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ELECTROCHEMICAL SELECTIVE DETECTION OF CADMIUM AND MERCURY ON BENZYLPYRAZOLYL NAPHTHOQUINONE MODIFIED WAX IMPREGNATED GRAPHITE ELECTRODE

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Abstract

A sensor probe has been synthesized with a facile one-pot reaction of molecules of 2-hydroxynaphthoquinone, P-Chlorobenzaldehyde and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one in water condition. These molecules were isolated as enol tautomers that exhibit intramolecular hydrogen bondMercury ion, Hg(II), has attracted extensive attention due to its highly toxic and bioaccumulative properties. As a result, this new phenyl benzopyrazole moiety is suited for use as a sensitive and selective “turn on” electrochemical sensor for Hg(II) ion.

Introduction

Heavy metal ions are natural components of Earth’s crust. Their content in soil varies from very low (femtograms) to high (milligrams). However due to anthropogenic activities their content can be elevated at the site of the action. High concentrations of heavy metal ions can injure human health and pollute the environment. It is a common knowledge that toxic heavy metal ions (lead, cadmium and mercury) are able to enter organisms and interfere with several important metabolic processes. The presence of toxic ions in a plant cell damages homeostasis, transpiration, etc. [1]. The result is that the plant lives and develops in the polluted environment and, moreover, accumulates the heavy metal ions in its tissues. If such plants are harvested, the foodstuffs derived from them may pose a threat to animal and human health [2, 3]. Due to the above-mentioned facts the development of simple analytical instruments, methods and procedures with low detection limits are needed [4]. Analytical methods and instruments for detection of cadmium(II) [5-7] and lead(II) [8-9] ions have been reviewed several times. Electrochemical ones are among the very sensitive analytical methods available for detection of heavy metal ions [10-12]. The classic instrument consists of a potentiostat/galvanostat with an electrochemical cell including three electrodes (working, reference and auxiliary). However the current trend of analytical techniques is to miniaturize the whole instrument due to the many advantages of small devices including portability, low costs and less demands on service and operations, sufficient sensitivity and selectivity [13, 14]. As the working electrode, a hanging mercury drop electrode (HMDE) is commonly used [15]. The HMDE can be also modified with biologically active substances to improve the sensitivity or selectivity of heavy metal ion detection [16, 17]. Due to the adverse effects of Hg(II) and many restrictions for usage of this metal, carbon electrodes have been promoted as an alternative [18, 19]. Moreover, in the miniaturization of whole instruments, carbon electrodes have many advantages compared to HMDE. Screen-printed carbon electrodes belong to the most suitable carbon electrodes for in situ environmental analysis [20, 21]. Besides the electrodes, the potentiostat controlling the electrode system also has to be miniaturized, portable and easy-to-use.

Mercury ion, Hg(II), has attracted extensive attention due to its highly toxic and bioaccumulative properties, possibly causing brain damage and other chronic diseases [22–24]. Therefore, it is urgently required to monitor and determine trace Hg(II) timely and accurately by developing highly sensitive and selective electrochemistry methods [25], etc. Compared with the above other ones, electrochemical methods simultaneously possess many advantages such as convenient and simple operation, rapid completion, low consumption, high sensitivity and selectivity, as well as possible application in field tests and on-site monitoring [26, 27]. As reported, anodic stripping voltammetry is mostly employed for heavy metal ions [28].

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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Cadmium is one of the most toxic heavy metals of prime environmental and health concern. This is evidenced by its incorporation in the initial priority metals established from the stand point of potential hazard to human health [29,30]. The FAO /WHO joint report committee on food additives has recommended a provisional maximum tolerable daily intake for cadmium from all sources generally 1-1.2 μg/kg of body mass[31].

Several papers [32, 33] have been published for Cd(II) reduction in aqueous media. Frischmann et al in their a.c. polarographic studies explained the abnormally high current and symmetric shape of the peak. These are typical of an electroactive reagent weakly adsorbed at the potential of the peak and they gave α and Ks values for different supporting electrolytes viz. 0.5M Na_2SO_4, 0.5M H_2SO_4, 1M H_2SO_4, 1M $NaClO_4$,1M KNO_3 , 1M HCl, 1M NaCl, and 1M KCl. The transfer coefficient values were 0.31 and 0.44 for 0.1M $NaClO_4$ and 0.1M KCl. The heterogeneous rate constants Ks is 0.34 and 1.2 for 0.1M $NaClO_4$ and 0.1M KCl respectively. Frumkin et al [34] reported the heterogeneous rate constant of the Cd(II) in aqueous sulphate, nitrate and perchlorate and chloride media.

The aim of this work was to utilize and compare electrochemical instruments for the easy and sensitive determination of heavy metal ions. The instruments were further employed to analyse real samples.

Materials and methods

Reagents

2-hydroxy naphthoquinone, P-Chlorobenzaldehyde, 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one, ethanol, Ammounium fluride, potassium chloride, copper sulphate, mecurous chloride, cadmium chloride, manganeous sulphate.

Materials and Methods

Electrochemical workstations of CHI. USA: Model 600D with potentiostate driven by electroanalytical measuring softwares is connected to PC computer to perform cyclic voltammetry (CV). An Ag/AgCl (3M KCl) and platinum wire are used as a reference and counter electrode respectively.

Polishing of Glassy Carbon Electrode

The glassy carbon electrode is polished with fine alumina powder (0.3micron) on a wet polishing cloth. To do so a part of the cloth is mode wet with deionized water and alumina powder is sprinkled on it. The glassy carbon electrode is then polished on this surface by pressing softly the electrode against the polishing surface in the end for 3-5 minutes. The electrode is then thoroughly washed with deionized water. At this point the electrode surface would look like a shiny black mirror.

Experimental

All of the chemicals used in the synthesis were purchased from Sigma-Aldrich and were used as received. Melting points were measured in open capillary tubes and are uncorrected. The ^{1}H-NMR, ^{13}C-NMR were recorded on a Bruker (Avance) 300 MHz NMR instrument using TMS as an internal standard and DMSO as a solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60-80^{o}C) and ethyl acetate as the eluent. Elemental analyses were performed on a Perkin-Elmer 2400 Series II Elemental CHNS analyzer. ESI mass was recorded using a Thermo Fleet-LC mass instrument.

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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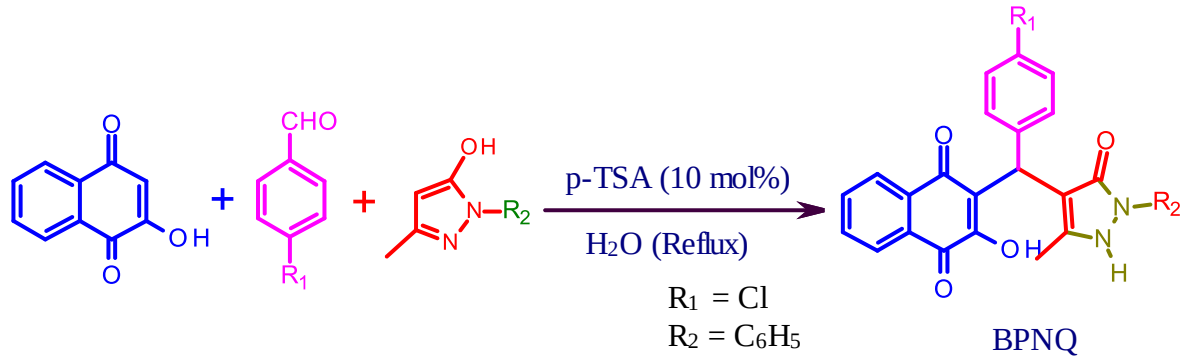
Synthesis of Benzylpyrazolyl Naphthoquinone (BPNQ)

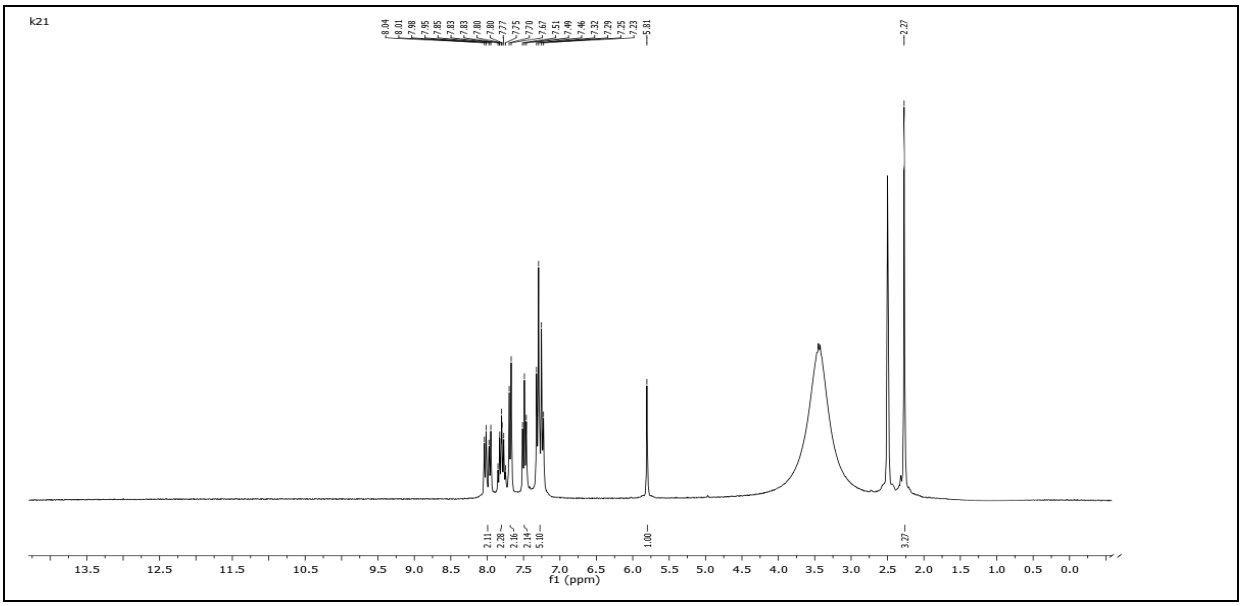
To a mixture of 10 mol% p-TSA and 5ml water, 2-hydroxy naphthoquinone, **1** (1 mmol), P-Chlorobenzaldehyde **2** (1 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **3** (1 mmol) were added and heated to reflux at 70ºC. The resulting clear solution that gradually became turbid, was stirred for the stipulated time 20 minutes. After completion of the reaction (indicated by TLC), the free-flowing solid was filtered and washed with ethanol (10 ml) to afford the desired products.



Scheme 1 Synthesis of Benzylpyrazolyl Naphthoquinone (BPNQ).

2-((4-chlorophenyl)(2,3-dihydro-5-methyl-3-oxo-2-phenyl-1*H*-pyrazol-4yl)methyl)-2-hydroxynaphthalene-1,4-dione.

Pale yellow solid; mp 256-258 ºC; ^{1}H NMR (300 MHz, DMSO, δ ppm): δ 7.99 (dd, *J* = 18.9, 7.5 Hz, 2H), 7.89 – 7.73 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.27 (dd, *J* = 20.2, 8.5 Hz, 5H), 5.81 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, DMSO, TMS, δ ppm): δ 183.83, 181.73, 160.29, 158.75, 147.39, 141.91, 135.82, 134.04, 132.93, 131.88, 130.55, 129.00, 126.02, 125.90, 125.45, 124.64, 120.26, 105.87, 104.61, 97.15, 54.93, 32.59,10.84. ESI-MS (M^{+} +1) calculated m/z 470.10. Found 471.02. Anal. Calcd for: $C_{27}H_{19}ClN_2O_4$: C, 68.87; H, 4.07; N, 5.95% found: C, 68.89; H, 4.09; N, 5.96%.



^{1}H-NMR spectrum of 2-((4-chlorophenyl)(2,3-dihydro-5-methyl-3-oxo-2-phenyl-1 *H*-pyrazol-4-yl)methyl)-2-hydroxynaphthalene-1,4-dione (Table 2, Entry 1).

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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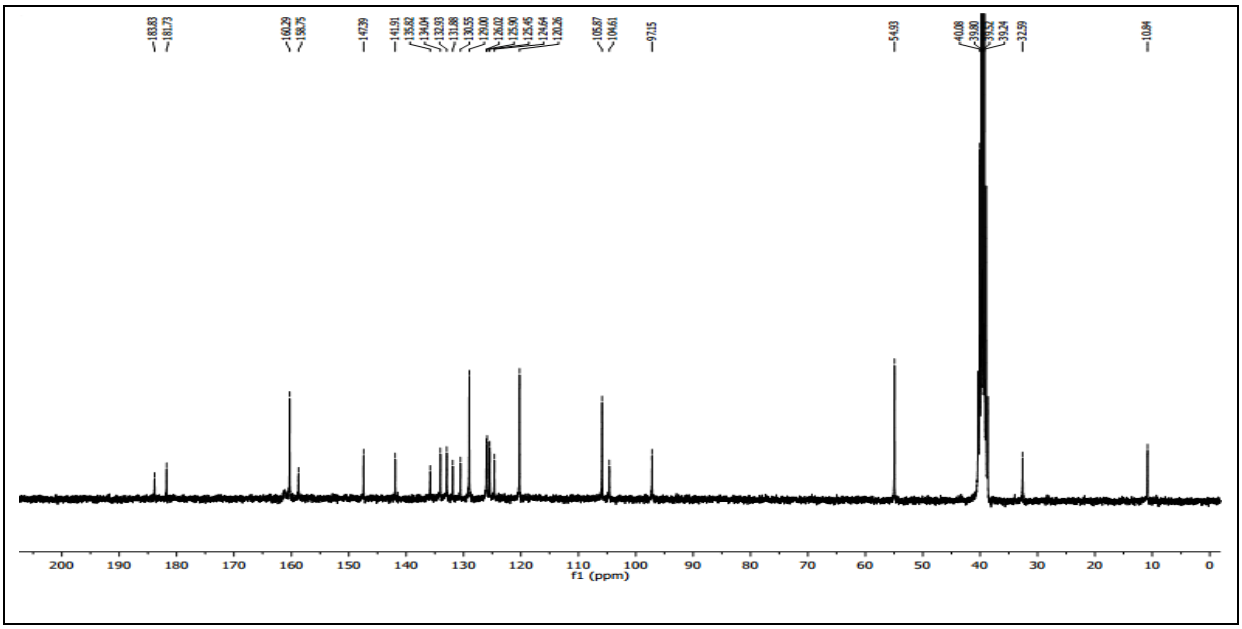
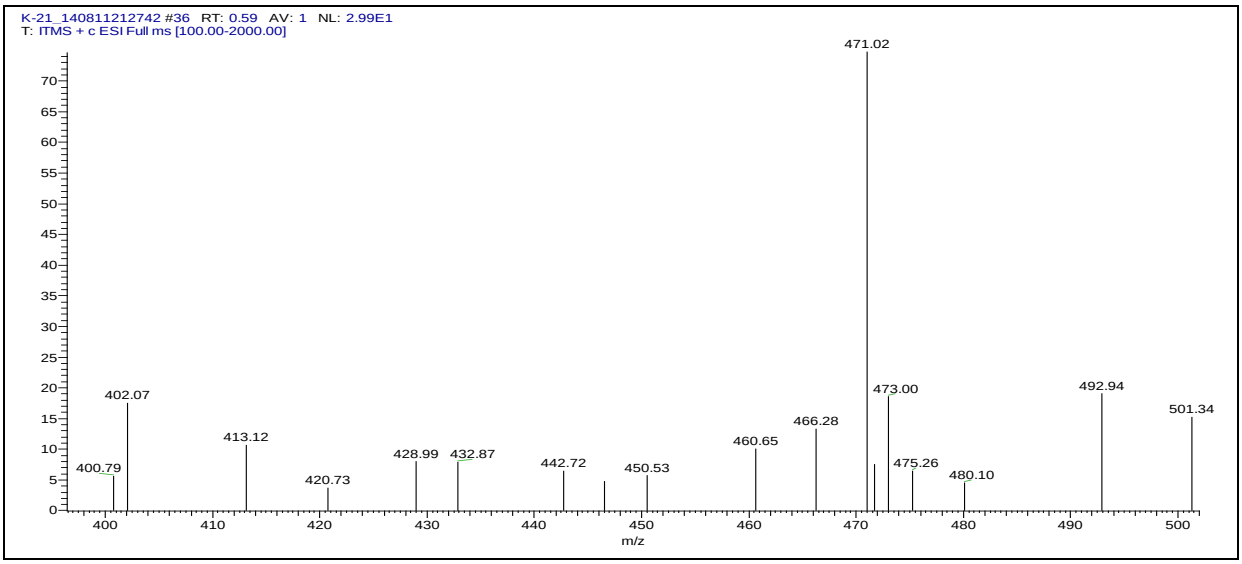


^{13}C-NMR spectrum of 2-((4-chlorophenyl)(2,3-dihydro-5-methyl-3-oxo-2-phenyl-1 *H*-pyrazol-4-yl)methyl)-2-hydroxynaphthalene-1,4-dione (Table 2, Entry 1).



Mass spectrum of 2-((4-chlorophenyl)(2,3-dihydro-5-methyl-3-oxo-2-phenyl-1 *H*-pyrazol-4-yl)methyl)-2-hydroxynaphthalene-1,4-dione (Table 2, Entry 1).

Results And Discussion

Intramolecular Hydrogen Bonding in Benzylpyrazolyl Naphthoquinone.

Typical cyclic voltammograms for compounds BPNQ is depicted in Figure 9 compared to the typical BPNQ voltammetric response. Two reversible pairs of peaks are present in the voltammograms of BPNQ such as those appearing in Figure 9. This behavior occurs typically for the reduction of quinones in aprotic conditions and is related to the transformation of the quinone into a stable semiquinone (peak Ic). The latter species is reduced at peak IIc into a dianion, being both electron transfer processes reversible under the time scale of the experiments (equations 1 and 2). The electrochemical behavior of BPNQ indicates that the hydroxy group is not acidic enough to protonate the semiquinone or dianion species.

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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Q + e– □ Q•– (1)

Q•– + e– □ Q= (2)

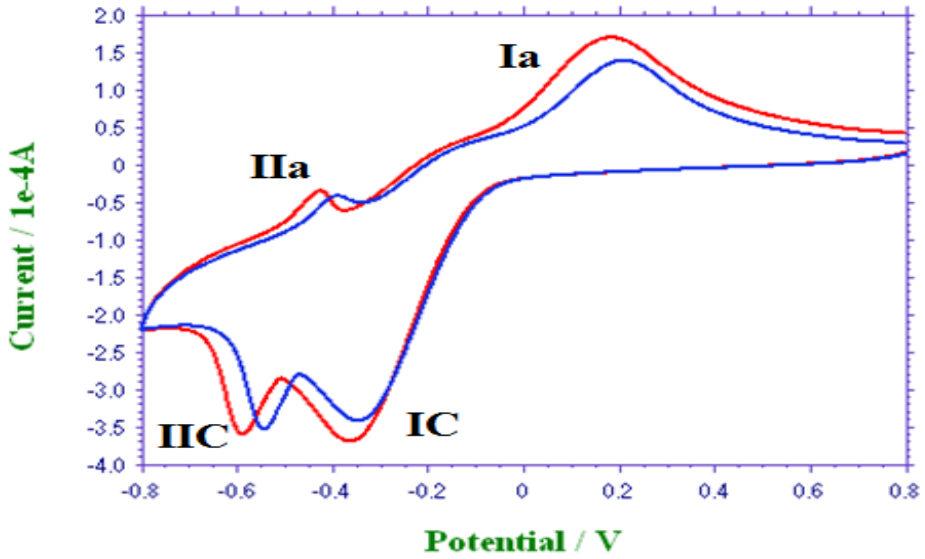

Figure 9. Typical voltammograms for BPNQ in DMSO + NH_4F 2.0 M medium on glassy carbon electrode.

Intramolecular hydrogen bonding Figure 10 shows the voltammetric behavior obtained for the Benzylpyrazolyl Naphthoquinone. The presence of hydroxyl groups in BPNQ structure does not affect reversibility of the two quinone reduction processes. However, it does modify the peak potential and diffusion coefficient. The peak current decrease results from the presence of hydroxyl groups, which can interact via hydrogen bonding with the molecules of DMSO (Table 1). The displacement of reduction potentials toward less negative values shows that hydroxylated molecules are easier to reduce. This behavior results from the presence of hydroxyls that may form inter- o intra-molecular bonds by stabilizing negative charge of the quinone carbonyl oxygen and products of their reduction. It was established that the presence of hydroxyl group in BPNQ affects both reduction processes. As a result voltammetric behavior of BPNQ system in the presence of methanol (CH_3OH) confirms the existence of hydrogen bonding in hydroxyl Benzylpyrazolyl Naphthoquinone. The voltammetric studies, in which the concentration of naphthoquinones was varied, suggest that during the reduction of hydroxyl Benzylpyrazolyl Naphthoquinone hydrogen bonding takes place Figure 11.

Table 1: Typical cyclic voltammograms obtained for a solution of Benzylpyrazolyl Naphthoquinone (2 mM) in 0.2 M NH_4F+ DMSO at different methanol concentrations.

S. No	I- Ipc	II- Ipc	I-Epc	II-Epc	I-Ipa	II-Ipa	I-Epa	II-Epa
1	-3.739	-3.690	-0.3699	-0.6556	2.072	-2.430	0.1634	-0.4457
2	-3.759	-3.646	-0.3742	-0.6093	1.786	-3.728	0.1760	-0.4371
3	-3.646	-3.578	-0.3659	-0.5884	1.695	-3.496	0.1886	-0.4245
4	-3.509	-3.464	-0.3616	-0.5547	1.582	-3.728	0.1929	-0.4036
5	-3.383	-3.409	-0.3405	-0.5506	1.408	-3.250	0.1095	-0.3951

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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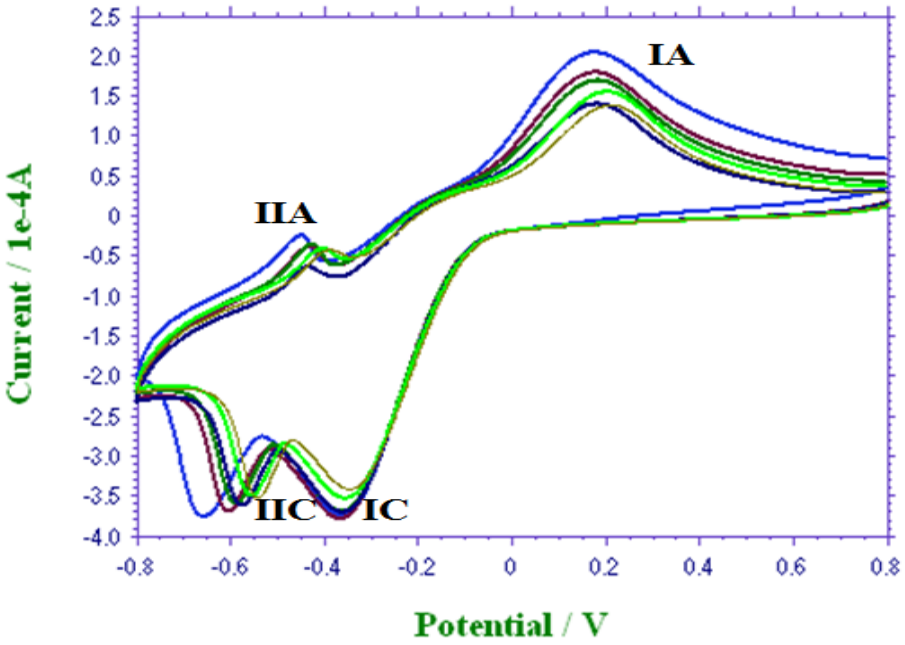


Figure 10. Typical cyclic voltammograms obtained for a solution of Benzylpyrazolyl Naphthoquinone (2 mM) in 0.2 M NH_4F+ DMSO at different methanol concentrations.

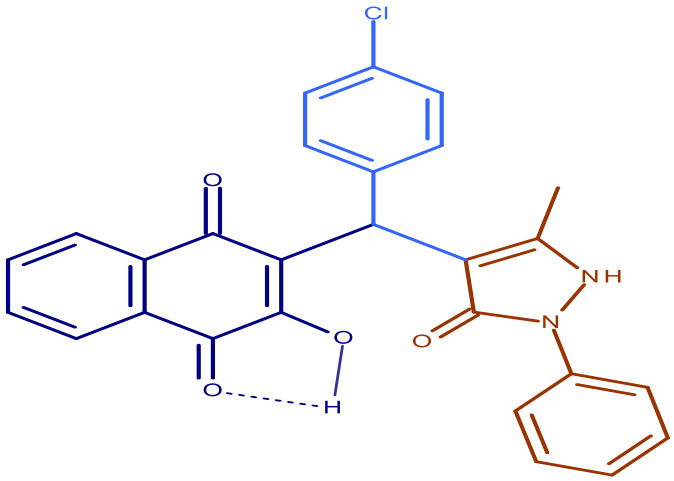


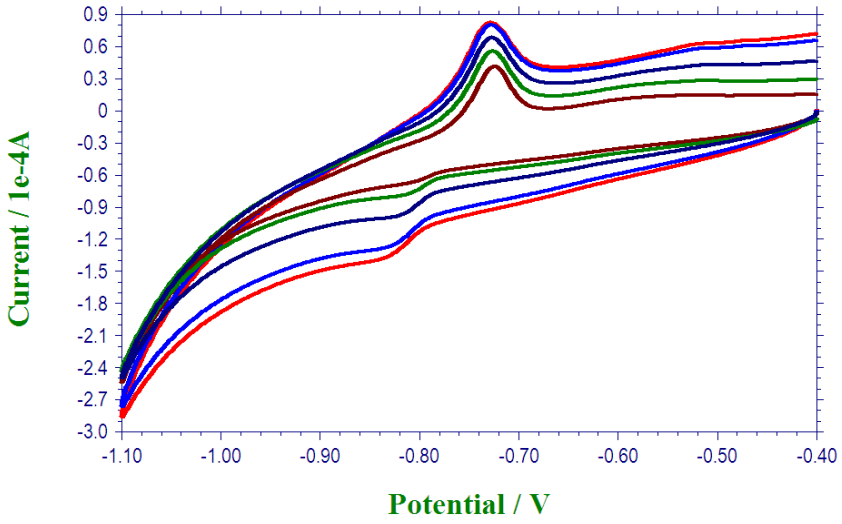
Figure 11. Intramolecular Hydrogen Bonding

Sensor Studies Of Cadmium Ions

The experiment was performed by taking 1mM of Cd^{2+} ion in bare different Sweep rates on wax impregnate graphite electrode 10,20,40,80,100mV/s in 0.5M NH_4F and is presented in fig (12). Anodically one peak appeared at potential -0.7852V to -0.7860V. In cathadic side observation of one peak appeared at potential -0.8220V to -0.834V. The experiment was repeated for 1mM of Cd^{2+} solution at different sweep rates 10,20,40,80,100 mV/s in 0.5M NH_4F and is presented in fig(12). Anodically one peak appeared at potential level -0.7348 to -0.7485V. In cathodic side observation of one peak. The redox reaction of Cd(II)/Cd(0) is surface absorbed process. This is because that the surface absorbed process becomes the rate determining step of the electrode reaction (Table 2).

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
ISSN: 2305-7246

$$Cd^{2+} + 2e^- \rightleftharpoons Cd$$



Figure(12) Cyclic Voltammetric Parameters for 1mM Cd^{2+} ion on modified WIGE at different sweep rates 10,20,40,80,100mV/s 0.5M NH4F medium

Table 2

Cyclic voltammogram for 1mM of cadmium at different Sweep rates on wax impregnate graphite electrode

S.NO	**Sweep Rate**	**Ipc**	**Epc**	**Ipa**	**Epa**
1.	10mV	-6.720	-0.8053	4.280	-0.7248
2.	20mV	-7.820	-0.8081	5.727	-0.7267
3.	40mV	-9.677	-0.8136	6.974	-0.7276
4.	80mV	-10.69	-0.8282	8.189	-0.7294
5.	100mV	-11.67	-0.8301	8.350	-0.7285

A plot of Epc Vs logV at different sweep rate is presented in fig(12). The potential values shifted to negative side. The linear regression equation are expressed as R^2=0.8973 and transfer co-efficient value 0.34. A plot of Ipc Vs $v^{1/2}$. The ipc values increases with increasing scan rates is presented in fig(13) diffusion process of cadmium redox system. The linear regression equation are expressed value as R^2=0.8973. The Voltammetric parameters for different scan rates are tabulated in Table 2.

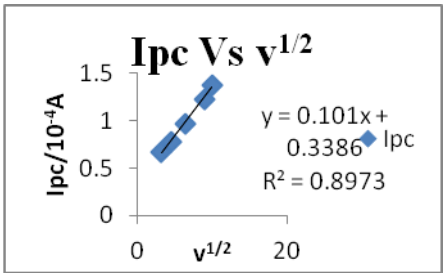


Figure (13) A plot of Ipc Vs $V^{1/2}$ for 1mM Cd(II) ion in 0.5M NH_4F medium at different sweep rates.

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
ISSN: 2305-7246

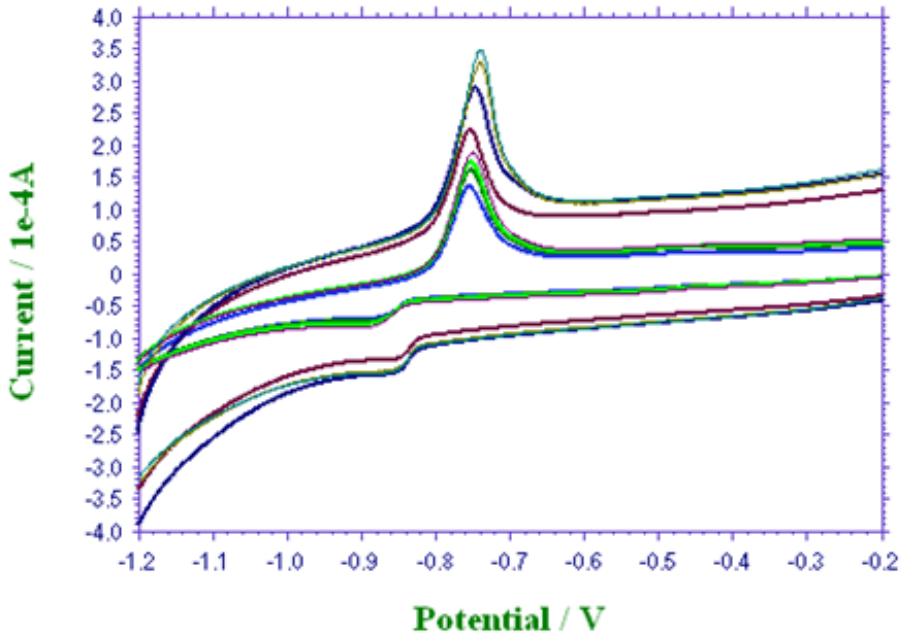
Table 3

Cyclic voltammogram for 1mM of cadmium at different concentration on wax impregnate graphite electrode

S.NO	Concentration	Ipa	Epa
1	1mm	1.351	-0.7528
2	2mm	1.564	-0.7528
3	3mm	1.776	-0.7501
4	4mm	1.837	-0.7501
5	5mm	2.230	-0.7553
6	6mm	2.897	-0.7475
7	7mm	3.261	-0.7423

The voltammogram for different concentration of Cd^{2+} ion on bare WIGE at 40mV/s in fluoride medium is presented in fig (14). The electrode is modified and corresponding cyclic voltammogram is obtained by taking different concentration 1mM to 5mM of Cd^{2+} at constant sweep rate of 40mV/s in 0.5M NH_4F medium and is presented in fig (15). Anodically one peak was appeared at potential level 0.1717V to 0.0.2221V and also similar one peak was appeared in cathode potential -0.3573V to -0.3533V. A cathodic side suggest that the reduction is single step two electron transfer.

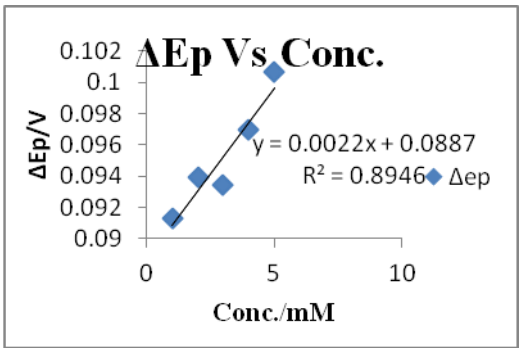
$Cd^{2+} + 2e^- \rightleftharpoons Cd$



Figure(15) Cyclic Voltammetric Parameters for different concentrations of Cd^{2+} ion on modified WIGE at 40mV/s.

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
ISSN: 2305-7246

A plot of ΔEp Vs Concentration is presented in fig(16). ΔEp values shifted to negative side. The linear regression equation are expressed as R^2=0.894. It is best good relation of reversible process. The voltammetric values for different concentrations are tabulated in Table(2).



Figure(16) A plot of ΔEp Vs Conc for different concentrations of Cd(II) ion in 0.5M NH_4F medium at 40mV/s.

Sensor Studies Of Mercury Ion

The experiment was performed by taking 1mM of Hg^{2+} ion in bare WIGE at different sweep rate 10,20,40,80,100mV/s in 0.5M NH_4F and is presented in fig (17). Anodically one peak appeared at potential 0.2387V to 0.4592V. In cathadic side observation of one peak appeared at potential -0.6998V to -0.9267V. The experiment was repeated for 1mM of Hg^{2+} solution at different sweep rates 10,20,40,80,100mV/s in 0.5M NH_4F and is presented in fig(17). Anodically one peak appeared at potential level 0.1508 to 0.1764V. In cathodic side observation of one peak. The redox reaction of Hg(II)/Hg(0) is surface absorbed process. This is because that the surface absorbed process becomes the rate determining step of the electrode reaction Table 3.

$$Hg^{2+} + 2e^- \rightleftharpoons Hg$$

Table 3

Cyclic voltammogram for 1mM of mercury at different Sweep rates on wax impregnate graphite electrode

S.NO	Sweep Rate	Ipc	Epc	Ipa	Epa
1.	10mv	1.288	0.229	-1.408	0.087
2.	20mv	-1.218	-0.282	-0.230	0.593
3.	30mv	-2.610	-0.2842	2.979	0.238
4.	40mv	-4.337	-0.4541	3.330	0.240
5.	60mv	-5.184	-0.4669	3.120	0.234
6.	80mv	-5.500	-0.2400	3.220	0.238
7.	120mv	-9.323	-0.6115	3.459	0.260

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
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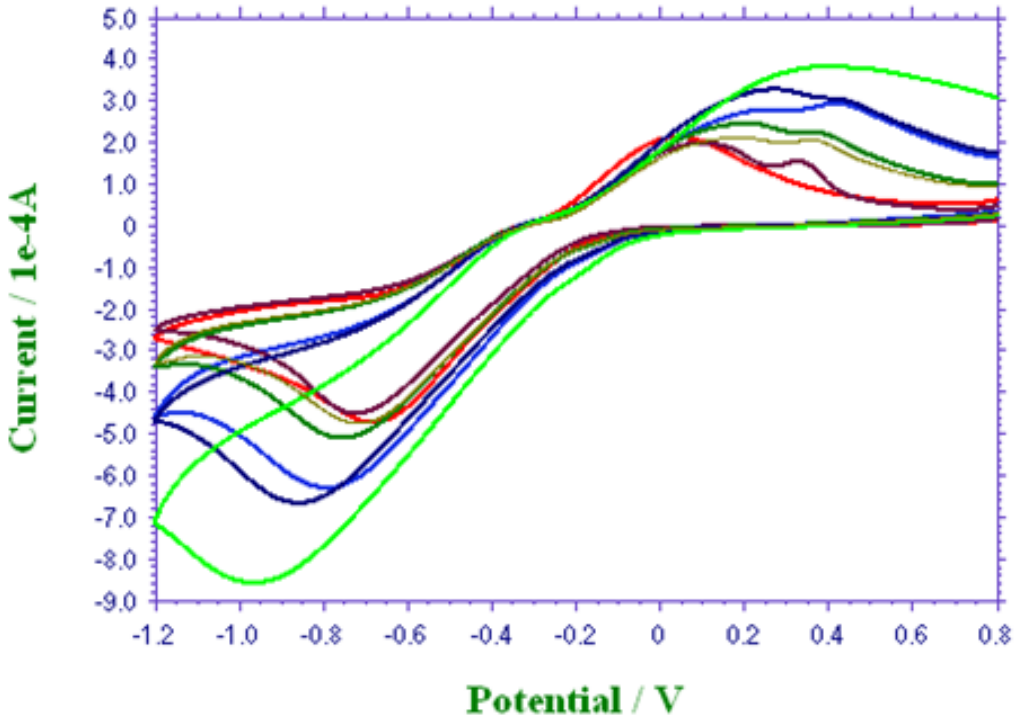


Figure(17) Cyclic Voltammetric Parameters for 1mM Hg^{2+} ion on modified WIGE at different sweep rates 10,20,40,80,100 mV/s 0.5M NH_4F medium

A plot of Epc Vs logV at different sweep rate is presented in fig(18). The potential values shifted to negative side. The linear regression equation are expressed as R^2=0.942 and transfer co-efficient value 0.36. A plot of Ipc Vs $v^{1/2}$. The ipc values increases with increasing scan rates is presented in fig(18) diffusion process of cadmium redox system. The linear regression equation are expressed value as R^2=0.997. The Voltammetric parameters for different scan rates are tabulated in table(1).

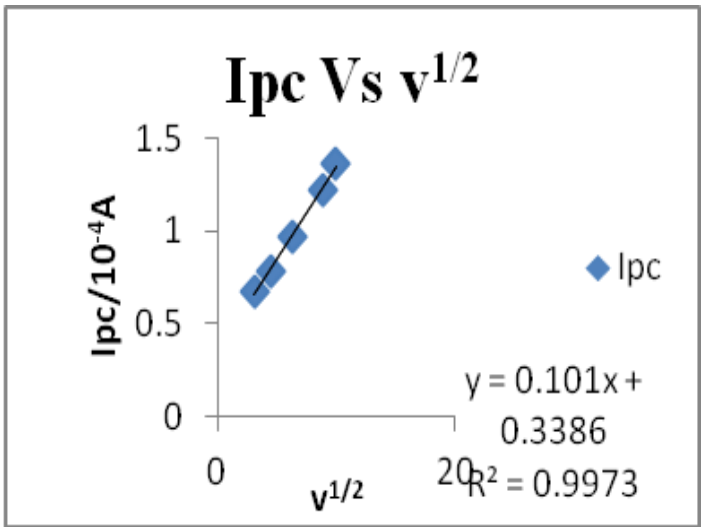


Figure (13) A plot of Ipc Vs $V^{1/2}$ for 1mM Hg(II) ion in 0.5M NH_4F medium at different sweep rates.

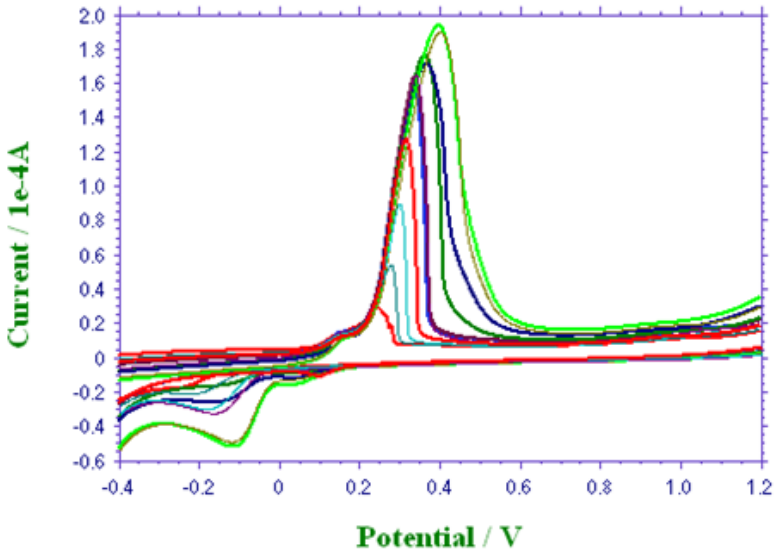
International Journal of Modern Agriculture, Volume 9, No. 4, 2020
ISSN: 2305-7246

Table 1 Cyclic voltammogram for 1mM of Mercury at different concentration on wax impregnate graphite electrode

S.No	Concentration	Ipa	Epa
1	1mm	2.861	0.2549
2	2mm	5.408	0.2780
3	3mm	8.800	0.2990
4	4mm	6.268	0.3179
5	5mm	5.683	0.3447
6	6mm	5.524	0.3361

The voltammogram for different concentration of Hg^{2+} ion on bare WIGE at 40mV/s in fluoride medium is presented in fig (19). The electrode is modified and corresponding cyclic voltammogram is obtained by taking different concentration 1mM to 5mM of Hg^{2+} at constant sweep rate of 40mV/s in 0.5M NH_4F medium and is presented in fig (19). Anodically one peak was appeared at potential level 0.1717V to 0.0.2221V and also similar one peak was appeared in cathode potential -0.3573V to -0.3533V. A cathodic side suggest that the reduction is single step two electron transfer.

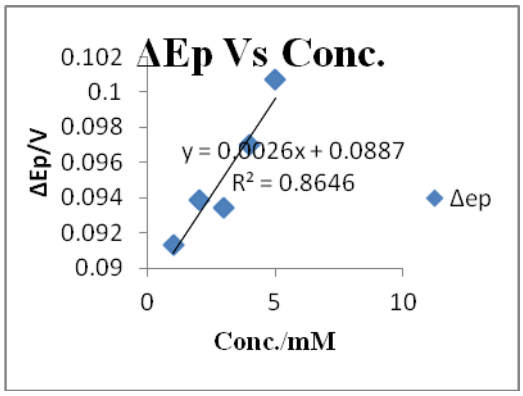
$Hg^{2+} + 2e^- \rightleftharpoons Hg$



Figure(19) Cyclic Voltammetric Parameters for different concentrations of Hg^{2+} ion on modified WIGE at 40mV/s.

A plot of ΔEp Vs Concentration is presented in fig (20). ΔEp values shifted to negative side. The linear regression equation are expressed as R^2=0.864. It is best good relation of reversible process. The voltammetric values for different concentrations are tabulated in Table (2)

International Journal of Modern Agriculture, Volume 9, No. 4, 2020
ISSN: 2305-7246



Figure(20) A plot of ΔEp Vs Conc for different concentrations of Hg(II) ion in 0.5M NH_4F medium at 40mV/s.

Interference Study

The interference study of different metals was conducted using Cd^{2+} ion 1mM of Cd^{2+}, 1mM Cu^{2+}, 1mM Zn^{2+} 1mM Mn^{2+} 1mM Ni^{2+} 1mM Co^{2+},1mM Fe^{2+} and 1mM of Hg^{2+} ion for bare WIGE and the corresponding the cyclic voltammogram is presented in fig (21). The experiment was repeated using Benzylpyrazolyl Naphthoquinone modified WIGE at constant sweep rate of 40mV/s in 0.5M NH_4F medium and is presented in fig (21) Only one peak was appeared for Cd^{2+} and one anodically peak was appeared for Hg^{2+} is presented in fig (21). Interference study shows that, simultaneously detection of Cd(II), and Hg(II) ions on the ligand modified WIGE is possible. The electron transfer is faster for mercury redox system as compared to the cadmium redox system. Thus well defined redox peak for mercury was obtained.

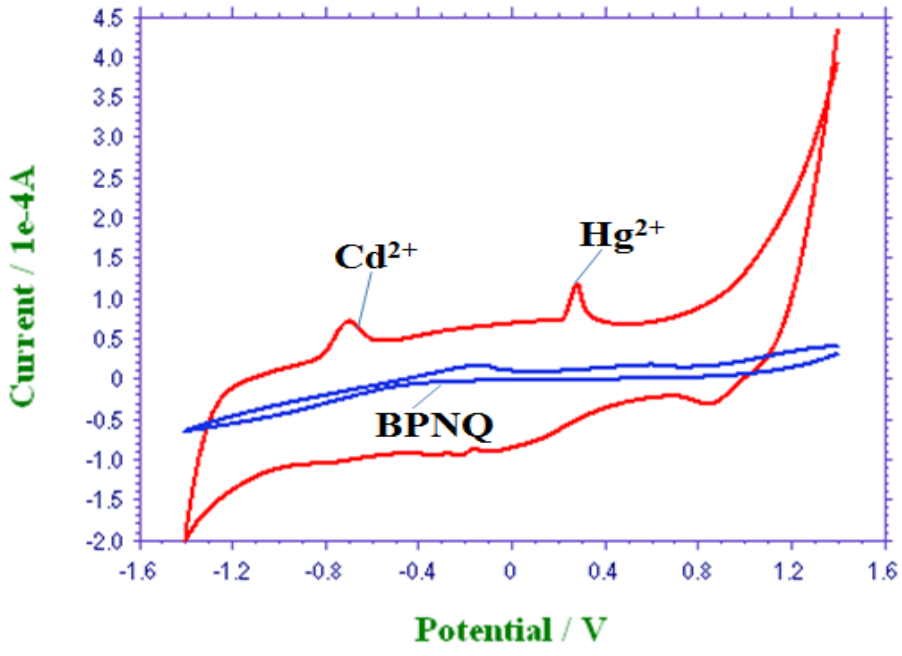


Figure (21) Interference study of metal ions like Cd and Hg.

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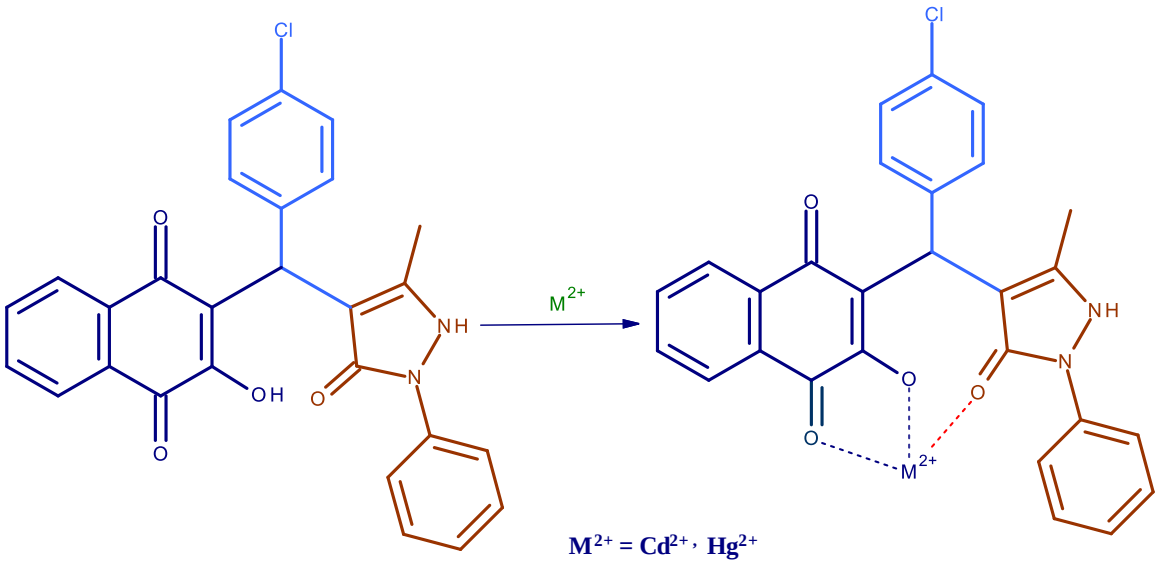

Scheme 4 Possible Sensor Mechanism

Conclusion

The results prove that the association via intermolecular hydrogen bonding, caused by the presence of weak proton donors in the reaction medium, modifies the reactivity of anion radicals and dianions formed by electroreduction of the corresponding quinones. The association constants show that as the number of possible intramolecular hydrogen bonds increases, the number of MeOH molecules that may associate decreases. This intermolecular association is dependent upon the proton donor concentration and may be more significant than the intramolecular interaction present in α-phenolic-quinones.

Refrence

1. Di Tioppi, S.L., Gabbrielli, R. *Environ. Exp. Bot.* **1999,** 41, 105-130.

2. Zehnalek, J. Adam, V., Kizek, R. *Lis. Cukrov. Reparske.* **2004,** 120, 222-224.

3. Zehnalek, J., Vacek, J., Kizek, R. *Lis. Cukrov. Reparske*. **2004,** 120, 220-221.

4. Soylak, M., Narin, I., Divrikli, U., Saracoglu, S., Elci, L., Dogan, M. *Anal. Lett.* **2004,** 37, 767-780.

5. Sneddon, J., Vincent, M.D. *Anal. Lett.* **2008,** 41, 1291-1303.

6. Ferreira, S.L.C., de Andrade, J.B., Korn, M.D.A., Pereira, M.D., Lemos, V.A., dos Santos, W.N.L., Rodrigues, F.D., Souza, A.S., Ferreira, H.S., da Silva, E.G.P. *J. Hazard. Mater*. **2007,** 145, 358-367.

7. Pyrzynska, K. *Crit. Rev. Anal. Chem.* **2007,** 37, 39-49.

8. Yantasee, W., Lin, Y., Hongsirikarn, K., Fryxell, G.E., Addleman, R., Timchalk, C. *Environ. Health Perspect.* **2007,** 115, 1683-1690.

9. Korn, M.D.A., dos Santos, D.S.S., Welz, B., Vale, M.G.R., Teixeira, A.P., Lima, D.D., Ferreira, S.L.C. *Talanta.* **2007,** 73, 1-11.

10. Lewen, N., Mathew, S., Schenkenberger, M., Raglione, T. *J. Pharm. Biomed. Anal.* **2004,** 35, 739-752.

11. Szlyk, E., Szydlowska-Czerniak, A. *J. Agric. Food Chem.* **2004,** 52, 4064-4071.

12. Mikkelsen, O., Schroder, K.H. *Electroanalysis.* **2003,** 15, 679-687.

13. May, L.M., Russell, D.A. *Anal. Chim. Acta*. **2003,** 500, 119-125.

14. Pei, J.H., Tercier-Waeber, M.L., Buffle, *J. Anal. Chem.* **2000,** 72, 161-171.

15. Fernandez-Bobes, C., Fernandez-Abedul, M.T., Costa-Garcia, A. *Electroanalysis.* **1998,** 10, 701-706.

16. Adam, V., Hanustiak, P., Krizkova, S., Beklova, M., Zehnalek, J., Trnkova, L., Horna, A., Sures, B., Kizek, R. *Electroanalysis.* **2007,** 19, 1909-1914.

17. Adam, V., Petrlova, J., Potesil, D., Zehnalek, J., Sures, B., Trnkova, L., Jelen, F., Kizek, R. *Electroanalysis.* **2005,** 17, 1649-1657.

18. Wu, K.B., Hu, S.S., Fei, J.J., Bai, W. *Anal. Chim. Acta*. **2003,** 489, 215-221.

19. Yantasee, W., Lin, Y.H., Fryxell, G.E., Busche, B.J. *Anal. Chim. Acta.* **2004,** 502, 207-212.

20. Palchetti, I., Cagnini, A., Mascini, M., Turner, A.P.F. *Mikrochim. Acta.* **1999,** 131, 65-73.

21. Guell, R., Aragay, G., Fontas, C., Antico, E., Merkoci, A. *Anal. Chim. Acta.* **2008,** 627, 219-224.

22. Tchounwou, P.B., Ayensu, W.K., Ninashvili, N., Sutton. D. *Environ Toxicol.* **2003,** 18, 149–175

23. Nolan, E.M., Lippard, S.J. *Chem Rev.* **2008,** 108, 3443–3480

24. Clemens, S., Monperrus, M., Donard, O.F.X., Amouroux, D., Guerin. T. *a review. Talanta* **2012,** 89, 12–20

25. Yin, Z., Wu, J., Yang, Z., *Microchim Acta***. 2010,** 170, 307–312

26. Mandil, A., Idrissi, L., Amine, A. *Microchim Acta.* **2010,** 170, 299–305

27. Pan, D.W, Wang, Y.E, Chen, Z.P, Lou, T.T, Qin, W. *Anal Chem.* **2009**, 81, 5088–5094

28. Niu, X., Ding, Y., Chen, C., Zhao, H., Lan, M. *Sensor Actuat B-Chem.* **2011,** 158, 383–387

29. Horrison, R.M. *The Royal Society of Chemistry*, Cambridge **1995.**

30. Bride, M.B.M. *Oxford University Press*, Yew York, *1994.*

31. Sancho, D., Vega, M., Deban L., Pardo, R., Gonzalez, G., *Analyst*, **1997,** 122, 727.

32. Lingane P., Christie, J., *J.Electroanal. Chem.* **1965,** 10, 284.

33. Hanelin, A. *Acad.Sci., Parris*, **1966,** 262, 520.

34. Frumkin, N., Physik, Z . *Chem., A.* **1937**, 64, 121.