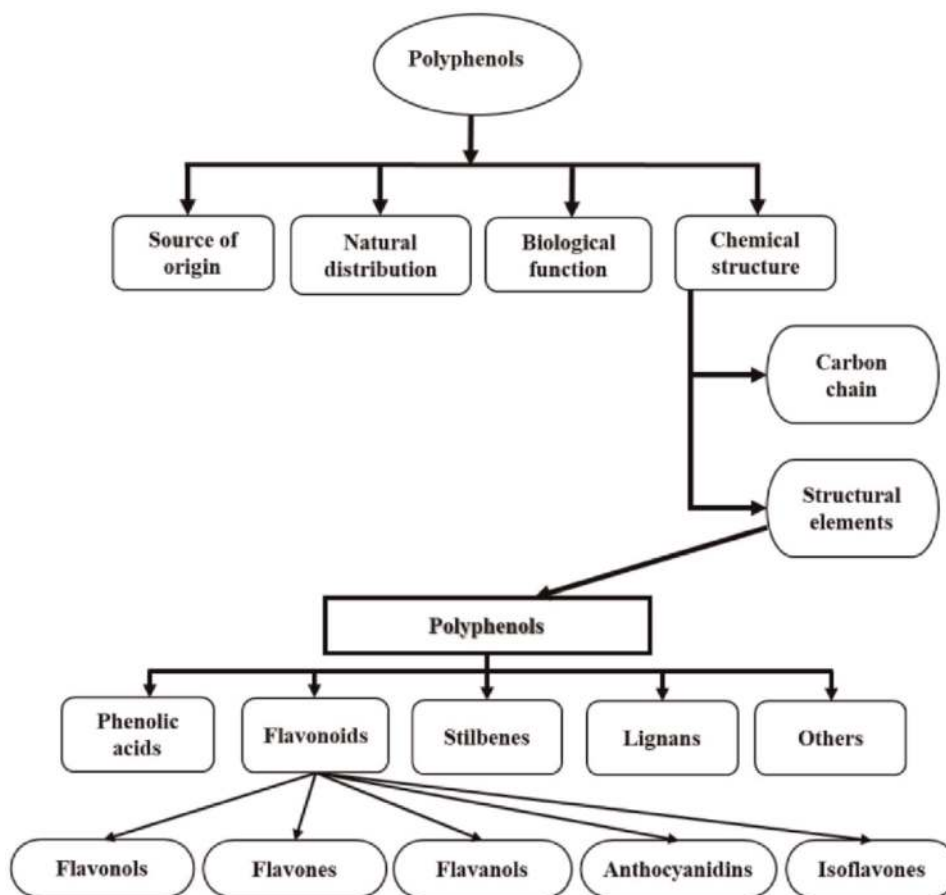


Figure 4. Main groups of polyphenolic compounds based on plants' biological functions (adapted from [5]).

biosphere. The phenolic secondary metabolites are produced through the shikimic and malonic acid pathways, as shown in **Figure 5** (adapted from [9]).

Since the synthesis of phenols can proceed by different pathways, phenols are a diverse metabolic group, and their chemical diversity is matched by their varied roles in plants (**Table 1**). Phenols' roles include these actions: function in mechanical support; protect the plant from harmful ultraviolet solar radiation and excessive water loss; attract pollinators and seed dispersers; serve as signals that induce defensive

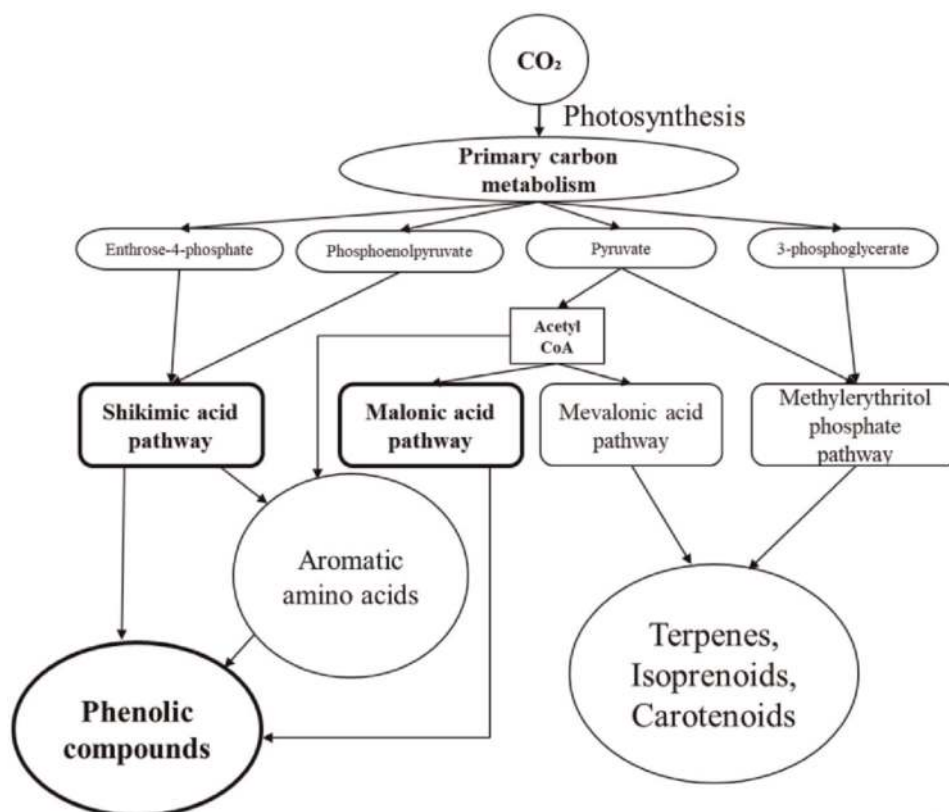


Figure 5. Main plant pathways for production of phenolic compounds (adapted from [9]).

Compound	Biological functions
Coumarins	Antibiotics, discourages herbivores
Cutin	External barrier to water and gas diffusion in aerial parts
Flavonoids	Antimicrobial, signals, pigments, UV protection
Lignan	Antibiotics, discourages herbivores
Lignin	Strengthen cell walls
Suberin	External and internal barrier to water and gas diffusion in roots
Stilbenes	Antibiotics, fungicides
Tannins	Fungicides, discourages herbivores

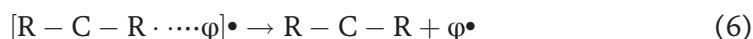
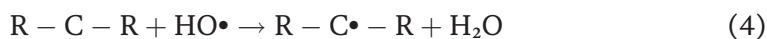
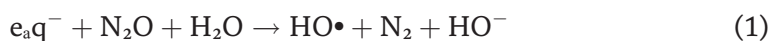
Table 1. The most prominent biological functions of phenolic groups.

reactions to biotic or abiotic stresses; suppress the growth of nearby competing plants (i.e., allelopathy); be attractive substances to accelerate pollination; provide coloring for camouflage and defense against herbivores; act as antibacterial and antifungal agents against pathogens; and provide protection against herbivores by repulsive taste or smell.

Phenolic acids constitute about one-third of the phenolic compounds in the human diet and are characterized by a remarkable antioxidant activity [10]. Phenolic acids can be divided into two groups: benzoic acids and their derivatives; and cinnamic acids and their derivatives. The benzoic acids are the simplest phenolic acids found in nature. Cinnamic acids are rarely found in their free form in plants and are generally in the form of esters.

1.3 Characteristics and reactions

Phenolics function as antioxidants in a number of ways. Phenolic hydroxyl groups are good hydrogen donors: hydrogen-donating antioxidants can react with reactive oxygen and reactive nitrogen species [11, 12] in a termination reaction, which breaks the cycle of generation of new radicals (reactions 1–5, adapted from [13] where, φ : phenolic antioxidant, \bullet : free radical species, R-C-R: organic molecule).



The antioxidant molecule (φ) reacts with the initial reactive species and forms the antioxidant radical ($\varphi\bullet$). The interaction between $\varphi\bullet$ and organic molecules produces an intermediate radical specie which has much greater chemical stability than the initial radical (reaction 5). The phenolics have the unique ability to produce stabilized free radicals due to delocalization of electrons between hydroxyl groups and the π -electrons of the benzene ring. These long-lasting radicals modify the oxidation processes and interrupt the free radical attack on other organic molecules (reaction 6) [14]. Similarly, the phenolic compounds can chelate metal ions and effectively stop the metal ions from producing free radicals. Another property which attributes to phenolic compounds antioxidant capability [10].

The phenolic compounds of plant origin act as antioxidants due to their redox properties, allowing them to act as reducing agents, hydrogen donors, free-radical quenchers, and metal chelators [15, 16]. In an organism, an oxidative process can be responsible for the generation of free radicals that attack the cells; the oxidative and nitrosative stress leads to serious diseases such as cancer, cardiovascular diseases, atherosclerosis, neurological disorders, hypertension, and diabetes mellitus [17, 18]. The principal function of antioxidants is to delay the oxidation of other molecules by inhibiting the initiation or propagation of oxidizing chain reactions by free radicals, consequently reducing oxidative damage [19]. Phenolic compounds can slow the oxidative degradation of lipids due to their antioxidant properties. Accordingly, the

food industry is showing increasing interest in application of phenolic-rich plant materials, such as crude extracts and oils of herbs, fruits and spices, to improve the quality and nutritional value of foods [20].

Phenolic compounds have also been associated with other bioactivities important for maintaining good health, such as anti-inflammatory, antimicrobial, and anti-proliferative activities [21, 22]. In addition to the pharmacological interest in these compounds, their biological activities have also been explored in other industry sectors such as food [23, 24], cosmetics [22, 25], packaging, and textiles [18, 26, 27].

2. Sources of phenolic compounds

About 370 million years ago, nature first produced phenols in woody plants. With the development of phenylpropanoid metabolic pathways, lignin (a major constituent of wood) was synthesized; this was a key evolutionary advancement for land plants. Lignin made the cell walls stiffer and stronger, making plants to bear up better, grow to larger size, and develop greater variety of tissues. Furthermore, an extensive range of phenolic compounds are produced through phenylpropanoid metabolic reactions. These phenols are responsible for pigmentation (leaves, fruits, and flowers), defense mechanisms, and signaling in plants. Also, the Natural organic matter (NOM) is mainly generated from plant phenolics and has a major role in ecosystem [28].

All plants including lower forms such as ferns, algae, and lichens can produce phenolics compounds. No animal species (with the exception of a marine sponge) however, has been found to be able to produce phenolic compounds in their bodies. As bacteria are unable to degrade polyphenolic compound, phenolics have also been found in coal, shale oil, and petroleum. The water pumped up along with petroleum in oil-production fields often contains elevated levels of phenolics. Phenolics are also found in water pumped from coal beds to extract methane from the coal beds; much of this water's acute toxicity is due to these aromatic and phenolic compounds.

Most phenolic compounds in plants are condensed tannins (proanthocyanidins) and act as flavors and pigments. These compounds are the cause of intense colors of flowers, fruits, and leaves. Flavonoids (anthocyanins) are responsible for autumnal foliage colors in plants. Condensed tannins are also cause the characteristic astringent tastes of many fruits and wines. An abundance of flavorful phenolics produces the identifying tastes of many fruits, leaves, and roots such as grapes, teas, cranberries, grapefruit, coffee, cinnamon, ginger, and vanilla.

Two classes of naturally occurring phenolic-based materials – humic and fulvic substances – are especially noteworthy with respect to ecosystem-level function. Humic and fulvic substances are products of plants, derived from partially degraded lignin, tannins, and other phenolics. These phenolic acids are negatively charged and rapidly form complexes with metal ions. The complex of humic acid and bivalent cations is almost insoluble in water. Even trace concentrations of humic compounds (below 1–5 mg/l) can effectively trap and reduce the toxicities of metals such as Cu, Zn, and Cd. Humic substances can also bound to chlorinated pesticides and reduce their bio-availability to aquatic organisms since the pesticide–humic complex would not be able to pass through cellular membranes [28].

In addition to plants' natural debris, phenolic compounds are released or condensed through industrial endeavors. Anthropogenic sources of phenolic compounds are described below for the food, cosmetics, packaging, and textiles industries.

In the food industry (agroindustry), phenolic compounds are widely distributed through plants, including vegetables, fruits, legumes, herbs, and spices. Raw fruits and vegetables are good sources of polyphenols. Being seasonally produced, they are often industrially processed and stored. Consequently, significant amounts of by-products (peel, pulp, seeds, stones, stems) are manufactured that contain valuable bioactive compounds such as flavonols, flavanols, anthocyanins, and phenolic acids such as ferulic acid, vanillic acid, and caffeic acid. Cereals (maize, wheat, rice, barley, sorghum, oats, and rye) and their by-products (like bran) are rich in a variety of phytochemical compounds such as phenolic compounds, carotenoids, vitamin E, γ -oryzanol, dietary fibers, and β -glucans. The phenolic compounds in legumes (chickpeas, beans, lentils, and peas) and their by-products are mainly represented by tannins, phenolic acids, and flavonoids. Polyphenols are present in beverages such as coffee, tea, wine, and beer and also in the by-products created during their production (e.g., coffee silverskin, spent coffee grains, grape pomace, brewers' spent grain). The agro-industrial residues of grapes are mostly solid byproducts such as stalks, pomace, and the liquid filtrate. These residues are composed of water, proteins, lipids, carbohydrates, vitamins, minerals, and compounds with important biological properties such as fiber, vitamin C, and phenolic compounds such as tannins, phenolic acids, anthocyanins, and resveratrol [29]. Olive oil and its by-products (olive leaves, olive mill wastewater and pomace) contain secoiridoids, phenyl alcohols, flavonoids, lignans, and phenolic acids. Cocoa and cocoa-derived products include flavanols such as epicatechin, catechin, and procyanidins. Many herbs and spices (coriander, thyme, sage, and rosemary) and waste extracts obtained from essential-oil production are good sources phenolic acids. Additionally, the antioxidant and antimicrobial activity of phenolic compounds in plant extracts have been crucial to the application of these compounds as preservatives, thus increasing the shelf life of several foodstuffs [18].

The cosmetic industry has been exploring natural additives as alternatives to artificial ones [25, 30]. Phenolic compounds have shown great potential for use as bioactive ingredients in skincare and beauty products [22]. Due to the presence of chromophores in their structure, these compounds can absorb ultraviolet radiation and protect the skin. Protection from UV-light has been measured for some phenolics such as quercetin, resveratrol, and hydroxycinnamic acids; presenting a sun protection factor (SPF) of 7–30 [30]. Hydroxycinnamic acids, such as p-coumaric and protocatechuic acids, can increase stability of lotions (up to 6 months) while maintaining their anti-inflammatory and antimicrobial activity, working as multifunctional ingredients [25].

In the packaging industry, some phenolics have been used to improve packaging formulations with antioxidant and antimicrobial properties [27, 31], as well as adding interesting colors and boosting antioxidant activity.

In the textile industry, textile production and dyeing is an important source of diverse chemical pollutants, since high amounts of water are contaminated with a heavy load of chemicals. In addition, allergic reactions have been associated with synthetic dyes [26, 32]. Consequently, there has been increased interest in the use of phenolic compounds as natural dyes with high biodegradability [26, 32]. In addition to being less harmful to the environment, natural dyes obtained from oak (*Quercus* sp.) bark and from red, black and green tea extracts, showed UV protection when applied to Tussah silk and cotton, respectively [26, 32]. Antimicrobial activity against *E. coli* and *S. aureus* was also achieved with the use of natural dye from oak bark [18, 26].

In the pulp and paper industry, bark and knotwood are the most economically available wood residues; they are collected in stems and transported to sawmills and

pulp mills, where bark is removed from the stems and knotwood is separated from wood chips. Many parts of cut trees such as leaves, branches, bark, roots, and stumps contain valuable phenolics but are considered waste material. Recently, more bark material is being used in energy, pulp, and paper production, and stumps have been collected for energy production due to restrictions on tree harvesting [33, 34].

3. Environmental fate and treatment of phenolic compounds

As previously stated, phenolic compounds are widely distributed through plants, and consequently, their dispensation in the environment, from either naturally discarded plant matter or decaying dead flora, is part of a balanced ecosystem. Plant phenolics have crucial impact on soil and fresh-water ecosystems mainly due to the large volume and variety of phenolic compounds in plants, the resistance of phenolics to degradation by bacteria; the low to average solubility of phenolic compounds in water; the conjugated system of C=C bonds, aromatic ring and hydroxyl group which translate into ease of absorbing certain wavelengths of light; and finally, their chemical energy content, available to potential decomposers.

However, many phenolic compounds are harmful to human health, causing necrosis, digestive problems, and liver and kidney damage in small doses and through chronic consumption of polluted water. Even in concentrations as low as 1 mg/l (1 ppm), phenolics can cause fish death in surface waters. At concentrations less than 1 mg/l, they are also toxic to other aquatic species and destroy the natural ecosystems. Phenolic compounds are phytotoxins, so their presence in soil would inhibit seed germination and the growth of local plants [35].

Phenolic compounds are present in the effluents of various industries such as oil refining, petrochemical production, pharmaceuticals production, resin manufacturing, and in pulp, paper, and wood products [36, 37]. Phenolic substances are widely used chemicals in several industries: as preservatives in the wood, lumber, and composites industries; as coke and coal gasifiers in coking operations; as antioxidants, flavorings, and other uses in the food industry; and in chemical production plants for the extraction and refining of minerals and metals, as well as the synthesis of organic chemicals, polymers, and plastics. Agricultural uses include pesticides, herbicides, and fungicides. Some of these phenolic substances are non-biodegradable and persistent in the environment and natural waters. Consequently, they will appear in treated water, as they usually cannot be treated through conventional methods and traditional treatment plants [36].

Nitrophenols and chlorinated phenols are usually labeled as priority pollutants since they are persistent and accumulative in nature [35, 38]. Phenol, cresols, and dimethyl-phenols have been considered as lesser environmental hazards because of their relative ease of biodegradation in activated sludge systems. However, as leachate from oil-shale waste, as well as in coal and coke leftover dumps, these short-chain phenols have become major pollutants of groundwaters [35, 39].

Phenolic common derivatives such as Bisphenol A (BPA), chlorophenols (CPs), and phenolic endocrine disrupting compounds (EDCs) are often listed at the top of lists of environmental pollutants. Phenolic compounds and their halogenated derivatives can also produce dioxin compounds [40]. Dioxins are notorious for their persistency in the environment and their high toxicity, so much so that they usually are at the top of “dirty dozen” lists.

Thus, the treatment of phenolic-rich agricultural and industrial wastes before discharge into the environment is a high priority. In the following sections, the environmental effects of phenolic compounds and their treatment techniques are discussed in more detail.

3.1 Phenolic compounds in air

Phenol is formed naturally in the atmosphere as a result of chemical reactions that occur in condensed water vapor that forms clouds. Natural background levels of phenolics in air are expected to be low, at about 1 ng/m [3] [38, 41]. Some phenolic compounds are typically emitted in ambient air by biomass burning, namely vanillin and acetosyringone [42]. Most phenolic compounds can be classified as volatile organic compounds (VOCs). VOCs are generally referred to as the highly reactive and/or toxic organics emitted from anthropogenic and natural sources, due to their high volatility in normal atmospheric conditions [43].

In industry, phenol is produced by extraction method from coal tar (tar being sourced from plants which contain high quantities of cumene). Phenol can be synthesized by a reaction between chlorobenzene and sodium hydroxide, or by oxidation of toluene, or by synthesis from benzene and propylene [41]. Phenol and its derivatives are used in several branches of industry: chemical production of alkylphenols, cresols, xylenols, phenolic resins, aniline and other compounds [44]; in oil and coal processing and metallurgy [45]. Phenol is also used in the production of pesticides, explosives, dyes, and textiles. Therefore, phenolic compounds are detected in industrial centers, especially near factories that incorporate wood in high concentrations. Phenol also enters the environment from vehicle exhaust and the use of disinfectants.

A large group of phenolic air pollutants are nitrophenols. The formation of nitrophenols happens under UV radiation from sunlight and in the atmosphere. The reaction of phenol, nitrite ions, and hydroxyl radicals leads to the formation of 2-nitrophenol and other nitrated compounds. Nitrophenols in the atmosphere are usually found in low concentrations (in the ng/dm [3] range). However, strong air pollution caused by industrial emissions leads to concentrations of nitrophenols up to 320 ng/dm [3, 41].

Nitrophenolic compounds mostly originate from anthropogenic emissions, such as automobile traffic, herbicide and insecticide use, coal combustion, and biomass burning [46–48]. Among these activities, biomass burning, traffic emissions, and coal combustion are regarded as the main sources, especially in urban areas [47–48]. Nitrophenols are a primary component of brown carbon (BrC), and the absorption properties of nitrated phenols in near-UV light can affect solar radiation and disturb atmospheric photochemistry, air quality, and regional climate [47, 49].

Incineration of phenolic waste contributes to phenolic pollutants in the air. Although the emissions from incinerators usually make up only a small proportion of air pollution, the secondary pollutants (heavy metals and polychlorinated dibenzo-p-dioxins and dibenzofurans) in the exhaust gases might pose greater health risks for the local populations [46, 50].

3.2 Phenolic compounds in water

The existence of phenolic compounds in water can be attributed to natural and anthropogenic activities. Natural sources of phenolic compounds in water include

decomposition of dead plants and animals (which is called natural organic matter). Phenolic compounds are also synthesized by microorganisms and plants in the aquatic environment. Industrial, domestic, agricultural, and municipal activities account for the anthropogenic sources of phenolic pollutants in surface and ground waters [4, 51]. Phenolics are found to be one of the most common contaminants of wastewater streams from manufacturers of petrochemicals, polymeric resins, or pharmaceuticals, along with coal-conversion plants and chemical industries. Due to their high aqueous solubility and weak adsorption to soils, phenolic compounds are widespread water pollutants. They are characterized by low biodegradability, making them difficult to remove from the environment by naturally occurring processes. Consequently, they can be found in drinking water reservoirs and underground aquifers. These compounds tend to accumulate in nature and living tissues, causing severe health problems for many species and disturbing the ecosystems. These toxic and non-biodegradable organic compounds cannot be effectively removed from industrial wastewaters by common treatment technologies, as will be discussed in Section 3.4.

The industries with the highest phenolic concentrations in their effluent discharge can be categorized into two classes: industries processing natural ingredients such as agro-industries; and production plants manufacturing new products from synthesized chemicals.

Examples of agro-industries with the highest phenolic discharge in their wastewaters are olive-oil mills, vineyards, avocado-oil producers, soy processing plants, coffee and tea production, beer and liquor breweries, and fruit or fruit-juice processing plants. Section 2 contains more specifics on polyphenols in the food industry.

The chemical manufacturing sectors producing great volumes of phenolic waste are paper production, dye synthesis, and pesticide manufacturing, among others [52–55]. Two examples of chemical processing (pulp and paper milling) and manufacturing (polypropylene plastic production) are presented in more details here.

Pulp and paper production is one of the most freshwater-consuming industries in the world; consequently, it is one of the largest producers of wastewater. Hence, the toxic load of pulp and paper mills (PPMs) is extremely high, and they are considered a major source of pollution [56]. They have a high chemical load of about 700 different organic and inorganic compounds including phenols, sterols, dioxins, and furans. Not surprisingly, these wastewaters have been shown to have detrimental impacts on the environment such as endocrine disruption, oxidative stress, and genotoxicity [56].

Another industrial wastewater with a high phenolic load comes from the production of polypropylene. Polypropylene, a synthetic resin produced through the polymerization of propylene, is one of the important plastic resins; it is used in products that require toughness, flexibility, light weight, and heat resistance. Polypropylene is used in carpeting and upholstery, reusable containers, paper, adhesives, and electronics, among others; the annual worldwide production of polypropylene (PP) is estimated at several thousand tons [57]. Massive amounts of phenolic VOCs and substituted phenols are used in the production of polypropylene to improve the resin's thermo-oxidation properties. The presence of these substituted phenols in industrial wastewater and VOCs in the air has been shown to be in the hundreds of ppm range [57]. Such considerable quantities of toxic chemicals in production effluents can cause serious damage to the aquatic environment and the health of many species.

The technologies for removing phenols from industrial wastewater are classified as either conventional methods or advanced methods. Treatment methods and their advantages are discussed in more detail in Section 3.4.

3.3 Phenolic compounds in soil

Phenolic compounds are considered a major water pollutant group because of their high solubility in water. The existence of phenols in waste materials from industrial processes such as oil refineries, coking plants, wastewater treatment plants, petroleum-based processing, and phenol-resin-industry manufacturing plants has been well established [58]. Usually, the small amounts of phenolic compounds in soil come from natural sources. Since phenolic compounds are stored in the leaves, roots, and stems of plants, decomposition of dead leaves, roots, and plants transfers the phenolic compounds to the soil. Also, the root and leaf secretions of plants contain phenolic compounds, which are finally emitted into the soil either by the exudates or the degradation of the plants' material.

However, the presence of phenolics in municipal solid waste is an important source of pollution in soil. Disinfectants and cleaning products are the common hazardous compounds reported to occur in a highly organic and heterogeneous mix of household waste and are often deposited into a municipal landfill. Landfill leachate is composed of a complicated chemical mixture including these compounds: phthalates; phenolics; pesticides; aliphatic and aromatic hydrocarbons; fatty acids and carboxylic acids; volatile compounds such as benzene, toluene, ethylene, and xylene; polyaromatic hydrocarbons; and polychlorinated biphenyls [59, 60].

The degradation of phenolic compounds under anaerobic landfill conditions has been established in a few reports [60]. The removal of phenolic compounds under anaerobic conditions is achieved with de-chlorination. Anaerobic bacteria can convert all phenolic compounds to phenol which then, can be degraded to CH₄ and CO₂ under anaerobic conditions.

One of the major controlling parameters for the degradation of phenolic compounds is the redox condition. Oxygen strongly affects the natural degradation of these compounds, and a positive correlation between oxygen concentration and enhanced degradation has been established. Under aerobic conditions, the removal of mono- and di-chlorinated phenols occurs rapidly. However, aerobic degradation becomes less effective for more highly chlorinated compounds such as TeCP and PCP. Nitrophenols are swiftly transformed to amino groups under aerobic conditions first and then degraded to CH₄ and CO₂ under anaerobic conditions.

Land disposal of solid waste increases the risk of surface and groundwater contamination with landfill leachate. Therefore, attention to aerobic treatment of landfills not only increases the degradation of solid waste, but also promotes the decomposition of toxic compounds such as phenols produced during the degradation process. Increased degradation rates would reduce the transfer of pollutants to groundwater and is applicable to both active landfills and in the reclamation of old landfills [59].

3.4 Treatment methods

As previously mentioned, phenolic compounds enter aquatic environments from natural, industrial, domestic, and agricultural activities. Their presence may be due to the degradation or decomposition of natural organic matter (NOM) present in the water, a natural part of the carbon cycle. However, the disposal of industrial and domestic wastes into water bodies and through runoff from agricultural lands requires awareness, action, and remediation.

Standard treatment methods are unable to reduce the concentration and toxicity of phenol-rich wastewaters, mainly due to the high solubility of phenolic compounds

and their toxicity to bacteria in activated sludge and anaerobic digesters; therefore, additional and alternate methods have been studied and implemented. The physical treatment processes include decantation (liquid-phase and solid-phase extractions), filtration (using reverse osmosis with micro, ultra, and nano membranes) and adsorption (activated carbon and ion exchange). The most-applied chemical methods are incineration, electrochemical methods, and advanced oxidation processes (AOP) [61]. Advanced technologies for removal of phenols include electrochemical oxidation, photo-oxidation, ozonation, UV/H₂O₂, Fenton reaction, membrane processes, and enzymatic treatment [36].

The main treatment methods of industrial effluents with biological processes are subdivided into microbial (aerobic and anaerobic) and enzymatic [61]. The microbial method involves the deployment of bacteria, yeast, and fungi in breaking down the phenolics into harmless products such as carbon dioxide and water. It has the advantage of comparatively low operational costs. Generally, the aerobic process is used for the degradation of phenolics with minimal halogenic substituents. On the other hand, the anaerobic process can efficiently reduce chlorinated phenolic compounds. The anaerobic system produces methane in addition to carbon dioxide and water. A major advantage of the anaerobic system of degradation is the absence of aeration cost, recovery of methane, and minimum excess biomass generation. Enzymes can also be used effectively to selectively eliminate pollutants in water, since they catalyze specific reactions under modest temperature, pH, and ionic strengths. Enzymatic reactions occur at much faster rates compared to other types of reactions and enzymatic systems can work under conditions unfavorable or toxic to bacteria. This method receives a high level of consideration due to its high pollutant-removal efficiency, its operation in a wide range of temperature and pressure, and the formation of harmless end products [4].

Considering the high value of phenolic compounds found in abundance in industrial waste discharge, however, it seems prudent to reclaim and extract the phenolic portion from effluent discharge. In addition to avoiding the extra cost and energy in treatment plants to process the phenolic compounds, the high levels of phenolic wastes could be viewed as resources. Therefore, reclaiming phenolic compounds offers a more attractive and sustainable solution to lowering the phytotoxicity of industrial waste. Wastes are residues of high organic load that are derived during raw materials processing and result in liquid or solid form. The fact that these substances are removed from the production process as undesirable materials defines them as wastes [62]. Since they contain high concentrations of valuable phenolic compounds, various recovery methods are being developed. The more popular ones are solid-liquid extractions, soxhlet extractions, pressurized fluid extractions and supercritical fluid extractions, ultrasound-assisted extractions, microwave-assisted extractions, pulsed electric field extractions, and enzyme-assisted extractions [63].

4. Industrial applications of phenolic compounds

Phenol derivatives have been attracting interest for decades as essential ingredients in various end-use industries due to their unique properties such as durability, chemical resistance, adhesion strength, plasticizing effect, and clear coating. These characteristics increase the sustainability of the phenol-derivatives market due to their applications in a broad range of industries such as electronics, paints and coatings, adhesives, household appliances, composites, textiles and packaging, pharmaceutical

drugs, wood products, agricultural products, and automotive products. Popular phenol derivatives include bisphenol A (BPA), chloro-phenols, alkylphenols, phenylalanine, caprolactam, and salicylic acid. The most common applications of phenolic compounds are in the paint and coating industry, wood processing, and bituminous construction; these uses are briefly reviewed below.

4.1 Paint and coating industry

Bisphenol A is used to produce epoxy resins and polycarbonate plastics. The most common epoxy resins (ERs) are produced from the ring-opening reaction of bisphenol and epichlorohydrin, followed by pre-polymerization of the produced diglycidyl ether through a reaction with bisphenol A. Epoxy resin is a type of thermosetting material that shows fascinating characteristics such as excellent adhesion properties, thermal stability, high heat and chemical resistance, and good mechanical strength [64–67]. These properties make epoxy resin suitable for different applications including coating [68, 69]. The significant adhesion strength of epoxy resin with various substrates, especially metal surfaces, is mainly due to high surface functional groups. Compounds with high molecular size provide adequate surface coverage in their role as inhibitors resulting in corrosion mitigation [70]. The adsorption of epoxy resin macromolecules at the interface of a metallic surface and the environment offers good surface covering and forms an oxygen-rich layer as a protective film against the aggressive atmosphere reaching the surface, leading to excellent corrosion resistance. Epoxy resin macromolecules can be effectively applied as anti-corrosive coating formulations for different metals and alloys in all kinds of electrolytic media due to their hydrophilic groups [71, 72]. Several literature studies have reported on the effectiveness of bisphenol-A-based epoxy resin to inhibit corrosion of E24 carbon steel in the acidic electrolyte and aluminum alloy in NaCl solution [73].

4.2 Wood processing

Phenolic compounds are the primary material used in the production of phenolic resins. Phenolic resins are the first class of synthetic polymers synthesized by the reaction between phenolic compounds and formaldehyde under acidic or basic conditions. Based on the formaldehyde/phenol ratio and the PH of the medium, the prepared resins are divided in two types: thermosetting phenol resins and thermoplastic phenol resins [74]. Phenol-formaldehyde resin (PF) is a thermosetting phenolic resin, known as resol, that is synthesized by electrophilic attack of the excess of formaldehyde to the aromatic ring of phenols under a basic condition. Thermosetting resins usually have strong mechanical properties, flame-retardant behavior, environmental resistance, and high bonding/adhesive strength, making them one of the promising adhesives used widely in wood composites [75, 76]. Phenol-formaldehyde resins are able to infiltrate the wood cell walls and improve their hardness [77–79]. Phenol-formaldehyde resins are the preferred thermoset adhesive for exterior wood composites such as manufactured plywood, oriented strand board (OSB) panels, laminated veneer lumber (LVL), medium-density fiberboard (MDF), and other structural wood products [80, 81]. Plywood is another popular wood-panel product manufactured as three layers of wood (veneers) assembled by an adhesive binder (such as phenol-formaldehyde for exterior-use plywood, or urea-formaldehyde for interior-use plywood) and then brought under heat and pressure [82–84]. The advantages of plywood over natural wood are

dimensional stability, resistance to splitting, and decorative value, making this product suitable for exterior and interior construction.

4.3 Bituminous construction

Bitumen, or asphalt binder, is the adhesive material that binds mineral aggregates together in an asphalt mixture. Bitumen is a waterproof and highly viscous material that is produced through vacuum distillation of crude oil. Because of the natural organic source of bitumen, oxidative aging is an inevitable phenomenon when a bitumen mixture is exposed to atmospheric oxygen. The major consequences of irreversible oxidative aging are the hardening of asphalt and the consequent pavement embrittlement, leading to deterioration of the asphalt's rheological properties and performance [85, 86]. During oxidation, the introduction of free radicals is believed to form new polar functionalities such as a carbonyl (C=O) group and also to break hydrocarbon side chains, leading to a reduction in aliphatic content in the bitumen [87, 88]. These structural changes in the bitumen fragments lead to further molecular agglomerations and unfavorable hardening of the bitumen mixture.

One of the counteractions to the aging of bitumen is adding "antioxidant" modifiers. Antioxidants are aimed at delaying the aging process and improving the aging resistance of bitumen by scavenging the free radicals generated in the process of oxidation [89–91]. The antioxidant mechanism of phenolic compounds through neutralizing free radicals and breaking the oxidation chain reactions has been previously discussed. Another group of compounds that function as free-radical scavengers and antioxidants for base bitumens and polymer-modified bitumens are hindered phenols [89, 91]. The antioxidation effectiveness of lignins and some of their derivatives in bitumen have already been studied [92–94].

To improve the performance properties and extend the service life of bitumen in the construction industry, it is necessary to use bitumen modifiers. Modifiers consist of fragments that are compatible with the bituminous environment and its processing temperatures. Thermosetting plastics, namely epoxy resins and phenolic resins, are important additives in bitumen modification, showing excellent adhesive ability, fatigue performance, and resistance to deformation. Blending phenol-formaldehyde resins (known as bakelite) or phenol-cresol-formaldehyde resins with bitumen causes significant improvements in rheological properties including the resistance to cracking and rutting, softening point, viscosity, and stability, reducing distresses during the bitumen's service life [95–98]. Besides the antioxidant nature of lignin, this polyphenol is also added as a modifier and renewable alternative into bitumen binder to improve the high-temperature and low-temperature performance and the resistance to rutting and cracking [99]. Adding bio-oils with high concentrations of phenolic compounds to bitumen binder increases resistance to ultraviolet exposure and decreases propensity to aging [100]. Phenol-rich bio-oils are effective at rejuvenating and restoring the properties of aged bitumen [101]. The thermomechanical properties of sulfur-extended bitumen can be tuned by introducing phenolic compounds. Phenolic compounds can activate the sulfur interactions within bitumen, so that the effect of sulfur can be more remarkable in the bitumen matrix [102].

Phenolic resins are used as curing agents in sulfur-containing synthetic rubbers, namely nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR), to increase the crosslinking density (vulcanization) and rigidity of the molecular network of rubber [103, 104]. Some study results show that the phenolic resins in the bio-oils activate rubber particles through their adsorption to the rubber surface. Their


curative effects improve the rubber-asphalt interactions and reduce the segregation between rubber and bitumen that commonly occurs in rubberized asphalt binder [105].

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