



Natural Quinone Dyes: A Review on Structure, Extraction Techniques, Analysis and Application Potential

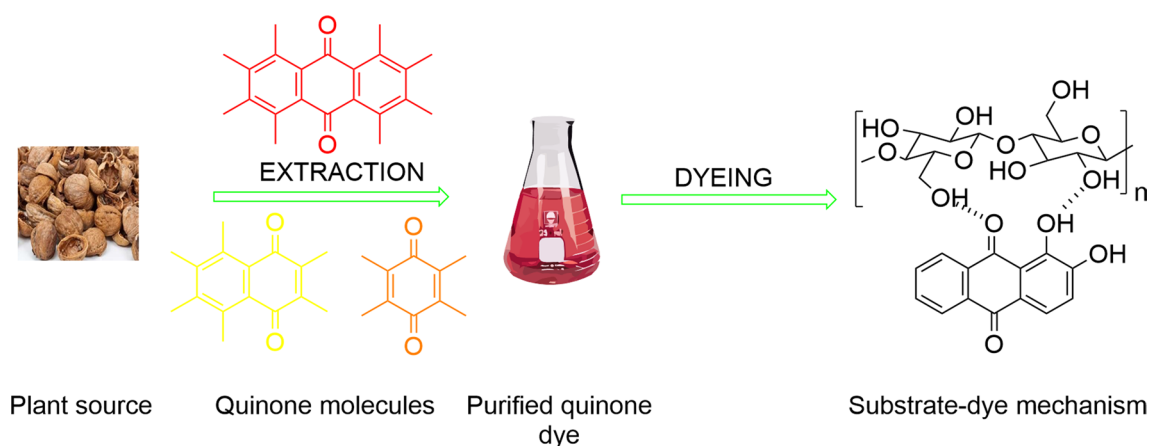
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Abstract

Synthetic dyes are by far the most widely applied colourants in industry. However, environmental and sustainability considerations have led to an increasing efforts to substitute them with safer and more sustainable equivalents. One promising class of alternatives is the natural quinones; these are class of cyclic organic compounds characterized by a saturated (C6) ring that contains two oxygen atoms that are bonded to carbonyls and have sufficient conjugation to show color. Therefore, this study looks at the potential of isolating and applying quinone dye molecules from a sustainable source as a possible replacement for synthetic dyes. It presents an in-depth description of the three main classes of quinoid compounds in terms of their structure, occurrence biogenesis and toxicology. Extraction and purification strategies, as well as analytical methods, are then discussed. Finally, current dyeing applications are summarised. The literature review shows that natural quinone dye compounds are ubiquitous, albeit in moderate quantities, but all have a possibility of enhanced production. They also display better dyeability, stability, brightness and fastness compared to other alternative natural dyes, such as anthocyanins and carotenoids. Furthermore, they are safer for the environment than are many synthetic counterparts. Their extraction, purification and analysis are simple and fast, making them potential substitutes for their synthetic equivalents.

Graphic Abstract



Keywords Natural dye · Extraction · Characterisation · Quinone · Sustainability · Biomass

Statement of Novelty

This paper evaluates natural quinone dyes as potential substitute for their synthetic equivalents. Sustainability and environmental safety will be achieved by the use of these dye extracts. Earlier studies concentrated on flavonoids and

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carotenoids whereas quinoids have not received similar attention, despite being at least as promising as the other two sources. The paper also presents an up-to-date overview of chemical analysis techniques and the use of natural quinone dyes.

Introduction

Dyes can generally be categorised as either synthetic or natural. While synthetic dyes are typically synthesised from petrochemical sources, natural colourants are abundantly available in nature and can be obtained from plants, microorganisms, animals or minerals. Of these sources, plants can potentially be a more sustainable source since plants biomass is more abundant in nature and contains dye molecules in higher quantities [1, 2]. These dyes have been used for centuries for colouration of natural fibres, such as cotton, silk, and wool, as well as for other substrates like leather, skin, hair, shoe polish, paper, wood, cane, candles and food [3]. However, in the beginning of the twentieth century, the introduction of synthetic dyes resulted in a drastic decline in the use of natural dyes due to the low cost, availability, simplicity of application, colour range, shade reproducibility and superior colour fastness of the synthetics [4]. Nevertheless, in the past two decades, an upsurge has occurred in the use of natural dyes because of their potential eco-friendliness, biodegradability, renewability and lower toxicity to humans and the environment [5–7].

Natural dyes can be classified based on the dye source, application method and chemical structure. However, classification based on the chemical structure might be more appropriate since the structure uniquely identifies dyes belonging to a certain chemical group with specific properties [5, 8]. On this basis, natural dyes are further grouped as indigoids, pyridine-based, carotenoids, quinoids, flavonoids, betalains, tannins and dihydropyrans [4, 5]. Of these groups, the quinoids, which include benzoquinones, naphthoquinones and anthraquinones are of particular interest since they resemble synthetic dyes [9] and may therefore be potential substitutes for the synthetic equivalents.

Synthetic dyes mainly consist of two major classes; azo dyes and anthraquinones dyes. The azo dyes, despite having many functional advantages, are now considered hazardous [10]. In fact, they are banned in many countries, such as the United States of America (U.S.A), India, and the European Union (E.U), among others [11, 12]. Many synthetic anthraquinones dyes, such as Disperse Blue 3, 2-aminoanthraquinone, and many others, have also been found to be highly toxic to humans and to the environment [13, 14].

The most abundant natural dyes are the carotenoids, flavonoids and quinones [15]. Of these, the carotenoids and flavonoids have been extensively studied and reviews are available [16–19]. By contrast, quinones have not been given similar attention, despite being at least as promising as the other two sources, since they can be considered the natural analogues of the more established synthetic quinone dyes. This review, therefore, aims to provide some insight into the potential of natural quinoid dyes. It gives a brief overview of the structure, occurrence, biogenesis, uses and toxicological analysis of these class of dyes. It also delves into quinone extraction, purification, identification, quantification and application in the context of dyeing. To ensure an exhaustive review, literature materials, such as text books, articles, abstracts and peer-reviewed publications listed in Web-of Science and Google scholar, were searched using the phrases “quinone dyes”, “natural quinone”, “natural dyes”, “quinone compound”, “natural anthraquinone”, “natural naphthoquinone” and “natural benzoquinone” within the period 1998–2019.

Structure, Occurrence, Use and Biogenesis of Natural Quinones

Though quinone compounds are structurally the most varied dye molecules [5, 20], they all share some features, sources, usage and biosynthesis pathways as described below.

Structure

Quinones are coloured compounds with a basic benzoquinone chromophore (Fig. 1a) consisting of two carbonyl groups with two carbon–carbon double bonds. The quinone dyes are fused benzenoid quinoid ring systems with sufficient conjugation to achieve colour. The three main classes of quinones are benzoquinones (Fig. 1a), naphthoquinones (Fig. 1b) and anthraquinones (Fig. 1c), which contains 1, 2 and 3 ring structures respectively.

Benzoquinone (Fig. 1a) is the basic subunit of quinone compounds [21]. Chemically, 1,4-benzoquinone (also called para-benzoquinone) is a non-aromatic compound which is easily converted into hydroquinone on reduction [22]. Benzoquinone units serve as building blocks in quinone synthesis and provide important moieties for the biosynthesis of active biological compounds [21]. Compounds with para-benzoquinones attached to one more benzene ring at position 2,3-C (carbon), are called naphthoquinones. The naphthoquinone structure (Fig. 1b) has two carbonyl groups on one benzene ring, normally at the o- or p- orientation [23]. Naphthoquinones also have α - and β -unsaturated carbonyls. The extended electron delocalisation through the double bonds and the carbonyl groups gives rise to intense

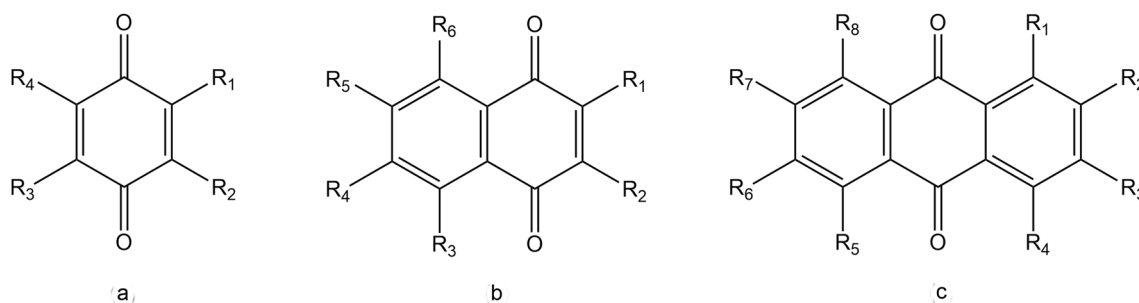


Fig. 1 Chemical structure of **a** benzoquinone, **b** naphthoquinone and **c** anthraquinone

colouration in the visible region [24]. The third class of quinones known as anthraquinones, are compounds containing the anthracene nucleus with two carbonyl groups, normally on the B-ring. They are derived from the basic structure 9,10-dioxoanthracene ($C_{14}H_8O_2$) (Fig. 1c), a tricyclic aromatic organic compound. The parent structure is also referred to as 9,10-anthracenedione, anthradione, 9,10-anthraquinone, anthracene-9–10 quinone, 9,10-dihydro-9, or 10-dioxoanthracene. Since quinone structures allow different substitution patterns, hundreds of derivatives exist in nature, especially for anthraquinones. Hydroxyanthraquinoids absorb visible light and are therefore coloured [25]. Generally, the colour of a quinone compound depends on the position, nature and number of hydroxyl and electron-donating/accepting constituents, also called auxochromes, on the different rings impacting on intra-molecular hydrogen bonding and steric effects [26]. Although the introduction of electro-donating substituents have little effect on quinones colouration, some substituents, such as amino or substituted amino groups, can have a significant impact on the dye's colour properties [26]. The structures and corresponding colours of commonly used coloured quinones are shown in Table 1.

Occurrence

Natural quinones constitute a large class of aromatic compounds that are prevalent in nature and can be found in several families of algae, fungi (including lichens), bacteria, flowering plants and arthropods [21, 24]. They are also found in insects like cochineal (*Dactylopius coccus*) [27], kermes (*Kermes vermilio*) [28] and lac (*Kerria lacca*) [25]. However, they are principally isolated from flowering plants, in which their colours are normally masked by other pigments [23, 29].

Among the subclasses of quinones, anthraquinones form the largest group, with around 700 compounds studied. Of these nearly half are from plants alone [26], While the remainder originate from fungi, bacteria, lichens, and insects [30]. The anthraquinones mainly occur in the *Rubiaceae*,

Leguminosae, *Polygonaceae*, *Bignoniaceae*, *Verbenaceae*, *Scrophulariaceae*, and *Liliaceae* plant families. These compounds have been reported to exist in almost all parts of plants tissues and organs, such as leaves, stems, pods, seed coats, fruits, nut shells, flowers, tubers, leaf glands, root bark and heartwood [20, 31]. The most commonly occurring anthraquinone is emodin, due to its presence in moulds, lichens, higher fungi, flowering plants and insects as well [20]. Anthraquinones may also be hydroxylated and may occur in vivo in free (aglycone) forms, or in combined (glycoside) forms, or in reduced forms [32]. In plants, anthraquinones are mostly present as glycosides, which makes them water soluble and gives them a lower chemical reactivity towards other plant cell compounds [33]. Normally, the aglycone forms are converted into glycoside anthraquinones by β -glycosidase activity or through an oxidative process [26]. This process occurs when one or more sugar molecules such as rhamnose or glucose are bound to the hydroxyl group at position R-6 or R-8 (Fig. 1) [30]. Conversely, hydrolysis of these glycosides also occurs [32]. An example is the aglycosylated alizarin formed by removal of the disaccharide primevorose (6-*O*- β -D-xylopyranosyl- β -D-glucose) by hydrolysis of a glycosylated ruberythric acid [31]. Pure non-glycosylated anthraquinones have also been reported to occur in plants as well [34]. Anthrones, a reduced form of anthraquinones, have also been isolated from plants, as have diathrone dimers, such as rheum emodindiathrone, physiondiathrone and sennosoids which are formed by coupling of two single anthrones [35].

Anthraquinone sources under active study for dyeing purposes include *Rubia cordifolia*, and *Rubia tinctorum* which contains alizarin, purpurin, emodin and rhein as common pigments [36, 37]; *Rheum emodi* which contains emodin and physcion colourants [38]; *Cassia nodosa*, which contains rhein [39]; and *Morinda angustifolia*, which contains rhein and emodin dye compounds [40]. Anthraquinone pigments have been isolated in concentrations in excess of 30 mg/(g dw) (dw: dry weight) from *Morinda citrifolia*, *R. emodi*, *Rheum undulatum*, *Rubia cardigolia* and *Tectona grandis* [38, 41, 42].

Table 1 Common quinone dye structures [20, 25]

Dye compound	Formula	Colour	R1	R2	R3	R4	R5	R6	R7	R8
Anthraquinones										
Alizarin	C ₁₄ H ₈ O ₄	Red	OH	OH	H	H	H	H	H	H
Emodin	C ₁₅ H ₁₀ O ₅	Yellow	OH	H	CH ₂ OH	H	H	H	H	OH
Carminic acid	C ₂₂ H ₂₀ O ₁₃	Red	OH	Glucose	OH	OH	H	OH	COOH	CH ₃
Kermesic acid	C ₁₆ H ₁₀ O ₈	Red	OH	H	OH	OH	H	OH	COOH	CH ₃
Lucidin- <i>O</i> -primeveroside	C ₁₅ H ₁₀ O ₅	Yellow	OH	CH ₂ OH	OH	H	H	H	H	H
Morindone	C ₁₅ H ₁₀ O ₅	Red, brown, orange	OH	OH	H	H	OH	CH ₃	H	H
Munjistin	C ₁₅ H ₈ O ₆	Red	OH	COOH	OH	H	H	H	H	H
Physcion	C ₁₆ H ₁₂ O ₅	Yellow	OH	H	CH ₃	H	H	OCH ₃	H	OH
Pseudopurpurin	C ₁₅ H ₈ O ₇	Red, yellow	OH	COOH	OH	OH	H	H	H	H
Purpurin	C ₁₄ H ₈ O ₅	Red	OH	OH	H	OH	H	H	H	H
Quinizarin	C ₁₅ H ₁₀ O ₃	Green	OH	CH ₂ OH	O-pr	H	H	H	H	H
Rhein	C ₁₅ H ₈ O ₆	Yellow	OH	H	COOH	H	H	H	H	OH
Ruberythric acid	C ₂₅ H ₂₆ O ₁₃	Yellow	OH	-pr	H	H	H	H	H	H
Rubiadin	C ₁₅ H ₁₀ O ₄	Yellow	OH	CH ₃	OH	H	H	H	H	H
Xanthopurpurin	C ₁₄ H ₈ O ₄	Red	OH	H	OH	H	H	H	H	H
Naphthoquinones										
Lawsonone	C ₁₀ H ₆ O ₃	Orange, brown	OH	H	H	H	H	H		
Alkannin	C ₁₆ H ₁₆ O ₅	Red, orange, brown	H	H	HO	H	H	H		
Shikonin	C ₁₆ H ₁₆ O ₅	Red, yellow, brown	H	H	HO	H	H	H		
Juglone	C ₁₀ H ₆ O ₃	Brown	H	H	HO	H	H	H		
Lapachol	C ₁₆ H ₁₆ O ₃	Yellow	OH	H	H	H	H	H		
Plumbagin	C ₁₁ H ₈ O ₃	Yellow	CH ₃	H	OH	H	H	H		
6-Methyl-naphthoquinone	C ₁₁ H ₈ O ₂	Yellow	H	H	H	CH ₃	H	H		
Benzoquinone										
Carthamine	C ₂₅ H ₈ O ₃	Yellow, green, red	O	O	H	HO				

-*pr* primeveroside

Numbers in Table 1 correspond with the numbers in Fig. 1

Naphthoquinones, with more than 120 sources studied, are the second most common group of quinones found in nature. They exist as several isomers, with the 1,4-naphthoquinones being the most common and the most stable [43]. This class of compounds is fairly broadly distributed among plants and microorganisms, while some are occasionally found in animals and specific fungi, and as metabolic product of some bacteria [23]. In plants, naphthoquinones frequently occur individually but sometimes co-exist with anthraquinones in the same species, particularly in the *Bignoniaceae* and *Verbenaceae* families [20]. They normally occur in the free form but sometimes exist in vivo as glycosides. In animals, naphthoquinones have been isolated from echinoderms, significantly from sea stars, starfish, sea urchins and from aphid species [20]. The commonly occurring 1,4-naphthoquinone compounds in plants are lawsone or henna in *Lythraceae* [24]; juglone in *Lawsonia inermis* [44]; and plumbagin in the *Juglandaceae* [45]; alkannin and shikonin in *Plumbaginaceae* [46] and lapachol pigment in the *Boraginaceae* [47]. Naphthoquinone pigment concentration

values as high as 50 mg/(g dw) have been obtained from *Juglans regia*, and *Tecomella undulata* [42, 48].

Of the three classes of quinones, benzoquinone is the least prevalent. However, it has been reported to occur in flowering plants, in fungi, in lichens, and in insects like beetles, millipedes and other arthropods capable of synthesising benzoquinone and its derivatives [20]. These compounds have been isolated from all parts of higher plants and usually occur as a single entity, with a few alkylated quinones and biquinones frequently occurring together [20]. The benzoquinone from plant biomass that is most commonly studied as a dye compound is carthamin, found in safflower (*Carthamus tinctorius*) [49]. A high concentration of about 30 mg/(g dw) have been isolated from safflower [50]. Common sources and occurrence of natural quinones are summarised in Table 2, together with the tissue from which the compounds are extracted and the colors and concentrations obtained.

Apart from plant sources, microbial organisms, such as fungi (including lichens), bacteria and algae, are other

Table 2 Survey of common sources of quinones components

Source	Common name	Part used	Compound	Colour	Concentration mg/(g dw)	References
Anthraquinones						
<i>Cassia occidentalis</i>	Kasunda-hindi	All parts	Emodin, rhein, physcion	Yellow	11.1	[60]
<i>Cassia fistula</i>	Indian laburnum	Whole plant	Rhein, sennoside, physcion, aloemodin	Yellow	Total glycoside in leaves 3.6 ± 0.16	[61]
<i>Dermocybe sanguinea</i>	Blood red redcap	Stem, cups, Fruit	Emodin, Physcion, Endurocin, Dermolutein	Yellow, orange, red and pink	0.0057	[9]
<i>Morinda citrifolia</i>	Indian Mulberry	Roots	Morindone	Red	0.6–1.2	[62, 63]
<i>Morinda angustifolia</i>	Noni, Indian Mulberry	Roots	Morindone	Brown/orange	40.0	[42]
<i>Oldenlandia umbellata</i>	Chay root, Indian madder	Roots	Hydroxy- and methoxy- anthraquinone	Brown	0.4	[64]
<i>Rhamnus frangula</i>	Buckthorn	Bark	frangulin (rhamnox)	Green, yellow	19.0	[65]
<i>Rheum emodi</i>	Himalayan rhubarb, Indian rhubarb	Rhizome	Rhein, Emodin, Physcion, Chrysophanol, Aloe-emodin, rutin	Yellow	Rhizome: 46.1	[38]
<i>Rheum undulatum</i>	Rhabarbarum	Leaves, Rhizome, Roots	Emodin, chrysophanol and physcion	Yellow	Roots: 34.0	[41]
<i>Rubia cordifolia</i>	Indian madder	Root, stem	Purpurin, alizarin, munjistin,	Red, red	Stem: 45.0	[42]
<i>Rubia tinctorum</i>	Dyer's madder	Root	Alizarin	Red	7.7	[66]
<i>Fusarium oxysporum</i>	Fusarium wilt	Tissue culture	Anthraquinone	Pink/violet	N.D	[54]
<i>Penicillium oxalicum</i>	Sorghum spp.	Tissue culture	Anthraquinone	Red	1.5–2 g/L	[67]
Naphthoquinones						
<i>Fusarium verticillioides</i>	Basal rot	Tissue culture	Naphthoquinone	Yellow	2.5 g/L	[68]
<i>Alkanna tinctoria</i>	Dyer's alkanet, alkanet	Whole plant, Root	Alkanin, Shikonin	Red, yellow, brown	Roots Alkanin: 14.1 Shikonin: 5.6	[69]
<i>Juglans regia</i>	Walnut	Bark, root, shell, leaf	Juglone	Brown	Shell: 50.0	[48]
<i>Lawsonia inermis</i>	Henna, Hina	Leaves	Lawsonone	Orange, brown	18.5–18.7	[70]
<i>Impatiens glandulifera</i>	Ornamental jewel weed	Leaves, stem, flowers	Lawsonone	Orange, brown	8.0–11.0	[71]
<i>Onosma nigri-caule</i>	Havacica	Roots	Shikonin/Alkanin	Red	2.2	[72]
<i>Tectona grandis</i>	Teak	Branches, leaves	Lapachol	Yellow	Leaves: 50.0	[42]
Benzoquinone						
<i>Carthamus tinctorius</i>	Safflower	Flower	Carthamin yellow and Carthamin red	Yellow, green, red	Red: 3.2–8.8 Yellow: 30.0	[50]

major sources of natural quinone dyes. The advantage of microbial colourants is that these sources can be cultured in different environments and due to the possibility of genetic modification, a high-quality colourant can be achieved [51]. In fungi, anthraquinones have been isolated from *Aspergillus* sp., *Eurotium* sp., *Emericella*

sp., *Fusarium* sp., *Penicillium* sp., *Mycosphaerella* sp., *Microsporum* sp., and as naphthoquinone from *Trypethelium eluteriae* [52], and benzoquinone from *Beauveria bassiana* [53], among others [54]. The fungi produce pigments, including chrysophanol and 1-acetyl-3, 8-dihydro-6-methoxyanthraquinone, which are capable of producing

a wide array of colourant shades, including red, bronze, maroon and red-brown [55]. In bacteria, quinones such as 2-hydroxy-9,10-anthraquinone and naphthoquinone have been isolated from *Streptomyces olivochromogenes* [56] and *Streptomyces* sp. [57], respectively. In algae, 2,6-dichloro-1,4-benzoquinone has been found in green algae [58], 1,4-naphthoquinone in brown algae [59] and 1-methyl emodin anthraquinone in red algae among others.

Table 2 shows that quinones can be found in all plant parts at varying concentrations: leaves (50 µg/g dw), stems (45 µg/g dw), pods (0.31 µg/g dw), seed coats (8.34 µg/g dw), fruits and nut shells (50 µg/g dw), flowers (8.8 µg/g dw), tubers/rhizomes (46.08 µg/g dw), root bark (190 µg/g dw), wood heart (36 µg/g dw), and whole plants (11.07 µg/g dw).

Biogenesis

Two different pathways have been proposed as biosynthesis routes for natural quinones in plants and other organisms (Fig. 2) [25, 73]. The first pathway is the polyketide or acetate-malonate pathway (Fig. 2a). The route involves systematic ring closure occurring on both aromatic rings and a substitution of at least two hydroxyl groups in the R1 and R8 positions (Fig. 1). This causes suitable folding and condensation of an octaketide chain derived from acetate and monolite. For example, in emodin pigment synthesis, the main precursor is the octaketide emodin anthrone, which results from a polyketide condensation reaction between acetyl-coenzyme A (-CoA) and malonyl-CoA fixed by a polyketide synthase (PKS) [74]. The anthrone is then oxidised into an emodin compound. The second proposed pathway is called the shikimate or chorismate/*O*-succinylbenzoic acid

pathway (Fig. 2b). Here, pigments eventually only have one of the rings unsubstituted and at least one hydroxyl group on the R1 (Fig. 1) position, as in alizarine, pseudopurpurin, purpurin and lucidin [74].

To increase the production yield of natural quinones for industrial applications, biotechnological methods have been attempted based on the simulation of quinone's biosynthesis pathways. In microbial organisms, for example, three production mechanisms are proposed: genetic manipulation by sequencing the microbial genome, molecular screening to improve gene expression and optimisation of secretion of quinones compounds and the use of strategic procedures under optimal conditions to increase the colourant excretion [75]. Other methods include tissue culture. For example, the enhancement of quinone yield from *Frangula alnus* has been investigated and has led to a total anthraquinone content of 1731 mg/100 g in the cultured plant leaf [76]. Precursor addition has also been investigated and was found to double anthraquinone yield in *Rubia akane* cell cultures [77]. Working with cell cultures has also been proposed to generate quinone extract of high purity [78]

Biological and Industrial Applications

Quinones are key secondary metabolites with vital biological functions, such as oxidative phosphorylation and electron transfer in photosynthesis and respiration processes within the plant system [30]. These compounds often act as an intermediates between a plant and its environment and are responsible for fragrance, flavour, defence, signalling, color and energy transduction [26, 79]. For humans, natural quinone components have found applications in pharmacology for inducing cytoprotection through antifungal [80],

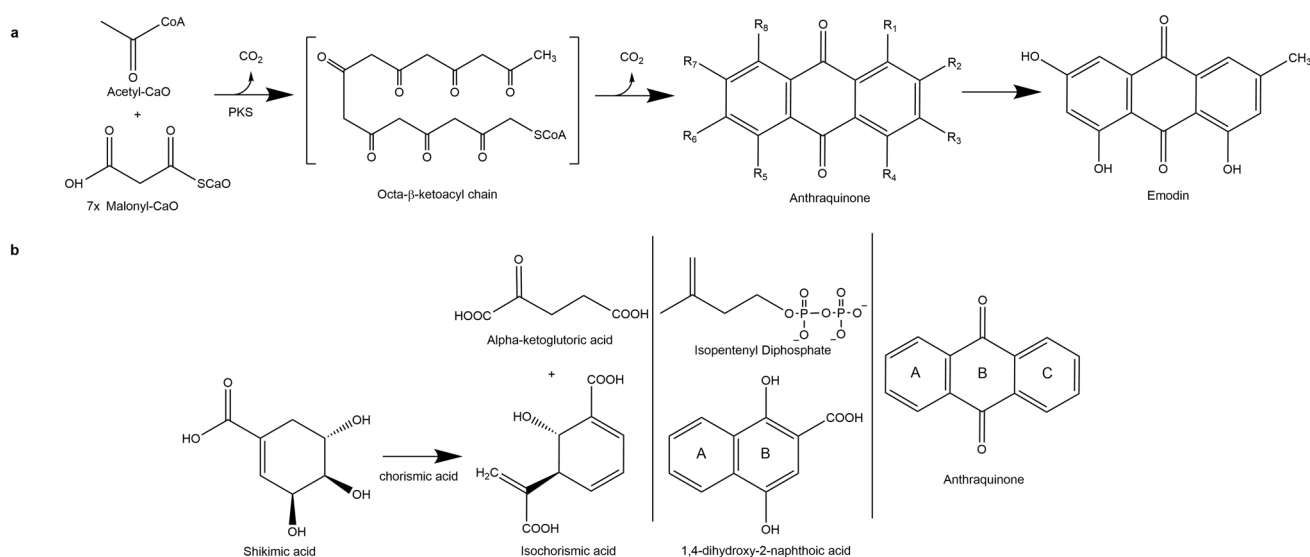


Fig. 2 Natural quinone biosynthesis pathways **a** acetic-malonate pathway [74] and **b** shikimate pathway [25]

antibacterial [81], antioxidant, anti-cancer, anti-inflammatory, laxative [26], anti-allergens and anti-moth properties [82]. They are also used as histological stains [8] and insect repellent [83] and in engineering technology for metallic corrosion protection [84], as pH indicators [64], in energy harvesting processes [85] and industrial colouration [26].

Quinones also have potential binding affinity to different cell receptor moieties. They display different affinity, selectivity, functionality and exchange dynamics towards different cellular binding sites. Hydrogen bonding, hydrophobic, electrostatic and van der Waals are among the dominant interactions between quinones and other receptors [86, 87]. Therefore, the many substitution sites in the long conjugated chain of quinone dye molecules lead to attractive affinity between a ligand molecule and a substrate. Quantitative structure–activity relationships studies have demonstrated at least an appreciable similarity between dye–substrate interactions and receptor–ligand interactions, indicating the possibility of modulating fiber–substrate affinity to benefit dyeing application [87].

Toxicity of Natural Quinones

The natural origin of molecules, in this case quinones, does not guarantee that they are harmless. Indeed, some natural quinones, such as anthraquinones from *Rumex patiens* that are used in the pharmaceutical and food industries, can cause pathological effects in vivo if used at high doses (≥ 4000 mg/kg), whereas lower doses produce slight or non-significant effects [88]. One report on the toxicity of various natural anthraquinones indicated a potential health and genotoxic effect on animals and humans if these quinones, and especially their aglycones, are directly ingested into the body in large quantity (≥ 1000 mg/kg) for a longer period (at least 2 weeks), despite their low bioavailability (< 0.1) [89]. Nevertheless, when compared with synthetic anthraquinone or azo dyes, the natural substances are less harmful. Indeed, the synthetic counterparts are non-biodegradable and recalcitrant in nature, so they cannot be easily removed by wastewater treatments. By contrast, the effluents from natural dyes like quinones are easily degradable and do not require the extensive and costly treatment plants needed for the synthetic counterparts [90].

One study that examined the use of natural naphthoquinones, such as juglone and plumbagin to control nuisance towards aquatic species showed that these two biocides had relatively short half-lives in saline water (5 h to 30 h), with juglone being more stable in fresh water [91]. The synthetic Reactive Blue 19 dye, in comparison, would take 46 years at pH 7 and 25 °C [92]. The study also determined that juglone, although stable in water, had little capacity for adsorption to suspended particulates or for bioaccumulation due to its low octanol–water partition coefficient (≈ 2). The study

concluded that, due to the rapid degradation, and especially in the marine environment, and the low adsorbency and bioaccumulation, the risk of residual toxicity is low for the release of juglone-treated water [91]. Generally, a reduction occurs in the pollution load when natural quinone dyes are used instead of their synthetic counterparts. A fact sheet on toxicological studies conducted on natural quinones, such as anthraquinones, reports that they are safe when used for non-food purposes [93]. An example is lawsone, a naphthoquinone dye, used in cosmetics; this dye has not been included among the 49 toxic cosmetic dyes banned by the EU as it presented low to negligible genotoxic risks to consumers [94, 95]. Contrarily, synthetic dyes such as Disperse Blue 3 displays acute toxicity [13], Vat Acid Blue 43 is potentially mutagenic, 2-aminoanthraquinone is identified as carcinogenic and Disperse Red 15 can cause allergic reactions [14]. However, these toxic effects, for either synthetic or natural quinone dyes, depend on the degree of exposure to the dye compounds.

The use of natural quinones as colorants has the advantage that these compounds also impart antibacterial [41, 96, 97], antifungal [98] anti-insect [83], and ultraviolet (UV) protection properties to textiles [99, 100]. Based on these findings, natural quinones are not without risk, and should not immediately be considered as ‘green’ and harmless, however, generally speaking, they might pose relatively lower risks compared to the synthetically produced quinone variants currently in use.

Purification of Quinone Dyes

The different subclasses and varying substitution patterns of quinones means that their identification and purification are not straightforward, but rather complex. However, recent advances in analytical techniques now allow a better understanding of their nature and extraction potential. Therefore, this section of the paper discusses the extraction and purification of, quinone molecules.

Extraction Parameters

As with other plants chemicals, the extraction of quinone is influenced by factors like the amount of solvent (s) used, extraction time and temperature, equipment design, selectivity of the target component, amount of sample used, extraction efficiency and nature and condition of the matrix. Of these factors, the nature of the solvents is the most important as this determines the solubility of the target compound and extraction efficiency. A good quinone solvent should have a high extraction capacity, low boiling temperature and low latent heat of evaporation to allow separation at low temperature, as this reduces the energy demand to a minimum, and

suppresses side reactions with colours and pigments to avoid loss of colour quality [36]. To a great extent, the solubility, and hence the extraction of substances, is dependent on the solute–solvent interaction [101]. The Hansen solubility theory illustrated in Eq. 1, can be used to predict this solubility [102]. The theory is based on three major intramolecular forces, namely dispersion (δ_d), polarity (δ_p) and hydrogen bonding (δ_h) [103]. The ability and efficiency of a solvent to dissolve a solute can therefore be estimated by determining the distance between the solute and the solvent or the relative energies according to Eq. 1:

$$D_{S-P} = \sqrt{4 * (\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2} \quad (1)$$

where $\delta_{i,P}$ and $\delta_{i,S}$ (MPa^{1/2}) are the *i*th component of quinone polymer compound and solvent, respectively [103].

Two chemicals are mutually soluble if their solubility parameters (thus D_{S-P}) are approximately equal. By plotting the Hansen solubility points on a 3D graph, the solubility of a compound can be predicted. Based on this solubility theory, the solvents for extracting quinones are predictable as shown in Fig. 3.

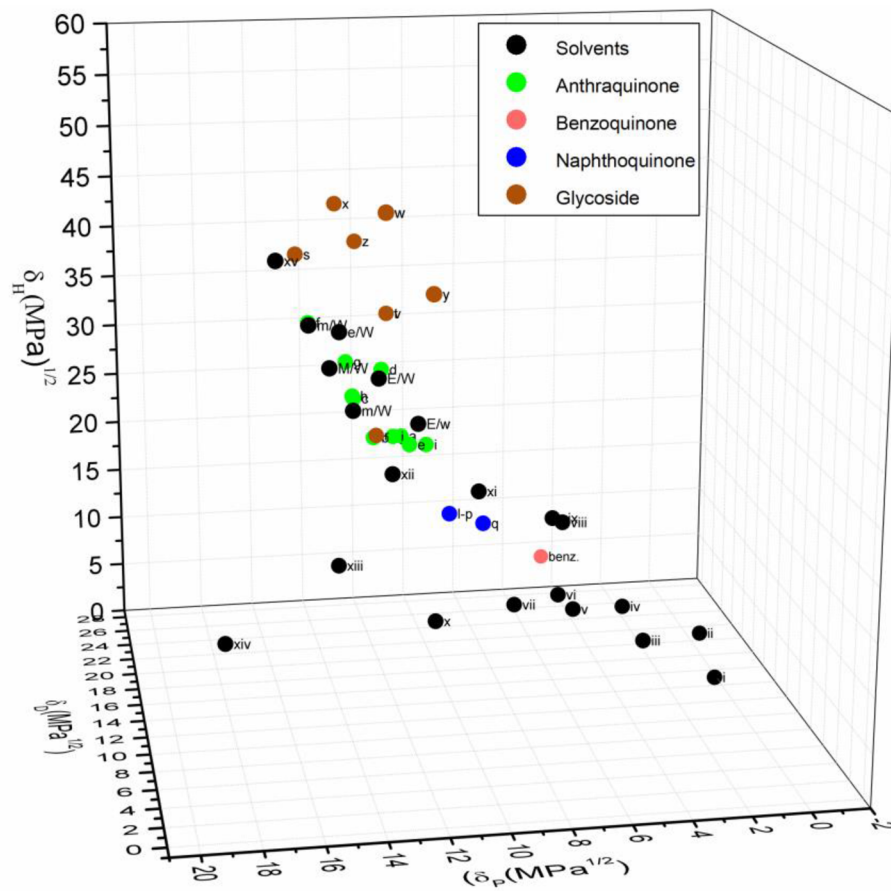
As shown in Fig. 3, methanol–water and ethanol–water mixtures are the recommended solvents for the extraction of anthraquinones. Methanol or ethanol are also good solvents for anthraquinones and naphthoquinones. Benzoquinone shows a high solubility in solvents with relatively lower polarity, such as ethyl acetate, tetrahydrofuran, dichloromethane and butanol. Glycosides seemingly dissolve best in water and water–alcohol mixtures, whereas aglycones appear to be more readily soluble in alcohol-based solvents. These predictions are supported by the findings listed in Table 3, which shows that alcohol–water based extracts, having lower relative energy differences (≤ 1), generates higher anthraquinone yields (about twofold) compared to solvents such as water, ethanol or benzene that all have higher relative energy differences (> 1) [104, 105]. Higher quantities (up to 7%) of anthraquinones were also obtained when methanol or ethanol were used as solvents rather than apolar solvents, again reflecting the lower relative energy towards anthraquinones [106]. Indeed, when comparing the quantity of the anthraquinone alizarin produced in different solvents, the yield decreased in the following order, in accordance with the increase in relative energy difference: methanol (0.15%), ethanol (0.03%), ethyl ether (0.018%), and acetone (0.018%) [36]. The same can also be seen for naphthoquinones extracted under similar conditions, where different solvents resulted in different yields: methanol (0.06%), chloroform (0.0146%) and ethyl acetate (0.009%) [107]. Another study showed that methanol gave a higher weight concentration of juglone (0.99%) than was obtained with acetone (0.88%) when extracted under what were otherwise the same

conditions [108]. Conversely, benzoquinone was obtained in a high quantity (1.45%) when chloroform was used as the extraction solvent [109] while alcohol–water mixtures gave higher values for glycosides (2.63–4.6%) [104].

Quinone isolation depends largely on whether aglycones or glycosides are targeted [36, 66]. However, sequential extraction with solvents of increasing dielectric constant or polarity is normally recommended when total quinones are of interest [33]. Additionally, since quinones vary in polarity and solubility, no particular solvent can be recommended for their complete extraction [20]. Another point of attention is that quinone extraction can be done at different temperatures. However, extracting anthraquinones at temperatures above 65 °C or over 78 °C in methanol or ethanol based solvents, respectively, for prolonged periods (> 9 h) can result in the formation of artefacts, such as 2-ethoxyethyl or 2-ethoxymethyl groups [33, 110]. Therefore, high-temperature extraction for longer periods should be avoided when using these two solvents [20]. These artefacts are undesirable since they modify the colour of the compounds [111].

Generally, quinone glycosides hydrolyses to their corresponding aglycones when exposed to high temperatures [112], in acidic conditions, for example, in (2–5%) sulphuric and hydrochloric acid solution at temperatures between 80 and 100 °C [113], they can also be partially hydrolysed by aqueous sodium hydroxide [114], and completely hydrolysed by enzymatic (such as β -glucosidase) treatment at a temperature of 50 °C and pH 5 [115]. Nevertheless, a comparison of solvents such as ethanol and water for extraction of alizarin from madder root [112], revealed that ethanol was preferable since it gave a higher yield of glycosides. This does not correspond with the Hansen solubility prediction, as water was expected to result in higher extraction yields of alizarin glycosides. However, the alizarin glycoside-to-aglycone ratio was found to be 237:1 mg/cm³ in ethanol and 22:1 mg/cm³ in water. The lower amount of glycoside in water possibly reflected hydrolysis of the glycosides due to the use of high extraction temperatures [112]. To mitigate this, the current literature suggests that quinones be extracted at room temperature up to about 70–90 °C and preferably during shorter time frames or with higher temperature (about 98 °C) for fewer hours (< 9 h) (Table 3).

Quinones also dissolve well in alkaline solutions [20, 50]. Teruyuki et al. [115] reported a selective and simultaneous extraction of both aglycones and glycosides using two phase extraction with chloroform and a potassium hydroxide solution. When potassium hydroxide solution was used as a solvent, both ruberythric acid and lucidin primeveroside were extracted, whereas only chloroform was used, anthraquinones primeverosides were not extracted and only small amounts of alizarin and lucidin were obtained. When both aqueous potassium hydroxide salt–chloroform solutions were used, alizarin and lucidin (in the chloroform phase) were



Key

Solvents		Anthraquinone		Glycosides	
i.	Hexane	a	Alizarin	r	Lucidin primeveroside
ii.	Benzene	b	Aloe-emodin	s	Carminic acid
iii.	Diethyl ether	c	Munjustin	t	Ruberythmic acid
iv.	Chloroform	d	Marindone	u	Quinizarin
v.	Ethyl acetate	e	Physcion	v	Emodin-8-o-glucoside
vi.	Tetrahydrofuran	f	Pseudopurpurin	w	Rhein-8-o-glucoside
vii.	Dichloromethane	g	Purpurin	x	Chrysophanol-8-ogluoside
viii.	Butanol	h	Rheum	z	Aloe-emodin-8-o-glucoside
ix.	Propanol	i	Rubidian		
x.	Acetone	j	Xanthopurpurin		
xi.	Ethanol	Naphthoquinones			
xii.	Methanol	k	Lawsone		
xiii.	Dimethylformamide	m	Alkannin		
xiv.	Acetonitrile	n	Shikonin		
xv.	Water	n	Juglone		
e/W	30 % Ethanol	o	Lapachol		
E/W	50 % Ethanol	p	Plumbargin		
E/w	70 % Ethanol	Benzo Benzoquinone			
m/W	30 % Methanol				
M/W	50 % Methanol				
m/W	70 % Methanol				

Fig. 3 Hansen solubility of quinones using common solvents

Table 3 Natural quinone dye extraction method and optimization conditions

Source	Target pigment	Extraction method	Solvent	Extraction system	Resultant dw yield (%)	Reference
<i>Rubia tinctorum</i>	Alizarin	Maceration	MeOH, H ₂ O, Et ₂ O, EtOH, Acetone	M:L 1: 40, temperature 25 °C for 12 h	Et ₂ O: 0.018, Acetone: 0.018 EtOH: 0.035 MeOH: 0.15, H ₂ O: 0.106 Alizarin ^T : 0.26 ^g , 0.21 ^a Naphthoquinones ^T : 0.8–0.11	[36]
<i>Impatiens glandulifera</i>	2-hydroxy-1,4-naphthoquinone, 2-methoxy derivatives	Maceration	35% EtOH	M:L 1:32, boiling for 30 min		[71]
<i>Carthamus tinctorius</i>	Carthamin	Maceration, alkaline	H ₂ O, Na ₂ CO ₃ solution	M:L 1:15, 1% salt, temperature range 20–25 °C for 30 min twice	Carthamin ^T : (0.32–0.88)	[50]
<i>Cassia fistula</i>	Rhein	Boiling	H ₂ O	M:L 1:10, 95–98 °C, 6–7 h	Anthraquinone ^{g,T} Decoated: 1.52, dry leaf: 0.36	[61]
<i>Rubia tinctorum</i>	Alizarin	Reflux	EtOH, MeOH, EtOAc	M:L 1:50, Successive EtOH and MeOH each at 50 °C for 1 h, then HCl hydrolysis of MeOH extract at 65 °C, for 24 h with EtOAc	5 months– 0.564 ^a , 0.259 ^g , 0.823 ^T , 15 months – 0.308 ^a , 0.372 ^g , 0.681 ^T 30 months – 0.356 ^a , 0.359 ^g , 0.715 ^T	[66]
<i>Rubia tinctorum</i>	Alizarin, Munjistin Pseudopurpurin Lucidin Premeveroside Ruberithric acid	Reflux	H ₂ O-EtOH	(1:1) v/v, M:L 1:40, Successive refluxing for 3 h, dried extract added to 2% H ₂ SO ₄ (v/v) and refluxed for 48 h	Anthraquinone ^T : 0.9	[128]
<i>Morinda parvifolia</i>	Marindone Naphthoquinone and Naphthohydroquinone	Reflux	EtOH-H ₂ O	(95:5×3) v/v, refluxing for 1.5 h, concentrated under reduced pressure, suspended in H ₂ O and successively partitioned with CHCl ₃ , EtOAc, and <i>n</i> -BuOH	Quinone ^T : 0.172	[40]
<i>Juglans regia</i>	Juglone	Reflux	Acetone, MeOH	M:L 1:50, particle size 200 µm, 8 h reflux, M:L 1:50, pre-treated for 4 min. by MAE 180 W, and 100 W ultrasound	Acetone – 0.88, 4.6, MeOH 0.99, 4.0 Non assisted and microwave assisted respectively	[108]
<i>Ficus foveolata</i>	2,6-dimethoxy-1,4-benzoquinone	Reflux	Hexane, CHCl ₃ , EtOAc	M:L 1:25, for 1 h	CHCl ₃ : 1.45	[109]
<i>Senna alata</i>	Rhein Aloe-emodin Emodin	Reflux	MeOH	1. MeOH and 2. MeOH plus 5% HCl M:L 1:20	Rhein – (1–0.02), (2.0–0.15) Aloe-emodin – (1.0–0.03), (2.0–0.04) Emodin – 1.0, (2.0–0.13)	[129]

Table 3 (continued)

Source	Target pigment	Extraction method	Solvent	Extraction system	Resultant dw yield (%)	Reference
<i>Rubia cordifolia</i> , <i>Morinda angustifolia</i> , <i>Tectona grandis</i>	Rubiadin Alizarin Munjistin Purpurin Marindone Lapachol and Tectoquinone	Reflux	H ₂ O, EtOH-H ₂ O, Petroleum ether, CHCl ₃ , Benzene	Successive reflux with H ₂ O at 90–95 °C for 3 h, then (70:30) EtOH: H ₂ O mixture, the dry mass extracted with Et ₂ O, CHCl ₃ or benzene	Anthraquinone ^T <i>Rubia cordifolia</i> : 4.5, <i>Morinda angustifolia</i> : 4.0 <i>Tectona grandis</i> : 5.0	[42]
<i>Polygonum cuspidatum</i>	Aloe-emodin, rhein, emodin, chrysophanol and physcion	Reflux	1. CHCl ₃ and H ₂ SO ₄ , 2. MeOH then H ₂ SO ₄ 3. MeOH	30 min heat for 1 h at 80 °C Sonication for 30 min	Aloe-emodin: 1.27, rhein: 4.65 Emodin: 2.12, chrysophanol: 7.68, and physcion: 1.46	[130]
<i>Rheum rhabarbarum</i>	Anthraquinone	Soxhlet	MeOH	L:R 1:10, 10 h	Anthraquinone range ^T : (0.064–7.032)	[106]
<i>Morinda angustifolia</i>	Aloe-emodin, Marindone, Emodin, Rhein, Marindone	Soxhlet	EtOH, Et ₂ O, Benzene	Successive extraction with EtOH for 10 h, then with Et ₂ O and benzene	Anthraquinones ^T : 2.0	[105]
<i>Juglans regia</i>	Juglone	Maceration, MAE, UAE	CHCl ₃ , EtOAc, MeOH, and H ₂ O	M:L 1:10, Maceration 45–50 °C, MAE 20 min, 150 W, 50 °C UAE: 40 ± 5 °C, 40 min	Maceration CHCl ₃ : 0.0146, MeOH: 0.06, EtOAc: 0.009, H ₂ O: 0.002 MAE and UAE: EtOAc – 0.0149, 0.0105 CHCl ₃ 0.02, 0.03 respectively	[131]
<i>Rheum emodi</i>	Emodin Aloe Physcion Chrysophanol	Maceration, heat-reflux, Soxhletion, ultra-sonication, sublimation	Petroleum ether, Et ₂ O, CHCl ₃ , EtOAc and EtOH	M:L – 1:50, shaken vigorously for 15 min and left undisturbed for 24 h, for native extraction. Hydrolyse with 10% HCl for 2 h	Soxhlet/acid: 4.0/4.6 Maceration/acid: 2.19/3.73 UAE: 4.56/8.31 Sublimation: 2.0/5.0 Soxhlet: 5.9, 12.13	[38]
<i>Rheum officinale</i> Baill, <i>Rheum palmatum</i> , and <i>Rheum tanguticum</i>	Aloe-emodin-8- <i>O</i> -glucoside, rhein-8- <i>O</i> -glucoside, chrysophanol-1- <i>O</i> -glucoside, emodin-1- <i>O</i> -glucoside, chrysophanol-8- <i>O</i> -glucoside, emodin-8- <i>O</i> -glucoside Emodin and Chrysophanic acid	UAE	MeOH-H ₂ O	M:L 1:20, (80:20) v/v, 40 mm size sample extracted at room temperature for 30 min	Anthraquinone ^{S,T} <i>Rheum tanguticum</i> : 4.6, <i>Rheum palmatum</i> : 3.56, <i>Rheum officinale</i> : 2.63	[104]
<i>Rheum emodi</i>	Emodin and Chrysophanic acid	Sonication	MeOH	M:L 1:15, 30 min at 45 °C	Emodin ^T HPLC: 0.335, HPTLC: 0.338, Chrysophanic acid ^T ; HPLC: 0.706, HPTLC: 0.78	[132]

Table 3 (continued)

Source	Target pigment	Extraction method	Solvent	Extraction system	Resultant dw yield (%)	Reference
<i>Rhizopus alpinus</i>	Emodin Aloe-emodin Physcion Chrysophanol	Maceration UAE, CO ₂ SFE	H ₂ O	60 min, 6 M HCl hydrolysed, Maceration- M:L 1:10, rt UAE- M:L 1:10, rt, 40 kHz, SFE-M:L 1:4, dynamic mode, 80 mPa, flow 3 mL/ min	Anthraquinone ^T Maceration: 0.142, UAE: 0.1425, CO ₂ SFE: 0.033	[133]

MeOH methanol, *H₂O* water, *Et₂O* diethyl ether, *EtOAc* ethyl acetate, *H₂SO₄* sulphuric acid, *HCl* hydrochloric acid, *BuOH* butanol, *CHCl₃* chloroform, *M:L* material to liquor ratio, *MAE* microwave-assisted extraction, *UAE* ultrasound-assisted extraction, *SFE* supercritical fluid extraction, *HPLC* high performance liquid chromatography, *SFE* supercritical fluid extraction, *r:t* room temperature

^T total, ^S glycoside, ^a aglycone

extracted along with their primeverosides (in the aqueous phase).

Another factor, the solid–liquid (S/L) ratio, is also important as this determines the interaction between the solute and solvent during the extraction. Table 3 shows that the S/L ratio ranges from 1:10 to 1:50. Typically, this ratio also depends on other extraction parameters, such as the solvent type, the extraction time and the method used.

Extraction Methods

Methods applied for extracting quinones include maceration [116], reflux [117], Soxhlet [118, 119], microwave assisted [118, 120, 121], ultrasonic assisted [118, 122], ultrasonic-microwave assisted [123], enzyme assisted [37, 124], supercritical fluid [125], sublimation assisted [38], and pressurised liquid [121, 126] extractions. The applicability, requirements and results vary considerably among these methods.

Some of these extraction methods, such as static and dynamic maceration, Soxhlet and ultrasonic extraction using n-hexane solvent, were compared for quinone extraction from the stem bark of *Diospyros anisandra* [127]. Soxhlet extraction was the most efficient technique, as it gave the highest yield of total quinone content at 11.5 mg/g dw, compared to 5 mg/g dw for dynamic maceration, 4.5 mg/g dw for ultrasound-assisted and 3.75 mg/g dw for static maceration methods. The efficiency of Soxhlet extraction is attributed to the continuous renewal of the solvent, which promote effective diffusion. Similarly, Aditya et al. [38], compared the efficiency of non-conventional methods, such as ultrasonication and sublimation, with the more classical methods, such as maceration, reflux and Soxhlet, to extract *R. emodi*. Refluxing was the most efficient method, with a recovery rate of 77.9%, whereas sublimation, ultrasonication and maceration achieved 53.32%, 51.79% and 37.31%, respectively. The highest impurity levels were obtained with Soxhlet and maceration, while sublimation gave the most selective, cost effective and environmentally friendly results, with minimum infrastructural and solvent requirements [26, 38]. Reflux extraction requires less time and has also proved to be suitable for commercialisation [26]. On the same note, extraction efficiencies of supercritical, microwave-assisted, enzymatic, solid–liquid and conventional extraction methods have also been compared. Supercritical fluid extraction and pressurised liquid extraction required shorter extraction times and were more environmentally friendly, at a similar equipment and operating costs [26]. Extraction methods for different quinone pigments, the optimised conditions, and the obtained yield are summarised in Table 3.

As indicated in Table 3, most researchers choose reflux, Soxhlet and maceration methods for quinone extraction, with yield and extraction time being the most considered

parameters. While reflux and Soxhlet give comparatively high quinone yields, Soxhlet requires a long extraction time making it comparatively more expensive. Conversely, the maceration method is preferred for quinone extraction mostly in medical application areas. Thus, trading off the scale of extraction yield, extraction time and cost reveals that the reflux method is clearly the most cost-efficient extraction method for quinone dyes. Here, extraction temperature normally ranges around 90–98 °C for 60 min.

Purification

Purification of the quinone crude extract is typically required to eliminate other interfering compounds. This separation is mainly achieved by methods such as thin layer chromatography (TLC) [134], high performance liquid chromatography (HPLC) [135] and phase separation [136]. Other methods include high-speed counter-current chromatography (HSCCC) [137], electrophoresis [106], and supercritical fluid chromatography (SCFC) [138].

TLC has long been used as a general procedure for separating quinones [32]. Generally, the TLC plate consists of a silica gel based stationary phase and a mobile phase containing a variety of eluents, typically mixtures of methanol, ethanol, water, chloroform, ethyl ether, acetate, toluene, hexane, ethyl acetate and propanol at different ratios. The TLC method separates lipid-soluble benzoquinones and naphthoquinones by carrying them along with the more nonpolar solvent mixture. At the same time, the complex and highly hydroxylated quinones require more polar solvent mixtures to mobilise them. The TLC method's main limitations are its slow speed and poor quality separation and difficult scalability. However, compared to other methods, it still shows advantages in terms of low equipment and consumables costs, as well as versatility in application [32, 48].

Compared to TLC, other chromatographic techniques show increased sensitivity and shorter purification times, but this comes with higher costs [139]. For chromatographic purposes, water–methanol–acetic acid, chloroform–methanol–formic acid or acetonitrile solutions are mostly used as eluents [26], although n-hexane–ethyl acetate–methanol–water or petroleum ether–ethyl acetate–water mixtures can be used in counter-current systems to give higher purities (> 90%).

A related method is SCFC, which is viewed as an environmental friendly method. Here CO₂ is used as the mobile phase and just a little solvent, either directly or in reverse phase, has also been applied to clean up quinone extracts [138]. The use of CO₂ permits a high flow and diffusion rate, thereby improving the selectivity and shortening the analysis time. Organic modifiers, mostly alcohols, are used to enhance dissolvability. However, based on the available

literature, this technique is not commonly used for quinone purification.

Alternatively, two-phase separation methods and precipitation are also used [140, 141]. In two-phase separation systems, the phase combinations have included polyethylene glycol/dextran, polymer/salt polyethylene, glycol/sodium sulphate, and non-ionic surfactant micellar systems, such as Triton X-114 [136]. While the method's significant strength has been the simplicity of the equipment used [140], its main challenges have been the slow segregation and re-extraction from the polymer phase [142]. However, a low cost, low viscosity, easy recoverable system using an alcohol/salt two-phase system has also been proposed [142]. The latter used 1-propanol and (NH₄)₂SO₄ to purify anthraquinones extracted from *Aloe vera*. A phase ratio of 0.34 (17.84/26.66 concentration of alcohol/salt % w/w), achieved a partition coefficient of 64, and an extraction efficiency of 96% were achieved [142]. Another example has demonstrated phase separation of alizarin glycoside and aglycone from *R. tinctorum* extract [113, 143]. The subsequent extraction with solvent from the Sep-Pak Plus silica has led to a recovery of 90–100% for bacterial quinones, compared to the conventional recovery of about 30 to 60% obtained with column chromatography and TLC [144].

Solid phase extraction or solid sorption is also becoming more popular since the sorbent materials used are stable in a narrow pH range and are capable of extracting polar and/or nonpolar compounds [145]. The main advantage of this method is the ability to separate the matrix from the target compound, automation ability, and ability to concentrate the final product [144]. Quinones have also been purified successfully by electrophoresis. For instance, the method was used to separate glycosidic quinone compounds from an extract of *R. emodi* [106]. The technique works well for an alkaline phase using a buffer and an ethanol, methanol or acetonitrile mobile phase. Compared with other liquid-phase analytical methods, the electrophoresis method is versatile, efficient and requires low amounts of solvent and reagent.

Quinones are known to have a high protein affinity [146], which means they can be separated by precipitating proteins from extract matrices [147]. The quinones are then recovered or separated from the protein-quinone complex through methods such as fractionation, centrifugal filtration and chromatofocusing [146, 148]. While purifying 1,4-benzoquinone, Brock et al. [149] reported purification of quinones through protein removal using ammonium sulphate fractionation, hydrophobic interaction, ion-exchange and affinity chromatography. Anthraquinones extracted from *Semen cassia* were purified by first precipitating the extracted cassia powder with saturated ammonium sulphate at 4 °C for 10 h, dialysing in deionised water and then recovering the anthraquinone by foam fractionation. A concentration of 94 mg/L was found in the foam, with a total recovery of

more than 48% [146]. A comparison of quinone purification techniques is provided in the Table S1.

From Table S1, suggests that HSCC may be a more appropriate method for quinone purification since the main limiting factor, namely the capacity of the column volume, is independent of the analyte itself and can be scaled up and automated to meet industrial dyeing demands. Its simplicity in terms of less sample preparation requirements, higher purity yield and total sample recovery also makes HSCCC comparably more economical for quinone purification. However, many of these techniques are analytical, rather than large-scale separation techniques. Therefore, further purification to yield a pure component would be a challenge industrially, also especially given the complexity of the quinone group.

Chemical Analysis

This section discusses various methods applied for quinones analysis. These include both qualitative and quantitative methods.

Qualitative Methods

Within this part, we mainly discuss phytochemical screening, which is a qualitative way to determine the presence of a group of compounds of interest. This type of analysis is often done by a colour reaction. For quinones, the success of these tests depends on one main distinctive property that distinguishes the quinone of interest from other typical colored compounds, which is the ability of quinones to undergo reduction and oxidation [20]. This property enables quinone molecules to be identified by reacting them with a range of reagents that generate different colours depending on the class of the quinones and/or position of hydroxyl groups on the benzoid ring. Important colour reaction tests are the Bornträger and alkaline reagent-based tests, which involve reaction of anthraquinones with an alkaline medium that results in production of their corresponding phenolate ion [150]. For example, the hydroxyls on 1,8-dihydroxyanthraquinones react with weak bases like ammonium hydroxide and are transformed into a phenolate ion. Anthraquinones having hydroxyls at positions 1 and 2 acquire a blue violet colour, whereas 1,8-disubstituted anthraquinones display a red colour [20]. Anthrones and dianthrones become yellow but rapidly oxidise to their corresponding anthraquinones to acquire red staining. The reaction mechanisms of anthraquinones are shown in Fig. 4a. For naphthoquinones and benzoquinones, an acid oxidation reaction (such as sulphuric or hydrochloric acids) gives a red or red–orange colour and is their preferred screening method (Fig. 4b).

Some quinones, especially those with C-glycosides, do not undergo hydrolysis when heated with dilute alkalis or acids. They are often screened by a modified Bornträger method, which involves heating with ferric chloride in hydrochloric or sulphuric acid medium to decompose them [61, 152]. The glucoside is then extracted in a suitable organic solvent, such as benzene, tetrachloride, dichloromethane or chloroform. Next, the lower layer, in the case of chlorinated solvents, is separated and diluted with ammonia where development of pink or red colour in the ammonia layer confirms the presence of anthraquinones [61].

These screening methods are preliminary tests that should be supplemented by other qualitative analysis, since the colours obtained can be greatly influenced by cross conjugation and other structural features [20]. A summary of screening methods is presented in Table 4, which shows that Bornträger and alkaline based reactions are used to detect anthraquinones while acid-based reactions are used to screen benzoquinones and naphthoquinones.

Quantitative Methods

These methods are used to characterise and/or quantify quinones. They include titrimetric, chromatography, UV–VIS spectroscopy and other related methods.

Titrimetry

This technique is based on the compound's ability to undergo a reduction reaction, which is unusual among other organic compounds. The reduction is achieved by reacting quinones with reducing agents or through catalytic hydrogenation. Different titrimetric methods have been investigated for quinones determinations. These include visual [157, 158], potentiometric [159], voltammetry [160], and differential pulse polarography [161] techniques. Here, a reducing agent in an aqueous acidic medium is used to stoichiometrically titrate quinone. The success of these methods depends on reagents used. Generally, the use of titrimetric methods has drastically declined, perhaps due to the numerous limitations associated with them.

Chromatography

Here, equipment such as HPLC and TLC are normally coupled with various detectors such as ultraviolet visible (UV–Vis) [36, 135], diode array detector (DAD) [128], fluorescence (FL) [154], mass spectrometry (MS) [162], chemiluminescence (CL) [155] and electrochemical detector (ED) [156].

Apart from being a quinone purification tool, TLC alone has also been used to identify quinones [134]. For GC–MS quantification, the volatility and thermal stability

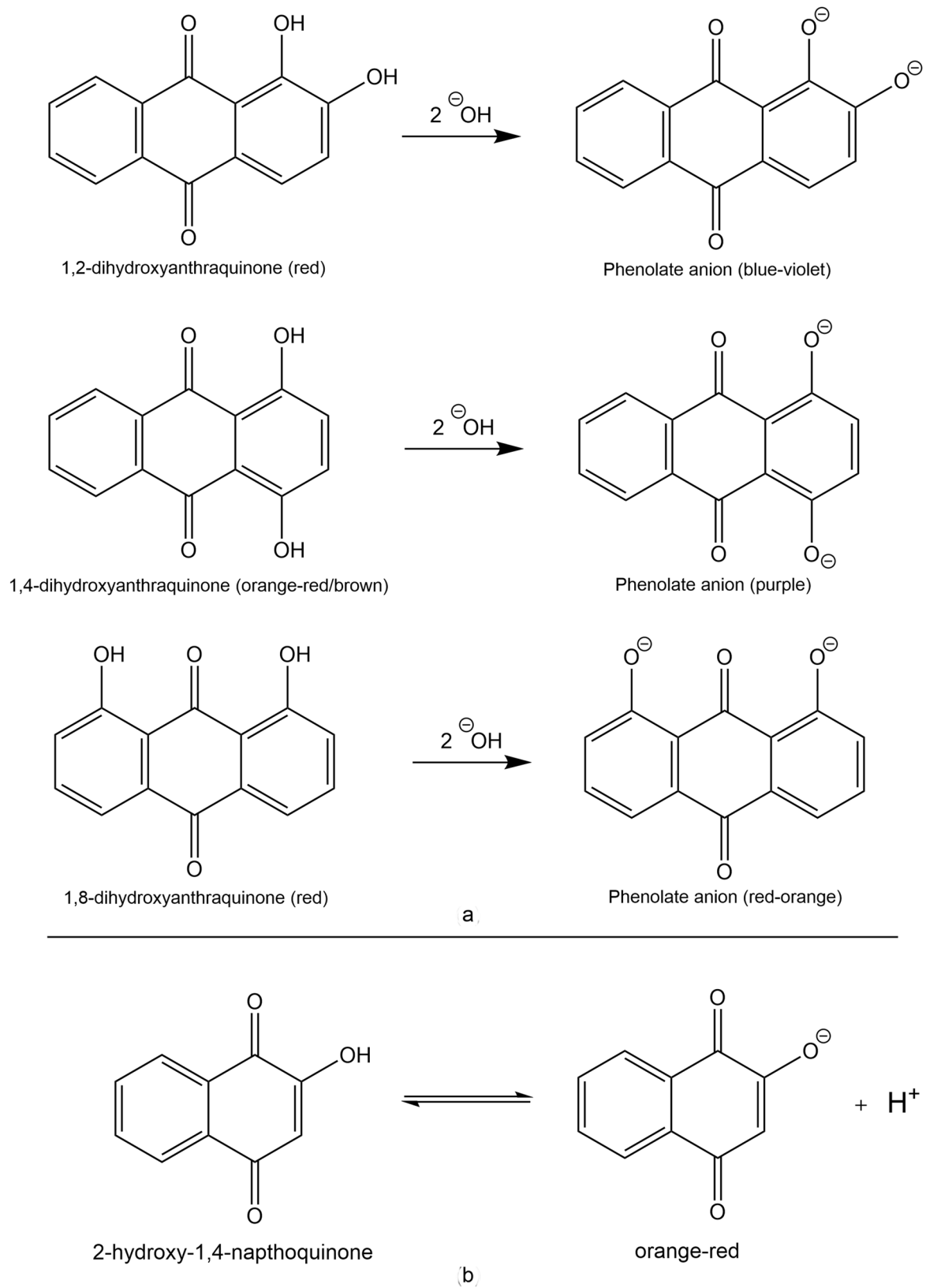


Fig. 4 Quinone colour reaction **a** Borntträger reaction [150], **b** pH-dependency of naphthoquinone compounds [151]

of the quinone is required. The quinone volatility is typically increased by derivatisation through silylation to obtain trimethylsilyl (TMS)-derivatives of the respective quinones [163]. This is a complex procedure and can result in a biased quantification due to the effect of low vapor pressure and ionisation efficiency of the quinone [26, 164]. MS has been used to detect juglone, plumbagin and maritinine from plant extracts after derivatisation [108, 127], as well as munjistin and pseudopurpurin from *R. tinctorum* [128] and anthraquinones from *Fusarium oxysporum* [134].

Quinones also undergo electrochemical reactions, making them suitable for analysis by ED. Electrochemical activity causes quinones to produce electromagnetic radiation when excited, so CL is also applicable. These methods are more

selective, sensitive and rapid compared to MS, but they are limited by a tendency for oxidation of the analyte by the dissolved oxygen from the mobile phase, which is mediated by degassing the instrument [164]. Methods like MS and CE also require that the quinone analyte be ionised, which can complicate the procedure especially when a buffer is required [26].

Important quinone identification methods are shown in Table 4, which demonstrates that each analytical method can be used to characterise any class of quinone. Furthermore, these analytical methods can detect both glycosylated and aglycone quinones. Figure 5 gives an overview of the different methodologies for analysing quinones based on the appearance of the molecule. It shows that photoreaction,

Table 4 Quinone molecule screening and other analytical methods

Quinone compound	Qualitative methods				Quantitative methods				
	Born-träger [150]	Modified Bornträger [61]	Bases (NaOH, NH ₄ sol., KOH, Mg(Ac) ₂) [153]	Acids (H ₂ SO ₄ /HCl) [153]	Chromatography [36]	Fluorescence [154]	Chemiluminescence [155]	Electrochemical [156]	Structural analysis [26, 105]
Anthraquinone	x	x	x	–	x	x	x	x	x
Naphthoquinone	–	–	–	x	x	x	x	x	x
Benzoquinone	–	–	–	x	x	x	x	x	x

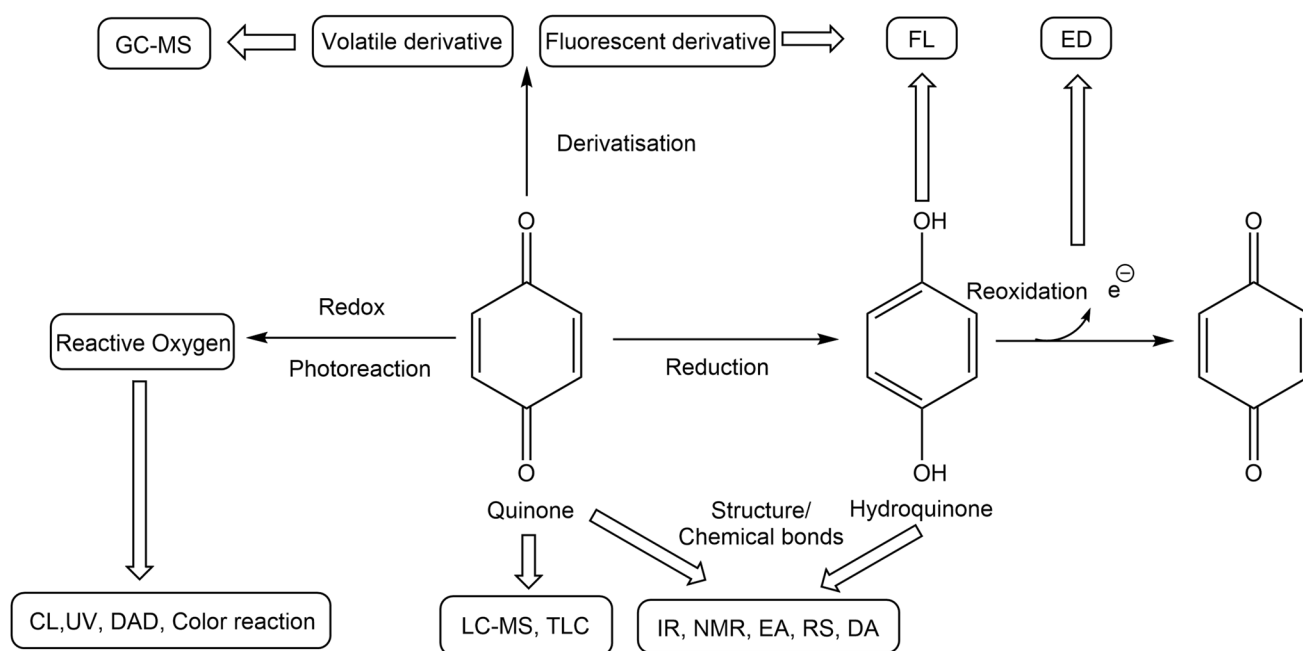


Fig. 5 Analytical methods for quinone compound. Modified from Naoya, Naotaka [164]. Key: GC-MS—gas chromatography coupled mass spectroscopy, FL—fluorescence detection, ED—electrochemical detection, IR—infrared, NMR—nuclear magnetic resonance,

EA—elemental analysis, DA—degradation analysis, CL—chemiluminescence, LC-MS—liquid chromatography mass spectroscopy, TLC—thin layer chromatography, UV—ultraviolet, DAD—diode array detection

electrochemical reaction-oxidation, derivatisation, chemical bond vibration, light absorption in the UV–Vis region, and mobility in the mobile phase are important properties for quinone analyses.

UV–Vis Spectroscopy

This is a method that makes use of the conjugated system in the quinone structure that absorbs specific wavelengths in the UV–Vis region. However, quinone derivatisation is sometimes necessary to enhance the peak absorbance [165]. The peaks formed are compared to those of known quinone standard compounds for identification. According to Harborne [32], all coloured benzoquinone spectra show two peak, one strong peak at 260–290 nm and a weak one at 375–410 nm. The spectra of all coloured naphthoquinones also characteristically display three to four peaks; one or two peaks below 300 nm, one peak at 330–340 nm and one peak above 400 nm, while all coloured anthraquinones typically show four to five peaks within the visible region; one peak above 430 nm and the rest below 300 nm. Note, however, that the peak positions depend on the solvent used.

UV–Vis measurement have also been used for quantification of quinones. Here again, derivatisation might be necessary, and the success of a derivatisation reaction depends on the reagents used. Reagents such as methanol have been investigated as a quinone derivatisation agents to quantify *p*-benzoquinone, methyl-*p*-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone and 1,4-naphthoquinone, but the derivatisation process takes time to complete [162]. Aniline was used as a reagent, but it only derivatised *p*-benzoquinone and chloranil quinone compounds [166]. Phenazine reagent has also been used [165], though, it only shows selectivity for benzoquinones and not to naphthoquinones and anthraquinones. A seemingly better derivatising reagent is piperidine [167]. The derivatization method is simple, sensitive, selective and can give 96% recovery. Another spectrophotometric method for determining quinones (1,4-benzoquinone, 1,4-naphthoquinones and *p*-chloranil) in 50% methyl-alcohol-water mixture solvents is their derivatisation by 1,3-dimethylbarbituric acid [168] and barbituric acid [169]. The advantage of this method is its increased sensitivity and colour stability. Anthraquinones have also been quantified after derivatising with alkaline reagents (Fig. 4a), such as NaOH containing 2% NH₃ [170], 5% magnesium acetate [61, 171], and ferric chloride [129], among others.

Using the UV–Vis method, the quantity of quinone can be determined via external calibration, i.e. a validated linear relationship between absorbance and quinone content, developed with a pure or standard quinone compound [66]. In addition to quinone quantity, the developed calibration curve can be used to determine the linear range, LOD and LOQ of

the quinone extract using methods like the signal-to-noise ratio [109]. The advantage of using quinone standards is the high accuracy and the ability to simultaneously identify and quantify quinone compounds. Many quinone standards are commercially available like alizarine, purpurin, quinizarin, 2-hydromethylantraquinone, 1,8-dihydroxyanthraquinone, 2,6-dihydroxyanthraquinone [128], *p*-benzoquinone, methyl-*p*-benzoquinone [162], aloe-emodin, chrysophanol, physcion, rhein, emodin [38, 172], juglone and lawsone [173], among others. However, the array of different standards required and the high cost involved, limits the use of these standards [106].

Other Analytical Methods

Other methods include IR spectroscopy [105], nuclear magnetic resonance (NMR) [42, 134], elemental analysis (EA) [42, 105], degradation analysis (DA) [105] and Raman spectroscopy (RS) [174]. IR analysis always presents a high and a low intensive bands. For 1,2-benzoquinone and 1,4-benzoquinone, the high intensity bands are shown at ~ 300–1650 cm⁻¹ whereas the low intensity band appears at ~ 3200 cm⁻¹. For 1,4-naphthoquinone, the most intensive peaks lie in the region from ~ 700 to 1800 cm⁻¹ while a low band is found at ~ 3200 cm⁻¹. For 9,10-anthraquinone, the intensive peaks fall in the region from ~ 400 to 1810 cm⁻¹, and a less intense peak appears around 3300 cm⁻¹ [175]. In most cases, only the principal band is being stated.

FT-IR spectroscopy is used to define the presence and absence of functional groups, and NMR spectroscopy can then be used to identify the organic structure of the compounds. Thus, these two methods are complementary and can be used together [105]. Compared to UV–VIS and FTIR, the use of NMR and GC–MS or LC–MS requires far more expensive equipment and the methods are more complex. On the other hand, normal RS and enhanced surface spectroscopy are used more to analyse quinone dyes in artefacts [176, 177]. Other methods, such as EA, DA or colourimetric techniques, and RS have been used but are not common thus are not discussed here.

The qualitative and quantitative methods for analysing natural quinones are summarised in Table 5, while characteristics used for their identification are given in Table 6.

Table 5, indicates that HPLC and UV–VIS are the preferred quinone identification and quantification techniques. A big advantage of HPLC is that it does not require quinone derivatisation. For UV–Vis, the use is justified since the method is simple, fast and sensitive [165]. IR and NMR are also popular especially where structural elucidation is required.

Table 5 Natural quinone analytical methods

Source	Quinone compound	Analytical condition	Analytical technique	Quantification range, LOD and LOQ ($\mu\text{g/mL}$)	Reference
<i>Ficus foveolata</i>	2,6-dimethoxy-1,4-benzoquinone	MeOH-5% acetic acid in H_2O (24:76, v/v)	RP-HPLC-DAD	LOD and LOQ: 0.97 and 3.90,	[109]
Various lignocellulose	1,4-benzoquinone, 2,6-dimethoxybenzoquinone	Eluent A: 0.1% (v/v) FA, Eluent B: Mixture of ACN/2-propanol (75/25% v/v) in 0.1FA, T = 30 °C	RP-UHPLC-ESI-Qq-MS	LOD: 0.0029, LOQ: 9.98	[178]
<i>Rubia tinctorum</i>	Alizarin	Eluent—MeOH-10% aqueous acetic acid (60:40); time: 30 min, followed by pure MeOH for 10 min	RP-HPLC-DAD	LOD: 3.8	[66]
<i>Lawsonia inermis</i> , <i>Juglans regia</i>	Lawson, Juglone	Lawson eluent, A: ACN, B: MeOH, C: 20 mM KH_2PO_4 buffer at pH 3.2 with H_3PO_4 flow rate 1 mL^{-1} . Elution starts at 15% A, 5% B and 80% C; Juglone eluent, A: 3% MeOH in 20 mM KDP at pH 3.2 with H_3PO_4 elution starts at 100% A and 100% B in 55 min, flow rate 1.3 mL^{-1}	RP-HPLC/UV-Vis	Lawson: LOD – 0.11, LOQ-0.36, Juglone: LOD – 0.6, LOQ: 1.8	[173]
<i>Rubia tinctorum</i>	Alizarin, pupurin, and lucidin	HPLC Pure MeOH (A) and 10% (v/v) aqueous acetic acid (B). Initial mobile phase 60% A, 40% B for 30 min then 100% A for 10 min, flow rate 0.6 $\text{cm}^{-3}/\text{min}$	RP-HPLC/UV-Vis	n.a	[36]
<i>Impatiens glandulifera</i>	a. 2-hydroxy-1,4-naphthoquinone, b. 2-methoxy-1,4-naphthoquinone	A: 0.05% TFA in H_2O , B: MeOH. Linear gradient A:B 70:30 to 35:65 in 40 min	TLC, RP-HPLC-DAD	a. -R _f : 33 min, b. -R _f : 35 min a. LOD (S/N) 0.00002 LOQ: 0.0001	[71]
Quinone compound in water	a. Benzoquinone, b. Hydroquinone	GC Eluent-Helium gas; HPLC eluent-acetonitrile	RP-HPLC-UV-DAD and GC-FID	a. LOD; GC: 50, HPLC: 2, b. LOD: GC: none, HPLC 32., a. LOQ 0.138	[145]
<i>Carthamus tinctorius</i>	Carthamin yellow, Carthamin Red	H_2O : i-BuOH:EtOH: FA (4:7:4:4)	TLC, UV-Vis	n.a	[50]
<i>Cassia fistula</i>	Rhein	Eluent: EtOAc:MeOH: H_2O (100:17:13)	TLC, UV-Vis	n.a	[61]
<i>Rubia tinctorum</i>	Lucidin, primeveroside, ruberythric acid, lucidin glucoside, alizarin glucoside, munjistin, alizarin, and purpurin	Eluent: (A) ammonium formate—FA buffer (0.2 M, pH 3 + EDTA, (B) acetonitrile (73% A, 27% B)	LC-DAD, HPLC-MS(MS) with ESI or APCI	n.a	[128]
<i>Diospyros anisandra</i>	Plumbagin, maritimon, 3,3'-biplumbagin, and droserone	Eluent: nitrogen gas, pressure 1.5 mL/min, at 180 °C for 5 min then 300 °C at 10 °C/min in 20 min	TLC-UV-Vis, GC-MS	n.a	[127]

Table 5 (continued)

Source	Quinone compound	Analytical condition	Analytical technique	Quantification range, LOD and LOQ ($\mu\text{g/mL}$)	Reference
<i>Rheum emodi</i>	Aloe-emodin Rhein Emodin, Chrysophanol, Physcion	Eluent-MeOH:H ₂ O containing 0.1% v/v of o-phosphoric acid (85:15) at 254 for UV detection and excitation and emission wavelength of 440 and 540 nm for FLD	RP-HPLC-UV and RP-HPLC-FLD	FLD—LOD: Emodin – 0.01087, rhein – 0.00385, chrysophanol 0.00421, physcion- 0.00198, UV: Rhein – 0.375, Aloe-emodin – 0.35	[38]
Quinone compounds	1,4-naphthoquinone,menadione, Chloranil and 1,4-benzoquinone	Derivatisation with 0.6 M piperidine, T = 30 °C for 10 min	FT-IR, UV-Vis	n.a	[167]
Quinone compounds	p-benzoquinone, p-naphthoquinone 025	Derivatisation with 0.05 M barbituric acid, at 30 °C for 15 min	UV-Vis	n.a	[169]
Quinone compounds	p-benzoquinone, p-naphthoquinones and p-chloranil	Derivatisation with 0.05 M 1,3-dimethylbarbituric acid, T = 30 °C for 10 min	M.P, elemental analysis, FT-IR, ¹ H NMR, Vis	Range—Benzo: (2.7–61.5), Naphtho: 3.7–37	[168]
Airborne quinone	a. p-benzoquinone, b. methyl-p-benzoquinone, c 1,4-naphthoquinone, d. 1,2-naphthoquinone, e 1,4-antraquinones,	Eluent: A. 30% MeOH, B 70% (H ₂ O containing 5 mmol/L Ammonia acetone and 0.1% FA) 1:1 v/v, MeOH derivatisation	RP-HPLC-ESI-MS/MS,	LOD $\times 10^{-2}$: a. 0.76, b. 6.32, c. 0.86, d. 0.06, and e. 0.34,	[162]
Kraft pulps	Quinones (o- and p-)	Derivatised by 30 mM Phenazine, at pH 5 for 30 min	UV-Vis	n.a	[165]
<i>Swietenia macrophylla</i>	Anthraquinone and benzoquinone	Eluent- EtOAc: MeOH: H ₂ O (100:17:13), hexane: EtOAc (17:3), and petrol-benzene: EtOAc (7:3), F ₂₅₄ silica plate	TLC-UV	n.a	[179]
<i>Morinda angustifolia</i>	Emodin, Marindon, Rhein	TLC Eluent: n-hexane: EtOAc (30:1, 20:1 or MeOH	TLC, FT-IR, UV-Vis, NMR, M.P., Elemental analyses	n.a	[105]
<i>Rheum officinale</i> , <i>Polygonum multiflorum</i> and <i>Cassia tora</i>	Physcion, chrysophanol, aloe-emodin, emodin, and rhein	ACN (conc. 10–35 v/v, pH 6–9) 24 mmol/L NaH ₂ PO ₄ buffer (pH 8.0)	CE-UV	n.a	[172]
<i>Nigella sativa</i>	Thymoquinone	Britton-Robinson buffer/methanol solution (3:7 v/v, pH 5.5)	DPP	LOD: 0.054	[161]
<i>Rhamnus frangula</i>	Alizarin, purpurin, physcion	Derivatisation using BSTFA + 1% TMCS at 70 °C, for 75 min	GC-MS	n.a	[180]

LOD level of detection, LOQ level of quantification, RP-UHPLC-ESI-Qq-MS reversed-phase ultra-high performance liquid chromatography-electrospray ionisation-triple quadrupole-mass spectrometry analysis, ACN acetonitrile, R_f retention factor, KH₂PO₄ potassium dihydrogen phosphate, DH₂PO₄ orthophosphoric acid, ESP electrospray ionisation, APCI Atmospheric pressure chemical ionisation, EDTA ethylenediaminetetraacetic acid, FA formic acid, MeOH methanol, H₂O water, i-BuOH isobutanol, EtOAc ethyl acetate, CE capillary electrophoresis, BSTFA bis-trimethylsilyltrifluoroacetamide, TMCS trimethylchlorosilane, S/N signal to noise, DAD diode array detector, M.P melting point, DPP differential pulse polarography, T temperature, n.a not applicable.

Table 6 Characteristics of quinones used for their identification

Compound	Colour	UV Vis λ_{max} (nm)	IR ν_{max} (cm^{-1})	MS (m/z)	1H -NMR δ	Reference
Emodin	Pinkish powder		(MeOH): 3390, 1675, 1631, 2950	[M] ⁺ : 269.2 [M-H] ⁻ , 241.3 [M-28] ⁻ and 225.2 [M-28-17]	(CDCl ₃): 12.30 (1H, s, OH-1), 12.80 (1H, s, OH-8), 6.69 (1H, d, H-2), 7.09 (1H, d, H-7), 7.37 (1H, s, H-4), 7.63 (1H, d, H-5), 2.46 (3H, H-3), 5.65 (1H, H-6)	[181]
Chrysophanol	Yellow powder	(MeOH): 228, 256, 279, 287, 429	(MeOH): 3470, 3080, 2940, 1680, 1630, 1590, 1460, 1470, 1260, 1210	284 [M] ⁺ : 253.3 [M-H] ⁻ , 225.3 [M-28] ⁻ , 209.1 [M-28-15] ⁻	(CDCl ₃): 2.45 (3-H, s, H-3), 7.15 (1H, d, H-2), 7.59 (1H, d, H-4), 7.30 (1H, dd, H-7), 7.86 (1H, dd, H-5), 7.69 (1H, d, H-6), 12.03 (1H, s, OH-1), 12.14 (1H, s, OH-8)	[181]
Physcion	Yellow needles		(MeOH): 1675, 1630, 1612, 1570, 1380	283.3 [M-H] ⁻ , 269.3 [M-15] ⁻ , 253.3 [M-31] ⁻ and 235.2 [M-31-18] ⁻	(CDCl ₃): 12.13 (1H, s, OH-1), 12.33 (1H, s, OH-8), 6.69 (1H, d, H-2), 7.09 (1H, d, H-7), 7.37 (1H, s, H-4), 7.63 (1H, d, H-5), 2.46 (3H, H-3), 3.94 (3-H, H-6)	[181]
Alizarin	Red-purple crystals	(MeOH) 245, 260, 271, 331, 431	(KBr) 3338 (-OH), 1662, 1628 (-C=O), 1580 (C=C-)	240 (M ⁺)	(DMSO- <i>d</i> ₆): 7.12 (1H, d, <i>J</i> =8 Hz, H-3), 7.72 (1H, d, <i>J</i> =8.5 Hz, H-4), 7.75–7.86 (2H, m, H-6 and H-7), 8.25–8.31 (2H, m, H-5 and H-8)	[182, 183]
Rubiadin	Yellow needles	(MeOH) 245, 275, 407	(KBr): 3400 (-OH), 1660, 1620 (-C=O), 1585, 1555 (C=C-)	254 (M ⁺)	(CDCl ₃): 2.21 (3H, s, -CH ₃) 7.20 (1H, s, H-4), 7.72–7.81 (2H, m, H-6 and H-7), 8.20–8.31 (2H, m, H-5 and H-8)	[182, 183]
Munjustin	Yellow needles	(MeOH): 245, 285, 415	(KBr): 3400 (-OH), 1675, 1650, 1630 (-C=O), 1594, 1585 (C=C)	284 (M ⁺)	(DMSO- <i>d</i> ₆): 6.90 (1H, s, H-4), 7.80–7.90 (2H, m, H-6 and H-7), 8.09–8.12 (2H, m, H-5 and H-8)	[182, 183]
Lapachol	Yellow needles	(EtOH): 246, 252, 270, 335	(KBr): 1660, 1620, 1595, 1330, 1300, 1265	243 [M+H]	(DMSO- <i>d</i> ₆): 1.71, 1.81 (2 s, 3H, (CH ₃) ₂ C=CH-), 3.38 (d, 2H, <i>J</i> =7 Hz, -CH ₂ -C=C-), 5.2–5.3 (m, 1H, -CH ₂ -C=C-), 6.8 (s, 1H, C ₃ -H) 7.7–8.15 (m, 4H, Ar H)	[182]

Table 6 (continued)

Compound	Colour	UV Vis λ_{max} (nm)	IR ν_{max} (cm^{-1})	MS (m/z)	1H -NMR δ	Reference
Tectoquinone	Pale yellow crystals	(EtOH): 255, 265, 274, 324	(KBr): 1700, 1665, 1580, 1320, 1290, 1050, 920, 700	222 [M ⁺]	(DMSO- <i>d</i> ₆): 2.5 (s, 2-CH ₃), 7.58 (br, <i>d</i> , <i>J</i> = 8 Hz, H-3) 8.08 (br, <i>s</i> , H-1)	[182]
Purpurin	Yellow needles	(MeOH): 215, 255, 280, 515	(KBr): 3350 (–OH), 1660, 1620 (–C=O), 1575, 1565 (C=C–)	256 (M ⁺)	(DMSO- <i>d</i> ₆): 6.57 (1H, <i>d</i> , <i>J</i> = 8 Hz, H-2), 7.75–7.80 (2H, m, H-6 and H-7), 8.20–8.32 (2H, m, H-5 and H-7)	[182]
3-ethyl-2,5-dihydroxy-1,4-benzoxinone	Light-yellow powder	228	(CDCl ₃): 3366, 2976, 2935, 2878, 1731, 1641	167 [M–H] [–]	(700 MHz, CDCl ₃) , (<i>d</i> , Hz): 1.21 (3H, t, <i>J</i> = 7.5, CH ₃), 2.49 (2H, <i>q</i> , <i>J</i> = 7.5, CH ₂), 6.01 (1H, <i>s</i> , H), 7.54 (2H, <i>s</i> , OH); 1H-	[184]
Juglone	Orange needles	(EtOH): 249, 345, 422	(KBr): 3660 ~ 3150 (O–H), 3066 (C–H), 1642 (C=O), 1452 (1226 (C–O), 750 and 697 (C–H)	174 [M ⁺]	(300 MHz, CDCl ₃): 7.02 s (2H, H-2 and H-3), 7.35 <i>dd</i> (1H, <i>J</i> = 7.8, 2.7 Hz, H-6), 12.1 s (1H, H-bonded OH)	[20] [185, 186]
Plumbagin	Yellow needles		(KBr): 3468 (O–H), 1654 (C=O), 1640 (H-band C=O)	188 [M ⁺]	(CDCl ₃): 6.99 s (1H, H-3), 7.36 <i>dd</i> (1H, <i>J</i> = 7.9, 2.6 Hz, H-6), 7.54 m (2H, H-7 and H-8), 11.98 s (1H, H-bonded OH), 1.8 s (3H, CH ₃)	[185]
Lawsonone	Yellow needles	(EtOH): 243, 249, 274, 332	(KBr): 3150, 1674, 1640	172 [M ⁺]	(DMSO): 6.14 (<i>s</i> ; H3), 7.75 (m; H6,7), 7.90 (<i>dt</i> ; H5), 7.96 (<i>dt</i> ; H8) 11.64 (<i>b</i> ; O H)	[20]
Shikonin	Red-violet needles	(MeOH): 552, 515, 486, 277, 216	(KBr): 3440, 1603	[M–H] [–] = 271.1	(CDCl ₃): 1.60 (3H, <i>s</i> , H-16), 1.70 (3H, <i>s</i> , H-15), 2.28 (2H, m, H-11), 2.60 (2H, m, H-12a, H-12b), 5.13 (1H, <i>t</i> , <i>J</i> = 7.1 Hz, H-13), 6.84 (1H, <i>s</i> , H-3), 7.21 (2H, <i>s</i> , H-6 and H-7), 12.48 (1H, <i>s</i> , OH-5) and 12.64 (1H, <i>s</i> , OH-8)	[20, 187]

Table 6 (continued)

Compound	Colour	UV Vis λ_{max} (nm)	IR ν_{max} (cm^{-1})	MS (m/z)	1H -NMR δ	Reference
Carthamin	Red amorphous powder	(EtOH) 515, 377, 244	(KBr): 3370, 1740, 1675, 1622, 1600, 1584, 1512	957.3 ([M + H] ⁺)	(DMSO, 1H , 800 Hz): 8.21 (d, 15.8), 8.03 (d, 15.6), 7.50 (d, 7.6), 6.87 (d, 7.6), 9.31 (s), 4.90 (d, 9.4), 4.45 (t, 9.4), 4.05 (t, 9.3), 4.11 (t, 9.3), 4.74 (br d, 10.8), 4.39 (br d, 10.8), 13C: 188.4, 113.1, 192.5	[188, 189]

$CDCl_3$, deuterated chloroform, *DMSO* dimethyl sulphoxide, *KBr*: potassium bromide, *EtOH* ethanol, *MeOH* methanol

Applications of Natural Quinone Dye

Quinone dyes have been used for various applications, such as histological staining, rust prevention on metal surfaces, and increasing the conversion efficiency of solar cells, and they have found use as sensors, pH indicators, pigments, inks and dyes for leather, wood, medicine, food and textiles [5, 64, 65, 190, 191]. Of these uses, the most popular one is colouration of textiles, whereas their application in bio-inspired systems for energy harvesting and storage is a more recent development. Natural quinones are used at the industrial scale to colour both natural (vegetable/cellulosic, animal/protein and mineral) and synthetic (regenerated and fully man-made) textile fibers. In energy harvesting and storage, they are applied in areas such as artificial photosynthetic platforms and dye-sensitised solar cell etc. [192]. The areas of applications of natural quinones are summarized in Table 7. Dyeing methods, substrates, mechanisms, conditions and results (such as colour fastness, colour strength, dye uptake and dyeing kinematics) are given.

Table 7 confirms that all common and important natural fibres, such as cotton, wool and silk, can be dyed with quinones. For synthetic fibres, polyester and nylon have been successfully dyed using quinone dyes. Other items of interest that can be dyed with quinone dyes are hair, leather and wood, among others. These substrates can successfully be dyed through the conventional exhaustion dyeing method, without the need of a mordant. The substrates are normally dyed at pH 3–8. For most substrates, the best dyeing temperature ranges between 90 and 100 °C. However, polyester dyes best at a higher temperature (130 °C). Most dyeing procedures give optimal fastness after one to 2 h of dyeing. Generally, dyeing results show high dye absorption and colour strength with or without mordants or substrate surface treatment, for all the substrates, although normally, lower substantivity is experienced when natural quinones dyes are used to colour cellulose based substrates as compared to non-cellulose substrates. Besides, good fastness to, wash, perspiration and rubbing (3–5) and light (7–8) are achievable as well. Additionally, just like using synthetic dyes, similar dyeing methods can be adopted, with similar dyeing parameters and similar dyeing substrates giving acceptable results.

Typically, many colour shades can be obtained when natural quinone dye is used to colour textiles. The shades obtained can be further modified by use of mordants to obtain an even wider colour spectrum. Colour modifications occur as a result of the coordinate covalent bonds formed between the dye molecule, mordant, and fibre (Figs. 6 and 7). In fact, it has been reported that when using natural alizarin dyes and different mordants, all colours are achievable except dark blue [196]. When wool fibre was dyed with Rheum dye, the final colour was yellow. However, orange

Table 7 Application of natural quinone dyes

Dye	Substrate/dyeing technique	Dye-substrate mechanism/binder/auxiliaries	Dyeing variables (temperature, time, pH dye concentration)	K/S, dye absorption and fastness properties	Remarks	Reference
Alizarin	Wool/exhaustion	Hydrogen bonding, no mordant	pH: 3, dye conc: 12 mg/L, T: 40 °C, t: 120 min, M:L: 1:100	K/S: 3.21–9.13, dyeing affinity: ($\Delta\mu^0$) -3.11 kJ/mol	Increasing pH, T, and dye conc increases K/S	[135]
Juglone	Cotton and wool/exhaustion	Chelation/mordant: $KAl(SO_4)_2$, $FeSO_4$	pH: 5.7, dye conc: 100 g/L, mordant conc: 10%, T: staggered, t: 120 min, M:L: 1:30	K/S: cotton 2–4.1, wool 0.6–3.5 w/f: 5, r/f: 3–5	Quinone gives good fastness even without mordant	[48]
Alkamin	Cotton/Padding	Chelation/mordants: $KAl(SO_4)_2$, $12H_2O$, $FeCl_3$, $Al_2(SO_4)_3$, $CuSO_4$, K_2CrO_7 , cross linkers, UV absorbers, cationising and finishing agents	3-dip-3-nip treatment with pick up of 80%, then drying for 3 min, at 120 °C then steaming at 100 °C for 10 min	K/S: 1.28–7.94 w/f: 4, Dry r/f: (4–5), I/f: 5	Cationisation improves K/S. Post treatment improved fastness, K/S and tensile strength	[193]
Juglone	Wool/Exhaustion	Chelation, mordant- $SnSO_4$, $FeSO_4 \cdot H_2O$, $Al_2(SO_4)_3$, no mordant	pH: 7, dye conc: (1–20) %, mordant conc: (1–10) %, T: 91–93 °C, t: 60 min, M:L: 1:40	K/S: $SnSO_4$ (1.38–7.95), $FeSO_4$ (2.17–11.51), $Al_2(SO_4)_3$ (1.13–6.14), unmordant- (1.12–4.27) w/f 3–5, colour change on wool and cotton 5, c/f 3–5,	K/S order: ferrous sulphate > stannous chloride > alum > unmordanted	[44]
Lawson	Polyester/Exhaustion	Hydrogen bonding, no mordant	Dye conc: 20%, T = 130 °C, t: 60 min, M:L: 1:40	K/S: -3.3, w/f, p/f, r/f—Staining (4/5–5)	K/S and depth of shade directly proportional dyeing temperature,	[190]
Marindone	Wool/Exhaustion	Chelation, Mordant: $CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, $SnCl_2 \cdot 2H_2O$, $Al(NH_4)(SO_4)_2 \cdot 12H_2O$, NaCl salt	pH: n.i, dye conc: 3%, T: 97–98 °C, t: 45 min., then salt conc: 2%, t: 15 min, M:L: 1:10	Absorption (12.5–31.58)%, K/S (9.53–14.88) I/f (3–5), c/f (3–6); W/f (4–6) for unmordanted, post- and pre-mordanting samples	Pre-mordant results to higher absorption. K/S increases with increase of dye concentration up to 3% dye	[105]
Aloe-emodin	Hair/exhaustion	Hydrogen bond, No mordant	pH: n.i, T: room temperature, t: 30 min	K/S: n.i w/f: 4/5–5,	No damage to cortex	[194]
Cochineal, Alizarin, Juglans	Wool/exhaustion	Chelation, mordant: $KAl(SO_4)_2 \cdot 12H_2O$, $CuSO_4$, $K_2Cr_2O_7$, $SnCl_2$, $FeSO_4$	pH: 5.5, Dye conc: Cochineal 12%, madder 80%, walnut 10%, mord conc: 4%, $KAl(SO_4)_2$: 25% T: 93 °C, t: 45 min., M:L: 1:40	n.i	Cochineal, Madder, and walnut weight loss due to bacteria: 0.18%, 0.017%, 4.31% respectively	[83]
Alizarin	Wool/exhaustion after vatting	Physical entrapment, Argan's pulp as the reducing agent, salt: Na_2CO_3 , NaCl	pH: 3, T: 60 °C, T = 45 °C, t: 30 min, salt conc: Na_2CO_3 (0.1–0.2) g/L, pH 8, NaCl 5 g/L, M:R: 1:100	Absorbance: (32–61) % Fixation rate: (20–52) % non-fixed dye: (2–14.5)%	Reducer increases, dye fixation, solubility and act as an electrolyte. NaCl salt increase dye substantivity	[37]

Table 7 (continued)

Dye	Substrate/dyeing technique	Dye-substrate mechanism/ binder/auxiliaries	Dyeing variables (tempera- ture, time, pH dye concen- tration)	K/S, dye absorption and fastness properties	Remarks	Reference
2-acetyl -3, 8-dihydroxy- 6-methoxy anthraquinone	Wool/exhaustion	Ionic bonding, salt: NaCl	pH: 3, Dye conc 2%, salt conc: 0 g/L, T: 100 °C, t: 60 min, M:R: 1:40	Dye uptake: 5.2 w/f, r/f, p/f: (4-5), l/f: (7-8)	Dye uptake is proportional to dyeing time	[134]
Anthraquinone	Cotton/exhaustion	Hydrogen bonding, Bio mordant— <i>Eurya acumi- nate DC var euprista</i> (Karh), Alum, CuSO ₄ , FeSO ₄	pH: 7.7, Dye conc: 10%, Mordant conc: 2%, T = 30–40 °C, t: 180 min	K/S: no-mordant 14.8%, bio- mordant 23.5% alum 33.5% w/f: (4-5), p/f: (3(4-4/5), r/f (3/4-4), l/f (4-4/5)	Bio-mordant gives good K/S and fastness due to aluminum content present	[183]
Anthraquinone	Cotton/exhaustion	Ionic bond	pH: 4, dye conc 2%, salt conc 0%, T = 80 °C, t: 60 min, Cationised with sandene 8425, T: 80 °C, t 60 min. M:L: 1:40	K/S: 6, l/f: 7, p/f: (4-5), r/f: 5, w/f: 4	Cationisation of cellulose under alkaline condi- tion enhances dye-fabric substantivity	[183]
Laccatic acid	Leather/exhaustion	Chelation, MgSO ₄ ·H ₂ O FeSO ₄ ·H ₂ O·Al ₂ (SO ₄) ₃	pH 6.5, dye conc: 6%, t: 80 min	No mordant K/S: 1.2, FeSO ₄ , Al ₂ (SO ₄) ₃ : 1.2, MgSO ₄ : 0.9, w/f, r/f, l/f: (4-4/5)	Acidic lac dye is acidic gives acceptable fastness	[195]

w/f wash fastness, r/f rubbing fastness, l/f light fastness, c/f crocking fastness, p/f fastness from perspiration, K/S colour strength, salt conc concentration on weight of fibre, dye conc concentration on weight of fibre, mordant conc concentration on weight of fiber, M:L material to liquor ratio, t time, T temperature, n,i not indicated

was obtained with alum as a mordant, while a chromium mordant retained the yellow colour [73]. Unmordanted alizarin gave a reddish-yellow colour on cotton and wool, while mordanting with alum gave cotton a dominant red colour and wool became pinkish [36]. Alizarin also gave yellow to purple colour on cotton after a vatting procedure, but this depends on the dyeing pH [37]. Juglans dyes gave a pinkish colour on non-mordanted wool but use of iron sulphate and stannous chloride mordant gave red and yellow colours, respectively [197]. Alkanet raw extract gave a greenish colour on cotton but a greyish and brownish colour when the same substrate was post-mordanted with CuSO_4 and alum respectively [193]. Angelini et al. [66] also reported a red colour on cotton, a rose/pink colour with silk and a red/rose colour with wool yarns when *R. tinctorum* anthraquinone dye extract was used with alum mordant. Thus, almost all

colours are attainable when natural quinone dyes are used to colour substrates. The dye-substrate dyeing mechanisms involved are explained below.

Cellulose-Based Fibres

Cellulosic polymer structures Fig. 6a. have hydroxyl groups ($-\text{OH}$) as the bonding sites responsible for attraction of dye molecules into the fibre [97]. However, cellulosic fibres have low substantivity to the natural quinone colorants resulting in poor dye affinity [29]. This limitation occurs due to the polar nature of cellulose and the varied polar quinone dyes inhibiting stronger dye-cellulose bonding, as well as the complexity of their molecules limiting dye diffusion [99]. To improve their substantivity, a number of techniques have been proposed. The use of mordants is the main technique

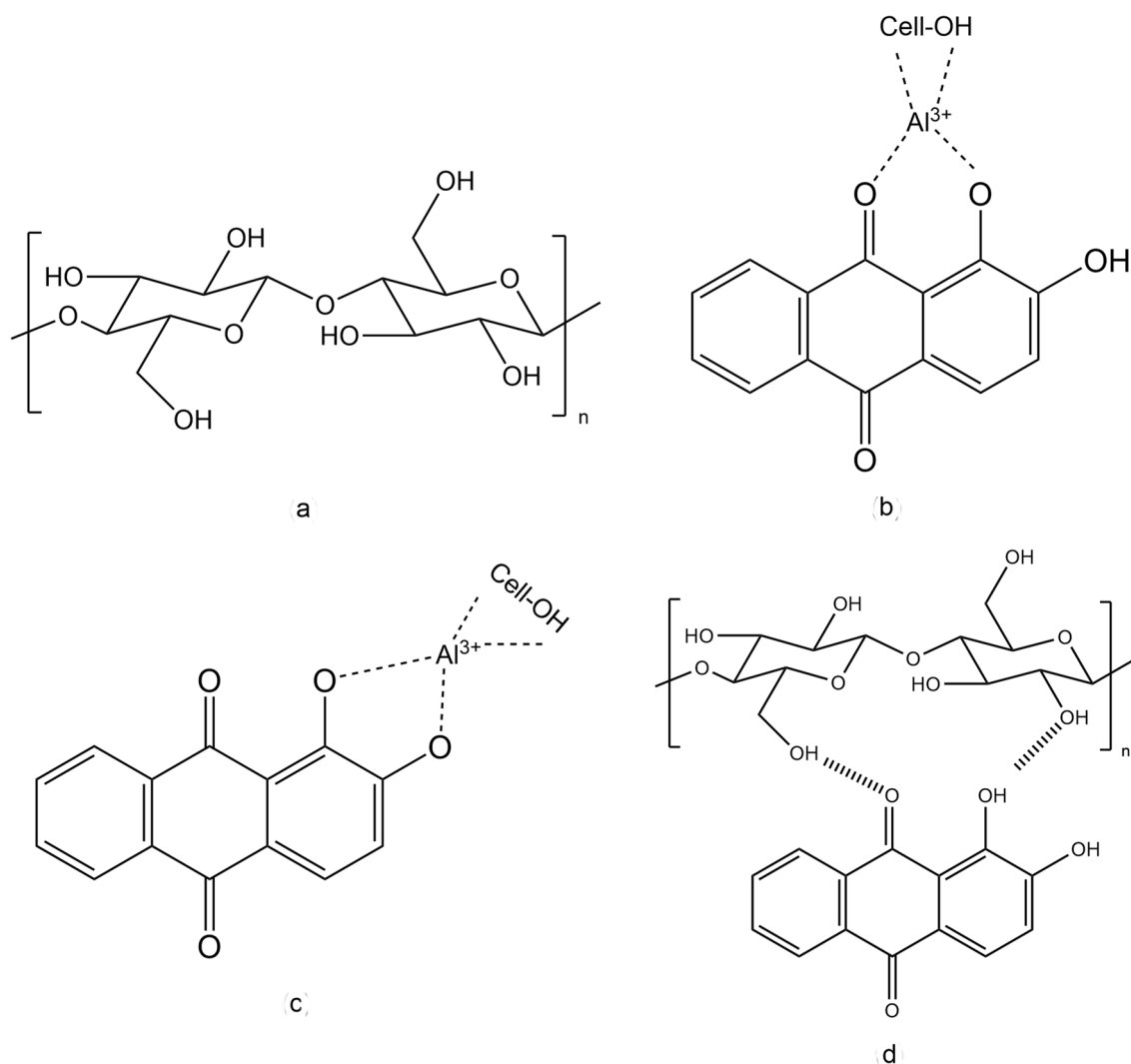


Fig. 6 Cellulose bonding **a** cellulose fibres structure [97], **b** chelation with carboxyl and hydroxyl, **c** chelation with di-hydroxyl moieties [183, 199], **d** hydrogen bonding [200]. Cell-OH represents the cellulose fibres

that has been extensively studied [29] and have included aluminium sulphate, copper sulphate, ferric chloride and potassium salts. Due to environmental and health issues, the use of alum and iron sulphate is encouraged [29, 36, 48] since they are less toxic than other mordants [36]. Vankar et al. [183] investigated the quinone-metallic salt mordant-cellulose bonding mechanism and proposed the formation of an insoluble dye-mordant coordination complex between alizarin and alum that generated a chelate ring with aluminium. The chelation was presumed to occur at two sites, one at the carbonyl and hydroxyl groups (Fig. 6b) and the other with di-hydroxyl moieties (Fig. 6c), and this formed coloured lakes capable of resisting stripping by water or organic solvent from cellulose substrates. The large dye structures also get entrapped within the complex cellulose structure further enhancing the chelation. The use of biomordants, such as tannin [105], karth (*Eurya acuminata* DC var. *euprista*) [183] and *Acacia catechu* [198] has also been studied and the results suggest the same bonding mechanism [183, 199], with improved overall colour fastness and dye uptake [198].

Quinone dyes could also adhere to cellulose fibre structures through hydrogen bonds formed between the hydrogen or oxygen atoms of the dye and the oxygen and hydrogen atoms of the cellulose hydroxyl groups [200], as depicted in Fig. 6. However, since quinone dyes and cellulose fibers bear the same overall negative charge, a repulsion occurs between the anionic dye and the fibres's negative surface potential, thereby reducing bonding efficiency. Different techniques have been suggested to mitigate against this effect. A case in point is the use of salts, such as Na_2SO_4 and NaCl , to overcome the repulsion [190]. Higher dye exhaustions were observed with increasing salt concentrations. Even so, the method is not popular due to the potential negative impact on the environment. Similarly, fibre surface modification by cationisation methods has been studied [183, 201], and cellulose becomes positively charged and forms ionic bonds with the anionic dyes. The mechanism has been explained to involve substitution of several $-\text{OH}$ groups of cellulose through grafting with the cationic agent [202]. The process has challenges, however, such as high cost, inadequate reactivity, fabric yellowing, excessive fabric tendering and toxicity. Nevertheless, this mechanism improves the dyeability of cellulose by quinone dyes. The cationised surface increases the wash fastness when compared to an untreated surface. The simultaneous use of both cationisation and mordanting processes further improves the cellulose fastness properties [203].

Other surface treatment methods, including UV-irradiation [204], oxygen plasma treatment [205], enzyme pretreatment [206] and biomimetic procedures [207] have been used mostly to improve substantivity, dye strength, dye uptake

and colour fastness to washing, rubbing and light. However, the surface modification methods are complex and give inferior results compared to mordanting [193].

Protein-Based Fibres

Silk and wool are the most important protein-based textile fibres. Their properties such as the ionic nature, are influenced by their carboxylic and amino groups (Fig. 7a) and the sequence and bonding of the groups within the protein chain. Generally, protein fibres are resistant to dilute acidic conditions. They react with dilute acids to protonate an amino group ($-\text{NH}_3^+$), which can easily attract anionic quinone dye molecules through an ionic bond (Fig. 7b) [151].

Compared to cellulose, protein fibres have better substantivity for quinone dyes due to the strong dye-fabric ionic bond formed between the cationic fibre and the anionic dye [209]. Further improvement in color fastness and modifications in the color shade can be achieved with metallic mordants, such as potassium aluminium sulphate [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], copper (II) sulphate (CuSO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), tin (II) chloride (SnCl_2), iron (II) sulphate (FeSO_4), copper(II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and tin(II) chloride (II) dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$). Bio-mordants (the bonding mechanism is shown in Fig. 7c), such as gallnut (*Quercus infectoria*), pomegranate peel (*Punica granatum*), babool (*Acacia nilotica*) and chitosan, have also been used with remarkable improvement of colour fastness and shade reproducibility [83, 210]. Moreover, as with cellulosic fibres, attempts have also been made to modify the protein fibres surface to further improve quinone dyeing. The effect of acid pretreatment on dyeing performance of walnut (the naphthoquinone juglone) dye on wool fibres has been studied [211]. The results showed better colour strength and fastness to washing, rubbing, and light when the substrate was pretreated with citric acid. Exhaustion after vatting of quinone dyes has also been used for coloring of textiles [37]. This technique showed a higher degree of dye fixation and wash fastness compared to the conventional exhaustion method, thereby increasing the anthraquinone substantivity for all types of textiles.

Synthetic Fibres

Nylon and polyester are the most important synthetic fibres coloured by quinone dyes [212, 213]. Acrylic and regenerated fibres, such as cellulose acetate, viscose and rayon, have also been dyed using natural quinone dyes [214, 215].

Nylon fibre is made primarily of a polar amide group ($-\text{CO}-\text{NH}-$) and amino groups ($-\text{NH}_2$). Absorption of quinone dyes is enabled by these amino groups, which are

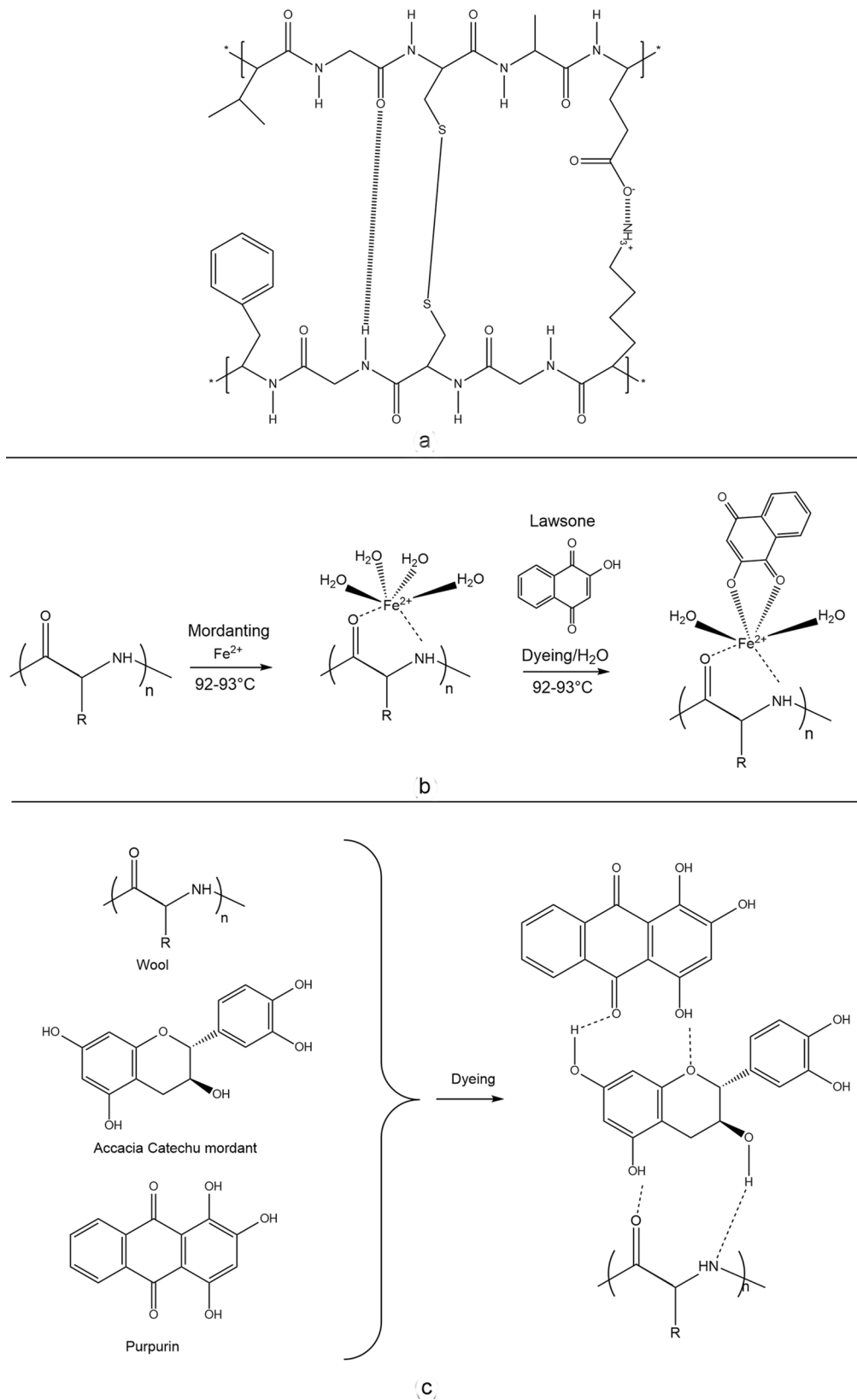


Fig. 7 Protein dyeing: **a** protein based fibres structure [190], **b** protein-metallic mordant-quinone dyeing mechanism [98], **c** wool-biomordant-dye interaction mechanism [208]

protonated in an acidic medium to form a cation that will support ionic dyeing. The presence of a carbonyl oxygen atom and the swelling of fibre due to the polar nature of the amide groups allow hydrogen bonding and dye diffusion into the fibre [208]. These fibres, and especially nylon 66 and nylon 6, are crystalline, cationic in acidic medium and possess hydrophilic properties. Recently, both electrostatic and non-electrostatic reactions have been proposed for the colouration of nylon fibres with quinone dyes [216]. Dyeing was hypothesized to occur due to higher numbers of electrostatic and non-electrostatic interactions between the quinone dye cochineal and polyamide at pH 3, whereas at pH 6, the predominant reactions are the electrostatic hydrophobic interactions between the dye and fiber molecules [216]. Another report showed similar result [217]. Other tests indicate that juglone and lawsone exhibit very high affinities for hydrophobic nylon fibres at high temperatures. Some evidence of dye aggregation was noted in the solution as well as inside the fibre. Purpurin, a non-ionic hydrophobic dye, was found to colour nylon better at 70 °C [217].

Another important synthetic polymer is polyester. Here, the fibre-dye bonding mechanism is influenced by the fibre properties, such as high crystallinity, hydrophobicity, glass transition temperature (T_g) and the ester linkages that makes it slightly polar. Due to its dense structure, the polyester fibre is frequently dyed at high temperatures up to 140 °C, certainly beyond its T_g , (which lies around 80–90 °C). This high temperature, in combination with an elevated pressure, opens up the pores of the polyester polymer and allows dye molecules to diffuse into the fibre [208, 209]. Under these dyeing conditions, natural quinones are still stable, thus making colouration possible.

Cosmetics, Food and Pharmaceutical Quinone Colouration

For centuries, quinones have been used in Arabic countries and India for cosmetic purposes to dye skin, nails and hair. The main colourant for cosmetic application is *L. inermis* (2-hydroxy-1,4-naphthoquinone), which can be found in henna [218]. The henna powder is mixed with water to form a paste and then applied to hair, nails or skin and left to dye at room temperature for about 30–40 min [218]. The dye binds to the keratin protein of the skin and securely stains the skin from pale orange to brown-black, depending on the skin type [80, 219]. Like protein textile dyeing, a mordant such as copper sulphate, is sometimes added to improve colour fastness or modify the final dye colour [219]. Juglone has also been studied as a potential cosmetic dye. Ferrous sulphate, tea, coffee, pomegranate rind, sumac extracts, oxalic acid, lactic acid, ethylenediaminetetraacetic acid (EDTA), alum and copper sulphate have been used as mordants. The dark-brown colour of hair samples obtained with the use of

ferrous sulphate exhibited appropriate colour strength (18), good washing resistance (4.5 after 15 number of washes) and good resistance to sunlight (4.5, after 72 h of sunlight) while maintaining its original morphology [220]. The same application procedure has also been used successfully with quinones to colour hides and skins and in histological staining [8, 220]

In the food and pharmaceuticals industry, quinones are used as food and medicine colourant in either liquid or solid state for various reasons, such as improving the product's natural colour, restoring and standardising the colour and appearance of food and medicine lost during processing or cooking, and to add a novel sensory attraction [25]. In Japan, for example, anthraquinone extracts from madder root are used as colourants for confectionery, boiled fish and soft drinks [73, 221]. These quinones are not allowed as a food additives in either the US or the EU. However, a natural red colourant anthraquinone, cochineal (additive E-120), with approximately 20% carminic acid content, is widely used as colouring agent in food processes in the EU (at dosage levels ≤ 500 mg/kg) and in the US (only up to 5 mg/kg) [73]. The advantage of this quinone food colourant over some synthetic colourants and even natural anthocyanins is its stability to chemical oxidation, light and oxygen. However, it is insoluble in low pH (> 4). Furthermore, as in the case of textile dyeing, for achieving a wide range of colors, carminic acid colourant comes in a metal form which acts like mordant [33]. Carminic acid dye is also used to colour drugs with the same results as in food colouration [221].

Other Functional Features of Natural Quinones

Quinone dyes have found other industrial uses apart from colouration. They are used in solar energy harvesting, as natural alizarin and lawsone quinone dyes can improve the efficiency of dye-sensitized solar cells to increase the photovoltaic properties [222]. When a quinone-dyed cell was exposed to sunlight, it showed a shift in absorbance towards a longer wavelength, resulting in to a significant increase in the short circuit current density and conversion efficiency. When hydroquinone and benzoquinone dye were used as a redox couple in a solar cell, the conversion efficiency of the cell improved from 4.7% using the conventional method to 5.2% [223].

An extract from *Oldenlandia umbellata*, commonly known as Indian madder, has been recommended for use as a pH indicator since it changes colour depending on the pH, i.e. it is yellow at pH 4.8–5.1, red at pH above 10 and green at an acidic pH below 3. The dye can be used to colour paper strips for use as a pH indicator strips or sensorial materials.

Other application areas where natural quinone dyes have been used are corrosion prevention on metal surfaces [84]

and as pigments for ink for felt tip pens, ball pens, stamp pads and jet printing ink [224, 225].

Conclusion

This review has covered natural quinones as a dyeing compound. The main areas considered are quinone structure, occurrence, biogenesis, toxicology, isolation, purification, chemical analysis and applications with respect to textile colouration. Quinones are shown to have varied structures, with many substitution sites, and this structure gives rise to wide range of colours. The review also reveals that, for the three classes of quinones, over 700 sources of anthraquinones, over 120 sources of naphthoquinones and a limited number of benzoquinones are known globally. The quinones are ubiquitous, though at limited concentrations. The main source is flowering plants, which accounts for more than half of the total currently in use, meaning that these sources are fully sustainable.

The paper also reviews the techniques for quinone isolation, identification, and quantification. As predicted by the Hansen solubility theory, solvent extraction using higher polarity solvents, like methanol, methanol–water, ethanol, ethanol–water, or water, is the recommended method for anthraquinones and naphthoquinones isolation and provides shorter extraction time at high temperatures (90–98) °C or at temperatures below the boiling points of solvents. For benzoquinones, lower polarity solvents, such as ethyl acetate and butanol, are recommended. Conventional extraction methods, such as reflux and maceration, are the preferred isolation techniques. Apart from classical methods, other techniques, like sonication, microwave assisted, sublimation, supercritical fluid, enzymatic and pressurised fluid extraction are also frequently used due to their speed, efficiency, selectivity and environmental friendliness. For a quick check of quinone compound occurrence in a plant extract, Borträger's test stands out as the preferred method for anthraquinones, while the acid reaction is useful for testing for the presence of naphthoquinones and benzoquinones. Additionally, HPLC seems to be the dominant method for purification due to its high separation quality, speed and reproducibility. For detailed analytical characterisation of quinones, UV, DAD and MS detectors are the most common, due to their ease of use and relatively low cost. For quantitative analysis of natural quinone extracts, UV–Vis spectrophotometry is a more popular analytical technique due to its simplicity, speed and ability to detect or determine purified or unpurified quinone samples with LOQ in the order of picograms. For accuracy in analysis for in-depth structure elucidation, MS is preferred.

The paper also revealed that natural quinone dyes can be used to dye both natural and synthetic textiles through the simple classical exhaustion method or through padding technique. Also, dyeing can be exhausted into the fiber after vating the dye. These methods yield almost all colour shades. Additionally, satisfactory results have been achieved with or without the use of mordants. Moreover, compared to other colourants, they also impart special finishing properties to textiles, including, antibacterial, anti-fungal, anti-insect and UV protection features. Cosmetics, food and pharmaceuticals are also being coloured by natural quinones. Compared with their synthetic counterparts, natural quinones are potentially more sustainable, comparatively safer and easily biodegradable. These features mean that they can be removed fast and efficiently by a less costly wastewater treatment systems, making them comparatively safer for the environment. Based on all these points, we conclude that the interest in natural quinone dyes will continue to increase, as will their market penetration rate, as such replacing their synthetic equivalents.

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Authors Contributions BD: investigation, writing- original draft preparation; KP: conceptualisation, writing- reviewing and editing. JG: supervision, conceptualisation, writing- reviewing and editing, sourcing for funds, resources: KR: conceptualisation, writing- reviewing and editing. SM: supervision, conceptualisation, writing- reviewing and editing, funding acquisition, resources.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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