Voltammetric analysis of mercury ion on nano structured polyaniline doped 2, 5bis (4-methyl piperaz-1yl-methyl) 1, 4 hydroquinone modified Wax Impregnated Graphite Electrode.

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Abstract

Polyaniline doped 2, 5bis (4-methyl piperaz-1yl-methyl) 1, 4 hydroquinone (ligand+PANI) was electrochemically deposited on Wax Impregnated Graphite Electrode (WIGE) by cyclic voltammetry method. The deposition was confirmed from their characteristic peaks of the polyaniline and the ligand. The morphology of ligand+ PANI modified WIGE was investigated by scanning electron microscopy.Electrochemical methods are used to detect mecury ion and to investigate interactions of PANI doped ligand with mercury ion. The redox peak current for mercury ion is increased with scan rate which suggesting the redox reaction is diffusion controlled. The adsorption of mercury ion on PANI doped ligand modified WIGE can be distinguished by cyclic voltammetry. The level of their current response is proportional to their concentration leads to the determination of unknown concentration of metals. The optimum detection limit of 2x10⁻⁸M for mercury ion on PANI doped ligand modified WIGE was calculated by linear sweep voltammetry method. The diffusion co-efficient values for mercury ion on modified electrode were calculated from chronoamperometry and chronocoloumetry methods. The interference study shows a way, detect the heavy metal ions on modified electrode.

Key words: Cyclic Voltammetry, Chronoamprometry, Chronocoloumetry, nano material, sensor

1 Introduction

Conducting polymers like polyaniline (PANI) has been popular lately due to its high electrical conductivity [1], unusual and unique redox properties [2] and favorable environmental stability. It had been the object of numerous studies because of its excellent processability and the presence of a number of intrinsic redox states. It had found potential applications ranging from light-emitting diodes [3], sensors, electronic noses [4,5], electromagnetic shielding and military camouflage [6] to intelligent materials and anti-corrosion protection.

PANI has a variety of oxidation states that are dependent on both the pH and potential and these result to a number of forms that have different chemical and physical properties. Literature have shown that PANI has three common forms namely leucoemeraldine (LEB, fully reduced), emeraldine (EB, half-oxidised) and pernigraniline (PNB, fully oxidized) [7]. The emeraldine base (EB-PANI) can be doped by protonic acids (Bronsted acids) allowing the coordination of the protons with the imine nitrogen of Emeraldine Base (EB) to produce emeraldine salt (ES-PANI), the conducting form of PANI [8,9]. Protonic acid doping is the most useful way to achieve high conductivity since this lead to the charge delocalization on the polymer backbone that gave increased dc conducivity [10,11] and increased spin density [12].

Mercury is one of the most toxic of the environment, because of its high reactivity, extreme volatility and relative solubility in water and living tissues. It can have several effects on human health and organomercury compounds even at low concentrations. Therefore, the determination of mercury is necessary and urgent at trace levels [13]. Some analytical techniques have been employed in metal analysis, such as atomic absorption spectrometry (AAS) [14], X-ray fluorescence [15] or UV spectrophotometry [16]. But complicated preconcentrations or multisolvent extraction techniques are also coupled with these techniques because of the complexity of the real samples and the low concentration of the analyte. Electrochemical methods, in particular cyclic voltammetry (CV), is the most favourable techniques for the detection of metal ions because of its low cost, high sensitivity, easy and ability for carry out speciation analysis.

Chemically modified electrodes (CMEs) have received increasing attentions which improve the sensitivity and selectivity of electrochemical analysis techniques in the past decades [17]. A few articles discuss determination of mercury(II) ion by CMEs. The modifiers used include organic chelating groups [18,19], polymer [20-24], sol-gel and nano particles [25-28]. Several calixaranes derivations have been successfully employed in modified electrode for determination of mercury ion [29-31]. There is no literature survey about the polyaniline doped hydroquninone modified carbon electrodes.

Since polyaniline (emeraline salt) doped 2, 5bis (4-methyl piperaz-1yl-methyl) 1, 4 hydroquinone(ligand) possess functional groups with high affinity towards heavy metal ion, this study try to look at its application as modifiers of Wax Impregnated Graphite Electrode (WIGE). WIGE is one form of Chemically Modified Electrodes (CME) wherein a material (Polyaniline doped ligand) to increase the selectivity of the electrode. The fabricated polyaniline doped ligand modified WIGE (PANI +ligand modified WIGE) was then used in the voltammetric analysis of mercury ion in aqueous samples.

2 Experimetnal

2.1 Reagents and materials:

N-methyl piperazine (spectro chem.),formaldehyde solution(rankem), hydroquinone (Himedia), ethanol (CHINA),aniline (sd fine), hydrochloric acid (s-d fine chemicals) potassium nitrate (sd fine-chem), mercurous chloride (universal laboratories reagent), lead nitrate (Rankem), copper sulphate pentahydrate (Rankem),Cadmium Chloride. All chemicalswere of analytical grade and were used without further purification. All the standard solutions were prepared using triple distilled water.

2.2 Electrochemical equipment:

All electrochemical experiments were performed in potassium nitrate medium(0.5M, pH 2) with a 600D electrochemical analyzer (CH Instruments) using a conventional threeelectrode system. The working electrode was a glassy carbon electrode; the counter electrode was a platinum wire and Ag/AgCl electrode served as reference. Solutions were degassed with N_2 before each measurement and kept under a N_2 atmosphere during the entire experiments period. All experiments were performed thrice to get concordant value. All experiments were run at 25°C.

3 Results and Discussion

3.1 Fabrication of polyaniline doped ligand(LH_2Q) modified Wax Impregnated Graphite Electrode

The fabrication of WIGE was already described [32]. The synthesis of PANI film was carried out in a standard one-compartment three electrode cell with WIGE as working electrode, Ag/AgCl(sat.KCl soln) as reference electrode and Pt wire as counter electrode. The polymerisation reaction was carried out in 20ml of 1M HCl solution with 0.30M aniline monomer and electrode potentials were swept for 2.5 cycles between -0.2 to 1.0V at a scan rate of 25mV/s at room temperature (Fig.1).



Fig.1: Electropolymerisation of aniline from 0.1M HCl solution of 0.03M aniline solution in the potential range of -0.2V to 1.0V at 0.025mV/s with 2.5cyles.

3.2 Electrochemcial behaviour of PANI modified WIGE

The importance of deposition conditions on the ensuing structure and properties of conducting polymers has been demonstrated on numerous occasions [33]. It has been reported that a compact PANI film superimposed with a fibrillar structure can be obtained by cyclic potential sweep deposition from 0.3M aniline solution from 1M HCl solutions. The compact layer is formed in the early stage of deposition and is resistant to polymer degradation. In HCl

electrolytes, however instead of compact layer, a granular film of high porosity is produced[34]. The open structure allows the solution constituents to have better access of the polymer interior. Electrosynthesis of polyaniline was performed by potential cycling between -0.0 V and 0.8 V vs.Ag/AgCl/ sat. KCl [35]. The higher anodic switching potential, the higher is the current, time and the higher amount of radical cation is generated.

A typical conducting polymer, polyaniline (PANI), has an acid base equilibrium in aqueous solution because the polymeric backbone contains amine and imine nitrogen atoms [36]. Due to this acid-base equilibrium, the electric conductivity of the PANI significantly depends on the solution pH. In acidic solution, the PANI acts as an electric conductor because most of the amine and imine nitrogen atoms are positively charged, and cation radical species (polaron species) as charge carriers can continuously exist [37]. Unfortunately, however, the positively charged amine and imine nitrogen atoms decrease in solution pH and the PANI acts as an electric insulator in a less acidic solution whose pH exceeds 3.5, which is the pKa value of the PANI [38]. These characteristic results in negating several useful functions of the PANI. If the PANI was transformed into an electric conductor in a less acidic solution, pANI would be applicable in more fields such as biosensors than has already been applied. Despite this possibility, little attention has been paid to such a transformation. In a less acidic solution, most of the electrode reactions of the dissolved species do not occur on a PANI film-modified electrode because the PANI film acts as an electric insulator [36].

For all peaks the currents increase, indicating progressive polymerization and film formating. The anodic limit was not lowered after the initiation period. The polymerization process is more difficult than for aniline because polyaniline deposition is catalysed by polyaniline itself [39,40]. Thus at high concentration more than one redox peaks were appeared during polymerization of aniline. The stability of the radical-cation obtained by oxidation is affected by the substituents. The presence of the bulky electron-withdrawing –SO₃H side-group greatly reduces nucleophilicity and increases steric hindrance. Such a phenomenon has been associated with the steric and electronic effects of the substituents and was already observed for several cases in polyaniline [41]. But in our study there is less steric hindrance due to the chloride ions and enhancement of anodic and cathodic peaks in uniformly and indicates the deposition of PANI.

3.3 Fabrication of ligand+PANI modified WIGE

The synthesis and characterization of ligand was already described [32]. The electrochemical deposition of ligand was carried out in 20ml of 0.2% of HCl solution of ligand and electorde potentials were swept for 5cycles between -0.2 to 1.0V at a scan rate of 25mV/s at room temperature (Fig.2).



Fig.2 Electrochemical deposition of ligand on PANI modified WIGE in the potential range of - 0.2V to 1.0V at 0.025mV/s with 2.5cycles.

Interestingly, however, we found that only a few hydroquinones selectively permeate through the PANI film and reach the electrode substrate, and the redox current is evident even using a PANI film modified electrode [42]. If the selective permeation is due to an electronic affinity between the PANI and hydroquinones, the electric conductivity might be improved.

On PANI-coated electrodes, the hydroquninoe moiety in ligand redox reaction takes place in the emeraldine potential region, and one can assume that the following reactions take place:

$$LH_2Q \longrightarrow LQ + 2H^+ + 2e^-$$

$$EM^{2+} + 2e^- \xleftarrow{kf}{kb} LE$$

$$EM^{2+} + LH_2Q \longleftarrow Luo.E + LQ + 2H^+$$

According to the studies on polaron-bipolaron existence, the literature offers various possibilities [43-48], and there is evidence that the presence of anions in the solution, or the oxidation potential may influence pre-dominance of polaron or bipolaron. In view of polaron lattice, two LQH_2 molecules would sterically be more favourably accommodated at one

emeraldine unit than at bipolaran lattice. However, one emeraldine unit can exchange only two electrons in both cases, and one QH_2 molecule is required for the above reaction to proceed. Therefore, it seems plausible to accept the concept of Matveeva [49], according to which bipolaron form of PANI is engaged in the adsorption of QH_2 molecules. Thus, the overall reaction can be described in scheme 1.

The applied potential, depending on the polarisation direction, will direct the electron transfer and, therefore, the redox form of PANI. Emeraldine centres (EM^{2+}) during anodic polarisation oxidise hydroquinone moiety in ligand according to the above reactions, but at the same time EM^{2+} transforms into LE.



Scheme1: Mechanism for formation of charge transfer complex between the ligand and polyaniline.

3.4 SEM study

Fig. (3) shows micrograph of the ligand + PANI coating at the potential range of -0.2 to 0.8V. It was observed that the spherical layer exihibited a porous nano structure with micropores which were relatively well separated and homogeneously distributed over the surface. The size of the sperical particles on the modified surface is 35.6nm.



Fig.3. SEM image of the surface of ligand+PANI modified WIGE

3.5 pH study

The redox reactions of organic compounds are influenced by the acid-base properties of the solvents. For the reversible processes, the number of hydrogen ions participating in the reduction can be determined from the pH-independence of the standard potential or the voltammetric half wave potential [50].



Fig.4. Cyclic Voltammogram for 1mM Hg²⁺ ion on ligand+PANI modified WIGE at different pH's.

pН	Ipc x 10 ⁴	Ipa x 10 ⁴	Epc	Epa	$E_{1/2}$
	(A)	(A)	(V)	(V)	
2	-1.249	2.917	-0.0827	0.3056	0.1114
4	-1.233	2.033	-0.0883	0.2710	0.0914
6	-1.183	2.026	-0.1086	0.2511	0.0712
8	-1.181	1.219	-0.0712	0.2481	0.0884

Table.1 Cyclic Voltammetric parameters for 1mM Hg²⁺ ion on lignd+PANI modified WIGE at different pH's.

The electrochemical behavior of Hg(II) on ligand+PANI modified WIGE was characterized on the pH value of the aqueous solution. Therefore, we studied the electrochemical behavior of Hg(II) in buffered solutions with different pH values (2 < pH>8 at higher pH mercury forms hydroxide precipitate) at the surface of ligand+PANI modified WIGE by cyclic voltammetry (Fig.4). In all the cases, the ionic strength was adjusted by adding HCl and NaOH. As seen from Fig. the best choice for the ability to give the best shape and highest peak current was pH 2. Also, can be seen in table.1 the half wave potential, $E_{1/2}$ of Hg(II) was pH dependent. The total number of protons that also participates in the redox process of Hg(II) may vary in accordance with the pH range. Depending on the number of protons taking part in the redox process with two electron transfer, the $E_{1/2}$ will shift by -59.2mV/pH (2H⁺), -29.6 mV/pH (1H⁺), and 0.0mV/pH (without H⁺) [51].

In our study $E_{1/2}$ value shift by less than nearly 0.0mV/pH. So there are no protons transferred in the redox reaction in the pH range of 2.0-8.0. The results obtained show that the pH 2 is the optimum for electrochemical behavior of Hg(II) by ligand+PANI modified WIGE.

3.6 Sensing of mercury ion on ligand +PANI modified WIGE

The background current for the ligand+PANI modified WIGE is less compared to the bare WIGE in 0.5M KNO₃ makes the feasibility of the electrode as sensor. The absence of any electroactive materials was confirmed from the fig.5. This only means that mercury ions in general bind with the polyaniline prepared using different dopants. Studies have shown that polyaniline preconcentrated mercury ions and methyl mercury [52,]. A composite of polyaniline with polystryrene successfully removed mercury ions from aqueous solutions. Desorption experiments showed that the process of Hg(II) ion adsorption by polyaniline was almost irreversible and chemisorptive in nature [53]. The absorbtion of

mercury ion on Ligand+PANI modified WIGE is confirmed from appearance of characteristic peak at 0.2V and enhancing of peak current for sensor.



Fig.5: CV for a)bare WIGE in 0.5M KNO₃ medium b) ligand+PANI modified electrode in 0.5M KNO₃ medium ; CV for 1mM Hg^{2+} ion on a) bare WIGE, b) ligand modified WIGE, c) ligand +PANI modified WIGE in 0.5M KNO₃ medium.

Table:2 Cyclic Voltammetric parameters for 1mM Hg	²⁺ ion on different electrodes in 0.5M
KNO ₃ m medium at 140mV/s.	

Type of electrodes	Ipc x 10^4 (A)	Ipa x 10^4 (A)	Epc (V)	Epa (V)
Bare WIGE	-1.187	3.201	-0.0854	0.1509
Ligand modified	-	3.533	-	0.1989
WIGE				
Ligand+PANI	-	5.001	-	0.1802
modified WIGE				

Cyclic voltammogram shows that both the cathodic as well as anodic peaks are enhanced as compared to the unmodified one (Fig.5.). The cyclic voltammetric parameters for 1mM Hg^{2+} ion on different types of electrodes was shown in table.2. This happens due to increased uptake of mercury ions by the chemically modified electrode through complexation. The co-ordination attachment of ligand with Hg (II) forming a complex is evident by the peak separation and enhancement of peak current.

3.7 Scan rate effect

Voltammograms were recorded for 1mM Hg(II) solution on ligand+PANI modified WIGE at varying scan rates(Fig.6). The peak currents (Fig.7) for mercury ion increased linearly with the scan rate in the range of 100 to 180 mV/s. The linear regression equations are expressed as Ipa= $0.430v^{1/2}$ -0.607 which suggesting that the redox reaction of Hg(II)/Hg(0) is surface – adsorbed process. This is because that the surface-adsorbed process becomes the rate

determining step of of the electrode reaction. However, the Ipa of mercury ion on ligand +PANI modified WIGE was proportional to the scan rate from 100 to 180mV/s with a coefficiency of 0.997, demonstrating that the diffusion process of mercury redox system is slower than the surface adsorbed process and the electrode reactions of mercury ion is controlled by diffusion of mercury ions from the solution to the modified electrode. Also, a shift in peak potentials is observed with the value of $Ipa/v^{1/2}$ increasing with increase in scan rates (Table 3). This implies that the chemical step does not precede electron transfer. From the voltammetric data, it has been observed that: (i) Epa values didn't change with increase of scan rate, (ii) absence of reduction peak due to the formation of the stable complex. This shows that the process is irreversible involving two electron transfer.



Fig.(6) Cyclic Voltammogram for 1mM of Hg(II) ion on low concentration of PANI+ ligand modified WIGE at different scan rate in 0.5M KNO₃ medium. Fig.(7) A plot of Ipa Vs $v^{1/2}$.

Scan rate	Ipa	Epa/V	Ipc	Epc/V	Ipa/V ^{1/2}		
(mV/s)	$x 10^4 A$		$x 10^4 A$				
100	3.737	0.2021	-1.681	0.0275	0.3737		
120	4.084	0.2021	-2.292	0.0296	0.3728		
140	4.459	0.2021	-2.563	0.0267	0.3768		
160	4.840	0.2050	-2.814	0.0296	0.3826		
180	5.200	0.2050	-3.075	0.0152	0.3876		

Table.3 Effect of scan rate on the behaviour of ligand + PANI modified WIGE for 1mM Ha(II) in 0.5M KNO₃ medium.

3.8 Effect of concentration

Fig.(8) shows the cyclic voltammogram and calibration curve of Hg(II) in different concentrations (1 mM to 5mM) in 0.5M KNO₃ respectively. At lower concentration no reduction

peak and at higher concentration two reduction peaks were found. This is due to the presence of following reaction was present at higher concentrations. Hg(II) + e- Hg(I) and Hg(I) + e- Hg(0). The cyclic voltammetric parameters were tabulated in table.4. The calibration plot (Fig.9) for Hg(II) was performed at the ligand+PANI modified WIGE Hg(II) solutions with a good linearity of anodic current versus concentration described by the linear regression equation Ipa = 0.473C+3.717 R²=0.983. The linearity of this equation shows that the redox process is diffusion controlled one.





Fig.(9)

Fig.(8) Cyclic voltammogram for different concentrations of Hg(II) ion ligand+PANI modified WIGE at 120mV/s in 0.5M KNO₃ medium. Fig.(9) A plot of Ipa Vs Conc.

Table 4. Cyclic Voltammetric parameters for different concentrations of Hg(II) ion on ligand+PANI modified WIGE at 120mV/s.

Conc.	lpc ¹	lpc ²	lpa¹	lpa ²	Epc ¹	Epc ²	Epa¹	Epa ²
(mM)	X 104	X 104	X 104	X 104	(V)	(V)	(V)	(V)
1	-	-	-	4.084	-	-	-	0.2021
2	-2.541	-3.041	2.375	4.729	0.0208	-0.6550	0.6218	0.2021
3	-2.777	-3.143	2.448	5.221	0.0325	-0.6433	0.6218	0.2021
4	-3.098	-3.281	2.540	5.679	0.0352	-0.6492	0.6306	0.2050
5	-3.236	-3.373	2.677	5.977	0.0469	-0.6492	0.6336	0.2050

3.9 Interference effect

Fig.(10) shows the cyclic voltammograms of Pb(II), Cu(II), Cd(II) and Hg(II) in their mixture on ligand +PANI modified WIGE and bare WIGE. The redox peaks of the three metal ions overlapped on bare WIGE (curve a), and the peak current is much lower than that on the ligand + PANI modified WIGE (curve b). At the ligand +PANI modified WIGE, four oxidation peaks appear obviously at about -0.75V (Cd), -0.43V (Pb), 0.04V (Cu) and 0.4V (Hg). This result demonstrated that the anodic peaks of Cd(II), Cu(II), Pb(II) and Hg(II) are well separated from each other on the ligand +PANI modified WIGE. Hence, it is possible to simultaneously detect Cd(II), Cu(II), Pb(II) and Hg(II) on the ligand +PANI modified WIGE. The presence of copper is highly interfered with the other heavy metal ions, even in nano molar level [54]. The nitrogen containing ligands are more preferable to form complex with copper as compared with mercury [55]. But in this study the presence of copper could not affect the oxidation peaks of the mercury on ligand+PANI modified WIGE.



Fig.(10) Cyclic Voltammogram for 1mM Pb(II), 1mM Cu(II), 1mM Cd(II) and 1mM Hg(II) on ligand modified WIGE in 0.5M KNO₃ at 120mV/s.

3.10 Optimum limit

Fig.11 shows the linear sweep voltammogram for Hg(II) in different concentrations $(2 \times 10^{-8} \text{M to } 2 \times 10^{-7} \text{M})$ in 0.5M KNO₃ respectively. The calibration plot (Fig. 12) for Hg(II) was performed at the ligand+PANI modified WIGE. Hg(II) solutions with a good linearity of anodic current versus concentration described by the linear regression equation Ipc= 0.011C-1.896 R²=0.887. The linearity of this equation shows that the redox process is diffusion controlled one. The detection limit of the method based on ligand+PANI modified WIGE for determination Hg(II) ion was found to be 2 x 10⁻⁸ M by linear sweep voltammetry.



Fig.11 Linear sweep voltammogram for different concentrations of 2 x 10^{-8} M to 2 x 10^{-7} M KNO₃ medium on low conc.PANI+ligand WIGE. Fig.12. A plot of Ipa Vs Conc.

3.11 Chronoamperometry and chroncoloumetry study

Fig (13) the monotonous rising and decaying current transient in accordance to the theoretical expectation of the cottrell equation [56,57]. Based on the diffusion process to a planar electrode, diffusion coefficient was determined for different concentrations of Hg(II) ion in 0.5M KNO₃ solution by chronoampermetry and chronocoloumetry methods and the parameters were tabulated in table.5, It was found that the current amount of charge transferred in Hg(II) is increased with increasing concentration. This shows that Hg(II) ions are more reducible on ligand + PANI modified WIGE as in Figure.(14).



Fig.(13,14) Chronoamperomogram and chronocoloumogram for different concentrations of Hg(II) ion on ligand+PANI modified WIGE respectively.

Table.5. Diffusion coefficient parameters for different concentrations of Hg(II) ion on ligand+PANI modified WIGE calculated by chronoamperometry and chronocoloumetry methods.

Chronoamperometry method			Chronocoloumetry method		
Conc.(mM)	Diffusion	Diffusion	Conc.	Diffusion	Diffusion
	coefficient	coeffcient	(mM)	coefficient	coeffcient
	$(Df cm^{-2}s^{1})$	$(Dr cm^{-2}s^1)$		$(Df cm^{-2}s^{1})$	$(Dr \ cm^{-2}s^1)$
	$x 10^3$	$x \ 10^2$		$x 10^3$	$x 10^3$
1	11.52	1.6931	1	1.592	2.335
2	2.864	0.4258	2	0.4977	0.6441
3	1.279	0.1908	3	0.2449	0.2943
4	0.7096	0.1039	4	0.1568	0.1682
5	0.6651	0.0798	5	0.1137	0.1143

Df – Diffusion coefficient value for forward scan; Dr – Diffusion coefficient value for reverse scan.

4 Conclusion

Sensing of mercury ion by polyaniline doped 2, 5bis (4-methyl piperaz-1yl-methyl) 1, 4 hydroquinone was proved by cyclic voltammetry method. This modified electrode is useful for detection of mercury ion in trace level. Nano structured nature of the particles on the electrode surface was confirmed from the scanning electron microscopy results. The diffusion controlled redox reaction for mercury ion was confirmed from scan rate effect, concentration effect, chronocoloumetry and chronoamperometry results. The interference study shows that ligand+PANI modified WIGE is useful for simultaneously detection of lead, cadmium, copper and mercury ion.

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