Sensors & Transducers

Gold Electrode Functionalized with Tridodecylamine for Impedimetric Detection of Acid Orange 10

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Abstract: In this work, we focus mainly characterize and develop a new type of impedimetric sensor for the detection of acid orange 10 (AO10: textile dye) which is a toxic element in waters polluted by industrial waste. A siloprene based membrane was chosen, the used ionophore is the tridodecylamine (TDA). The results are interesting because the developed sensor gives a linear response range of concentrations 10^{-13} M - 10^{-3} M for acid orange 10 in aqueous medium with a good correlation coefficient of 0.9862 and a low detection limit of 10^{-13} M, indicating the sensitivity of the sensor overlooked the target element. Ion sensitivity of sensor has been tested for acid orange 10 via methyl blue (MB). A layer of tridodecylamine deposited on gold electrode has been characterized by impedance spectroscopy and cyclic voltammetry methods. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Impedimetric sensor, Acid orange 10, Tridodecylamine, Cyclic voltammetry.

1. Introduction

Azo dyes are used by a wide number of industries. While textile mills predominantly use them [1-3], azo dyes can also be found in the food [4-5], pharmaceutical [6], paper and printing [7, 8], leather [9, 10], and cosmetic industries [11]. Many of these dyes find their way into the environment via wastewater facilities.

Recent estimation indicates that approximately 12 % of the synthetic dyes used in textile processes each year are lost to waste streams during manufacturing and processing operations, and that 20% of these losses are released into the environment through effluents from wastewater treatment plants [12]. These compounds are quite difficult to be removed in water treatment procedures, and can be transported from municipal sewers through rivers because of their high water solubility [13, 14].

The majority of dyes may cause allergic responses [15], skin dermatoses, eczema, affect the liver, the lungs, the vasco-circulatory system, the immune system, and the reproductive system of experimental animals as well as humans.

Azo dyes contain at least one nitrogen-nitrogen double bond (-N=N-) [16-20]; however, many different structures are possible. Azo dyes are of great concern because dye precursors or their

biotransformation products such as aromatic amines show carcinogenic and mutagenic effects [21, 22].

Acid orange 10 is an anionic azo dye with molecular formula: $C_{16}H_{10}N_2Na_2O_7S_2$ (MW= =452.37 g.mol^{-1}). It is well know that has been used in paper printing,

Textile dyeing and it causes irritation of the eyes, skin and digestive tract if inhaled/ Swallowed.

The detection and quantification of acid orange 10 in water are generally performed using analysis instruments such as chromatographs and spectrometers. The complexity, high costs and big size of these instruments are reasons that led us to develop a simple analytical tool that consists of a chemical sensor, i.e., a sensitive membrane including a selective ionophore.

The electrochemical sensors described in this paper are based on electrochemical impedance spectroscopy (EIS) transduction. A polymeric membrane including tridodecylamine was employed for selective measurements of acid orange 10. Tridodecylamine has been shown to be an efficient extractant for separation and purification of a number of azo dyes because of its excellent chemical stability.

2. Materials and Methods

2.1. Dyes and Chemicals

All chemical reagents were provided by SIGMA ALDRICH.

Acid Orange 10 (abbreviation: AO10; C.I. number: 16230; Synonyms: Orange G: 7-Hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid disodium) was purchased from Aldrich and was used as received. The molecular structure of Acid Orange 10 (C.I. 16230) is shown in Fig. 1.
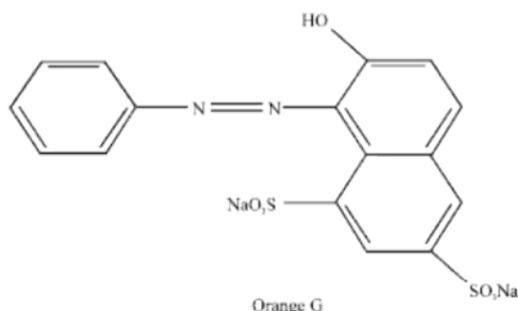

Fig. 1. Chemical structure of acid orange 10.

2.2. Gold Electrodes Transducers

The gold electrodes were designed to be suitable for use in a three electrode cell. The active surface was about 0.3 cm^2. It was cleaned for about 5 min in a piranha solution (1/4(H_2O_2 35 %) +3/4 (H_2SO_4

96 %) mixture) [23]. After this treatment, the gold electrode was rinsed thoroughly with ultrapure water in order to remove weakly physisorbed species and was finally dried with nitrogen.

2.3. Composition and Deposition of the Membrane

The membrane composition was optimized by using the mixture of tridodecylamine (ionophore), siloprene (polymer), cross-linker (plasticizer) in the following proportions: 90 mg, 65 mg, 6 mg respectively, diluted in 0.2 ml of tetrahydrofuran (THF). These masses of siloprene and cross-linker are chosen according to a study of membranes deposited on glass electrode in order to obtain a better behaviour of the membrane [24]. 5 µl of this membrane was deposited carefully on the gold electrode. The solvent being then evaporated.

2.4. Electrochemical Measurements

All potentiometric measurements were made with a voltalab 40 (radiometer analytical S.A) and PGZ301 as a potentiostat, software Volta master 4 was used for the acquisition of the data and the control of the experiments. A three-electrodes cell was used to make the impedance measurements and cyclic voltammetry, the reference electrode was saturated calomel electrode (SCE), platinum wire of 1 mm diameter as the auxiliary electrode and the modified gold electrode as working electrode. The electrolyte used in all experiments was potassium phosphate (KH_2PO_4) at 10^{-1} M with pH 6.8.

3. Results and Discussion

3.1. Choice of the Measurement Conditions

Electrochemical impedance spectroscopy (EIS) appears to be an excellent technique for the investigation of bulk and interfacial electrical properties of any kind of solid or liquid material connected to or being part of an appropriate electrochemical transducer [25].

Tridodecylamine functionalized gold electrodes were used to determine the optimal experimental conditions, in term of voltage and frequency. Nyquist diagrams (Fig. 2 (a, b) were plotted for different overvoltages from - 600 mV to 0 mV versus SCE in a frequency range situated between 100 mHz - 1 Hz.

It was found that the good response occurs for polarization of -600 mV with the appearance of the semicircle in a Nyquist plot as shown in Fig. 3.

The electrical behaviour of gold /membrane /electrolyte interface can be modeled by a resistance, the electrolyte resistance (R_s), in series with a parallel

combination of the capacitance of the electrode (C_m) and the polarization resistance R_p.
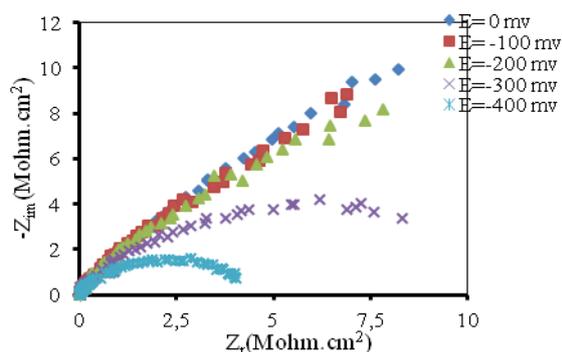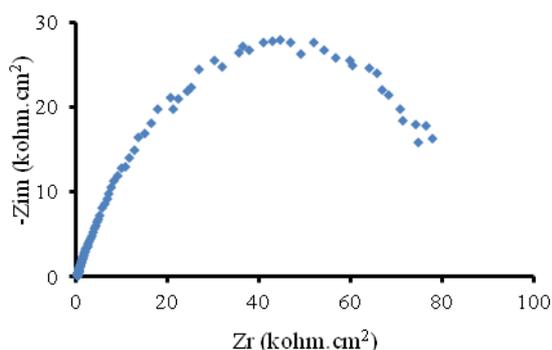

(a)
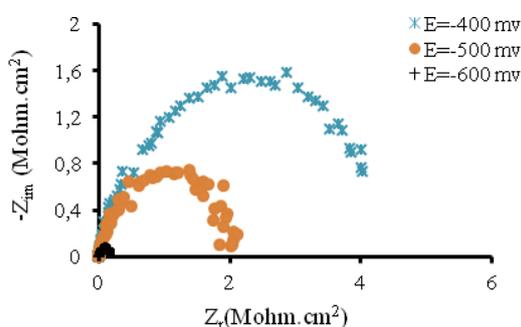
(b)

Fig. 2. Impedance spectra in Nyquist representation (a): From -400 mV to 0 mV, (b): From -600 mV to -400 mV.

Fig. 3. Spectrum impedance polarization of -600 mV.

A fitting is required to exploit impedance spectra of Fig. 2, in order to extract the values of the polarization resistance (R_P) and the correlation coefficient (ζ) which are summarized in the Table 1.

From Table 1, we see that the minimum of the polarization resistance is at potential E = - 600 mV, with a good correlation coefficient of about 0.997. For this polarization, the Warburg impedance is

minimized. These conditions (polarization -600 mV, range of frequencies 100 mHz - 1 Hz) will be maintained to carry out further impedance measurements.

Table 1. Test Results of Electrochemical impedance.

E (mV)	$R_P(Mohm.cm^2)$	ζ
-600	0.089	0.997
-500	2.094	0.942
-400	4.548	0.994
-300	12.18	0.995
-200	29.84	0.996
-100	38.39	0.992
0	50.07	0.998

3.2. Characteristic of Modified Electrode

3.2.1. Electrochemical Impedance Method

We performed impedance measurements for gold electrode and the electrode covered by our membrane. It noticed that the Nyquist diagram of a bare gold electrode is completely different from that obtained with a modified electrode. Fig. 4 has a semi-circular characteristic of the resistance in parallel with a capacity. It is noteworthy that the diameter of a semi-circle increases significantly after the deposition of the membrane. This allowed us to say that gold is a metal substrate suitable for the development of type ISE electrode for the detection of acid orange 10.
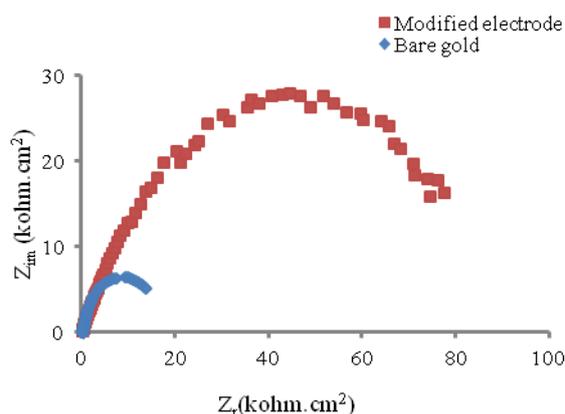
Fig. 4. Impedance spectra for bare and modified electrode.

3.2.2. Cyclic Voltammetry Method

a) Cleaning Transducers.

Gold working electrode was activated by a Piranha solution, washed in water and then activated by cycling in NaOH (0.5 M) at a potential range

between - 400 mV and -1400 mV and scan rate of 50 mV/s until the cycle voltammogram stabilized, indicating that the surface electrode was cleaned and efficiently reduced.

b) Characterization of Electrodes.

The cyclic voltammograms of the gold electrode and the electrode covered by polymeric layer containing the tridodecylamine in 0,1 M KH_2PO_4 (pH=6.8) are presented in Fig. 5. The scan rate is 50 mV / s.
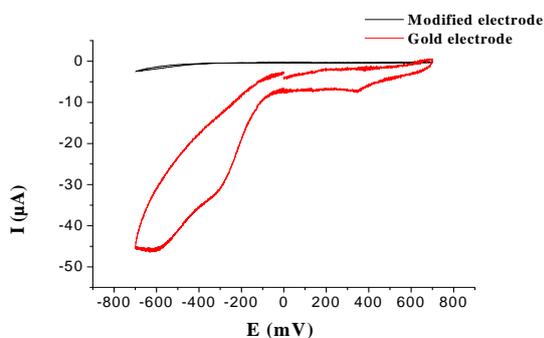

Fig. 5. Voltammogram for a bare gold and modified electrode.

From Fig. 5, it appears that the major change in the character of voltammogram occurs between -700 mV and +700 mV (Versus SCE). The formation of the polymeric layer on the surface of gold has resulted in disappearance of the peaks of the current and a total shift in the peaks of the potential. The cyclic voltammetry shows the formation of the polymer layer on the gold surface.

3.3. Effect of the Concentration of AO10

Once we have ensured the stability of the sensor response developed, we then approached the study of the effect of the concentration of AO10 on the sensor response. The injections of textile dye solution, from 10^{-13} M to 10^{-3}M, were carried out. The obtained results are listed in (Table 2).

Table 2. Evolution of R_P as a function of dye concentration.

[AO10] (M)	R_P (Kohm.cm²)	ζ
0	89.73	0.997
10^{-13}	81.42	0.991
10^{-12}	71.43	0.989
10^{-11}	67.86	0.991
10^{-10}	61.86	0.982
10^{-9}	58.13	0.974
10^{-8}	55.17	0.984
10^{-7}	48.49	0.978
10^{-6}	46.98	0.983
10^{-5}	45.26	0.978
10^{-4}	41.51	0.968
10^{-3}	36,56	0,927

From these results, we can see that the polarization resistance depends on dye concentration; of the system, it increases when the concentration of the target substance decreases, indicating that the kinetics of charge transfer is favored for high concentration of dye.

In order to obtain the calibration data set, the values of membrane resistances ΔR_P versus the added dye concentration were plotted in Fig. 6. The change of membrane resistance was calculated according to the equation [26]:

$$\Delta R_p = R_{withoutAO10} - R_{withAO10}, \quad (1)$$

where $R_{without\ AO10}$ and $R_{with\ AO10}$ are the values of the polarization resistance before and after injection of acid orange 10.

As can be seen in the Fig. 6, the sensor has a linear response in the range of AO10 concentration between 10^{-13} M and 10^{-3} M with a good correlation coefficient of about 0.9862. The detection limit is about 10^{-13} M, which cannot be detected when using other instruments.
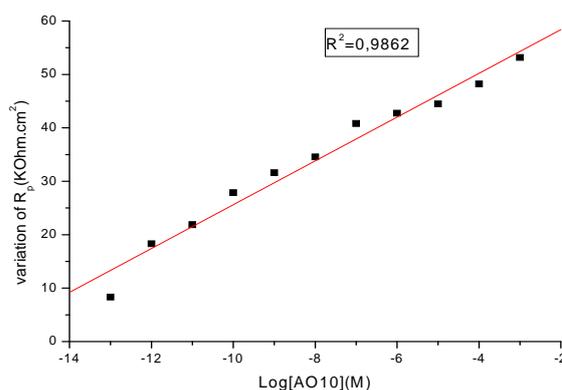

Fig. 6. Calibration plot of the AO10 sensor.

3.4. Selectivity Against Interferences

The most important characteristic of a sensor is selectivity. In this work, we sum interested to study the response of the sensor developed for the detection of acid orange 10, overlooked other dyes such as methyl blue (MB). For this study the selectivity of the sensor was carried out in the absence of the AO10 and by varying the concentration of methyl blue from 10^{-13}M to 10^{-3}M, in order to compare their calibration curves. Fig. 7.

From these curves, we note that for concentrations lower than 10^{-8} M of the two dyes, the two calibration curves are superimposed, which means that the MB is a disturbing element for the detection of AO10. By cons, for concentrations higher than 10^{-8} M, there is a remarkable difference between the two calibration curves, which meant that the presence of methyl blue does not interfere with the determination of acid orange 10.
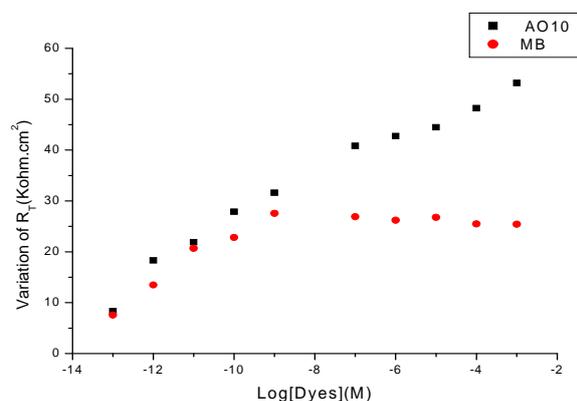
Fig. 7. Calibration curves of the two dyes.

4. Conclusion

In this study, we have proposed a new impedimetric sensor for detection of acid orange 10. The tridodecylamine gold-electrode based device has shown a better limit of detection (10^{-13}M) and larger linear range between 10^{-13}M-10^{-3}M. This result can be obtained in specific conditions (polarization -600 mV for a frequency ranging between 100 mHz and 1 Hz).

From a general point of view, studies should be continued to determine the lifetime of the sensors also developed their selectivity for practical application in situ analysis if possible.

Acknowledgements

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