

Electrochemical Study of the capacity of *Moringa oleifera* to chelate 4-Nitroaniline

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ABSTRACT

In this work we describe the electrochemical analysis of 4-NA chelation by a modified phosphate carbon paste electrode (NP-CPE) and SEM of the surface both with and without *Moringa Oleifera*. The electrochemical characteristic of complex *Moringa Oleifera* - 4-NA was evaluated using cyclic voltammetric (CV) and square wave (SQWV). The optimum potential window of the wide range of -1 V to 1.7V is selected. The kinetics of electron transfer from the NP-CPE to the analytic detection was determined by studies of exchange rate effects and changes in concentration of scanning. Common redox peaks represented a linear dependence on complex MO- 4-NA.

The results showed that *Moringa Oleifera* is able to chelate 4-NA with an electrochemical sensor (NP-CPE), which shows excellent performance to detect this complex (MO-4NA).

1. Introduction

4-nitroaniline, (C₆H₆N₂O₂, 4-NA), a significant aromatic nitro compound, has been widely used as a precursor in the chemical synthesis of various azo dyes, antioxidants, antiseptic agents, drugs of the poultry, fuel additives, and significant corrosion inhibitors [1, 2]. However, the stability and chemical toxicity also makes it dangerous [3, 4]. Its treatment and disposal has emerged as an important concern for the environment. In addition, it is toxic, mutagenic, and carcinogenic toward various and different experimental models [5-8]. Consequently, many developed and developing countries have committed 4-NA priority pollutant and imposed restrictions on the production, use and disposal, etc. [1]; However, despite numerous applications of 4- AN and its substituted in the ortho position derivatives, 4-nitroaniline has attracted much attention, as a special prominent member of the family nitroanilines isomers, because of the specific effects of a nitro group electron withdrawing and electron donating amino group being in the para position of his aromatic system [9-10].

2. Experimental Reagents

Sulfate sodium was dissolved into Bidistilled deionized water (BDW) to form 0.1 mol.L⁻¹ stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with BDW. Carbon paste was supplied from (Carbon, Lorraine, ref. 9900, French). All chemicals were of analytical grade and used without further purification.

2.1. Electrodes preparation

Firstly, the carbon-paste electrode was prepared according to the following procedure [11]. The carbon-paste electrode was prepared by mixing the graphite powder with paraffin oil used as a binder.

The mixture was grinding in an agate mortar and then a portion of the resulting composite material was housed in PTFE cylinder. The geometric surface area of the working electrode was 0.1256cm². A bare of carbon vitreous inserted into a carbon paste provided the electrical contact, and then the natural phosphate film is electrodeposited onto carbon paste electrode. The deposit of natural phosphate on carbon paste electrode

surfaces was processed at 20 V during 30 min. The current was maintained by a galvanostat with a function generator.

2.2. Prepared electrode characterization

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrode was a natural phosphate modified carbon paste electrode (NP-CPE).

2.3 Apparatus

Electrochemical experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software).

3. Results and discussion

3.1. Preliminary characterization voltammetry

Voltammetry preliminary characterization of the performance of the phosphate newly developed modified carbon paste electrode is based on the 4-NA pre-concentration from an aqueous solution on the surface of the electrode modified by adsorption on the surface modification. Probable electrochemical reactions of 4-NA is shown in the scheme 1.

Schem1: Mechanism of the electrochemical redox reaction of 4-NP NA-CPE.

CV and SQWV was used to study the electrochemical behavior of 4-NA on NP-CPE in buffer solution 0.1 M Na_2SO_4 [12] at a scan rate of $100 \text{ mV} \cdot \text{S}^{-1}$ which is optimal for detection. was 18.1 mM used, optimum for detection, The figures 1 and 2 show that 4-NA has two oxidation peak and a reduction peak on NP-CPE with EPA successively (anodic peak potential) at 0.3V and 1.2V, and the EPC (cathodic peak potential) at 0.25V.

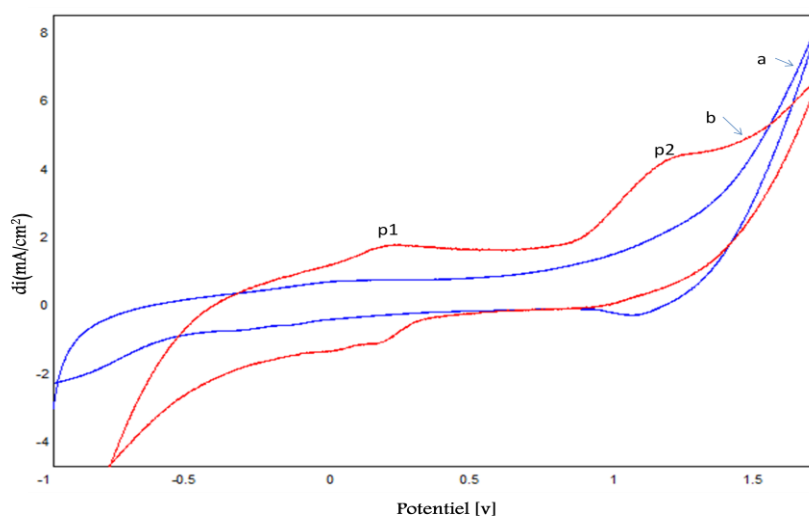


Figure 1: Cyclic Voltammograms recorded in electrolytic solution at 100 mV/s , phosphate natural modified NP-CPE (a) and NP-CPE when adding 18.1 mM 4-NA (b).

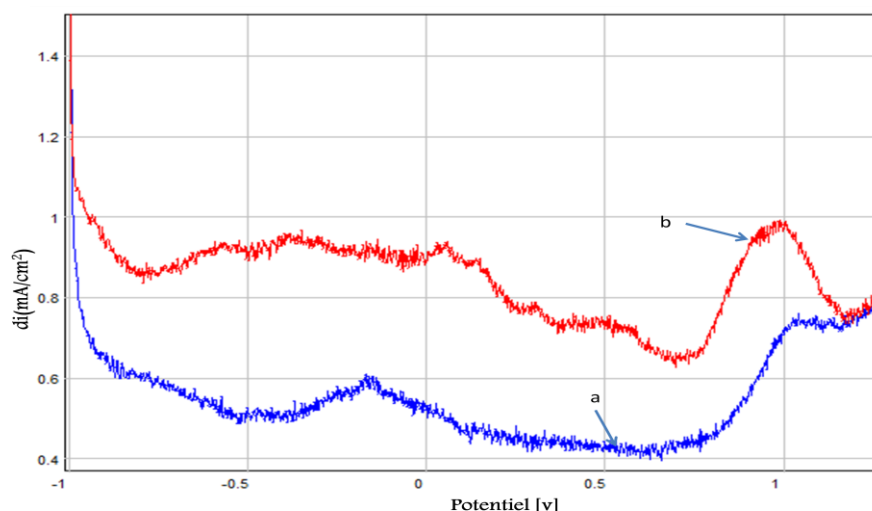


Figure 2: Square wave voltammograms recorded in electrolytic solution at 100 mV/s, phosphate natural modified NP-CPE (a) and NP-CPE when adding 18.1 mM 4-NA (b).

3.2. Chelating effect of *moringa oleifera*

Moringa oleifera is the best known species of the Moringaceae family. Moringaceae is a family of plants belonging to the order Brassicales. It is represented by fourteen species and a single genus (*Moringa*), being considered an angiosperm plant. It is a shrub or small tree, which is fast growing, reaching 12 meters in height. It has an open crown and usually a single trunk. It grows mainly in the semi-arid tropics and subtropics. Since its preferred habitat is dry sandy soil, it tolerates poor soils, such as those in coastal areas [14]. Several researches show that *moringa oleifera* capable of chelating lead and cadmium [15], paraquat and diquat [16], another result shows that isolates capable of eliminating toxic (heavy metals) products from domestic and industrial waste water [17].

Firstly, the *Moringa oleifera* was prepared according the following procedure [13]. *Moringa oleifera* seeds collected for the analysis were shelled off and sundried to maintain constant weight. The sundried seeds were grinded into powdered form using the machine. The powdered was added to the solutions containing 4-NA. After 15 min of contact with *moringa oleifera*, the solutions were purified by removal of 4-NA via analysis in electrochemical sensor.

The VC and SQWV are recorded at carbon paste electrode modified with NP film, in supporting solution containing 4-NA (curve (a)) and after the addition of the *moringa oleifera* (curve (b)), are shown in Figure 3 and 4 respectively. The peak current decreased considerably after *moringa* treatment. This current density reduction is due to a sharp decline in 4-NA, which suggests that *moringa* has a strong complexing power of 4-NA. We noted that the solution pH was decreased after *moringa* treatment.

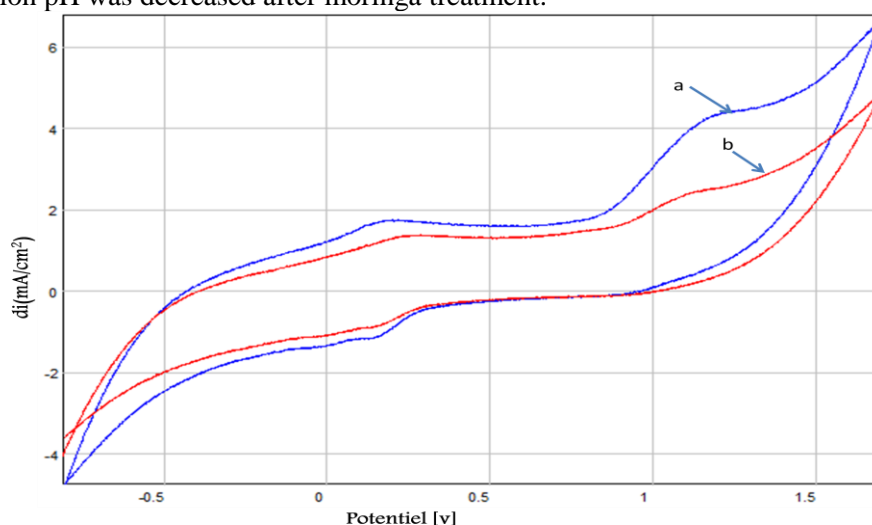


Figure 3: Cyclic voltammograms obtained for NP-respectively, in supporting solution, after exposing electrode to the 4-NA contaminated solution. (a) – before *Moringa* treatment, (b) – after *Moringa* treatment.

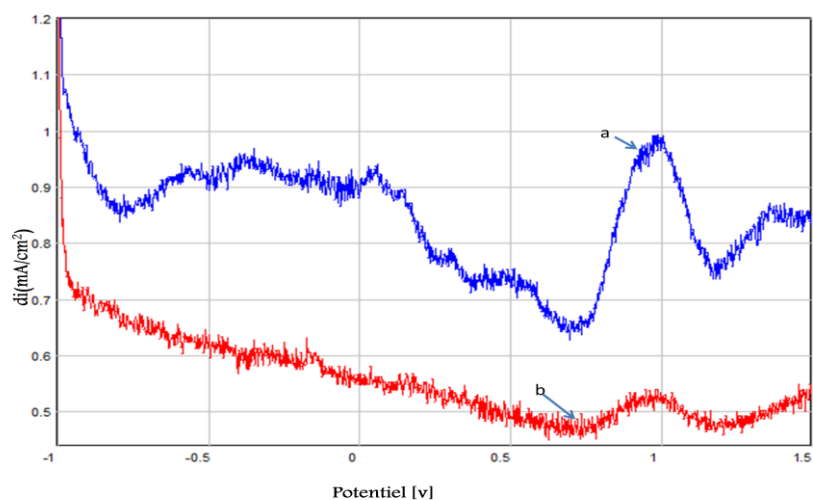


Figure 4: square wave voltammograms obtained for NP-respectively, in supporting solution, after exposing electrode to the 4-NA contaminated solution. (a) – before Moringa treatment. (b) – after Moringa treatment.

3.3. *Moringa Oleifera* concentrating effect of 4-NA

After the electrochemical analysis (VC and SQWV) Figure 5 and 6 who recorded the moringa concentration effect of 4-NA, which shows that the current density decreases by adding the Moringa oleifera, which we think the Moringa chelate the 4-NA.

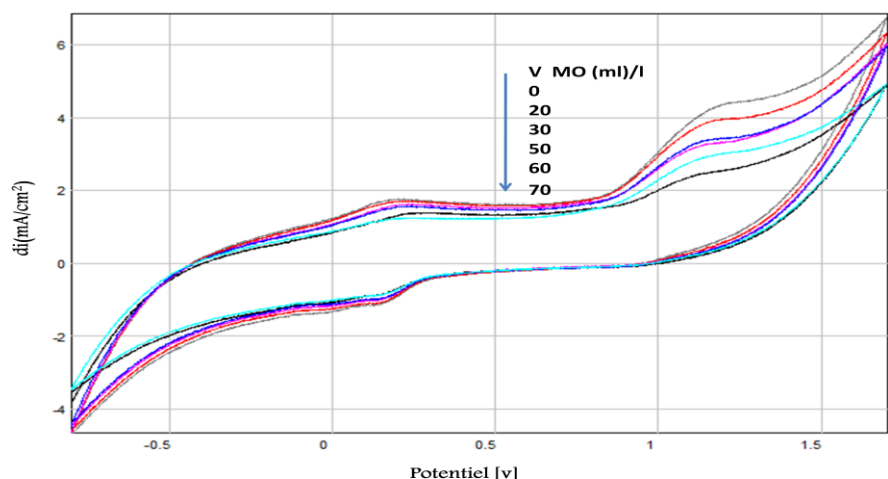


Figure 5: Cyclic Voltammogram of different concentration of MO (0 ml/l to 70ml/l) in (18.1mM) 4-NA at NP- CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s.

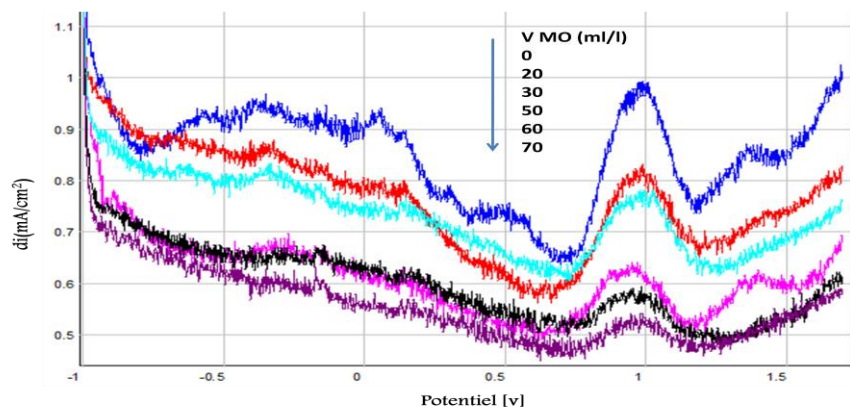


Figure 6: Square wave voltammogram of different concentration of Moringa Oleifera (0 ml/l to 70ml/l) in (18.1 mM) 4-NA at NP- CPE in 0.1M Na₂SO₄, Scan rate 100 mV/s.

3.4. Calibration curve

Figure 7 shows that the density of current decreases linearly with the addition of moringa oleifera according to the following equation $I_{p2} = -0,067[MO] + 0,971$ with a coefficient regression $R^2 = 0,993$.

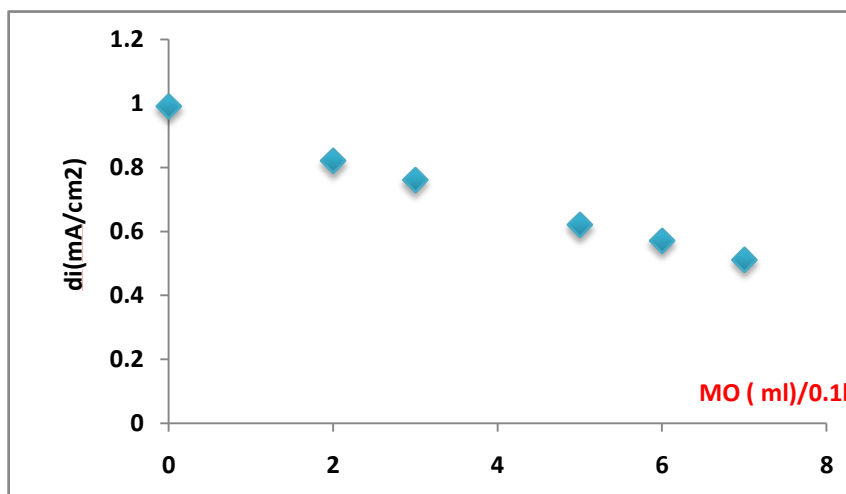


Figure 7: Peak area of land depending on the volume of added MO on Peak 2 using SQWV.

Similarly, the efficiency of the Moringa Oleifera to chelate 4-Nitroaniline increases considerably with the MO volume (figure8).

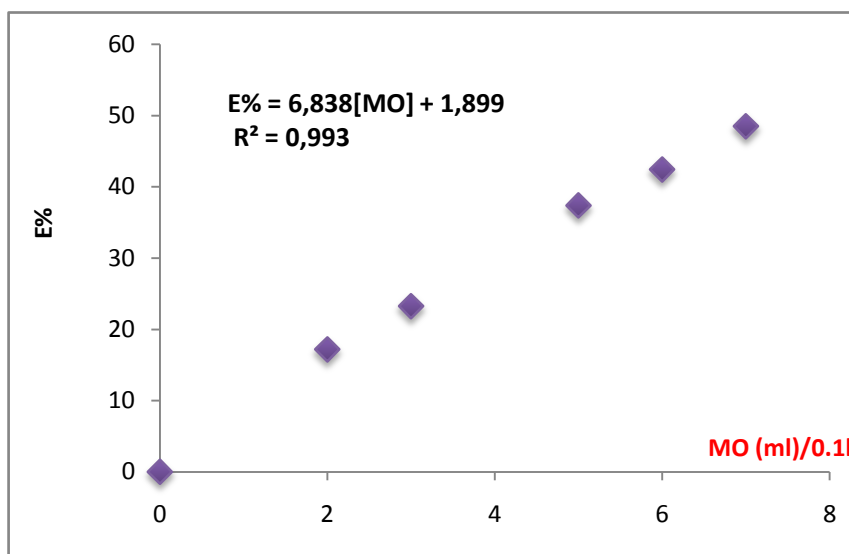
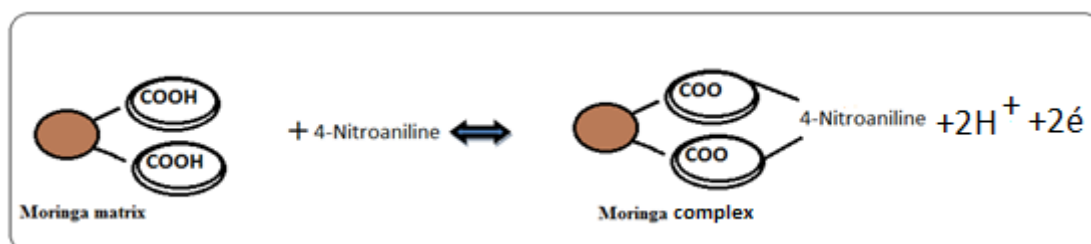


Figure 8: The MO efficiency is 18.1 mM [4-nitroaniline] in different MO volume

The decrease of the pH solution treated, suggests to us that the Moringa exchanged two protons against the metal ion. The Proposed mechanism is as Follows (scheme 2):



Scheme 2: Proposed mechanism of the *Moringa* exchanging two protons.

Moringa oleifera analysis proposed mechanism is confirmed by the IR as shown in figure 9:

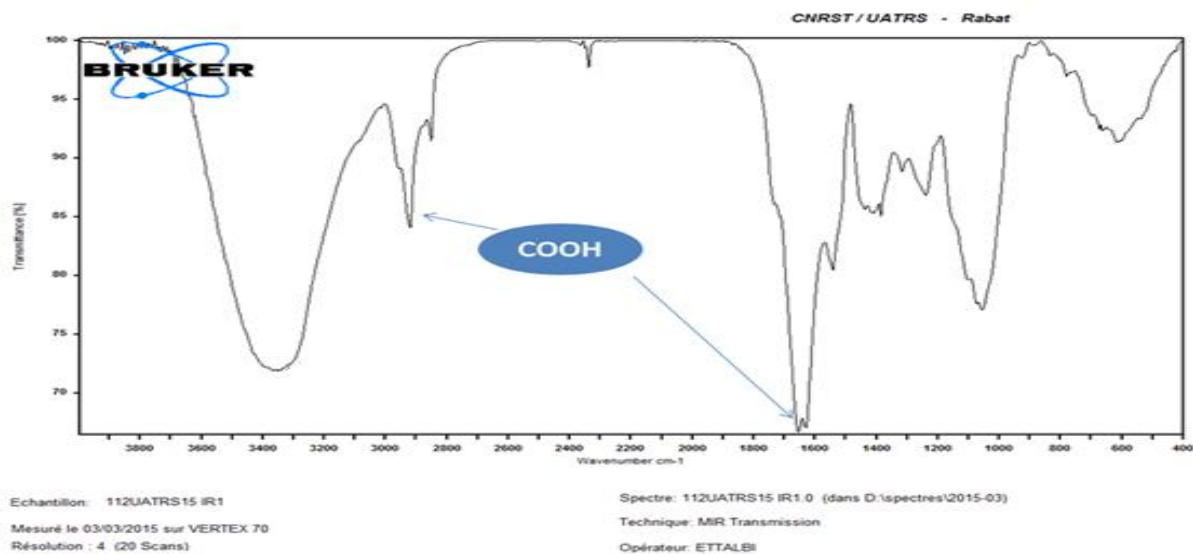


Figure 9: Infrared Spectrum of *Moringa Oleifera* MO.

In Figure 10, we present the SEM images, taken from the surface of the modified electrode; we can see that after MO treatment, the surface morphology has changed dramatically with the advent of large compact crystals, which made us suggest that *Moringa Oleifera* complex 4-nitroanilines (4-NA) adsorbed on the electrode by forming a continuous film.

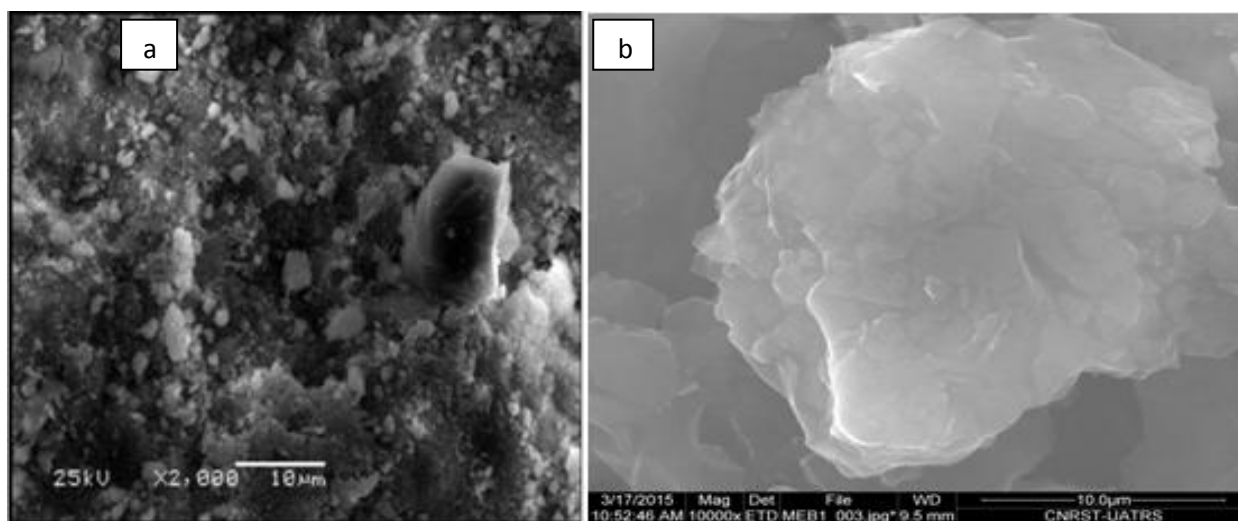


Figure 10: SEM pictures of NP modified carbon paste electrode, a- before treatment and b- after treatment

Conclusion

In conclusion, it was possible to demonstrate the potentiality of the proposed electrodes for determining and detecting the 4-NA. This sensor is characterized by a higher sensitivity and reproductibility.

The *Moringa oleifera* seeds have the ability to chelate the 4-NA. This last is sequestered by chemical sites naturally present in the moringa matrix. The chelating process is rapid and takes place under normal temperature and pressure. *Moringa oleifera* is an environmentally-friendly natural complexing most suitable for the treatment of water containing undesirable 4-NA concentrations. The removal efficiencies were 70% of the 4-NA and it is an eco-friendly technology that is economically more advantageous than other treatment alternatives.

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