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Applications of Metal Complexes Dyes in Analytical Chemistry

Mariame Coulibaly

Abstract

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment since they have a significant effect on ecological quality. Commonly, the analytical methods for the determination of trace metals are the spectrometry techniques. While, the electroanalytical methods are recognized as a powerful technique for trace metals owing to its remarkable sensitivity, relatively inexpensive instrumentation, ability for multi-element determination at trace and ultra trace level. New alternative electrode materials are highly desired to develop sensitive stripping sensors for meeting the growing demands for on-site environmental monitoring. Dyes aromatic heterocyclic compound, used in food, textile and cosmetic industries has been used for spectrophotometric determination of metals. In electrochemistry, methods for metals determination based on their complexation with dyes were proposed. In this chapter, a brief summary of spectrometry methods and electrochemical sensors for heavy metals detection based on the formation of metals dyes complexes is presented.

Keywords: heavy metals, dyes, dye/complexation, electrochemical analysis, metal complex dye, spectrometry

1. Introduction

Dyes are known to be used in the textile industry, printing, food industry, as well as cosmetic industry. Since the invention of synthetic dyes in 1856, chemistry has been enriched by these large group of chemical compounds. More than 800,000 tons are manufactured by year [1–4]. Dyes are organic substances with chromophore and auxochromic groups (**Figure 1**) classified into several groups (indigoid dyes, xanthene dyes, etc.) of various structures for different applications.

These applications depend on dyes chemical structure, their hue and their entire light absorbing system. The chromophores are the groups of atoms responsible for the dye colour and auxochromes are an electron withdrawing or donating substituents that cause or intensify the colour of the chromophores [6] in shifting the adsorption towards longer wavelength along with an increase in the intensity of absorption. Some commonly known chromophores groups are: azo ($-\text{N}=\text{N}-$), carbonyl ($-\text{C}=\text{O}$), methine ($-\text{CH}=\text{}$), nitro ($-\text{NO}_2$) and quinoid groups. The auxochromes are acids or bases; the most important are amine ($-\text{NH}_3$), carboxyl ($-\text{COOH}$), sulfonate ($-\text{SO}_3\text{H}$) and hydroxyl ($-\text{OH}$).

The use of dyes in analytical chemistry is well known. Dyes applications in analytical chemistry are feasible because of the presence of chromophores and auxochromes [7]. Most of dyes form complexes with pollutants in aqueous media [8].

Figure 1.
Structure of the azo reactive dye [5].

They are used as titrations indicator in analytical chemistry, and their complexes with the metal ions in aqueous media are used in spectrophotometric analysis. The complexation between dyes and some essential metals including Cu(II), Hg(II) allows the detection of them by the spectrophotometric method or chromatography [9–11].

As in spectrophotometry, titration, colorimetry or chromatography, dyes are also used in electrochemistry specially in metal ions detection. Electrochemical analysis is recognized to be a method for industrial process control, environmental monitoring, and different applications in medicine [12–16]. The electrochemical technique, especially stripping voltammetry for the trace analysis of metal ions, obtained considerable interest because of its low cost, easy operation, good sensitivity, high selectivity and accuracy [17]. The usual working electrode for stripping voltammetry was a mercury electrode [18] and bare electrodes. However mercury is toxic and causes harm to the environment and human bodies. Concerning bare electrodes, they have numerous limitations such as poisoning, low sensibility, poor stability. Therefore, many groups tried to develop mercury free-electrodes and modified electrode to determine metal ions by voltammetric analysis [19–22]. These chemically modified electrodes (CME) have received an increasing attention in recent years in the fields of electroanalysis due to well recognized advantages in comparison with conventional electrodes [23]. Several reagents and techniques are used to modify the electrodes surfaces [24–28]. The complexation reactions with organic or inorganic reagents on electrodes surfaces, incorporate in electrode paste or in solution for electrochemical analysis have been reported [29–32]. Among them, the dyes which are important complexing agents for metals. Electrochemical methods for metal ions determination based on their reaction with dyes, their complexation with dye film on electrode surface or inside of electrode paste have been studied [33–35].

2. Metal-complex dyes in spectrophotometric analysis

2.1 Overview

Many studies have been based on the spectrophotometric determination of metal ions after their reactions with complexing reagents including dyes [36–38]. The dyes are organic substances with chromophore and auxochrome groups which can be classified in different type. Among these different type of dyes, azo dyes represent the largest production volume. They make up about 70% of all synthesized dyes annually [39]. The importance of these may increase in the future and also their use in a variety of applications such as complexing agent in spectrophotometric analysis. However, their stability causes environmental pollution once the dyes are discharged with liquid effluents without adequate treatment before release into the natural environment.

The formation of dye complex depends of the number of ligands in the dye structure, and the coordination number of the metal. The electron donating ligand or ion

combines with the metal ion to form the complex. For instance, for copper ion which is a bivalent ion with coordination number four, it can complexed with two bidentate ligands in an acid dye or a trivalent or a tetravalent one [40]. Metal-complex dyes formed may be broadly divided into two classes: 1:1 metal complexes and 1:2 metal complexes [41]. These complexes have versatile application in various fields include the dyeing of nylon and protein fibers, paint, toners for photocopiers, laser and ink-jet printers, photoconductors for laser printers, nonlinear optics, singlet oxygen generators, dark oxidation catalysts, and high-density memory storage devices [42]. Their colors span the entire spectrum allowing their use in spectrometry.

By UV-Vis Spectrophotometry, the absorption spectra of solutions allows the determination of metals concentration. The absorption spectra of dye solution and metal ions solutions are measured first. Then, after the mix of the dye and the metal ion, the formation of coloured complex between the both compound give a new color peaking and a new absorption spectra.

2.2 Spectrophotometric determination of trace metal by formation of complexes with dye

It well know that dyes can form a stable complexes with metal ions. Dyes applications in spectrophotometric analysis are possible because of the presence of chromophores and auxochromes (**Figure 2**) [7]. Dyes especially the azo dyes are used as spectrophotometric chemosensor. These compounds interact easily with metal ions through the heteroatoms S, N, and O and can chelate with a large number of metal ions to form a metal-dye complex (**Figure 3**). Numerous works have been dedicated to the synthesis and spectral characterization of new azo dyes and their metal complexes [44, 45]. These studies allow to establish the optimal conditions of formation of the complexes (ratio metal: dye, pH, temperature, the maximum light absorption, the influence of foreign ions ...) and the determination of the constants of complexes.

The complex formation equilibrium and formation constant of the complex can be represented by Eqs. (1) and (2) [46].

$$K = \frac{[ML_n]}{[M][L]^n} \quad (2)$$

Figure 2.
 The light absorption system of dyes [43].

Figure 3.
Chemical structure of the azo-metal chelates [44].

[M], [L] and [ML_n] represent the molar equilibrium concentrations of the metal ion, ligand dye and the complex, respectively.

Thus, several new spectrophotometric methods for determination of metal ions based on their complexation with dyes have been developed and tested in real samples [47–49]. Bonishko et al. [48] have developed, a simple spectrophotometric method for the determination of osmium (IV) ions, based on the formation of a complex of this metal with Congo Red. While, the orange G has been used as a complexing reagent in spectrophotometric determination of osmium(IV) by Rydchuk et al. [49]. They showed that the optimum conditions for the formation of coloured complex compound between Os(IV) and acidic monoazo dye Orange G (OG) were: the stoichiometric ratio in the complex was 2:1 at pH = 5.80. Moreover, their study showed that at the room temperature Os(IV) practically did not interact with OG. Os(IV)-OG compound was almost fully obtained after 30 min of heating on a boiling water bath (~98°C).

In general, the formation of complexes lead a significant decreases in the absorption band of the dyes and the emergence concomitantly of a new absorption band with different absorbance. Thus, the formation of complex species between mercury and indigo carmine((Hg)IC and (Hg)₂IC) allowed a optical determination of mercury [36]. The interaction between Cu(II) ions and indigo carmine forms Cu₂(IC) complex characterized by the stoichiometric ratio between indigo carmine and copper 2:1, the molar absorptivity $1.17 \times 10^4 \text{ mol L}^{-1} \text{ cm}^{-1}$ at 715 nm and the stability constant of the complex $\log K = 5.75$, at pH 10, obtained by spectrophotometric data. This complex has been successfully tested for determination of copper in pharmaceutical compounds [37].

3. Electrochemical method for the determination of trace metal by formation of complexes with dye

3.1 Electrochemical behaviour of dye

The electrochemical behaviour of dyes depends of their chemical characteristics, the working electrodes and the pH of supporting electrolyte. According

nature of electrodes, the voltammograms of dyes exhibited irreversible oxidation peaks [50] or can be involved in a two or more steps redox reaction [51]. The voltammetric response of indigo carmine shows two well separated peak pairs on graphite electrode (**Figure 4**) at pH 7, while the first pair of peak disappear at pH more basic.

As indicated previously, azo dyes are an important class of organic dyes which consist of at least a conjugated chromophore azo ($-N=N-$) group. This is the largest and most versatile class of dyes. These dyes are characterised by the presence in their molecules of one or more azo groups $-N=N-$ which form links with organic groups, of which at least one is usually an aromatic nucleus (**Figure 2**). Taking account their potential toxicity, electrochemical methods was developed for the analyzing of azo dye. The mechanism based on the reduction of the azo group with a classical dropping mercury electrode or static mercury drop electrode has been described in detail [52]. Recently, several modified electrodes have been used to study the electrochemical characteristics of azo dyes and their electrochemical determination [54–57]. On a glassy carbon modified, the voltammograms exhibited a irreversible oxidation peaks and a well-resolved oxidation wave was observed at approximately 0.74 V for the azo dye sudan I, sudan II, sudan III, and sudan IV [50] and similar irreversible oxidation peaks was obtained with the congo red on graphene oxide modified electrode [56]. However, the release potential of anodic peak depends of dye and electrode.

These studies show that some of azo dyes are electrochemically reactive. They can reduced or oxidized on different bare or modified electrode (**Table 1**). These electrochemical behaviour allows the detection of dye by voltammetric technique but also the detection of trace metals based on the decrease of dyes oxidation/reduction peak after their complexation.

Figure 4.
 Cyclic voltammograms recorded at graphite electrode for 10^{-3} M IC. Experimental conditions: supporting electrolyte 0.1 M phosphate buffer (pH 7); start potential, -1.0 V vs. Ag/AgCl, KCl_{sat}; scan rates: 25, 50, 100, 250, 500 and 750 mV/s. [51].

Electrode	Dye/structure	Electrochemical behaviour	Reference
Graphite	Indigo carmine	Two pairs reversible oxidation and reduction	[51]
Nanoclay modified carbon electrode	Sunset yellow	Irreversible oxidation	[58]
Amalgam electrodes	Amaranth	Irreversible reduction	[52]
Amalgam electrodes	Allura Red AC	Irreversible reduction	[52]
Graphene oxide casted glassy carbon electrode	Congo red	Irreversible oxidation	[56]
Carbon nanotube ionic liquid gel modified glassy carbon	Sudan I, II, III and IV	Irreversible oxidation	[55]

Electrode	Dye/structure	Electrochemical behaviour	Reference
Glassy carbon electrode.	Reactive Brilliant Red x (RBR x-3b); Acid Red 6b (AR 6b); Reactive Yellow x-rg (RY x-rg); Reactive Orange x-gn (RO x-gn) <div><div> <p>RBR x- 3b</p></div><div> <p>AR 6b</p></div><div> <p>RO x- gn</p></div><div> <p>RY x- rg</p></div></div>	Irreversible oxidation	[59]
Graphite carbon electrodes.	Novacron Deep Red C-D; <div> </div> Novacron Orange C-RN <div> </div>	Reversible oxidation reduction	[60]

Table 1.
Electrochemical behaviour of some dyes investigated in electrochemistry.

3.2 Detection of metals using their reaction with dyes

The coordination complexes of metals with azo-ligands are used in several applications due to the interesting material properties synthetized. The metal complexation by dyes modify the photophysical and coloristic properties of dyes. The formation of complexes are influenced by several by parameters such as dye concentration, dye

structure, pH, temperature, solvents and ionic strengths [61]. This reaction is due to the interactions by Van der Waals forces, hydrogen bonds and hydrophobic interactions [62]. In electrochemistry, the metals complexation with dyes has been investigated for the selective determination of metals trace by voltammetric techniques. For this, the oxidation/reduction current of dye is measured in the presence and the absence of metal ions. The decrease of the redox peaks caused by the formation of electro inactive complexes is function of the metals concentration and allows their determination. Thus, an electrochemical method for Cu(II) determination based on its reaction with indigo carmine (IC) in alkaline medium and differential pulse voltammetry performed at graphite electrode, was elaborated [51]. When Cu(II) ions are added to an alkaline solution of IC, the Cu₂IC complex is formed [51]. This complex electro-inactive at the working potential trains the decrease of the oxidation peak current, which is depending on Cu(II) concentration. The detection limit was 4.74 μ M [51]. The complexation studies between the indigo carmine food dye and mercury were carried out [63] and used for the determination of Hg (II) by electrochemical method. These studies show the suitability of voltammetric detection of metals trace using a decrease of oxidation/reduction current of dyes due to the formation of electro inactive metal -dye-complexes. However, there is very little work in literature concerning this approach. In general, these are electrodes modified by dyes which are used for the detection of metals in electrochemistry.

3.3 Dye modified electrodes for the determination of metal

The chemically modified electrodes have received an increasing attention in recent years in the fields of electroanalysis due to well recognized advantages in comparison with conventional electrodes [23]. The methods for modified electrode preparation are varied. The construction of dyes modified electrodes can be done by electrodeposition [64], by sol-gel method, by incorporation of dye into the carbon paste [65], by composite dye film or by the polymerization of dye on electrode surface. Thus, electrodes modified by chitosan -dye-enzyme composite film or copper complex dye (C.I. Direct Blue 200) film have been reported [64]. Studies have also been carried out on the polymerisation of dyes as modified agent. The poly-congo red (PCR) has been used to modified electrodes by electro-deposition [66, 67] or by polycondensation [5]. However, in voltammetric measurement, the polymerizations of congo red reported are generally carried out with the incorporation of poly congo into other components. These components can be polymers such as aniline [58] or nanoparticles [66]. We will notably encounter the synthesis of poly pyrrole on glassy carbon in the presence of Congo red in view of the detection of dopamine [67], but also the use of poly Congo red in composition with nanoparticles such as CdS for the quantification of α -1-fetoprotein [66], several studies also relate to the use of Congo red in the presence of nanotube [59]. However, the use of dye as modifying reagent in electrochemical analysis is limited. Very little works about this topic have been reported in literature.

4. Conclusion

Dyes are widely used for industrial, printing, food, cosmetic and clinical purposes as well as in analytical chemistry. They play an important role in spectrophotometry and electrochemistry analysis as complexing reagent for the detection of metal ions but they potential is still underestimated in electroanalysis.

It is well known that thousands tons of synthesis dyes are annually produced worldwide. Despite considerable work in recent years on the synthesis of new dyes which can be used reagent for the determination of trace amounts metals, the use of dye as modifying agents is still limited in electroanalysis. Further investigations are

required to synthesis dyes in function of metal and use them to modified electrodes for electrochemical determination of metal ions.

5. Future outlook

The ill effects of metals on health and the environment are well documented, yet there is a lack of reliable, robust, cheap, and accurate sensors for monitoring toxics metals level in environment. Although much progress has been achieved in the last few decades in the field of chemically modified electrodes, techniques developed so far in electroanalysis have used very little the properties of dyes. This signifying that more research and development of new electrodes or new metal complexes for spectrophotometric analysis are required. The inconvenients of current sensors concern largely on their reproductibility, sensitivity and their selectivity toward target metal. The cost associated with portable nature and speciation analysis are also a limiting factor.

Thus there is an urgent need to synthesis new dyes in function of target metal for the application to the electroanalysis of metal cation and in spectrophotometric analysis. Several investigations can therefore be carried out: synthesis of new dye as ligand for metal complexation; study of physicochemical characteristics of new synthesis ligands; study of their electrochemical behavior and complexation; characterization of metal dyes complexes for the electro and spectro analysis; polymerization of dye; thermodynamic study of the complexation of metal cations in poly-dye/poly film dye; study of chemically modified electrodes (ECM) by dye and their application to the detection of metal ions, etc.

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