



## Cyclic Voltammetry And Chronoamperometry Study Of Polyaniline-MnO<sub>2</sub> Nanostructured Urease Biosensor Using Stainless Steel Electrode For The Detection Of Heavy Metal Ions In Water

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### Abstract

The rapid and sensitive measurement of heavy metal ions and pesticides are required in various fields such as Water pollution, Juice Content Determination, waste water monitoring and Soil pollution. Biosensors have found a vast range of important applications in the field of clinical, industrial, environmental and agricultural analysis. Out of all the environmental issues, water pollution by heavy metal ion such as Mercury, Lead, Arsenic, Cadmium, Chromium etc. is directly related with health of human being individually as well as society health too. In the present work, we have developed electrochemical amperometric biosensor by immobilizing biological element as enzyme 'Urease', to the transducer surface 'Stainless steel'. The biosensor was prepared using stainless steel electrode modified with PANI/MnO<sub>2</sub> nanocomposites with different weight percentage of MnO<sub>2</sub> such as 5% 10% and 15% by the method of electropolymerization. The modified transducers were characterized by Cyclic Voltammetry and Chronoamperometry. From the Cyclic voltammograms reveals the presence of MnO<sub>2</sub> changes the electrode behavior during the electropolymerization of aniline. The Cyclic Voltammetry of PANI/MnO<sub>2</sub> shows that the adsorption/desorption process of the ions are very fast during cycling. The oxidation current for PANI/MnO<sub>2</sub> nanocomposites was found to be increased with an increase in concentration of MnO<sub>2</sub>. The Chronoamperometry curve of PANI/ MnO<sub>2</sub>/Urease (15%) electrodes shows that the immobilization of urease on modified PANI/ MnO<sub>2</sub> (15%) film results in getting larger saturation current in the time of 10 sec. But the curve obtained is not stable for long time. Thus the PANI/ MnO<sub>2</sub> matrix show degradation of the Urease from the electrode surface.

**Kywords:** Cyclic Voltammetry, Chronoamperometry, Polyaniline, Urease, Heavy metal ions.



### 1.1 Introduction

With the advancement in the field of nanoscience and nanotechnology in the recent years, nanocomposites of different metals and conducting polymers or metal oxide polymer have become an important class of materials. These materials find potential applications as sensors, UV detectors, catalysts, biosensors, and piezoelectronic materials [1]. As with conventional composites, the properties of nanocomposites can display synergistic improvements over those of the component phases individually. However, by reducing the physical dimension(s) of the phase(s) down to the nanometer length scale, unusual and often enhanced properties can be realized. An important microstructural feature of nanocomposites is their large ratio of interphase surface area to volume [2]. The electrochemical methods based on the in situ polymerization allow single-step synthesis of polymer inorganic nanocomposites in the presence of polymer or monomer[3]. An addition of nanofillers in the polymer matrix results in remarkable improvement of mechanical properties and glass transition temperature of the polymer. Nanoparticles settle polymers by reducing the degree of mechanical non-homogeneity [4].

It is reported that conducting polymers shows some more ion exchange with the help of dopant and other polymer modifier to form composites or blends. This will not only change total pH sensitivity but give stable immobilization matrix also[5]. In biosensors, active materials are playing most important factor governing the electrochemical performance. Generally, the electrode materials of biosensors are of three types, carbon materials, conducting polymers and transition metaloxides [6]. In the recent research scenario Polyaniiline (PANI)–MnO<sub>2</sub> nanocomposites are attracting increased interests from both academic and industrial scientists. PANI is one of the most promising conducting polymers and has many advantages such as high doping/de-doping rate during sensing process, easy polymerization and high environmental stability [7]. MnO<sub>2</sub> is taken as a promising electrocatalytic agent for electrode material due to its natural abundance, low cost and high theoretical selectivity [8]. Furthermore, MnO<sub>2</sub> based nanocomposites are known to be used in neutral aqueous electrolytes that can meet the requirements of “green electrolyte” [9].

*E. Çevik et.al.*, 2012 [10] constructed urea biosensor based on the direct covalent attachment of urease onto a polymeric electron transfer mediator, poly(glycidyl methacrylate-covinylferrocene)- and observed response time about 3 sec. *R. Balint et.al.*, 2014 [11] suggested a



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conductive polymer as a novel type of electroactive biomaterial and biocompatible and biodegradable properties promises its huge applications in the field of biomaterials. Recently, our research group [12] developed biosensor based on immobilization of urease on polypyrrole (PPy) / (MWCNT) composite on stainless steel electrode and used for heavy metal ions detection in water. The detection limit for cadmium and lead was found to be in the range of 1-10 mM. A. Y. Obaid *et.al.* 2014 [13] presented electrochemical characterization of PANIs as well as obtaining a thin polyaniline films on Stainless Steel (SS) in aqueous acidic solutions. Voltammetric characteristics of PANI showed that the nature of the voltammograms in 0.5M and 1M of H<sub>2</sub>SO<sub>4</sub> are similar. J. L. Camalet *et.al.*, 2000 [14] obtained electropolymerized Aniline on platinum and mild steel electrode from neutral aqueous electrolytes. They found the properties of the resulting Polyaniline (PANI) films are similar to those obtained in acidic media. The films are generated with less metal dissolution than when acid electrolytes are used. B. D. Malhotra *et.al.*, 2011 [15] have been Capitalized the properties of NSMOs, and opened up a new horizon in materials science with a synergistic effect of the individual components. M. U. AnuPrathapa, *et.al.*, 2013 [16] have studied PANI/MnO<sub>2</sub> nanocomposite and showed that it exhibit high-current sensitivity for guanine, adenine, thymine, and cytosine analytes compared to individual MnO<sub>2</sub> and PANI modified electrodes. L. Cui *et.al.*, 2015 [17] have summarized inorganic, organic, and bio-material modified electrodes for electrochemical detection of heavy metal ions and suggested importance of development of simple, sensitive and accurate methods for their detection in environment and food.

### 1.2 Materials and Methodology

All chemical used were of analytical grade. Aniline, ammonia solution (min 25%), zinc nitrate (96%), acetone, Sulphuric acid, MnSO<sub>4</sub>, KMnO<sub>4</sub> from Merck Ltd, Mumbai, Urease (Jack bean mill) from LobaChemie, mercury nitrate, lead nitrate, phosphate buffer solution and Urea were procured from Sigma-Aldrich, were used as received without further purification except aniline. Aniline was used after distillation by a known technique. Double distilled water was used throughout this work.

#### (a) Chemical Synthesis of Nano-sized MnO<sub>2</sub>

A mixture of MnSO<sub>4</sub> (1.0M) and KMnO<sub>4</sub> (0.5M) solution was stirred for 4 h at 70 °C. The obtained precipitates were washed several times with distilled water followed by ethanol to



remove impurities, and then dried in vacuum at 110 °C for 5 h. The dried powder was put into muffle and heated at 300 °C for additional 3 h. These powders were acidified with 2.0M H<sub>2</sub>SO<sub>4</sub> at 90 °C for 2 h. Finally, the product was washed with distilled water and vacuum dried [18].

### **(b) Electropolymerization of PANI/MnO<sub>2</sub>nanocomposite**

The solution of 0.4M aniline was prepared in 100 ml of 1M H<sub>2</sub>SO<sub>4</sub>. The electrodeposition was performed using Potentiostat model CH-600 D. Platinum wire was used as Counter electrode, Ag/AgCl<sub>2</sub> as reference electrode and Stainless Steel as working electrode. The layer of PANI-MnO<sub>2</sub>nanocomposites with different weight percentage were deposited on Stainless Steel surface by linear swiping the voltage in range -200 mV to +1100 mV at 50 mVs<sup>-1</sup> for 50 cycles. After 50 cycles the sufficient amount of layer was deposited. The electrodes are washed with distilled water and dried at room temp and used for further studies.

### **(c)Urease Immobilization**

The immobilization of Urease on PANI / MnO<sub>2</sub>matrix on Stainless steel electrode was done using Physical Adsorption method. The electrodes were dipped in a pH 4 acetic acid solution, washed with water and then left overnight at 5<sup>0</sup> C in contact with an urease solution containing 2 mg of the enzyme (urease) per ml of pH 5.6 phosphate buffer. The next day, the membrane was washed with a pH 7 phosphate buffer solution. The prepared PANI/ MnO<sub>2</sub>/Urs electrodes will be always stored dry at 4<sup>0</sup> C [19].

### **(d) Cyclic voltammetry study**

A steel electrode, platinum wire and silver/silver chloride electrode have respectively been used as working, counter and reference electrodes. Potentiostat/Galvanostat (Model CHI600D Electrochemical Analyzer) has been used to record the cyclic voltammogram of the constructed biosensor under study.

*PANI/MnO<sub>2</sub> coated SS electrode:* For electropolymerization of aniline, different weight percentage of nanostructure MnO<sub>2</sub> (5%, 10% and 15%) were added in 1 M H<sub>2</sub>SO<sub>4</sub> containing of 0.4 M aniline. Then PANI/MnO<sub>2</sub>composite were electrochemically polymerized by applied potentials to Pt working electrode at 100 mV/s between the scanning potential -0.2 to 0.8 volt. For comparison, pure PANI was also polymerized in the same condition as mentioned above, but MnO<sub>2</sub> is not added in the polymerization electrolyte.



### ***(e) Chronoamperometric study***

A steel electrode, platinum wire and silver/silver chloride electrode have respectively been used as working, counter and reference electrodes. Potentiostat/Galvanostat (Model CHI600D Electrochemical Analyzer) has been used to record Chronoamperometry Curves of the conducting polymers and their nanocomposites under study. The fabricated PANI/MnO<sub>2</sub>/ Urease electrodes with different weight percentage of nanostructure (5%, 10% and 15%) were investigated in phosphate buffer solution (PBS). Chronoamperometric study was performed by immersing modified steel electrodes in PBS with constant stirring at 100 rpm [20]. Chronoamperometric scan was taken by biasing the electrode at 0.85 V vs Ag/AgCl reference electrode.

### **1.3 Results and discussion**

#### ***(a) Mechanism of PANI film formation by electropolymerization***

The voltammogram indicates oxidation proceeding on stainless steel surface in two stages. The anodic peak situated at more positive potentials ( $E_{pa} = +0.3$  V/S.C.E.) is particularly intense in the anodic branch of the first spinning cycle and can be attributed to the initial monomer oxidation. The dimer formation is the rate determining step, which is accompanied by the loss of an electron ( $e^-$ ) and of a proton for every aniline molecule increasing rate of polymer chain, of about  $10^4$  times higher than the initiation one [21]. The dimer is then oxidized in one step to the diiminequinoiden form, with participation of two electrons, due to its low oxidation potential in comparison with aniline. The redox couple situated within the range of less positive potentials has a progressive evolution (intensities of Voltammetric currents increase with increasing the number of scanning cycles) and might be attributed to the dimer and, subsequently, to the polymer forming on the stainless steel electrode surface [22]. In cyclic voltammetry studies, the “nucleation loop” commonly observed on the first scan is characteristic of conducting phase formation by a nucleation and growth mechanism [23]. From the **Figure 1** it is observed that, the anodic–cathodic peaks of the polymer (5<sup>th</sup> cycle onward) are narrower than anodic peak of monomer (1<sup>st</sup> cycle). This indicates that the charge transfer in the case of the monomer is small than in the case of the polymer. This will lead to high conductivity of the polymer layer formed at electrode surface. In the 5<sup>th</sup> cycle one oxidation peak is observed at 0.51 V vs Ag/AgCl which was related to the oxidation of aniline [24].



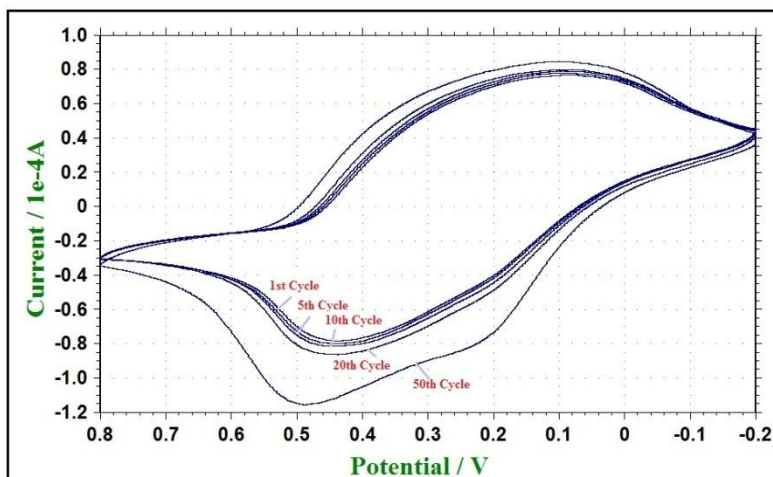


Figure 1: Growth of PANI on SS electrode.

**(b) Co-deposition of PANI/MnO<sub>2</sub> nanocomposites by cyclic voltammetry**

Figure 2 shows the voltammograms obtained during aniline polymerization in the presence of nanostructure MnO<sub>2</sub> 15% composition. The potential peak for aniline without MnO<sub>2</sub> shows significant difference which can be attributed to the incorporation of the anionic metal oxide into the polymer backbone, which favors the charge transference processes during the conducting polymer-metal oxide formation [25]. The formation of charged species such as Manganese-SO<sub>4</sub><sup>-</sup>, confirmed the monomer oxidation is the key to its electropolymerization, which would allow to obtain positive sites, and hence, the incorporation of the metal oxide into the polymer backbone [26-27].

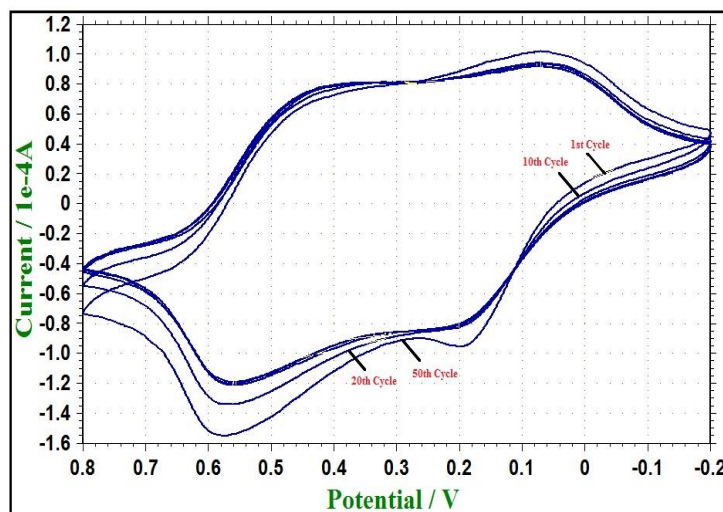
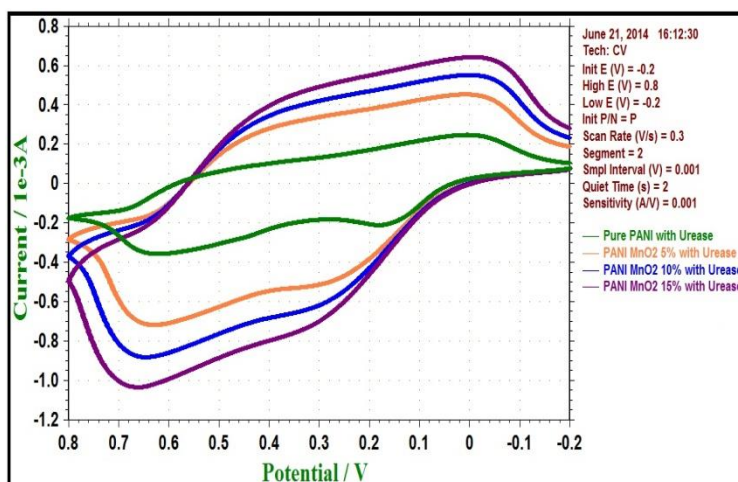


Figure 2: Growth of PANI/MnO<sub>2</sub> 15% on SS electrode

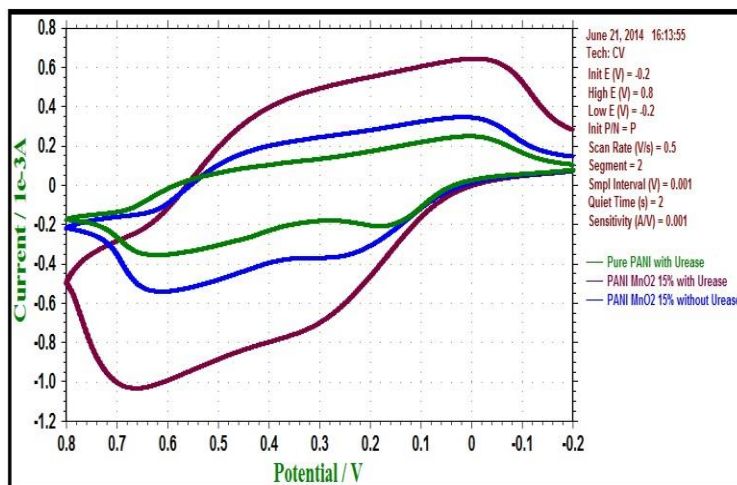
**(c) Cyclic Voltammetry of PANI/MnO<sub>2</sub>/Urease electrode:**

**Figure 3** shows the cyclic voltammograms of PANI/ MnO<sub>2</sub>/Urs electrode with 5%, 10% and 15% compositions in phosphate buffer solution. It was observed that potential reversals at the potential limits are fast and instantaneous. This suggests that the adsorption/desorption process of the ions are very fast during cycling. The oxidation current for PANI/MnO<sub>2</sub> nanocomposites was found to be increased with an increase in concentration of MnO<sub>2</sub>. Thus, conducting polyaniline having amine functional group can be utilized as a suitable matrix for the physical adsorption of urease [28].

The effect of Urease is shown in **Figure 4**, it can be seen that current is higher at higher urease concentration. This may be due to the increase in proton concentration in the electrolyte, which favors rapid protonation–deprotonation giving rise to larger currents [29].



**Figure 3:** CV of PANI/MnO<sub>2</sub>/Urease electrode



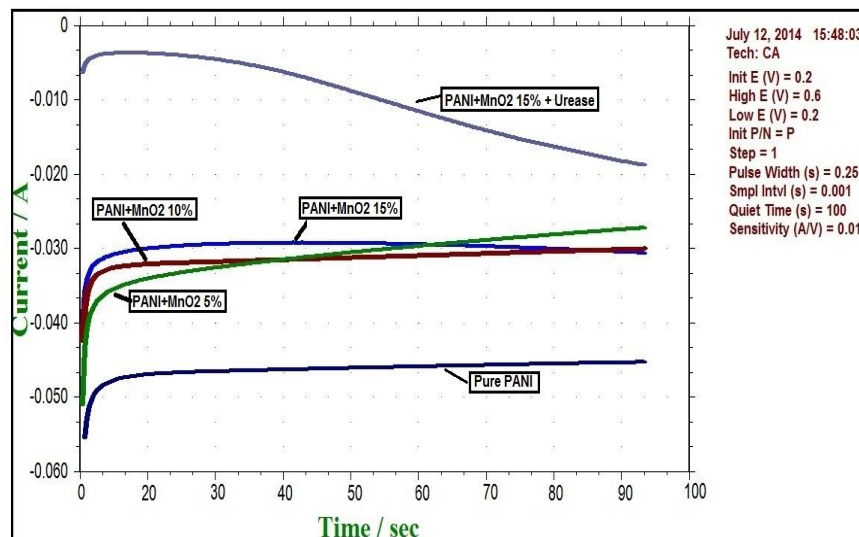
**Figure 4:**Effect of Urease on the PANI/MnO<sub>2</sub> 15% electrode surface.

**(d) Chronoamperometry of PANI/MnO<sub>2</sub>/Urease electrode**

**Figure 5** illustrates the chronoamperometric response of the Pure PANI, PANI/MnO<sub>2</sub> (5%, 10% and 15%) and PANI/ MnO<sub>2</sub>/Urease (15%) electrodes in the potential range 0.2 to 0.6 volt vs. reference electrode for time interval of 100 Sec in PBS of pH 7. The nature of the all curves for three weight percentage composition (5%, 10% and 15%) shows similar behavior. Thus increase in the MnO<sub>2</sub> weight percentage in the PANI matrix does not attribute towards the larger saturation current and hence does not guarantee for the fast electron transfer at the modified electrode surface.

The Chronoamperometry curve of PANI/ MnO<sub>2</sub>/Urease (15%) electrodes shows that the immobilization of urease on modified PANI/ MnO<sub>2</sub> (15%) film results in getting larger saturation current in the time of 10 sec. But the curve obtained was not stable for long time. Thus the PANI/ MnO<sub>2</sub> matrix showed degradation of the Urease from the electrode surface. This might be due to low Isoelectric point (IEP) of MnO<sub>2</sub> (4 to 5) compared to ZnO (9 to 9.5). The Isoelectric point is the value of pH at which the material become non-conducting [30].

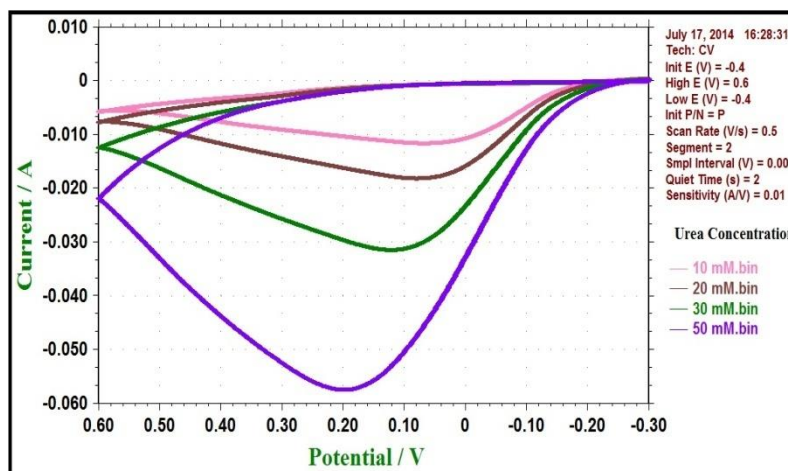




**Figure 5:** Chronoamperometry of PANI/MnO<sub>2</sub>/Urease electrode.

#### (e) Biosensor Response

It can be seen from **Figure 6** that the response current increased linearly with the addition of urea in the range of 10 mM to 50 mM which is due to the produced ammonium from the enzymatic reaction, then reached saturation. The results show that this biosensor exhibits an excellent response for urea at working potential of -0.3 V to 0.6 V.



**Figure 6:** Response of PANI/MnO<sub>2</sub>/Urease biosensor

#### 1.4 Conclusions

From the Cyclic voltammograms obtained for electropolymerization of aniline, it has been observed that the presence of MnO<sub>2</sub> changes the electrode behavior during the electropolymerization of aniline. The CV for PANI/MnO<sub>2</sub> shows that the potential reversals at



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the potential limits are fast and instantaneous. Thus the adsorption/desorption process of the ions are very fast during cycling. The oxidation current for PANI/MnO<sub>2</sub> nanocomposites was found to be increased with an increase in concentration of MnO<sub>2</sub>. The CV for PANI/MnO<sub>2</sub>/Urease shows that the current is higher at higher urease concentration, which favors rapid protonation–deprotonation giving rise to larger currents. Thus, conducting polyaniline having amine functional group can be utilized as a suitable matrix for the physical adsorption of urease. The Chronoamperometry curve of PANI/ MnO<sub>2</sub>/Urease (15%) electrodes shows that the immobilization of urease on modified PANI/ MnO<sub>2</sub> (15%) film results in getting larger saturation current in the time of 10 sec. But the curve obtained is not stable for long time. Thus the PANI/ MnO<sub>2</sub> matrix show degradation of the Urease from the electrode surface.

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