Journal of materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 1, Page 324-331

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Electrochemical Study of the capacity of *Moringa Oleifera* to chelate chloroaniline

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Received 29Aug 2016,
Revised 01Oct 2016,
Accepted 04 Oct 2016

Keywords

- ✓ *p*-Chloroaniline
- ✓ Carbon paste electrode
- ✓ cyclic voltammetry
- ✓ *Moringa Oleifera*
- ✓ phosphate Natural

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Abstract

We provide a method of electrochemically sensitive voltammetry for analytical chelating *p*-chloroaniline by *Moringa Oleifera* using a carbon paste electrochemical (PEC) modified by a porous material, for example natural phosphate. *P*-Chloroaniline - *Moringa Oleifera* strongly adsorbed on a surface of PN-CPE and provides easy quantitative electrochemical methods to electro-*p*-chloroaniline (p-CA) - *Moringa* operational parameters have been optimized, and performance voltammetric stripping was studied using square wave voltammetry of. The current intensity peaks are reduced very linear, with good sensitivity PN-CPE. These results can lead to widespread use of electrochemical sensors to detect chelating p-chloroaniline (p-CA) by *Moringa* in an aqueous solution contaminated with *p*-chloroaniline (p-CA) for purified water.

1. Introduction

The interest for chloroanilines in the environment is due to their recognised toxicity associated to their ubiquitous diffusion. Chloroanilines can be present in industrial effluents, sludges and agricultural soils; they are produced in biodegradation processes of phenylurea, acylanilide and phenylcarbamate herbicides [1], can derive from azodye synthesis and industrial applications [2] and are important intermediates in production of polymers, rubber additives, dyes and pharmaceutics. Due to the high persistence in the environment and the low natural biodegradability, remediation strategies have been developed for their destruction, based on different processes and reagents [3]. Particular attention is devoted to the degradations of 2-chloroaniline [4] and especially of p-chloroaniline (p-CA) [5]. Degradation pathways of p-CA induced by differently-catalysed chemicals and microbiological treatments are reported. A photodegradation process catalysed by TiO_2 [6] and Fe (III)-assisted do not lead to complete mineralization but to the formation of polymeric products, often red- colored [7]. Some remediation strategies are based on H_2O_2 oxidation catalysed by mixed metal oxides, metals and Fentontype heterogeneous mixtures. The oxidation with hydroxyl radicals leads to the formation of aminohydroxybenzene and HCl and then to complete mineralization, the kinetics depending on the kind of the catalyst [8]. The photolytic reaction performed at 313 nm and assisted by electron transfer reactions to organic solvents leads to the formation of hydrogen chloride and dimeric forms [9] while ozonation at different pH values leads to the formation of products characterized by lower toxicity [10]. The electrochemical oxidation in cyclic voltametry (acetonitrile as the solvent) leads to the formation of dimeric products [11] and evidences the role of the halogen substituents in the electroxidation process [12]. Pulsed laser-induced transient absorption spectroscopy in acetonitrile has also been applied in the degradation of p-CA [13]. Degradation reactions conducted in a photoreactor containing a fluorescent lamp, in the presence of phosphate, leads to the formation of many products, among which the purple colored 4, 40-dichloroazobenzene [14]. In acetonitrile 4- A undergoes heterolysis and in polar media gives rise to photodechlorination, formation of organic species and of hydrochloride, while nanosecond laser flash photolysis experiments showed the effect of the solvent polarity on the degradation pathway [15]. Photoirradiation of p-CA in acetonitrile in the presence of alkene was shown to form diamine and aniline [16]. Ionisation radiation has also been employed in the development of new technologies for the treatment of waste waters. In particular the degradation of p-CA has been studied by ionising radiation, utilising a 60Co g-rays source: the reaction leads to the formation of NH_3, chloride, aldehydes, acids and chlorophenols [17]. In soil remediation, degradation processes based on microbiological and enzymatic activity are also employed. Biodegradation by gram negative bacteria and by ‘‘natural attenuation’’ methods, consisting in natural processes have been also experimented [18]. Enzymatic activities were employed to degrade p-CA to polymeric species [19]. P-CA has been also destroyed by means of sequential airlift bioreactor SABR [20] and by sun light exposure in the presence of riboflavin-50-phosphate and sodium [21]. Some literature papers deal with the degradation reactions of p-CA in natural waters but no distinction is made among the possible contributions of sun light irradiation, temperature and bacteria, microbial microorganisms and humic acids present in water [22-24]. Aim of the present work is to evaluate the behaviour of p-CA in aqueous solution, without at with *Moringa Oleifera.*

2. Experimental Reagents

P-CA, sodium sulfate, and nitric acid were of analytical grade and from Aldrich. Stock solutions of p-CA were prepared by dissolving p-CA in Deionized Water (DW). All preparations and dilution of solutions were made with deionized water. For reproducible results, a fresh solution was made for each experiment.

2.1. Electrodes preparation

The electrode was prepared by mixing a pure graphite powder and synthesis phosphate natural described above. The mixture was grinding in a mortar. The mixture paste was packed into working electrode. The geometric surface area of the working electrode was 0.1256cm^2. The electrolytic solution Na_2SO_4 (0.1M) was deoxygenated with nitrogen during experiment at ambient temperature.

2.2. Apparatus and electrochemical procedures

Voltametric measurements were made using a potentiostat PGSTAT 100 driven by the General Purpose Electrochemical Systems data processing software (voltalab master 4 software). The auxiliary electrode was platinum, the reference electrode a saturated calomel electrode (SCE). The working electrode consisted of an NP-CPE with a drop area of 0.1256cm^2. The pH measurements were carried out with a pH meter. All experiments were performed at 25°C. Test solutions for voltammetric experiments were prepared in 20 ml volumetric flasks containing a suitable amount of p-CA solution, 0.1M sodium sulfate. All solutions were added deionised water to a final volume of 20 ml and transferred to the electrochemical cell. Before the voltammetric scan, the solutions were stirred and de-aerated by bubbling nitrogen gas (purity 99.95%) at flow rate of 50 ml for 5 min. Current-potential curves from -1 V to 1.7 V.

3. Results and discussion

3.1. Voltammetric characteristics of 4-chloroaniline

Figure 1 shows a cyclic voltammograms (CV) in the potential range -1 V to 1.7 V recorded for NP modified carbon paste electrode at 100 mVs -1. No peak is observed in the case of NP-CPE for the absence at p-CA (Figure 1a), contrary to the Figure 1b shows as p-CA exhibits has two oxidation peaks at Epa(1) = 0.25V and at Epa(2)= 0.85V , in addition to reduction peak at Epc3 = - 0.025V.

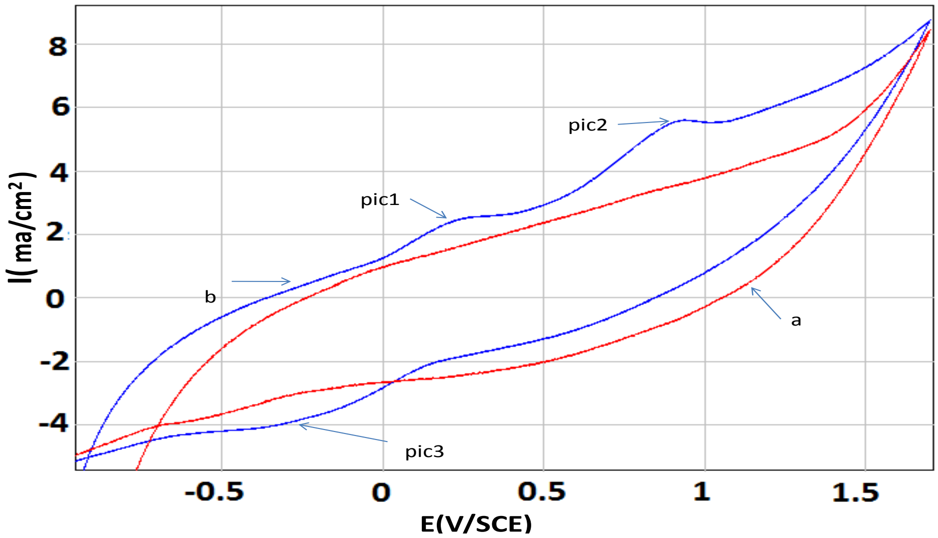


Figure 1*:* voltomogram cyclique recorded in electrolytic 0.1 Na_2SO_4 solution, at 100 mV/s at pH=7 at bare PN -CPE (a) and PN -CPE/p-CA(1.18mM) (b), scan rate 100 mV/s

3.2. *Square wave voltammograms of 4-chloroaniline*

There is of (figure2) after that Square wave voltammograms pic1 and pic2 oxidation of p-chloroaniline increases with concentration of p-chloroaniline adition

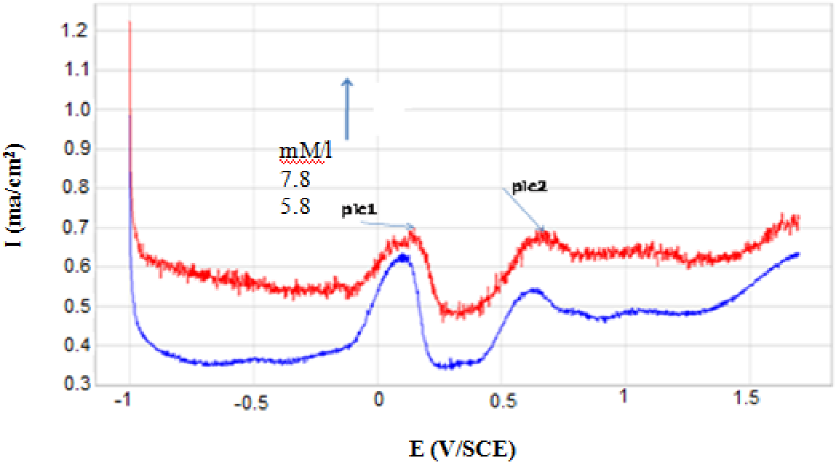


Figure 2*:* Square wave voltammograms recorded for (7.8-5.8)mM p-CA at pH=7 at bare pn -CPE), scan rate 100 mV/s, preconcentration timetime (tp) =15min.

3.3. *Chelating effect of moringa oleifera*

Moringa oleifera Lamarack (English: Horseradish, Drumstick;Hindi: Saijan; Sanskrit: Shigru) belongs to the Moringaceae family,is widely distributed in tropics and sub-tropics of Asia and Africa. The young leaves and green pods are common vegetables in India [25], another result shows that isolates capable of eliminating toxic (heavy metals) products from domestic and industrial waste water [26].

Firstly, the *Moringa oleifera* was prepared according the following procedure [27]. Moringa oleifera

Seeds collected for the analysis were shelled off and sun- dried to maintain constant weight. The sun-dried seeds were grinded into powdered form using machine. The powdered was added to the solutions containing p-chloroaniline. After 15 min of contact with moringa oleifera, the solutions were purified and analysis in electrochemical sensor. The SQWV recorded at carbon paste electrode modified with NP film, in supporting solution containing p-chloroaniline (curve a) and after addition of the moringa oleifera (curve b), The peak current decreased considerably after moringa treatment. This current density reduction is due to a sharp decline in p-chloroaniline concentrations which suggests that moringa has a strong complexing power of p-chloroaniline (Figs. 3and 4).We not that the solution pH was varied after moringa treatment. It was decreased from 7.2 to 6.5.

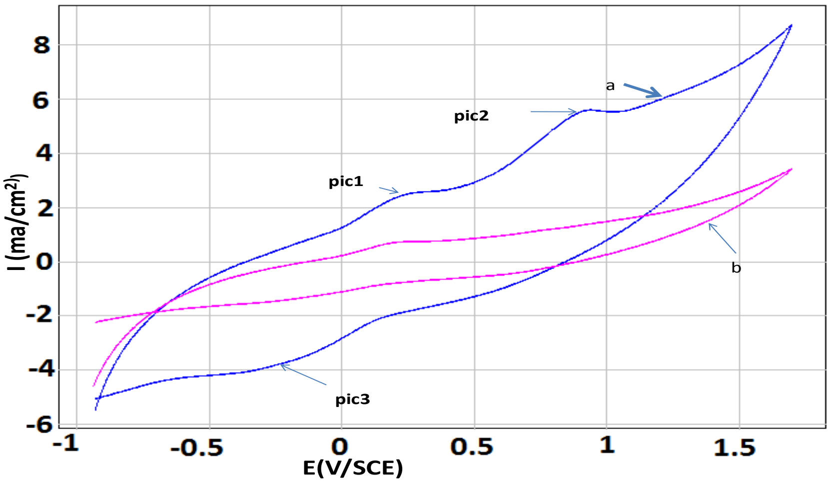


Figure 3: Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, phosphate naturel modified carbon pas, in 0.1 M Na_2SO_4 after exposing electrode to 1.18mM/l p-chloroaniline contaminated solution. (a) - before moringa treatment, b - after moringa treatment.

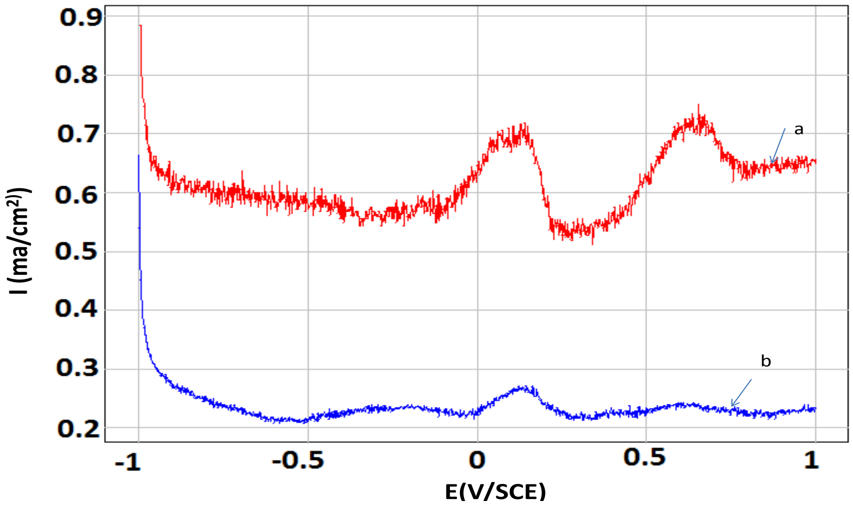


Figure 4: square wave voltammograms obtained for NP-respectively, in supporting solution, after exposing electrode to the 1.18 mM/l p-chloroaniline contaminated solution. (a) – before moringa treatment, (b) – after moringa treatment.

significantly of the oxidation peak current of 1.18 mmol l^{-1} p-chloroaniline is greatly reduced succevement with adition of Moringa oleifera concentration (0ml, … , 11 ml) .sug- manages *Moringa oleifera* us that a complexing effect on p-chloroaniline.

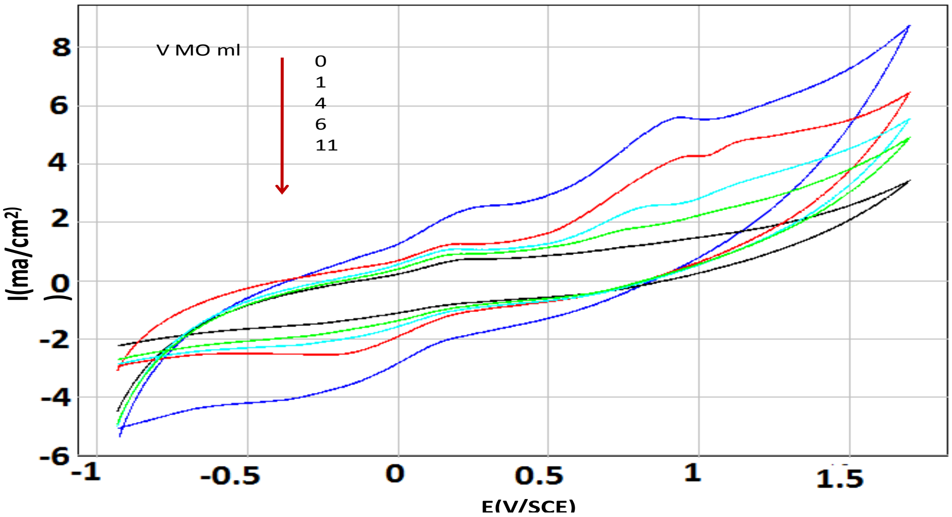


Figure 5: Cyclic voltammograms of different concentration of MO (0 ml to 11ml) in (1.18mM) p-chloroaniline at NP- CPE in 0.1 M Na_2SO_4, Scan rate 100 mV/s.

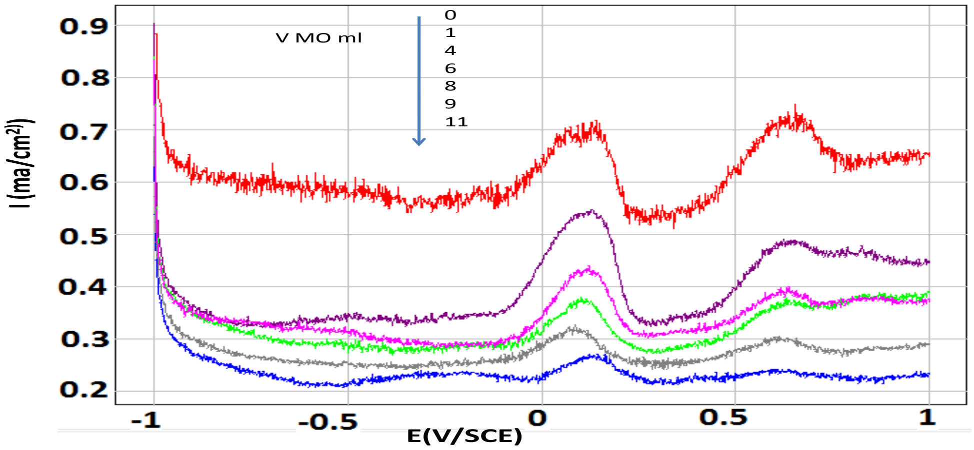


Figure 6*:* Square wave voltammogram of different concentration of moringa oleifera (0 ml to 11ml) in (1, 18 mM) p-chloroaniline at NP- CPE in 0.1 M Na_2SO_4, Scan rate 100 mV/s

3.5. Calibration curve

It was established that the current peaks of p-chloroaniline decreases linearly relative *Moringa oleifera* added in solution (figure 7) .and the zero waiting moringa were 65% for 1.18mM / l p-chloroaniline (Figure 8).

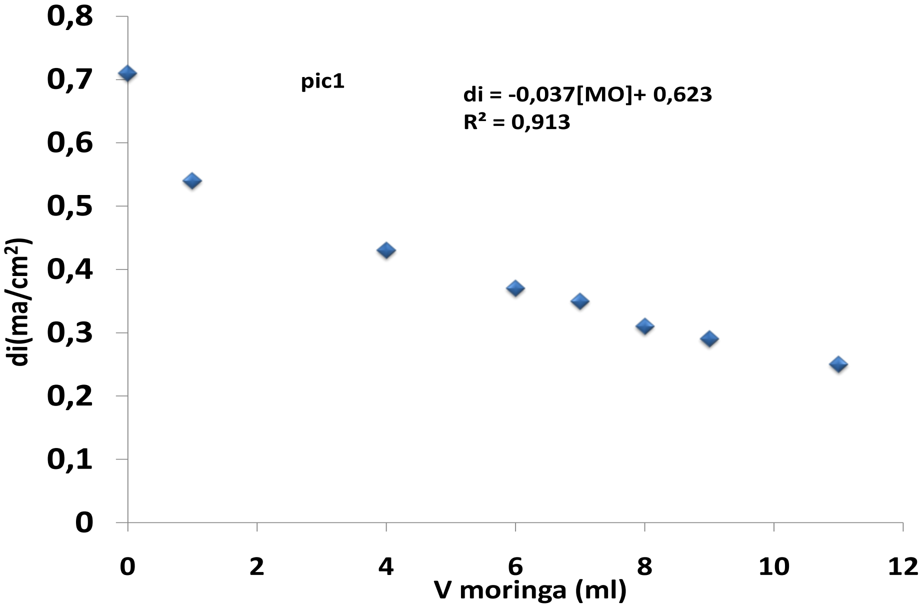


Figure 7: Peak area of land depending on the concentration of added MO on Peak 1

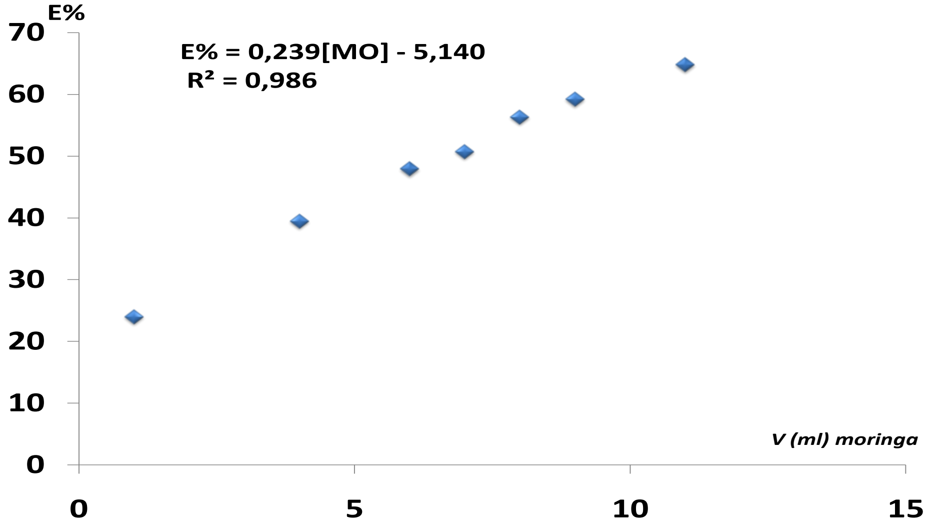
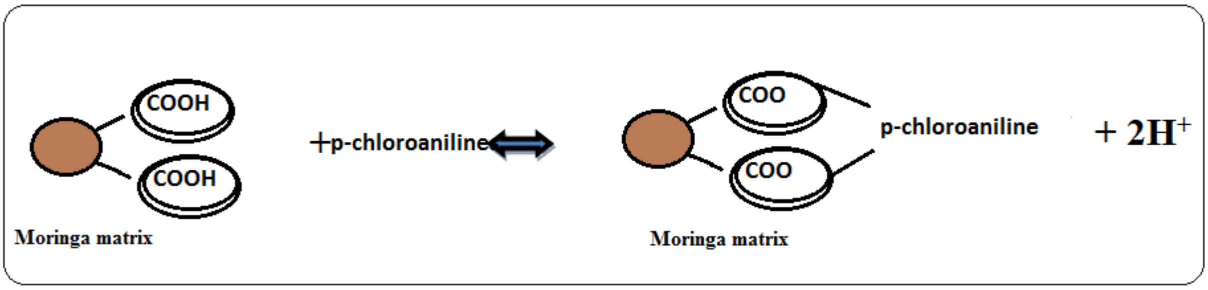


Figure 8: Moringa oleifera efficiency of 1.18 mM / l p-chloroaniline (pic1) versus volume added Moringa

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 1):



Scheme 1*:* proposed mechanism for chelating Moringa oleifera p-chloroaniline by and exchange of two protons

It is also proposed another mechanism based on morphology for comparing the two surface without and with Moringa oleifera (fig9 a and b)

In Figure 9, 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-chloroanilines (4-CA) adsorbed on the electrode by forming a continuous film.

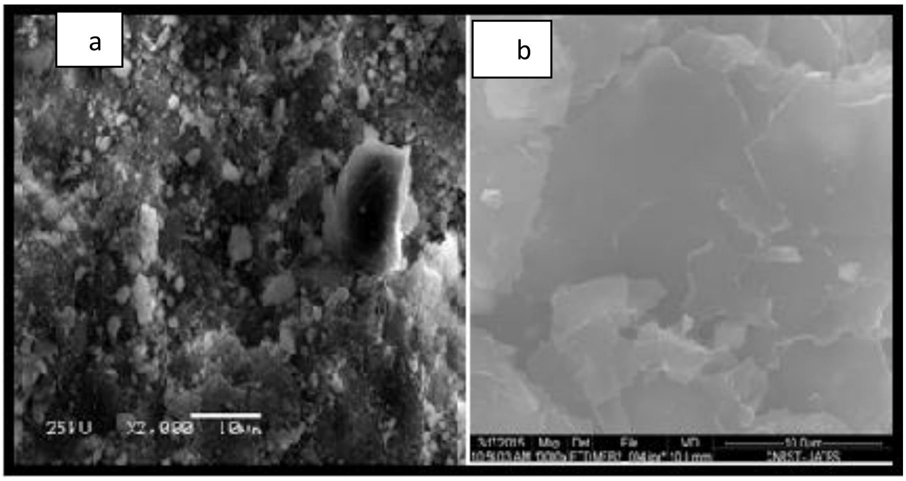


Figure 9: SEM pictures of NP modified carbon paste electrode, a- before treatment and b- after treatment MO.

Conclusion

In conclusion, it was possible demonstrating the potentiality of the proposed electrodes for determining p-chloroaniline. Such a sensor is characterized by a higher sensitivity and reproducibility.

The *Moringa oleifera* seeds have the ability to chelate *p*-chloroaniline. The metal 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 p-chloroaniline concentrations. The removal efficiencies were 65% *p*-chloroaniline. It is an eco-friendly technology that is economically more advantageous than other treatment alternatives.

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(2017) ; http://www.jmaterenvironsci.com