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### Heavy Metal ions Detection in real samples by using Polyaniline doped 2, 6bis (4-methyl piperazin-1yl-methyl)-1, 4hydroquinone Wax Impregnated Graphite Electrode

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2,6bis(4-methyl piperazin-1yl-methyl)-1,4hydroquinone (ligand) + Polyaniline (PANI) Wax Impregnated Graphite Electrode is used for analysis of equimolar mixture of  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  ions in the interference study at pH 4. Similar procedure is applied for the analysis of heavy metal ions in real samples such as tap water, rubber industry effluent and dye industry effluent by using cyclic voltammetry and differential pulse anodic stripping voltammetry techniques.

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*Keyword:* Interference study, Cyclic Voltammetry, Differential Pulse-Anodic Stripping Voltammetry, Heavy Metal ions, Effluent Study.

#### 1. Introduction

Heavy metal pollution, always caused by the waste streams of many industries, such as metal plating facilities, mining operations, and tanneries, has become a serious threat to human health, living resources, and ecological systems. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders to the nervous, immune, reproductive and gastrointestinal systems<sup>[1]</sup>. Thus, different sensitive methods have been developed to the simultaneous determination of heavy metals. The typical methods for the simultaneous analysis include X-ray fluorescence spectrometry (XRF)<sup>[2]</sup> and atomic absorption spectrometry (AAS)<sup>[3]</sup> However, time consuming process, high cost of maintenance, expensive and sophisticated instruments severely restrict their practical applications. Electrochemical method is one of the most favourable techniques for the determination of environmental pollutants

because of its low cost, high sensitivity and easy operation. Among different electrochemical methods, anodic stripping voltammetry (ASV) has been proved to be a simple and effective method for the determination of heavy metal ions. Traditional working electrodes for simultaneously voltammetric determination were generally based on a hanging drop mercury electrode (HDME)<sup>[4]</sup>. However, the toxicity of Hg and its precursors made these materials undesirable for disposable in situ sensing applications. Therefore, various mercury free electrodes including bismuth film electrode<sup>[5]</sup> gold-coated electrode<sup>[6]</sup> carbon paste electrode (CPE)<sup>[7]</sup> and glassy carbon electrode<sup>[8]</sup> were applied for sensitive metal determinations. In the fabrication of these modified electrodes, Wax Impregnated Graphite Electrode (WIGE) was usually preferred for its low cost and simple preparation procedure. In this study ligand+PANI modified WIGE is used for simultaneous detection of heavy metal ions.

## 2 Materials and Methods

### 2.a Reagents

N-methyl piperazine, formaldehyde solution, hydroquinone, ethanol, aniline, acetate buffer, potassium chloride, copper sulphate, mercurous sulphate, lead nitrate, cadmium chloride. All chemicals are of analytical grade and are used without further purification. All solutions are prepared with triple distilled water.

### 2.b Apparatus

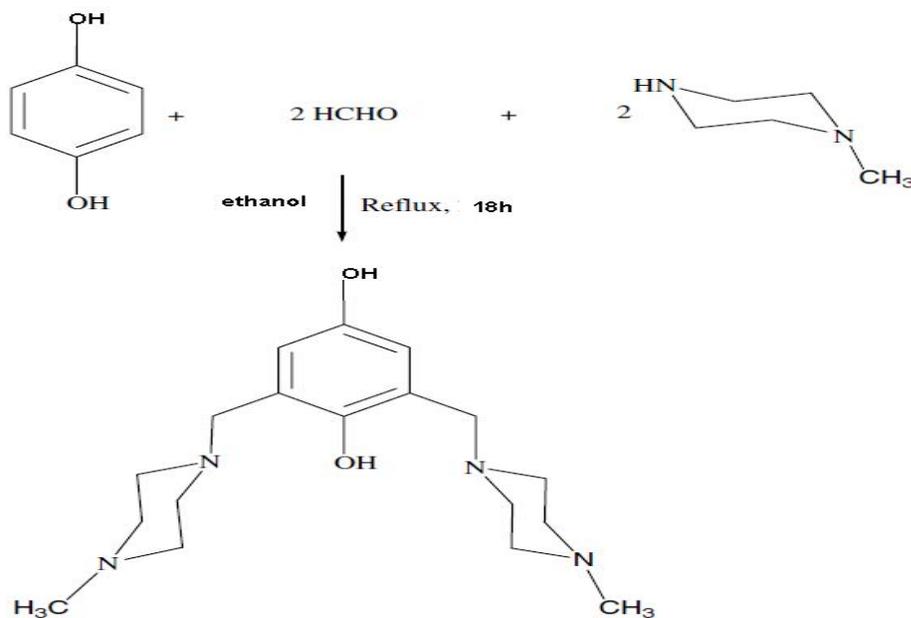
Cyclic Voltammetry (CV) and differential pulse-anodic stripping voltammetry (DPASV) are performed with a CHI 720C electrochemical workstation (CH Instruments, Austin, USA). The working electrode is a wax impregnated graphite electrode (WIGE, 3mm in diameter). An Ag/AgCl (saturated KCl) electrode and platinum wire are used as the reference electrode and counter electrode, respectively. All electrochemical experiments are carried out in a

single compartment electrochemical cell at room temperature.

## 3 Results and Discussion

### 3.a Synthesis of 2,6bis(4-methyl piperazin-1yl-methyl)-1,4hydroquinone(ligand L)

The ligand is synthesized by taking mixture of formaldehyde solution (3.5ml, 0.035mol), N-methyl piperazine (3.8ml, 0.035mol) in ethanol (15ml) and 5ml of glacial acetic acid and stirred for 24hours. Then p-hydroxy phenol (2g, 0.017mol) in ethanol (10ml) solution is added and stirred for 12hours. The resulting solution is refluxed in oil bath at 50°C for 18hours. The excess of ethanol is evaporated and allow the mixture to stand for 24hours. The brown colour solid is obtained. The crude sample is recrystallized from ethanol. The scheme of the reaction is presented in Fig.1.



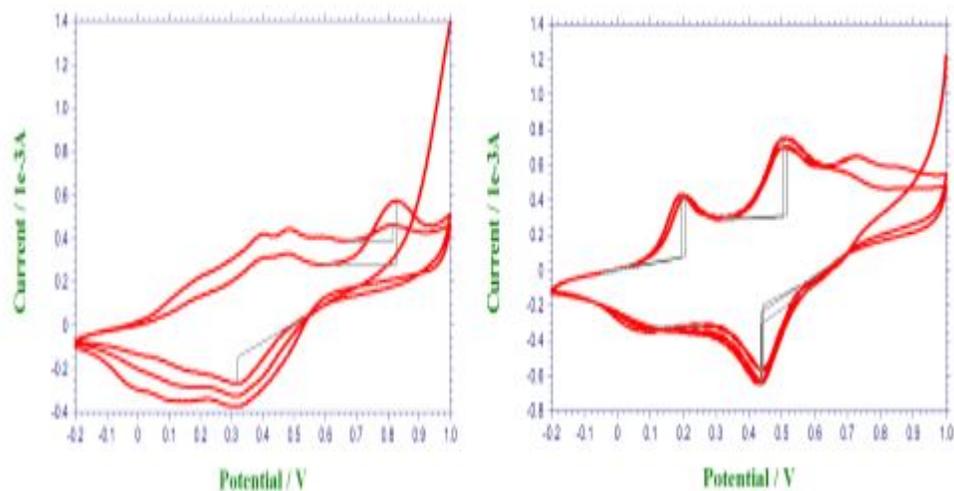
**Fig 1:** Scheme for the synthesis of 2,6bis(4-methyl piperazin-1yl-methyl)1,4hydroquinone

### 3.b Fabrication of 2,6bis(4-methyl piperazin-1yl-methyl)-1,4hydroquinone (ligand) + Polyaniline (PANI) Wax Impregnated Graphite Electrode.

The polymerisation reaction is carried out in 20ml of 0.1M HCl solution with 0.3M aniline monomer and electrode potentials are swept for 2.5cycles between -0.2 to 1.0V at a scan rate of 25mV/s at room temperature for all the peaks

current value increase, indicating progressive polymerization and film formatting. The cyclic voltammogram for the polymerization of aniline is shown in Fig.2. The electrochemical deposition of ligand on PANI modified WIGE is carried out

in 20ml of 0.2% of HCl solution of ligand and electrode potentials are swept for 2.5cycles between -0.2 to 1.0V at a scan rate of 25mV/s at room temperature (Fig.3).

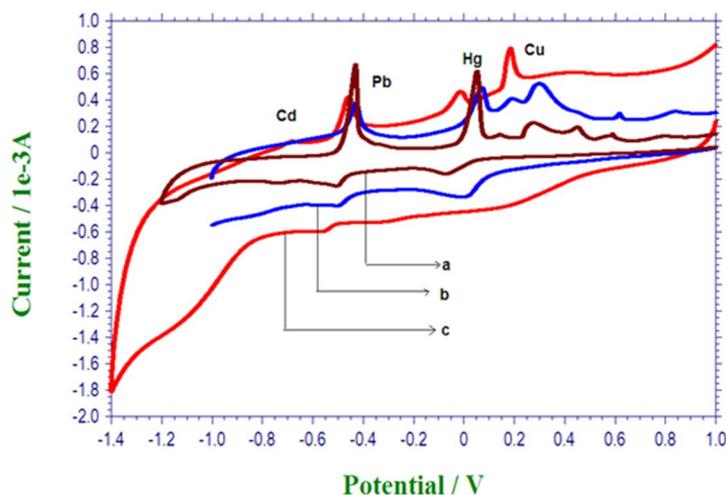


**Fig 2:** Electrochemical polymerization of aniline on WIGE from 0.1M HCl solution with 0.3M aniline solution in the potential range of -0.2V to 1V at 25mV/s with 5cycles. **Fig.3** Electrochemical deposition of ligand on PANI modified WIGE was carried out in 20ml of 0.2% of HCl solution of ligand and electrode potentials were swept for 2.5cycles between -0.2 to 1.0V at a scan rate of 25mV/s at room temperature.

### 3. C Interference study

Fig.4 shows that cyclic voltammogram for mixture of 1mM Zn(II), 1mM Cd(II), 1mM Pb(II), 1mM Cu(II) and 1mM Hg(II) ions on A) bare WIGE, B) ligand modified WIGE, C) ligand+PANI modified WIGE in nitrate medium at pH 4. The peak intensity of copper ion is enhanced as compared to the other metal ions on

ligand+PANI modified WIGE. On bare WIGE complicated peaks are appeared for metal ions may be due to the formation of oxides of metal ions on bare WIGE. But on ligand+PANI modified WIGE well separated peaks for metal ions are appeared.

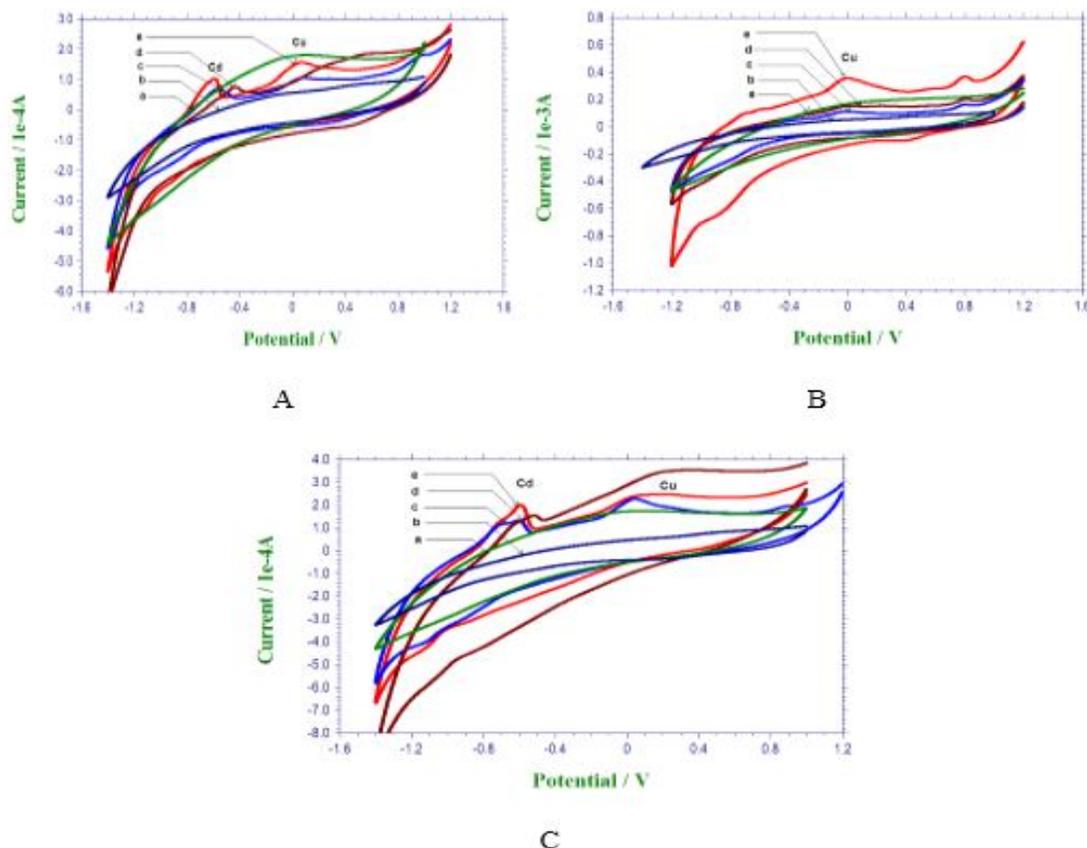


**Fig 4:** Cyclic Voltammogram for 1mM Cd<sup>2+</sup>, 1mM Pb<sup>2+</sup>, 1mM Hg<sup>2+</sup>, 1mM Zn<sup>2+</sup> and 1mM Cu<sup>2+</sup> ions on a) bare WIGE b) ligand modified WIGE c) ligand +PANI modified WIGE at 140mV/s at pH.4.

Hence, it is possible to simultaneously detect Cd(II), Cu(II), Pb(II) and Hg(II) on nano structured ligand +PANI modified WIGE. The presence of copper is highly interfered with the other heavy metal ions, even in nano molar level<sup>9</sup>. The nitrogen containing ligands are more preferable to form complex with copper as compared with mercury<sup>10</sup>. According to HSAB (Hard and Soft Acids and Bases) theory, the N-methyl piperazine is a kind of hard base, while the Cu(II) is beyond border line acid, and then it can be adsorbed onto the surface of ligand modified WIGE. Ligand +PANI modified WIGE has special selection of Cu(II) even in presence of Pb(II) and Hg(II). Symmetrical ligands has special selective and sensitive on copper ion which is proved from the results<sup>11</sup>. Thus nano structured ligand +PANI modified WIGE behave as a copper ion selective electrode.

### 3. d Cyclic Voltammetric analysis of tap water, rubber industry and dye industry effluent

Cyclic voltammogram for tap water, rubber industry effluent and dye industry effluent are performed by taking the 10ml real sample and 10ml on 0.5M KNO<sub>3</sub> solution and the pH of the solution is adjusted to 4 by addition of HCl acid or NaOH. At high pH most heavy metal ions form hydroxide precipitate. Thus pH 4 is used for analytical purpose. Cyclic Voltammogram for 0.5M KNO<sub>3</sub> medium on bare a)WIGE b) ligand+PANI modified WIGE are shown in fig.5(A-C). It show that electrode surface have not any metal ions. Cyclic Voltammogram for tap water, rubber industry effluent and dye industry effluent on c) bare WIGE, d) ligand modified WIGE e) ligand+PANI modified WIGE are shown in figs.5 (A-C).



**Fig 5:** Cyclic Voltammogram for 0.5M KNO<sub>3</sub> medium on a) bare WIGE b) ligand+PANI modified WIGE. Cyclic Voltammogram for A) tap water B) rubber industry effluent C) dye industry effluent on c) bare WIGE d) ligand modified WIGE e) ligand+ PANI modified WIGE at pH4.

It shows that electrode surfaces have not any metal ions. Cyclic Voltammogram for tap water, rubber industry effluent and dye industry effluent on c) bare WIGE, d) ligand modified WIGE e) ligand+PANI modified WIGE are shown in figs.5 (A-C). It suggests that ligand +PANI modified WIGE is highly sensitive towards copper ion even in presence of lead, cadmium and mercury ions in all the real samples. The presence of lead, mercury, copper ions in real samples is confirmed from the OCP-Emission Spectroscopy results. Therefore, the ligand+PANI modified WIGE can provide effective method for detection of copper ion in real samples.

### 3.e Differential Pulse-Anodic Stripping Voltammetry (DPASV) analysis of dye industry effluent

The electrochemical cell used a three electrode configuration, consisting of ligand+PANI modified WIGE, Ag/AgCl (filled with 1M KCl) reference electrode and platinum wire counter electrode. For stripping analysis, there are two main steps: accumulation and stripping. The accumulation time or deposition time  $t_d$  was 240s for all of the metal depositions unless specified otherwise. After depositing metals on

ligand+PANI modified WIGE, the reduced metals are stripped by using Differential Pulse Voltammetry. Differential Pulse Voltammetry parameters: Initial potential = -1.2V; Final potential = 1.4V; Amplitude = 0.05V; pulse width = 0.07sec; sampling width = 0.0167sec; pulse period = 0.25sec. The stripping peak currents are used to quantify the metals after baseline correction. The stripping peak potentials are used to assign the metals.

Fig.6 shows Differential Pulse Anodic Stripping Voltammogram at ligand+PANI modified WIGE for the detection of heavy metal ions in dye industry effluent at pH 4.5 in different deposition time. Sharp stripping peaks are obtained for Cu, broad stripping peak is observed for other heavy metals and the metals have distinctive stripping potentials  $E_{p,Cd} = 685\text{mV}$ ;  $E_{p,Cu} = 66\text{mV}$ ;  $E_{p,Pb} = 180\text{mV}$ ; single peaks are obtained for  $\text{Pb}^{2+}$  &  $\text{Cd}^{2+}$ , whereas some broad peaks between -400mV and -800mV and a shoulder to the left of the main peak are obtained for  $\text{Cu}^{2+}$ . These broad peaks do not increase or decrease very much with changes in deposition time. A single peak for copper stripping is obtained at the WIGE with ligand+PANI.

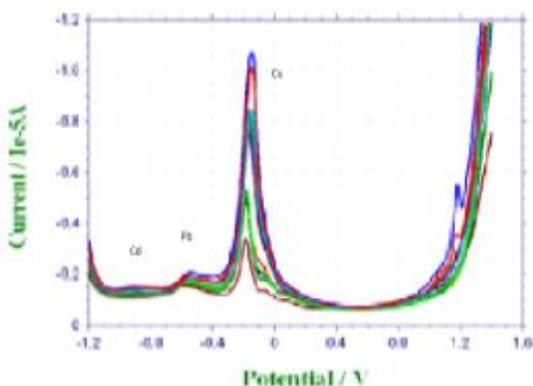


Fig.6

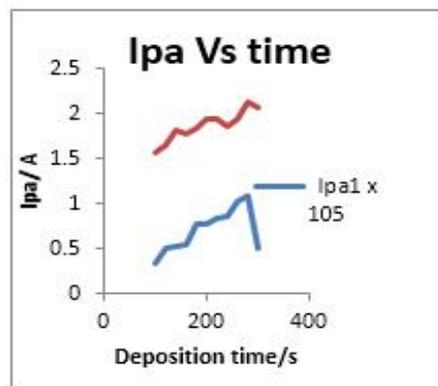


Fig.7

Fig 6: Differential pulse-anodic stripping voltammogram for dye industry effluent on ligand+PANI modified WIGE at different time in the range of 100, 120, 140... 300s at pH 4.5. Fig.7 A plot of Ipa Vs deposition time.

Earlier voltammetric studies indicate that the electrochemical behaviour of  $\text{Cu}^{2+}$  in water depends strongly on the presence of ligands such as chloride and ammonia<sup>[12]</sup>. Generally, the shoulder peaks of  $\text{Cu}^{2+}$  stripping can be positive

or negative of the main wave of  $\text{Cu}^{+}$  depending on the ligands<sup>[13]</sup>. Waves between -0.2 and -0.4V vs. SCE were reported for detecting copper in alcohol where the waves were attributed to copper-lead interactions where lead concentration

can be as high as micromolar <sup>[14]</sup>. The broad peaks between -400mV and -800mV results from the presence of trace metal residues from prior determinations, while the shoulder peaks are characteristics for Cu detection.

The effects of deposition potentials in the range from -0.8 upto -1.5V on metal stripping signals are studied. High peak current is observed at the potential of -1.4V <sup>[15]</sup>. The dependence of the differential pulse anodic stripping current on the accumulation time is examined. As expected for anodic stripping experiment the peak current increased with increasing accumulation time. From the plot (Fig.7) deposition time longer than 280s the stripping signals became almost constant. Because the accumulation time depends on the analyte concentration, it takes longer for the peak current to level off at lower concentrations of metal ions. On the other hand, at higher concentrations the rate of the metal ion uptake is faster and the binding sites of the modified electrode can be saturated during short time <sup>[16]</sup>. Thus the measurement range can be controlled by the adequate selection of the preconcentration time.

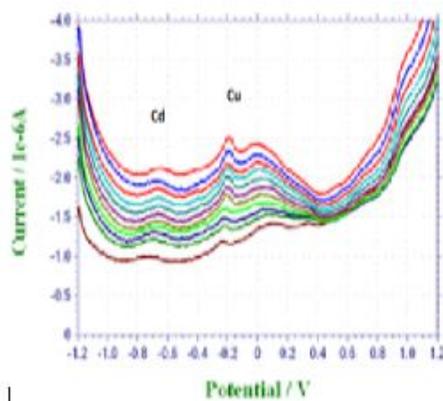


Fig.8

**Fig 8:** Differential pulse-anodic stripping voltammogram for rubber industry effluent on ligand+PANI modified WIGE at different time in the range of 100, 120, 140... 300s at pH 4.5. Fig.9 A plot of Ipa Vs deposition time.

### 3.f Differential Pulse-Anodic Stripping Voltammetry (DPASV) analysis of rubber industry effluent

Fig.8 shows Differential Pulse Anodic Stripping Voltammogram at ligand+PANI modified WIGE for the detection of heavy metal ions in rubber industry effluent at pH 4.5 in different deposition time. Sharp stripping peaks are obtained for Cu, broad stripping peak is observed for other heavy metals and the metals have distinctive stripping potentials  $E_{p,Cd} = 685\text{mV}$ ;  $E_{p,Cu} = 66\text{mV}$ ; single peak is obtained for  $\text{Cd}^{2+}$ , whereas some broad peaks between -400mV and -800mV and a shoulder to the left of the main peak are obtained for  $\text{Cu}^{2+}$ . These broad peaks do not increase or decrease very much with changes in deposition time. A single peak for copper stripping is obtained at the WIGE with ligand+PANI. The dependence of the differential pulse anodic stripping current on the accumulation time is examined. As expected for anodic stripping experiment the peak current increased with increasing accumulation time. From the plot (Fig.9) deposition time longer than 240s the stripping signals became almost constant.

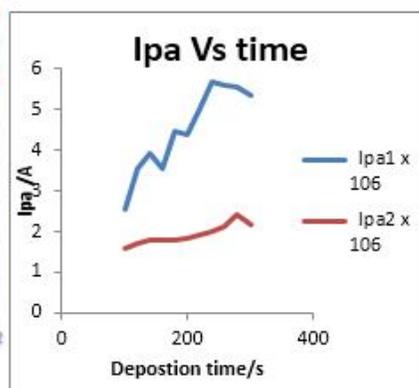


Fig.9

### 3.g Sensing of metal ions in real samples by ligand+PANI

From the figs.(10,11) sensitivity of the ligand is observed from enhance of peak current as compared to the unmodified one in dye industry

and rubber industry effluent respectively. Thus the presence of heavy metal ions could be detected in simultaneously by using ligand+PANI modified WIGE

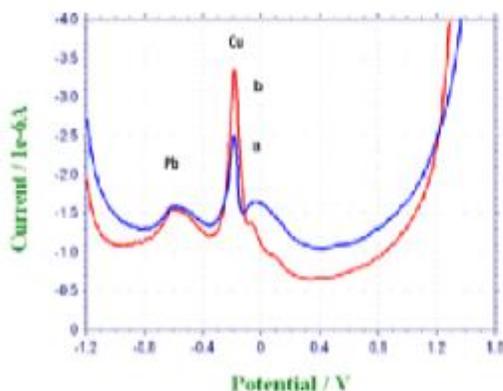


Fig.10

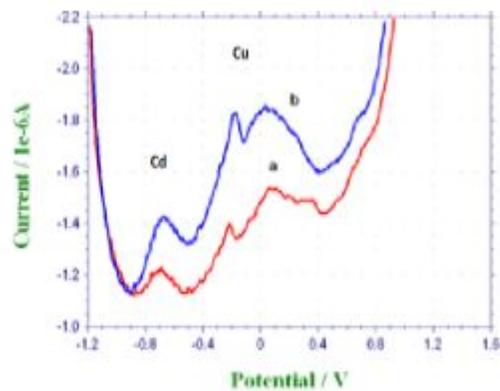


Fig.11

**Fig 10:** Differential pulse voltammogram for dye industry effluent on a)bare WIGE b) Polyaniline+ligand modified WIGE at pH 4.5  $t_{\text{deposition}} = 280\text{s}$ . **Fig.11** Differential pulse voltammogram for rubber industry effluent on a)bare WIGE b) polyaniline+ligand modified WIGE at pH 4.5  $t_{\text{deposition}} = 240\text{s}$ .

#### 4. Conclusion

The interference study shows that ligand +PANI modified WIGE is highly sensitive towards copper ion even in presence of lead, cadmium and mercury ions. The peak currents for the  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  ions in the real samples are enhanced as compared to the bare electrode. Thus the ligand is useful for easier detection of the heavy metal ions in real samples. Both the cyclic voltammetry and differential pulse anodic stripping voltammetry techniques proved that sensing of ligand on copper ion in real samples. Because symmetrical ligands are easily complexed with copper ion.

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