Original Article: Chemistry and Applications of Azo Dyes: A Comprehensive Review

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ABSTRACT

Azo dyes have a long history and establish a significant constituent in our daily lives. These compounds and their derivatives have several potential applications in different fields, including industry, environmental and biological researches. Different azo compounds were successfully modified to other derivatives, complexes, and polymers. In this work, we reviewed the chemistry and applications of azo dyes investigating organic chemistry of azo dyes, inorganic chemistry of azo dyes, analytical chemistry of azo dyes, and azo dyes-polymers.

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1. Introduction

Historically, we can divide the dyeing into two great periods; the pre-aniline era starts at the beginning and lasts until 1856. The post-aniline is the second epoch. Some of the colors in the former were based on dye-producing plants and animals which gave it its distinctive look. In Asia and Europe, from madder root were extracted the main vegetable dyes available. In India, indigo plant leaves and vivid red dye are used to produce the blue dye that is still used in jeans today [1-3]. Azo dye has received significant interest due to its environmental stability, ease of manufacturing, and optical and electrical qualities [4-8]. Around the year 1858, when what is regarded as the founding moment of modern organic chemistry began, diazo compounds were discovered [8-10]. Quantitative and qualitative studies on azo dyes as derivatives have garnered increased attention due to their uses in various fields, azo complexes and polymers with specific characteristics [11-13]. In this article, organic, inorganic, analytical, and polymer chemistry of azo dyes have been reviewed.

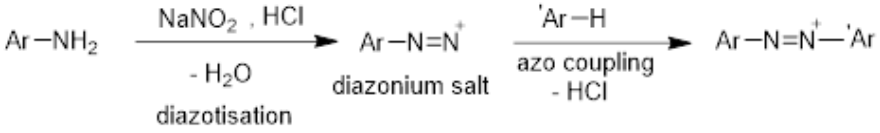
2. Organic chemistry of azo dyes

Azo dyes are substances with one or more azo groups (-N=N-) coupled with two mono- or polycyclic aromatic systems in their structure. Unlike most organic compounds, azo dyes possess color; as a result, azo compounds have various usages. They are important and widely utilized as coloring agents in the leather and textile industries [14]. Theoretically, azo dyes characterized with colors to make a complete rainbow of colors based on the molecule's precise structure. Practically, azo dye compounds are found in yellow, orange, red, brown, and blue. Different substitutions for aromatic rings cause variances in the conjugation degree of the system in the azo dye, resulting in color variations. As known [14, 15], the wavelength of visible light that a molecule will absorb depends on how extensive its conjugated system is; this is demonstrated as follow:

(Shortest π system) → yellow → orange → red → green → blue (longest π system).

2.1. *Synthesis of azo dyes*

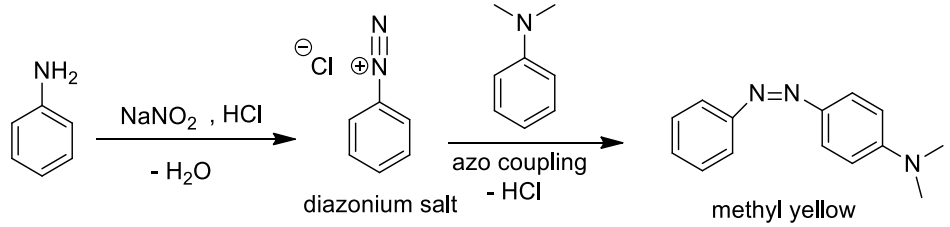
Two-stage reaction sequence as diazotization and azo coupling is illustrated in **Scheme 1**. In the first stage, diazotization involves the treatment of a primary aromatic amine ($ArNH_2$), referred to as the diazo component, with sodium nitrite under conditions of controlled acidity and at relatively low temperatures to form a diazonium salt (ArN^+Cl^-). In the second stage of the sequence, azo coupling, the formed relatively unstable diazonium salt is thus reacted with a coupling component, which may be a phenol, an aromatic amine or a *β*-ketoacid derivative, to form the azo dye or pigment [16].



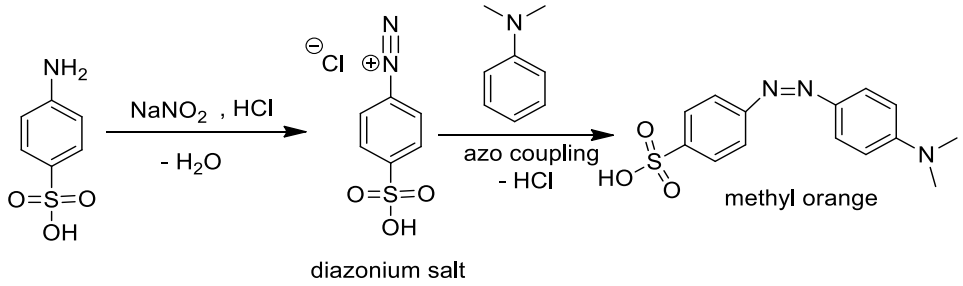
Scheme 1. Diazotization and azo coupling

2.1.1. *Examples of synthesis of some azo dyes*

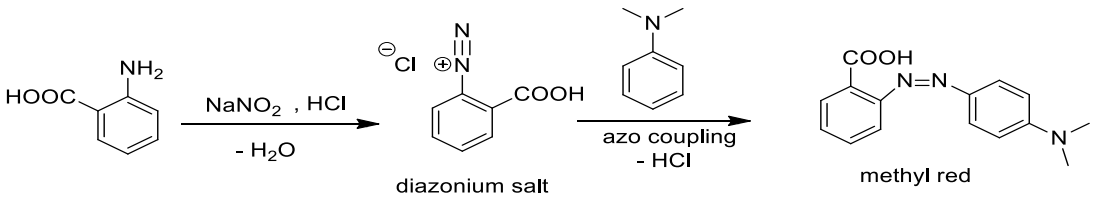
A class of compounds known as azo dyes, which include popular pH indicators like methyl yellow, methyl orange, methyl red, Congo red, and alizarine yellow and include two aromatic fragments connected by an N=N double bond, is the subject of numerous investigations. They are easy to make and have industrial relevance. Azo dyes are produced in a two-step reaction, the first of which entails converting an aniline derivative into an aromatic diazonium ion. Then, an aromatic molecule is added to the diazonium salt. In **Schemes 2, 3,** and **4**, the synthesis of methyl yellow, methyl orange, and methyl red is depicted [3].



Scheme 2. Synthesis of methyl yellow



Scheme 3. Synthesis of methyl orange



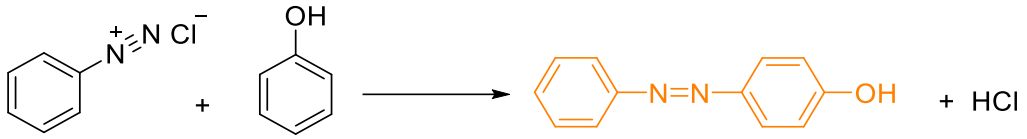
Scheme 4. Synthesis of methyl red

2.1.2. Diazo coupling reactions

The diazonium salt reacts as an electrophile with another arene, such as the benzene ring, in a diazo coupling process [3, 17].

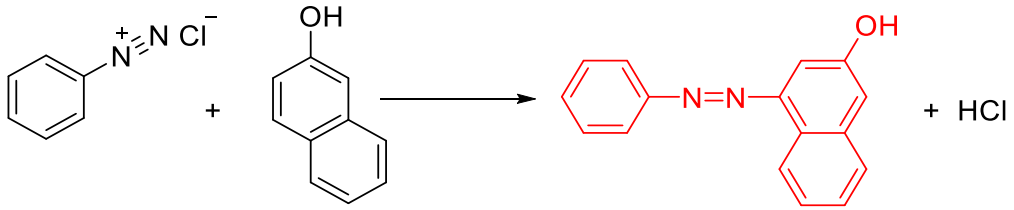
2.1.3. Coupling with phenols [18-20]

When the diazonium salt reacts with a phenol, an azo compound that is yellow or orange is created (**Scheme 5**).



Scheme 5. Synthesis of an azo compound (yellow or orange)

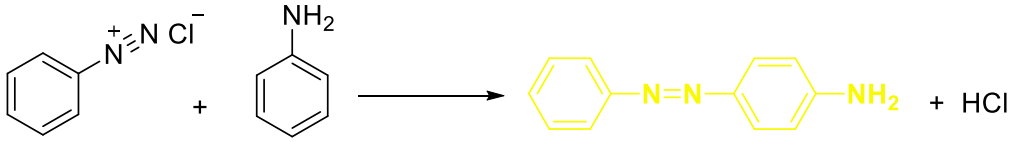
When napthalein-2-ol is dissolved in an alkaline solution, a crimson azo compound is created (**Scheme 6**).



Scheme 6. Synthesis of crimson azo compound

2.1.4. Coupling with amines

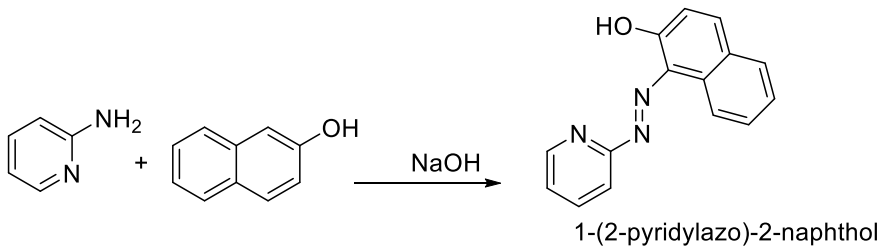
When an aryl amine and a diazonium salt combine, yellow dye is frequently produced (**Scheme 7**) [19, 21]:



Scheme 7. Synthesis of an azo compound (yellow)

2.1.5. Synthesis of 1-(2-pyridyl azo)-2-naphthol (PAN)

PAN synthesis is depicted in **Scheme 8**.



Scheme 8. Synthesis of PAN

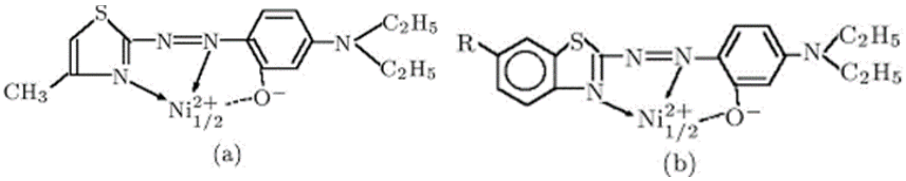
3. Inorganic chemistry of azo dyes

Known for their exceptional chelating abilities with all types of metal ions, azo ligands with O and N donor atoms also demonstrated noteworthy biological activity [22-25]. As an illustration, Cr(III) and Co(III) are frequently used to dye wool and synthetic polyamides[26]. Furthermore, Ni(II) and Cu(II) azo dye complexes are employed in antibacterial, anticancer, and analytical applications [7-30]. In most cases, azo ligands are created by combining

diazonium salts with heterocyclic compounds [31-33]. The current attraction is also focused on the coordination complexes of transition metals with azo ligands because of their intriguing physical, chemical, photophysical, catalytic, and diverse material properties. This section of the review will concentrate on the synthesized, studied, and characterized metal complexes of azo dyes.

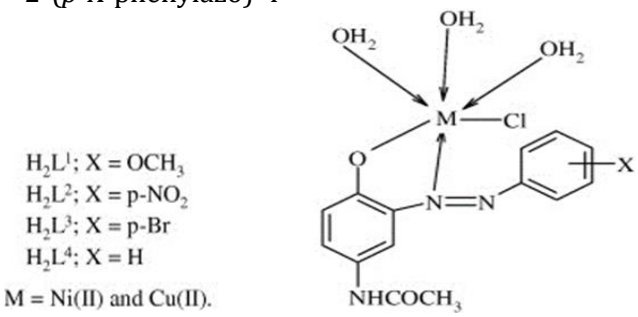
In 2003, Wei Bin *et al.* have reported the synthesis of three novel Nickel-azo dyes; Ni-2(4-methyl2-thiazolylazo)-5 diethyl aminophenol (Ni-MTADP), Ni-2(-benzothiaazolyazo)-5-diethylamino phenol-(Ni-BTADAP) and Ni-2-(6-methyl-2-benzothiaazolyazo)-5-diethylamino-phenol are used for digital versatile disc recordable film [34]. Molecular structures of the nickel-azo dyes are displayed in **Scheme 9**.

3.1. Azo dyes complexes



Scheme 9. Molecular structures of the nickel-azo dyes: (a) Ni- MTADP, (b) R = H for Ni-BTADP and R = CH_3 for Ni- MBADP

The findings suggest that the 4-methylthiazole-based nickel-azo complex is a good option for a digital versatile disc-recordable recording medium. The synthesis of four azo compounds (H_2L^{14}), namely 2-(*p*-X-phenylazo)-4-acetamidophenol (X = OCH_3, NO_2, Br, and H for H_2L^1, H_2L^2, H_2L^3, and H_2L^4, correspondingly) by *Abdallah et al.* [35] the structure of the azo-metal complexes is presented in **Scheme 10**.

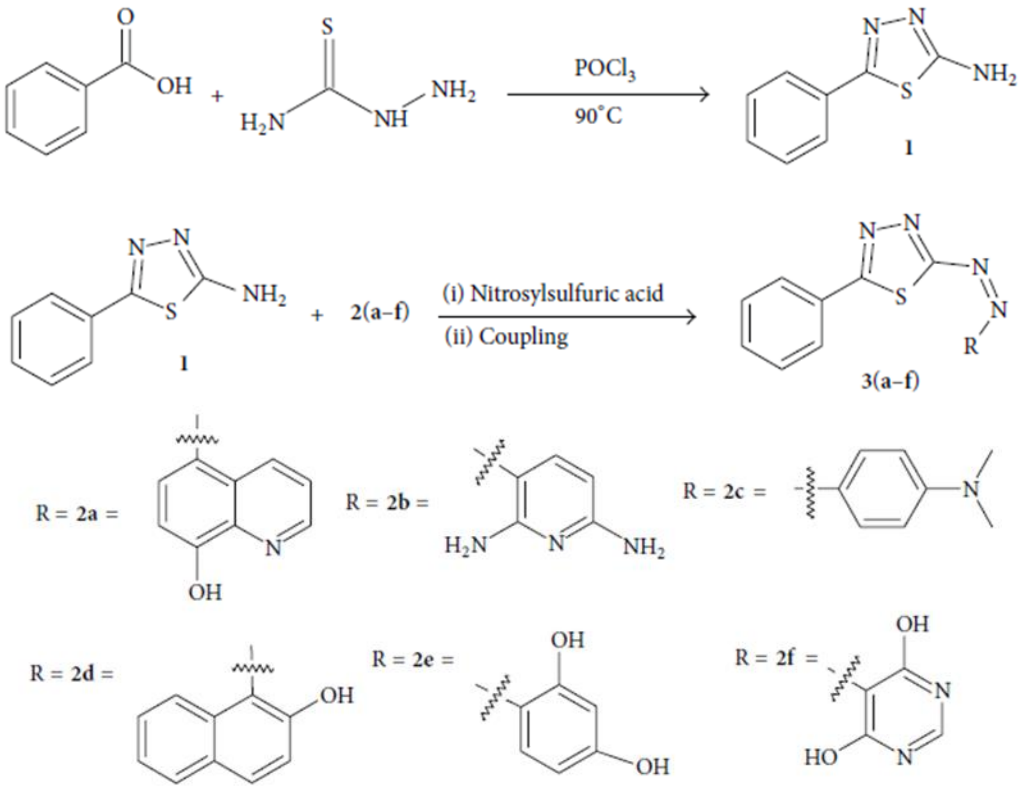


Scheme 10. The proposed structure of the azo-metal complexes

According to the IR spectra, azo ligands are coupled to the metal ions in a uninegative bidentate manner by using the azo N and deprotonated phenolic O as NO donor sites. When tested against adult *Tribolium Confusum* mortality, the synthesized compounds and their metal complexes showed impressive biological action.

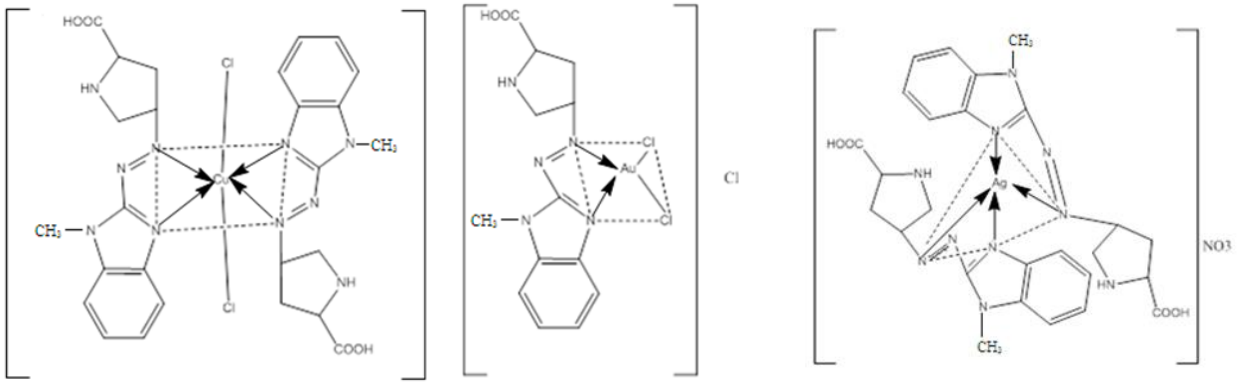
Kumar *et al.* [36] have synthesised and characterised a series of heterocyclic azo dyes, as illustrated in **Scheme 11**. The new heterocycles azo dyes exhibit significant antimicrobial and antioxidant activities specially 1,3,4-thiadiazole which coupled with 8-hydroxyl quinolone demonstrate higher antimicrobial and antioxidant activity.

3.2. Heterocyclic azo dyes



Scheme 11. Series of heterocyclic azo dyes

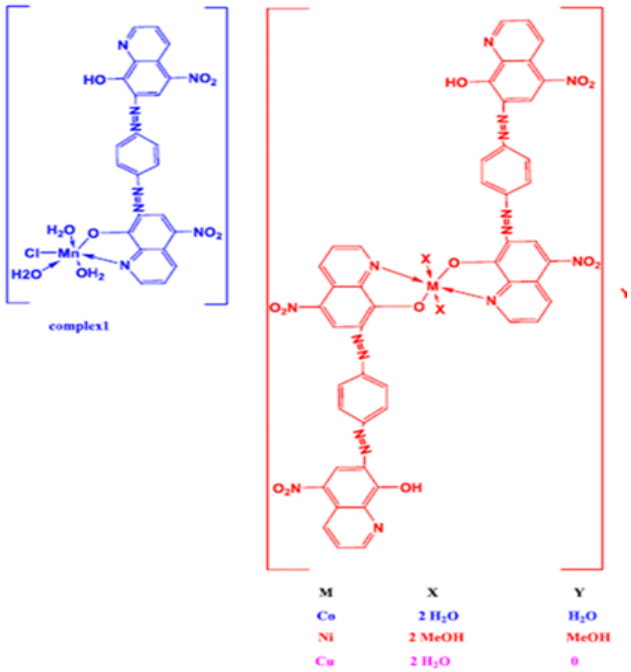
The synthesis of metal complexes of Cu (II), Ag (I), and Au (III) with azo ligands (MBP) produced from proline and 1-methyl -2-aminobenziimidazoe as diazotized components were described by Abbas and Kadhin [37]. The nitrogen and the imidazole moiety of the ligand (MBP) function as a natural bidentate to coordinate with specific metal ions. All substances exhibit potent deactivation capacity against the observant microorganisms. On wool cloth, all compounds were applied. The dyes have produced colors on the fabric that are in the range of orange, brown, red, and purple with a good shine (**Scheme 12)**.



Scheme 12. Complexes of Cu (II), Ag (I), and Au (III) with azo ligands

El-Wakiel *et al.* [38] described the synthesis of new 5-nitro-8-hydroxyquinoline (Mn(II), Ni(II), Cu(II), and Co(II) complexes of an azo dye ligand constructed from *p*-phenylene diamine (see **Scheme 13**). The analytical results reveal that the azo ligand functions as a mono basic bidentate ligand by deprotonating OH and nitrogen atom of the quinoline ring. A 2:1 ligand to metal ratio has been observed for all complexes with the exception of the Mn (II)

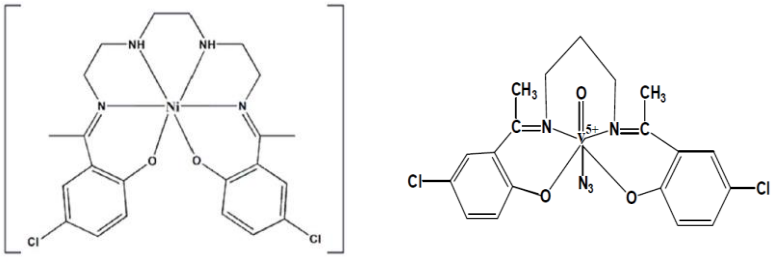
complex. Entire complexes possess an octahedral structure. The produced complexes were tested for color fastness in polyester fabrics and against light washing, perspiration, sublimation, sublimation, and rubbing. The findings show that ligand and the affinity of its complexes for poly ester fibres is good to moderate.



Scheme 13. 5-nitro-8-hydroxyquinoline (Mn(II), Ni(II), Cu(II), and Co(II) complexes of an azo dye ligand constructed from *p*-phenylene diamine

3.3. Azo Schiff base ligands

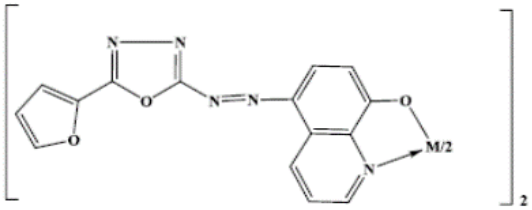
Majumdar [39] has successfully synthesised a new compartment azo linked Schiff base ligands (H_4L& H_2L] derived fom *N-bis*-(2-amino-ethyl)-ethane-1,2diamine and 1-(5-chloro-2-hydroxy-phenyl)-ethaneone (H_4L), propane-1,3-diamine and 1-(5-chloro-2-hydroxy-phenyl)-ethanone (H_2L). The prepared ligands are applied for the synthesis of Ni(H_2L) complex and VO(H_2LN_3) complex, as indicated in **Scheme 14**. The Ni complex exhibits octahedral structure, while VO complex appears square pyramidal structure. The biological activities of synthesised complexes are under study.



Scheme 14. Ni(H_2L) and VO(H_2LN_3) complexes

3.4. New azo ligands

Patel [40] reported the synthesis of new azo ligand of Cu (II), Ni(II), Co(II), Mn(II), and Zn(II) with 8- hydroxyquinoline and 1,3,4-oxidazole. All metal ligand ratios are found in 1:2 M: L. Metal complexes of M(II)$(DAFOHQ)_2$, as depicted in **Scheme 15**. Four strains were used to study the biological activity of azo metal chelates, and the results revealed the benefit of coordination for these kinds of heterocyclic azo ligands.

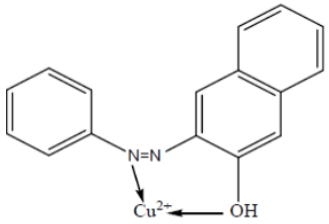


Metal complex of DAFOHQ

M = Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)

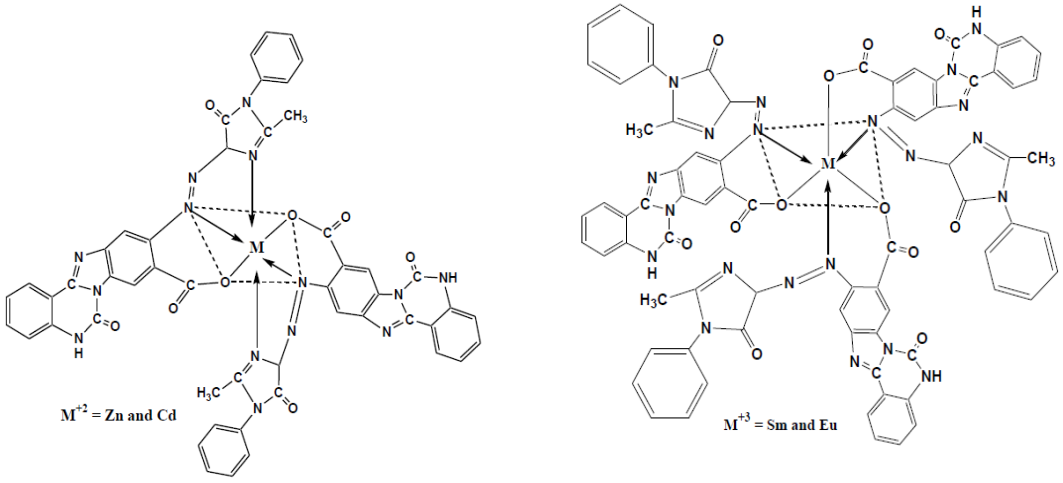
Scheme 15. Metal complexes of M(II)(DAFOHQ)$_2$

The novel azo ligand and their metal chelates were tested against four fungi for their antifungal properties; the results revealed that the compound exhibited good to moderate activity against tested fungus. The Cu(II) indicated the maximum consequence compared with all the experienced fungus. Recently, Rathod *et al.* [41] reported the synthesis of β-naphthol azo dye, which is used to complexation study with Cu^{2+} ions. The result shows that azo dye has good complexing ability to Cu^{2+} metal ions. The stoichiometry was found between M: L 1:1 as well as the pH value effect on the formation of complex. Molecular structure of the complex is represented in **Scheme 16**



Scheme 16. Molecular structure of the azo-Cu (II) complex

Al-Tahan [42**]** reported the synthesis of azo ligand 10-(2-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-imidazole-4-ylazo)-6-oxo-5,6-dihydro-benzo[4,5] imidazole [1,2-*c*] quanozoline-9-carboioxylic acid. The synthesised azo ligands were applied in the preparation of metal complexes of Zn^{2+}, Cd^{2+}, Sm^{3+}, and Eu^{3+}. Flame atomic absorption, elemental analysis, and UV-Vis spectroscopy were used to characterize each compound. The octahedral structures of the complexes resulted in 1:2 and 1:3 metal: ligand ratios, respectively. Molecular structures are depicted **Scheme 17**.



Scheme 17. Octahedral structures of metal complexes

4. Analytical chemistry of azo dyes

In this part of this review, we discuss about analytical chemistry of azo dyes as an analyte and a reagent used for other determinations.

4.1. Analyses of Azo dyes

In the last few decades, concern over the discharge of industrial effluent from the textile industry that contains a significant number of dyes into the environment is developing on a global scale. The colors may enter surface and drinking waterways since industrial water treatment cannot totally eliminate these types of toxins [43]. Some non-ionic azo dyes have mutagenic and carcinogenic activities, according to the International Agency for Research on Cancer (IARC), which acknowledged this in 2010 [44]. The main source of risk connected with the use of azo dyes is the breakdown products formed by reductive cleavage of the azo group into aromatic amines. Due to the toxicity and carcinogenicity of the aromatic amines generated, the use of several azo dyes as textile and leather colorants creates serious health issues. The EU Commission has identified 22 amines as known or perhaps known human carcinogens that can be released by reductive cleavage of one or more azo groups [45, 46].

A diode array UV-Vis detector and spectrophotometry are used in the currently known approaches [47-49]. Recently, many hyphenated systems have been used to simultaneously measure and quantify low concentrations of disperse azo dyes and identify disperse dye residues in environmental samples, such as solid phase extraction and liquid chromatography coupled to electrospray ionization mass spectrometry (LC-ESI-MS/MS) [50]. Because of its great sensitivity and capacity to gather structural data on unidentified chemicals, HPLC directly coupled to mass spectrometry (HPLC-MS) is the preferred method for monitoring dyes [51, 52]. The determination of azo dyes in consumer products is generally based on the analysis of the amines after chemical reduction. LC-MS is a suitable technique to determine these amines [53]. However, routine laboratories often rely on UV based detectors to perform such type of analyses. This is primarily caused by the expensive MS detectors. The lack of selectivity is the fundamental disadvantage of non-MS detectors. As a result, it is crucial to separate all amines [54]. Practically, the diazo group and two aromatic amines are formed when the azo group of the majority of azo dyes is reduced in the presence of sodium dithionite at pH = 6 and 70°C. By using liquid-liquid extraction and t-butyl methyl ether (MTBE), the generated amines can be isolated, and then subjected to GC-MS analysis. Prior to GC-MS analysis, the directly reduced amines can alternatively be separated and pre-concentrated via solid phase extraction [55].

4.2. Analytical application of azo dyes

Azo dyes are of high significance due to their unique complexing properties, sensitivity as chromogenic reagents, and usage in the spectrophotometric and extractive photometric detection of various metal ions. In addition, some of them have been demonstrated to be especially helpful as indicators in complexometric titrations. As a result of their reactivity with metals, particularly with some transition metals to generate stable chelates, azo dyes are used in spectrophotometry to create colors and like many other organic reagents; they can be employed in separation procedures. In general, the solubility of the reagents and their metal complexes in aqueous solutions is quite low, whereas it is much higher in organic systems, where they can be extracted or extracted by using alternative techniques such solid phase extraction, cloud point extract, or co-precipitation [56-59].

Azo dyes, and particularly heterocyclic azo dyes, are a vital kind of the numerous organic chemicals employed in the measurement of metal ions because of their exceptional photometric sensitivity. They belong to aromatic azo compounds, but they make up an individual group of organic reagents, because of their synthesis, their reactivity, and good analytical characteristics [60, 61]. The versatility of aromatic azo dye is coming from various function groups which can be attached to the aromatic rings next to the azo group. Strong

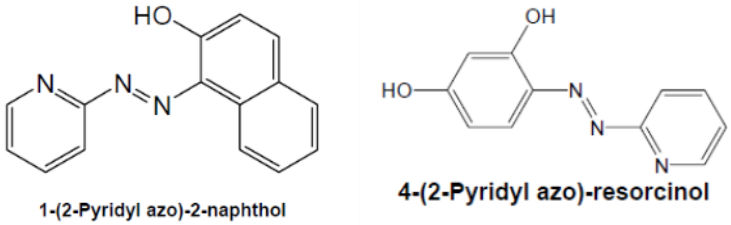
chelating agents, azo dyes with two donor groups (hydroxy, carboxy, or amino) ortho to the azo linkage can be used to determine various metal ions including Al, Fe, Mg, Ga, Ni, U, Zr, Cr, Zn, In, Mn, Mo, Pb, Sb, Co, and Ti [62]. The complex can either be reduced after it has been dissolved in an organic solvent or can be formed as a slightly soluble complex and the A typical use of azo dyes is in the direct titration of metals against EDTA, such as with Eriochrome Black and in acid-base titration, such as with Methyl orange and Methyl red.

4.3. Common azo reagents

In the following, as an example, the most common azo reagents and their applications will be discussed. According to certain studies, the azo-dyes 1-(2-pyridyl azo)-2-naphthol (PAN) and 4-(2-pyridyl azo)-resorcinol (PAR) demonstrate the highest sensitivity and the best precision when utilized in certain techniques [63, 64].

1-(2-Pyridyl azo)-2-naphthol (PAN)

The majority of 1-(2-pyridyl azo)-2-naphthol (PAN) chelates are extracted by using organic solvents since they are insoluble in water. The metal transitions from the an aqueous to the organic layer following chelation by using substances such as chloroform, isopentyl alcohol, benzene, and o-dichlorobenzene, ether and carbon tetrachloride. Structures of PAN and PAR are depicted in **Scheme 18**.



Scheme 18. Structures of PAN and PAR

A well-known spectrophotometric reagent called 1-(2-pyridylazo)-2-naphthol (PAN) is used to identify metals using extraction-spectrophotometric methods or, when non-ionic surfactants are employed through direct spectrophotometric methods. It has also been used for metals determination in highly acidic medium [65, 66]. Complexes with PAN are mostly insoluble in water but can be extracted in CH_3Cl, CCl_4, and benzene. They are soluble in various miscible solvents (acetone, methanol, and dioxane) and mostly are red with the exception of Pd(II) and Co(III) complexes which are green. Almost all the methods of metal determinations by using PAN include extraction procedure. Similar to its chelates, PAN has the drawback of being insoluble in water, which necessitates the heating of numerous solutions during titration. However, when used as an indicator, PAN can be dissolved in acidified deionized water.

4-(2-Pyridyl azo)-resorcinol (PAR)

Unlike PAN, PAR reacts with metal ions to form water-soluble complexes of intense red to red-violet color, with 1:1 and 1:2 metal-ligand ratios. The structure chelate ring is analogous to PAN reagent structure [67]. The PAR sensitivity for metal ions is greater than that of PAN. PAR complexes show a very high molar absorptivity and they are stable for several hours. It can be used for metal speciation analyses [68-71]. In addition, PAR can be employed in the liquid chromatography of metal ions as a complexing agent. The degree of complexation and the oxidation state are the factors that determine the metal ion form because metal ions can exist in many distinct forms. Direct UV absorbance cannot be used to identify the majority of transition metals. To create a light-absorbing complex, the metal complexing agent 4-(2-pyridylazo) resorcinol (PAR) is added in the postcolumn [72].

PAN creates cationic chelates from trivalent ions and neutral chelates from divalent metal ions. The deprotonation of the -OH group at a

position para to the azo group causes the chelates with PAR to have varied charges, ranging from 0 to 2 for divalent metal chelates to 1+ to 1 for trivalent metal chelates. As a result, PAN and PAR chelates can both be separated by using reversed phase HPLC and reversed phase ion-pair HPLC, respectively [73-77]. PAN and PAR can cover a wide spectrum of the analytes, and as a chelating agent they can be used in different techniques in analytical sample preparations like solid phase extraction, liquid-liquid extraction, cloud point extraction, and many others. There are many different structures derived from PAN and PAR with various function groups localized in different positions on the aromatic rings attached to Azo group to enhance the selectivity of the reagent toward the underlying analyte(s).

5. Azo dyes-polymers

5.1. Synthesis and applications of dye-containing polymers

Dyes could be covalently or non-covalently linked to synthetic and natural polymers. The non-covalent bond between the dye and polymer can be ionic, dipole-driven, or produced by inclusion complexes. The adsorption of either cationic or anionic azo dyes in dye waste water extraction, for instance, depends on natural polymers like polysaccharides. Polymer-analogous attachment, polymer condensation, or polymerization of coloured monomers can all be used to create covalent attachment in the main chain or as an end group. According to the number of publications, coloured monomers are generally produced via (meth) acrylation, as are many azo dyes, whereas poly condensation and polymer-analogous reactions demand sufficient functional groups in the monomeric or polymeric building blocks [78].

Incorporation azo dyes to natural and synthetic polymers improves their properties and applications. For instance, methyl orange dye (MO, **Scheme 3**) was successfully employed in controlled synthesis of polypyrrole (PPy) with to enhance its behaviour as a conducting polymer [79]. PPy has recently been applied in electrodes [80-82], sensors [83, 84], biomedicine [85], and antibacterial compositions [86]. In another work, adding MO to chitosan and starch-based biopolymers created a thin film with great selectivity and sensitivity that may be used for low doses of processes including food irradiation, sterilization of medical devices, polymer crosslinking, and degradation [87]. Unfortunately, MO is extremely cancer-causing, mutagenic dye, and excessively employed in dyeing industries [88, 89]. Thus, it was tremendously significant to eliminate this dye from waste watercourse before its discharge to aqueous systems. Thus, starch was introduced as a good candidate for the removal of anionic dye MO from an aqueous medium [90].

Due to the importance of MO dye in both industry and environment in this part of review, we would want to provide a summary of the many synthetic pathways that result in polymer-MO interaction and the various applications of such materials.

5.2. Azo dyes-synthetic polymers preparation

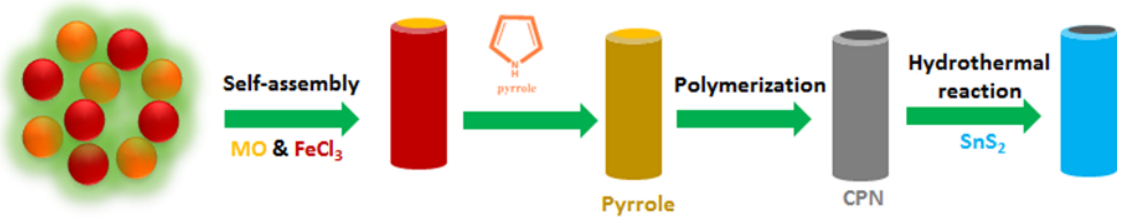
5.2.1. Disperse Red 1 and disperse orange 25-poly (methyl methacrylate)

The penetration of poly (methyl methacrylate) (PMMA) films with the azo dyes Disperse Red 1 and Disperse Orange 25 in supercritical carbon dioxide (**Scheme 19**) was examined in 2003 by using in situ UV/Vis spectroscopy [91]. In addition to serving as a polymer swelling agent, supercritical carbon dioxide works effectively as a substitute for water in the transport of dye molecules. It was found that the dyes adhere to the polymer through hydrogen bonding or dipole-dipole interactions, but that the diffusion process is hampered by relatively potent dye-dye interactions. This issue was resolved by the employment of a color combination. The diffusion rate is larger than it would be with pure dyes in this situation because intramolecular dye-dye interactions prevail over dye polymer interactions.

Scheme 19. Loading of PMMA film with dyes

5.2.2 Methyl orange-polypyrrole

Chen *et al.* used in situ polymerization, carbonization, and a hydrothermal method to create a novel anode material for lithium ion batteries [92]. Tin disulfide (SnS_2) nanosheets were used to adorn the carbonaceous polypyrrole nanotubes to regulate their size. A conductive substrate made of hollow carbonaceous polypyrrole nanotubes could be used to increase conductivity and prevent the agglomeration of active components. The synthetic path of the experimental procedure is schematically indicated in **Scheme 20**, along with self-assembly mechanism of the "reactive self-degradation template method". Methyl orange and ferric chloride spontaneously self-assembled in an aqueous solution at the start of the synthesis stage, resulting in a one-dimensional rod-like structure. As soon as they were added, the pyrrole monomers clung to the surface of the rod-like structure, and under the effect of ferric chloride, polymerization occurred to produce polypyrrole. During the polypyrrole formation process, the obtained one-dimensional rod-like structure self-degraded and gradually fell off leaving the remaining polypyrrole to form a hollow tubular structure. Carbonaceous polypyrrole nanotubes (CPN) were created through high-temperature carbonation. The SnS_2 nanosheets were then grown on the surface by using CPN as a support and template, resulting in CPN-SnS_2 core-shell nanocomposites after a hydrothermal reaction.



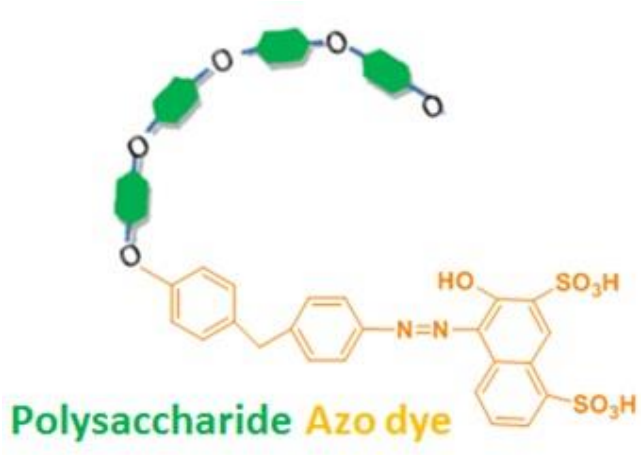
Scheme 20. Polypyrrole nanotubes preparation

5.3. Azo dyes-natural polymers preparation

5.3.1. 4,4'-Diaminodiphenylmethane-maltodextrine

The inclusion of a hydrophilic polysaccharide component in the design of an azo dye may result in increased solubility, with the dye being soluble across the entire pH range. As a result, the technological applicability of these dyes will be significantly increased, and they may be extended to non-traditional fields of application. To fulfil that a strategy was devised by Sisu *et al.* to create azo compounds that contain 4,4'-diaminodiphenylmethane (DADFM) and low molecular weight maltodextrine in their structure (**Scheme 21**). The model compounds were created by functionalizing DADFM with maltodextrine, converting the amino functionalized maltodextrine into a diazonium

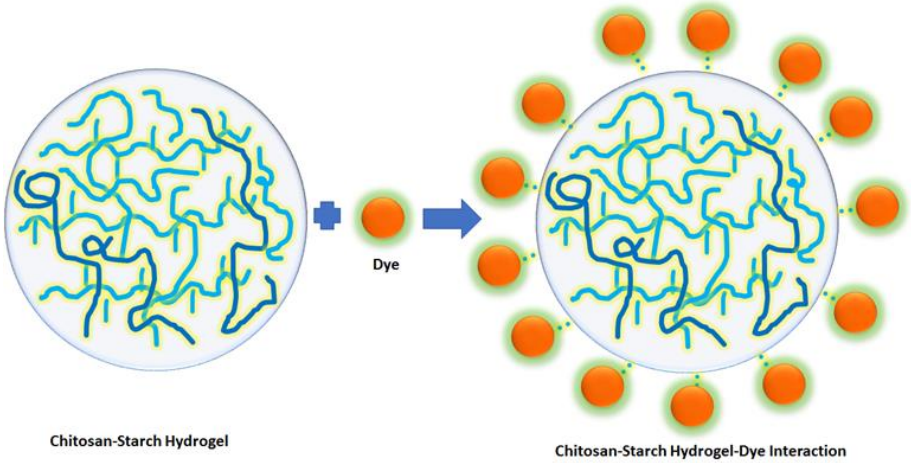
salt, and coupling the reaction with H and R acids. The UV-VIS, infrared, mass spectroscopy, and thermal analysis were used to characterize the compounds [93].



Scheme 21. Polysaccharide-azo dye

5.3.2. Multi azo dyes-(chitosan-starch) gel

Besides covalent coupling of azo dyes with polysaccharides, non-covalent interaction could be done via adsorption of polysaccharides onto small molecules [94]. By using chitosan hydrogel as the adsorbent, numerous researches on the interaction of dyes from aqueous solutions have previously been conducted [95-97]. However, due to limitations such as chitosan's low mechanical properties and specific gravity, this interaction rate and swelling capacity of hydrogel in water are slow [96]. A chemically cross-linked chitosan was created with starch hydrogel which improved the hydrogel's stability and swelling capacity [97]. The goal of the research was to create a chitosan-starch hydrogel with increased swelling and sorption capacity in an aqueous solution. The hydrogel's performance was then assessed in terms of interacting with DR80 dye from the aqueous phase (**Scheme 22**). The temperature dependant data showed that the contact mechanism was endothermic and spontaneous based on the obtained DG° and DH° values. The produced protonated amine functionality of hydrogel allowed for the effective removal of the multi-azo dye (DR80) from an aqueous solution. Natural polymers were a useful, economical, non-toxic, and safe substance that may be used to treat industrial wastewater in this study [97].



Scheme 22. Dyeing of chitosan-starch hydrogel

6. Conclusion

Azo dye and its monomeric and polymeric derivatives are characterized by their environmental stability, ease of preparation, and its photo-electro properties, making them a workable alternate to the more expensive commercial dyes. While wide-ranging research into the diverse modification and applications of azo dyes is presently continuing, more emphasis on the use of azo dyes as chemical reagents, complexes, or modified with synthetic or natural polymers. There is a continuous demand for additional development and research on azo dyes, particularly to improve progress in terms of environment, technology, and sustainability awareness.

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Conflict of Interest

The authors declared no conflict of interest.

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