Int. J. Electrochem. Sci., 11 **(2016)** 8027 – 8045, doi: 10.20964/2016.09.53

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Dithiocarbamate Induced Catalytic Hydrogen Wave for the determination of Iron (II) in Waters and Leafy Vegetables: Experimental and Computational Approach

Suvardhan Kanchi[1,*†], *Giridhar Chembeti*[2†], *Deepali Sharma*[1], *Phumlane Selby Mdluli*[1], *Krishna Bisetty*[1,*], *Venkatasubba Naidu Nuthalapati*[2,*] *Myalowenkosi Innocent Sabela*[1]

[1] Department of Chemistry, Sri Venkateswara University, Tirupati-517502, A.P. India.
[2] Department of Chemistry, Durban University of Technology, P.O. Box 1334, Durban 4000, South Africa.
[*]E-mail: nvsn69@gmail.com, ksuvardhan@gmail.com

Received: 8 March 2016 / *Accepted:* 13 July 2016 / *Published:* 7 August 2016

A simple, sensitive, selective and robust catalytic hydrogen wave method was developed by novel dithiocarbamates (ammonium 2,6-dimethyl morpholine dithiocarbamate and ammonium 3-methyl piperidine dithiocarbamate) using DC polarography. This method was based on the interaction of Iron(II) with dithiocarbamates in the presence of buffer (NH_4Cl-NH_4OH) at pH 6.6/6.4 to produce catalytic hydrogen currents at -1.39/-1.32V vs SCE respectively. The optimized experimental conditions were established by investigating the pH effect, supporting electrolyte (NH_4Cl-NH_4OH), and concentration of ligand. Thereafter, adverse ions effect on wave height was evaluated to enhance the selectivity of the present method. Additionally, the density functional theory calculations of ammonium 3-methyl piperidine dithiocarbamate revealed a smaller HOMO-LUMO energy gap than ammonium 2,6-dimethyl morpholine dithiocarbamates, suggesting that ammonium 3-methyl piperidine dithiocarbamates have a superior propensity to act as an electron donor to Iron(II). The reported analytical method was successfully applied for the detection of Iron (II) in different water and leafy vegetable samples with recoveries ranging from 97-99 %.

Keywords: D.C. polarography; Catalytic hydrogen currents; Iron (II); Ammonium 2,6-dimethyl morpholine dithiocarbamates; Ammonium 3-methyl piperidine dithiocarbamates; Water and Leafy vegetable samples; Density functional theory and HOMO-LUMO calculations

1. INTRODUCTION

The most important transition metal in living system is Iron and serves more in the biological system than any other metal. Its main role in the body is to carry oxygen to the tissues where it is needed besides other vital functions. The Iron is responsible for the appropriate function of protection against microbes and free radicals, energy metabolism and DNA synthesis [1]. The total Iron content present in an adult body is approximately 4.0 g, i.e. 70 mM, of which about two third is in haemoglobin. The majority of Iron is stored mainly in the spleen, liver, and bone marrow which contain about one-quarter of the body's Iron and rest is in myoglobin and other heme proteins. It is widely distributed in foodstuffs and normally about 1.0 mg of Iron is absorbed from food every day [2]. Due to intermediate bioavailability of Iron in vegetarian diets are the common cause of Iron deficiency in the developing countries [3]. The average Iron content in human milk is less than 1.0 μg mL^{-1}, therefore, Iron spiked foods make a significant impact to the Iron intake, which is insufficient in certain groups of the population [4]. The main gastrointestinal side effects are associated with net high doses of supplemental Iron, especially when taken on an empty stomach. Excess of Iron in domestic water causes staining of clothes and imparts astringent taste [5-7].

Several analytical techniques such as Chromatography [8], X-Ray fluorescence [9], Radio-analytical [10], UV-Visible Spectrophotometry [11], and Atomic absorption spectroscopy [12], Flame atomic absorption spectrometry [13], Inductively coupled plasma-mass spectrometry [14] have been reported for the analysis of Iron (II) in various samples of environmental importance. In spite of the fact that the above-mentioned instruments are sensitive and able to achieve lower detection limits, they have few drawbacks like non-available of instrumentation facility in all laboratories, the requirement of specialist to handle, and cost implications. Therefore, it is necessary to develop a sensitive, selective, reliable and alternative method for the trace and ultra-trace analysis of Iron (II) in various water and leafy vegetable samples. In view of these circumstances, simple polarography technique coupled with a catalytic hydrogen wave (CHW) methodology was used in the present study.

A new technique in which flow-injection-cloud point extraction coupled with flame atomic absorption spectrometric method was reported for the determination of Iron (II) and Copper (II). In this method, Eriochrome Cyanine R has been used as a ligand and extraction medium [15]. A froth flotation method for the separation and pre-concentration of Cobalt (II), Nickel (II), Iron (II) and Copper (II) using phenyl-2-pyridyl ketone oxime prior to flame atomic absorption spectrometric analysis has been developed by Karimi et al [16]. While Tsuyoshi Nomura developed a method based on the indirect polarographic analysis of Iron (II) by means of catalytic oxidation of 5-aminosalicylic acid [17].

Iron (II) was detected in nanograms amounts using catalytic waves with H_2O_2 in the presence of N,N'-bis(salicylidene) ethylene diamine complex [18]. The catalytic hydrogen waves due to organic thiol compounds of Iron (II) and (III) were also identified. Thiourea was used as a complexing agent for Iron (II), Cobalt (II) and Manganese (II) in sodium perchlorate medium by Ravinskii et al [19]. Toropova et al. [20] reported the catalytic hydrogen waves of Iron (II), Cobalt (II) and Nickel (II) with bis-(2-hydroxyethyl) dithiocarbamate in water-ethanol medium and using acetate buffer. Fogg and Lewis [21] presented the kinetic behaviour of Iron (III)-Solochrome Violet complex at pH 4.7 and monitored the polarographic waves at the concentration of 10^{-3} M due to the excess of Iron (III).

EDTA was employed as a ligand for the separation and determination of Iron (II) and Iron (III) in the presence of acetate-buffer at pH 4.0 in different environmental samples [22]. Bond et al [23] reported a method for the analysis of Iron(II), Iron(III) and total Iron from zinc plant electrolyte samples using EDTA as a chelating agent in 0.1 M citrate solution and adjusted to pH 6.0 with ammonia. The results obtained under optimal conditions suggested a reversible reaction which was essentially independent of whether Iron (II) or Iron (III) standard solutions were used for calibration purposes [23]. A simple screen printed-ion selective (Fe-phosphotungstate ion-associate) electrode and tricresylphosphate as a plasticizer were developed for the analysis of Iron(II) in various polluted waters using potentiometric method [24]. Mendil et al [25] developed 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline as a co-precipitating agent for the separation and determination of Copper(II), Lead(II), Zinc(II), Iron(III) and Chromium (III) in food and water samples using flame atomic absorption spectrometry.

The present work deals with catalytic hydrogen wave based polarographic determination of Iron(II) with ammonium 2,6-dimethyl morpholine dithiocarbamates (ADMM-DTC) and ammonium 3-methyl piperidine dithiocarbamate (AMP-DTC) in the presence of NH_4Cl-NH_4OH medium. The results revealed that Iron(II) reduction wave followed a catalytic wave function. Moreover, theoretical calculations performed at the density functional (DFT) level to calculate the HOMO-LUMO energy gaps of these ligands, confirmed their electron donating capacities during complexation with the electron deficient metals.

2. EXPERIMENTAL

2.1. Apparatus

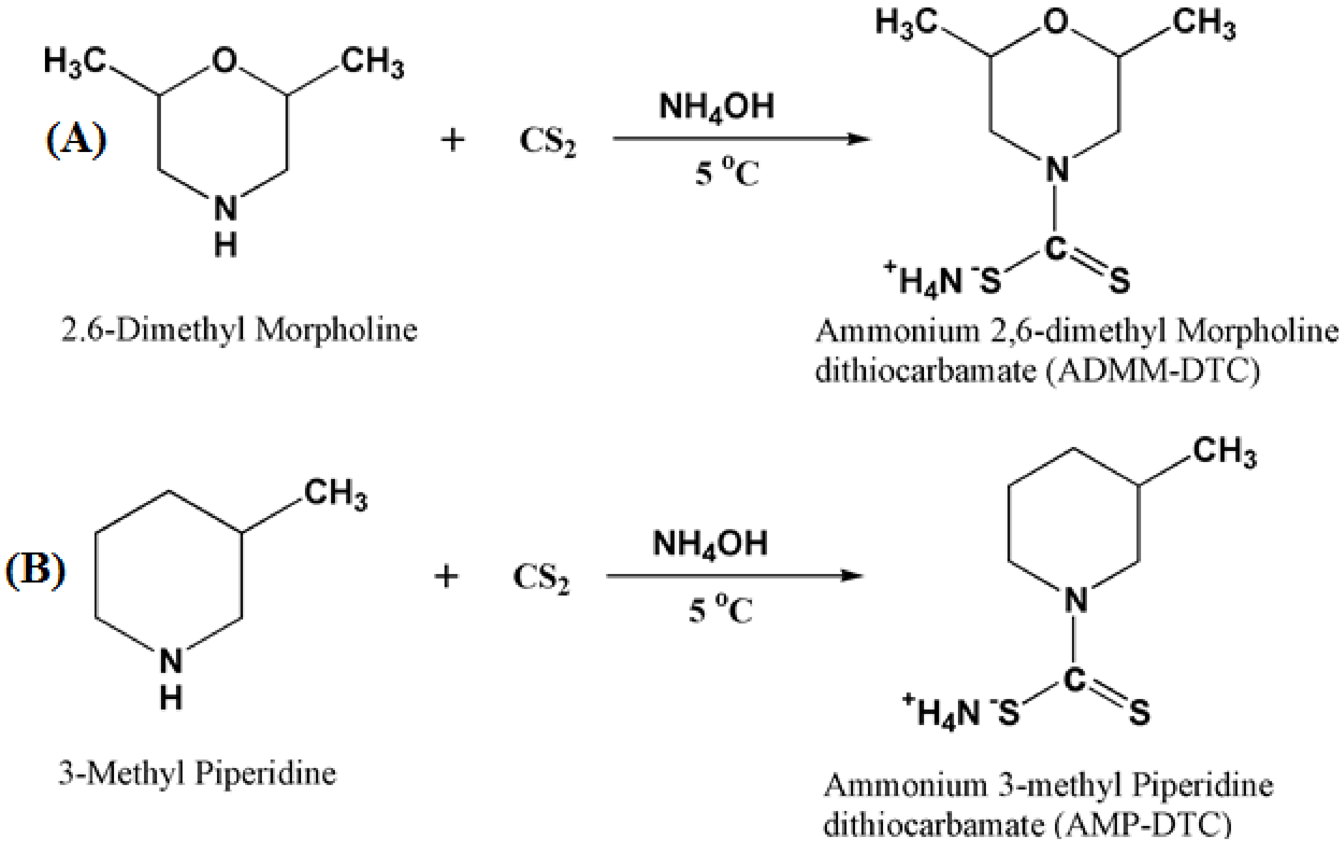
DC polarographic analyzers with model CL-357 and CL-25 (Elico Private Ltd, India) coupled with LR-101 strip chart recorder were used to measure the current-voltage curves and mercury height effect on polarographic currents. LI-120 (Elico Private. Ltd, India) with combined electrode of pH range 1-13 was used to record the pH of all the standard and sample solutions. UV–visible spectra for ADMM-DTC/AMP-DTC and their Iron (II) complexes were performed using a UV2450 spectrophotometer (Shimadzu). FT-IR Varian 800 was used to confirm the interaction of Iron(II) with ADMM-DTC/AMP-DTC.

2.2. Chemicals and reagents

2,6-dimethyl morpholine, 3-methyl piperidine, carbon disulphide, ammonium chloride, and ammonia solution were purchased from S.D. Fine Chemicals, India. Standard solution of Iron (II) (1.0 $\mu g\ mL^{-1}$) was prepared by weighing 3.928 g of $Fe(NH_4)_2 (SO_4)_2$ (S.D.Fine chemicals, Mumbai, India) and dissolved in de-ionized doubly distilled water and diluted to 1.0 L in a standard flask. ADMM-DTC (0.01 M) was prepared by dissolving 0.208 g and 0.192 g of ADMM-DTC and AMP-DTC respectively with de-ionized doubly distilled water in separate 100 mL volumetric flasks. Freshly prepared solutions were stored in amber bottles to avoid oxidation/reduction. Stock solutions of ADMM-DTC, AMP-DTC and NH_4Cl, NH_4OH were prepared by appropriate addition of reagents in 250 mL standard flasks and stored in dark place. All reagents were of analytical grade used without further purification.

2.3. Preparation of ammonium 2,6-dimethyl morpholine dithiocarbamates (ADMM-DTC) and ammonium 3-methyl piperidine dithiocarbamates (AMP-DTC)

The two novel dithiocarbamates were synthesized as per to the earlier literature reports [26-39] with slight modification: To 2,6-dimethyl morpholine/3-methyl piperidine (45 g) in 25 mL of de-ionized double distilled water, carbon disulphide (40 g) was slowly added at 5 ^{o}C with constant stirring, followed by steady addition of ammonium hydroxide to neutralize the final product (see Scheme 1a-b). Thereafter the mixutre was heated to ambient temperature and two to three washing were given with purified acetone to get the final product. The obtained product was further purified and recrystallization in acetone with an melting points of 176-182 ^{o}C (ADMM-DTC) and 192-195 ^{o}C (AMP-DTC) at pressure of 740 mmHg.



Scheme 1. Schematic pathway for the preparation of (**A**) Ammonium 2,6-dimethyl Morpholine dithiocarbamate (ADMM-DTC) (**B**) Ammonium 3-methyl Piperidine dithiocarbamate (AMP-DTC)

2.4. Experimental procedure

In a 100 mL standard flask, measured volume of electro-active species, Iron(II), supporting electrolyte (NH_4Cl-NH_4OH) and ligands (ADMM-DTC/AMP-DTC) were added by maintaining the optimum pH of 6.6/6.4 and the solutions were diluted with de-ionized doubly distilled water and then 15 mL was transferred into a polarographic cell. Thereafter, degassing step was carried out for 15 mins to remove the dissolved oxygen. The ligand or the metal on its own do not show the any CHW's at the optimal experimental conditions. The polarogram of the solutions was recorded using DC polarography.

2.5. Computational methodology

The computational method was carried out using Gaussian 09 software. The structures of ligands and the complexes were drawn in GuassView 5.0 and saved as Gaussian input files. These input and job files were run on the supercomputer located at the Centre for High-Performance Computing at Cape Town, South Africa. The geometry optimization of the ligands and complexes were done using 6-31g(d) basis set and the band gap energy was calculated from the energy of HOMO-LUMO orbitals respectively. The UV-visible and FTIR calculations were performed using B3LYP basis set for the geometrically optimized complexes.

2.6. Sample preparation

The CHW method developed by ADM-DTC/AMP-DTC was employed to detect the Iron (II) in different water and leafy vegetable samples. One litre of water samples collected from Renigunta Industrial Estate and around Amaraja Batteries, Tirupati, India were pre-concentrated to 100 mL and filtered using Whatman filter paper with a pore size of 0.45 µm prior to analysis. The 5 mL of this solution was taken for further electrochemical analysis. 5 g of the leafy vegetables grown in the nearby villages of Tirupati, India were collected, analysed as per to the reported method in the literature [28]. And thereafter, dissolved in 500 mL triple distilled water except curry leaves which were dissolved in 50 mL. The leafy samples include Amaranth viridis (Kuppakeerai), Amarnath polygonoides (Siri Keerai), Mentha spicata (Mint leaves), Piper Betle (Betle leaves) and Murraya koenigi (curry leaves) for the detection of Iron (II) using CHW method.

3. RESULTS AND DISCUSSION

Different optimized experimental conditions were developed for the analysis of Iron (II) by CHW method was discussed in this section. The polarographic studies of Iron (II)-dithiocarbamates in NH_4Cl-NH_4OH buffer medium was examined and found that it gives a pronounced catalytic hydrogen wave with peak potential at -1.39 and -1.32 V Vs SCE with Amm 2,6-dimethyl Mor-DTC and Vs SCE with Amm 3-methyl Pip-DTC respectively. The Iron (II) diffusion current wave with $E_{1/2}$ is at -1.45 V Vs SCE in NH_4Cl-NH_4OH buffer which was found to be similar with the earlier reports from the same laboratory [39]. The typical current-voltage curves of Iron (II)-dithiocarbamate complexes were depicted in the Figures 1A-B.

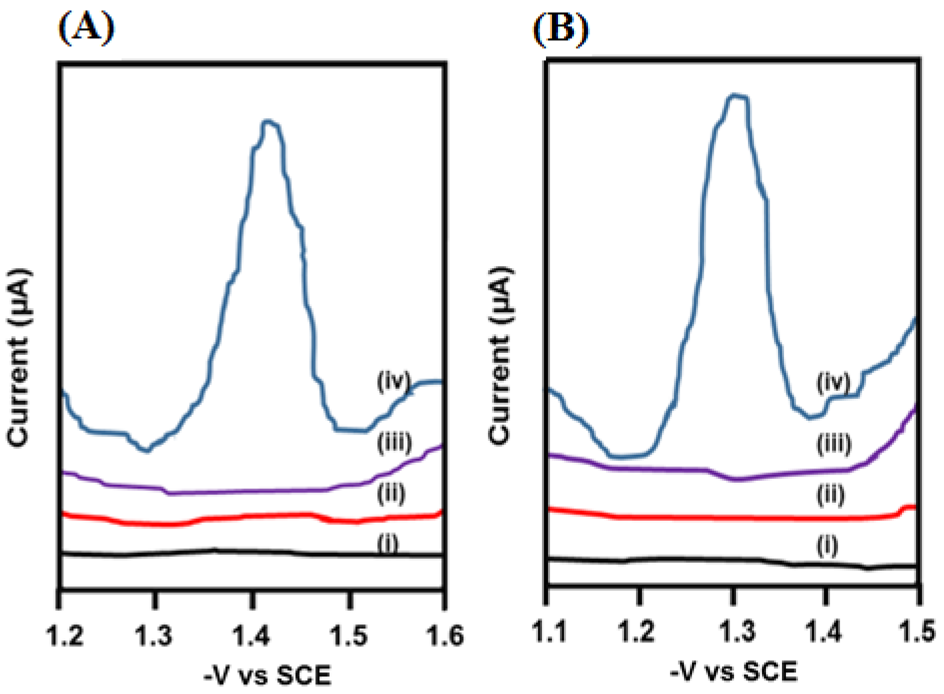


Figure 1. DC polarographic curves of Iron(II) with **(A)** ADMM-DTC (i) 0.4 M NH_4Cl, pH~6.6 (ii) a+2.0 mM ADMM-DTC (iii) a+ 3.0 ppm Iron(II) (iv) b+ 3.0 ppm Iron(II) **(B)** AMP-DTC (i) 0.4 M NH_4Cl, pH~6.4 (ii) a+3.0 mM AMP-DTC (iii) a+3.0 ppm Iron(II) (iv) b+3.0 ppm Iron(II) in presence of NH_4Cl-NH_4OH medium

3.1. Experimental and computational characterization of dithiocarbamates and their metal complexes with FTIR and UV-Visible spectroscopy

FTIR is the preliminary technique to confirm the chelation of ligand with metal ions. In generally, dithiocarbamates are the flexi-dentate ligands and can be involved in the symmetrical coordination by donating electrons from both sulphur atoms as well as unsymmetrically by donating electrons from one of the two sulphur atoms in chelation which was confirmed from our previous studies [29, 30]. Our FT-IR results suggest that ν(C-N), ν(C-S) and ν(M-S) are critical frequency modes to be taken into the consideration to find out the nature of dithiocarbamate (monodentate or bidentate) moiety and complexation capability. Interestingly, with reference to Table 1, the Iron (II)-dithiocarbamate solid complexes showed most intense and sharp bands.

Table 1. FT-IR data obtained from experimental and computational techniques for ADMM-DTC/AMP-DTC

Complex	Experimental			Computational		
	Frequency modes			Frequency modes		
	γ(C-N) cm^{-1}	γ (C-S) cm^{-1}	γ (M-S) cm^{-1}	γ(C-N) cm^{-1}	γ (C-S) cm^{-1}	γ (M-S) cm^{-1}
ADMM-DTC	1510	985	391	1514.54	914.21	395.56
AMP-DTC	1512	984	387	1517.63	965.8	394.75

The experimental results suggests that the peak corresponding to ν(C-N) stretching was observed at 1510 cm^{-1} and the ν(C-S) peak was found at 985 cm^{-1}. The ν(M-S) stretching frequency was observed at 391 cm^{-1}.

Table 2. UV-Visible data obtained from experimental and computational techniques for ADMM-DTC/AMP-DTC and their Iron(II) complexes

Dithiocarbamate/ Complexes	Experimental			Computational
	Stability studies Wavelength (nm)/Intensity			Simulation Wavelength (nm)/Intensity
	Day-1	Day-2	Day-3	
ADMM-DTC	309/0.461	309/0.460	309/0.451	315/0.462
AMP-DTC	321/0.573	321/0.572	321/0.572	320/0.580
Iron(II)-ADMM-DTC	404/0.826	404/0.821	403/0.820	410/0.834
Iron(II)-AMP-DTC	420/0.935	420/0.935	420/0.931	417/0.933

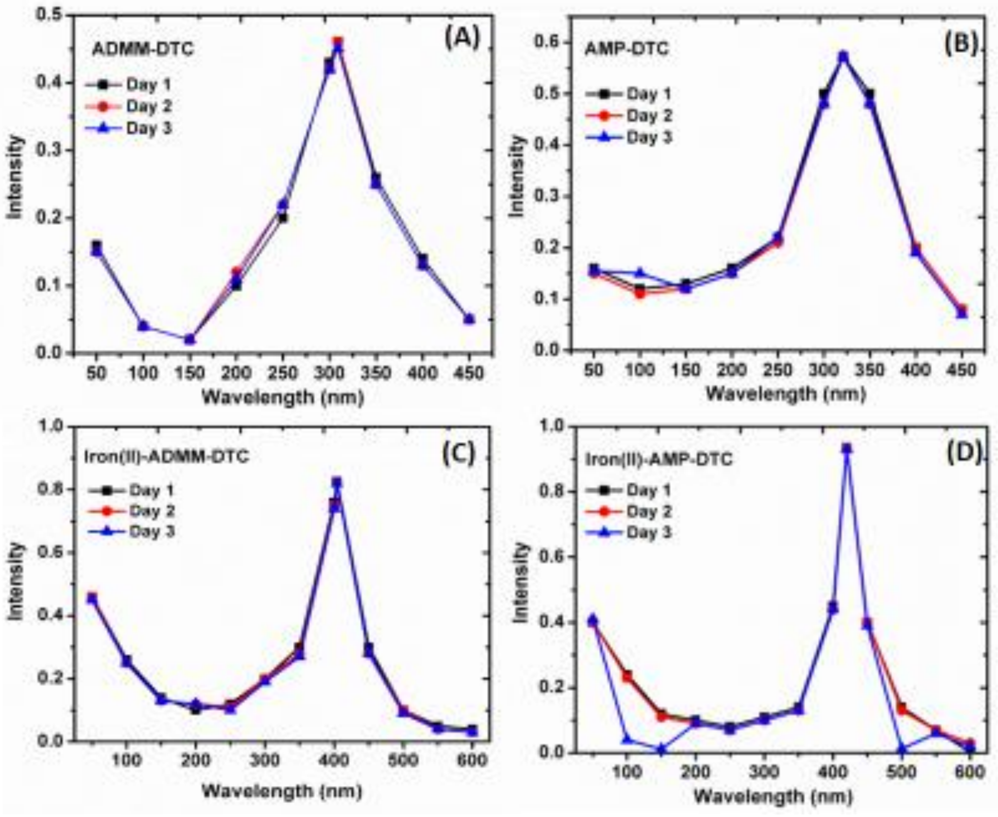


Figure 2. UV-visible spectroscopic studies of (A) ADMM-DTC (B) AMP-DTC (C) Iron(II)-ADMM-DTC and (D) Iron(II)-AMP-DTC for examination of stabilities

On the other hand, the computational results indicates the peaks corresponding to ν(C-N) stretching, ν(C-S) and ν(M-S) stretching frequency were found at 1512, 984 and 387 cm^{-1} respectively for Iron(II)-dithiocarbamte complexes. Based on the obtained FTIR experimental and computational data, dithiocarbamates exhibits bidentate nature with strong bonding capability towards Iron (II) [29, 30, 40]. The UV-visible spectra of two dithiocarbamates and their metal complexes were measured at room temperature for three consecutive days as represented in Table 2 and illustrated in Figure 2. The first spectra was recorded immediately after complexation and afterwards in successive 24 h against the blank. The results shows that absorbance remains relatively unaltered over a period of 3 days. This significantly confirmed the co-ordination and stability of Iron(II)-dithiocarbamate complexes under the optimum experimental conditions (Iron(II)-ADMM-DTC:-pH: 6.6, NH_4Cl-NH_4OH: 0.4 M, ADMM-DTC: 2.0 mM, Iron(II): 3.0 ppm and Iron(II)-ADMM-DTC:-pH: 6.4, NH_4Cl-NH_4OH: 0.4 M, AMP-DTC: 3.0 mM, Iron(II): 3.0 ppm. Nevertheless, minor variations in the absorbance of distinctive bands were noticed with time; without a substantial shift in the absorption peak of spectra.

3.2. CHW method optimization

The effect of pH on solutions containing 3.0 ppm of Iron (II) in 0.4 M NH_4Cl-NH_4OH for both ADMM-DTC (2.0 mM) and AMP-DTC (3.0 mM) was studied in the range of 5.0-10. With the increase in the pH, the height of the catalytic hydrogen currents increased until the pH of 6.6 and 6.4 was reached using ADMM-DTC and AMP-DTC respectively. Beyond that, current response decreased linearly with increase in the pH. With further increase in pH, the peak potential of the catalytic currents started shifting towards positive potential, hence pHs 6.6 and 6.4 were selected as optimum to attain the maximum CHWs as illustrated in Figure 3.

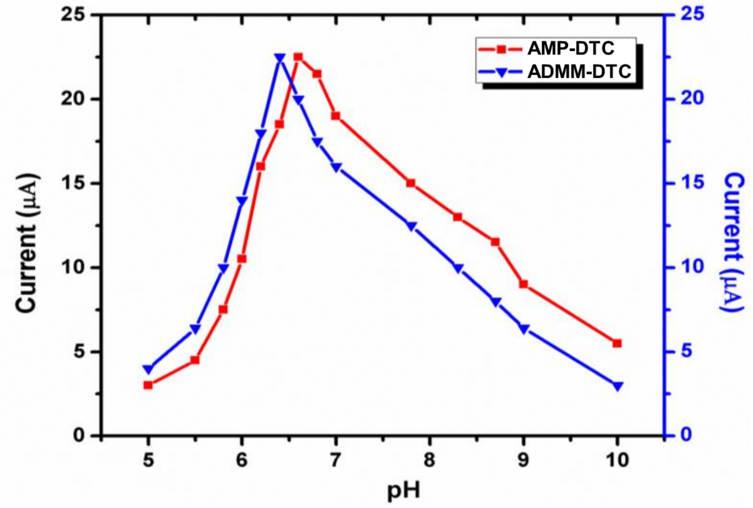


Figure 3. Effect of pH on Iron(II)-ADMM-DTC/AMP-DTC complexes.

The effect of the concentration of the supporting electrolyte (NH_4Cl-NH_4OH) was carried out in the range of 0.1 to 0.8 M while keeping the ADMM-DTC/AMP-DTC concentration fixed at 3.0/4.0 mM respectively. The well-defined and increase in CHW's were observed at 0.4 M NH_4Cl-NH_4OH

with both the dithiocarbamates (ADMM-DTC/AMP-DTC). The peak height of CHW's started decreasing linearly beyond 0.4 M NH_4Cl-NH_4OH and the peak potential of the CHW's shifts towards a positive potentials with an increase in NH_4Cl-NH_4OH throughout the concentration range of study. Hence, the optimum concentration of 0.4 M NH_4Cl-NH_4OH was maintained for further investigation as represented in Figure 4.

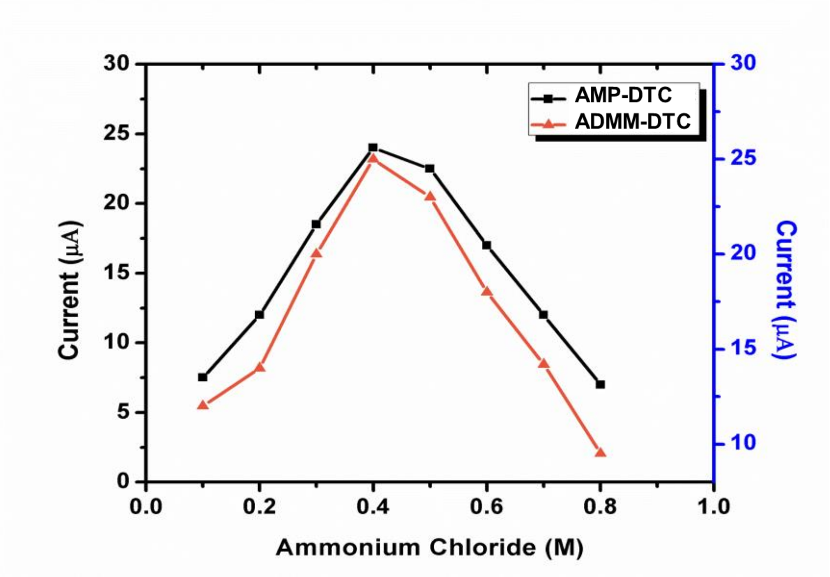


Figure 4. Effect of supporting electrolyte concentration on Iron(II)-ADMM-DTC/AMP-DTC complexes

The solutions containing 3.0 ppm of Iron (II), 0.4 M supporting electrolyte (NH_4Cl-NH_4OH) for both ADMM-DTC/AMP-DTC were fixed and the dithiocarbamate concentration was varied from 0.5 to 6.0 mM maintaining the pH of the solution at 6.6/6.4 for ADMM-DTC/AMP-DTC respectively. The peak current does not vary linearly with all concentrations of ligand which are typical characteristic nature of catalytic waves as shown in Figure 5.

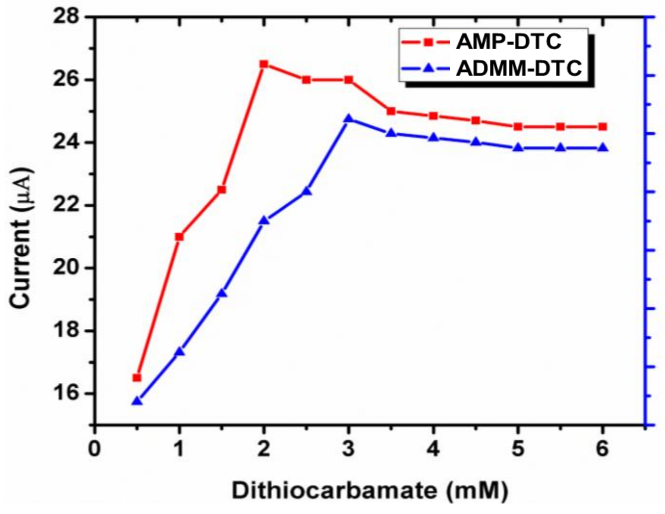


Figure 5. Effect of ligand concentration on Iron(II)-ADMM-DTC/AMP-DTC complexes.

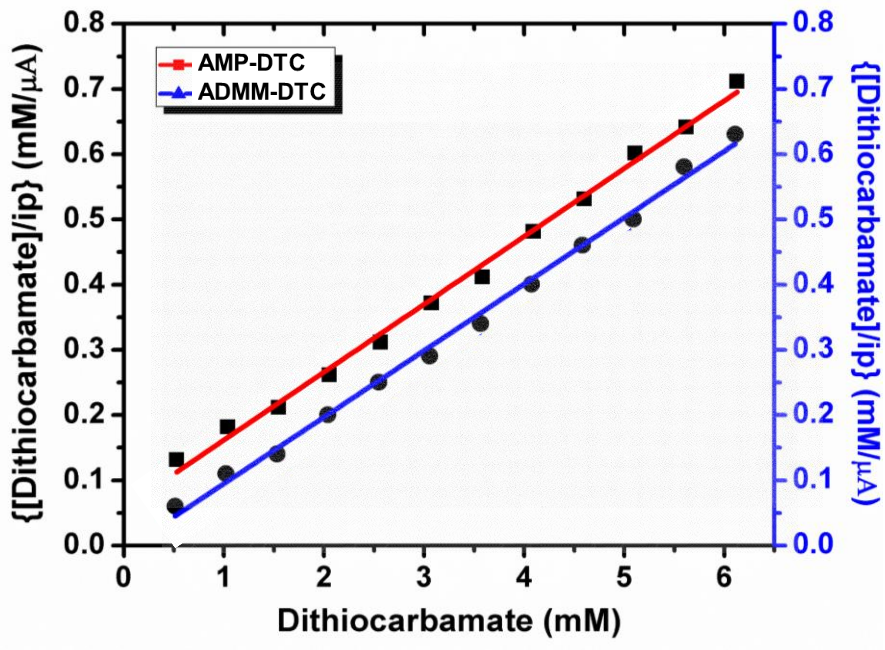


Figure 6. Langmuir adsorption isotherm plot of Iron(II)- ADMM-DTC/AMP-DTC complexes.

The obtained results indicated that the wave height of Iron(II)-dithocarbamate complexes increased linearly with the concentration of dithiocarbamate up to 2.0/3.0 mM for ADMM-DTC/AMP-DTC respectively. With further increase in concentration, the CHW's height are independent to concentration and shows that the complexes were highly stable. Therefore, 2.0/3.0 mM concentrations were fixed for further quantitative studies. The plot of {[dithiocarbamate]/i_p} V_S {dithiocarbamate} results in straight lines (Figure 6) and authorizes the adsorption process on the surface of working electrode.

The effect of mercury column height was studied by varying it volume and the polarograms were recorded for 3.0 ppm of Iron(II) to optimize experimental conditions for quantification. In the analytical data shown in Table 3, it was found that CHW's as well as $i_C/\sqrt{h}$ decreased with the height of the mercury column suggesting that the waves are catalytic in nature which was confirmed from our previous studies [46].

Table 3. Effect of height of mercury column on Iron(II)-ADMM-DTC/AMP-DTC systems.

Height of the mercury column, cm	Iron(II)-ADMM-DTC		Iron(II)-AMP-DTC	
	Current, µA	$i_c/\sqrt{h}$	Current, µA	$i_c/\sqrt{h}$
21	24.00	5.487	27.00	6.142
26	23.50	3.224	26.50	4.257
31	22.25	2.551	26.00	3.548
36	21.00	1.984	25.00	2.596

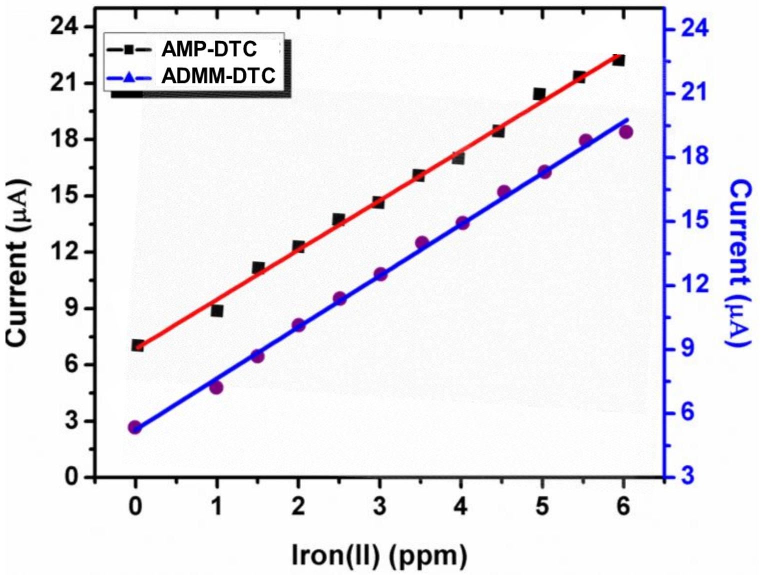


Figure 7. Effect of concentration of Iron(II) on peak current of Iron(II)-ADMM-DTC/AMP-DTC complexes.

The polarograms of the system with Iron (II)-ADMM-DTC/AMP-DTC complexes were recorded at temperatures varying from 15 to 45 ^{o}C. It was noted that with an increase in temperature, the CHW height and temperature coefficient value decreased gradually. Therefore, the $i_{C,}$ CHW's were completely independent above 30 ^{o}C. The effect of Iron(II) concentration in the range 0.1 to 6.0 ppm was studied on the peak current in the presence of optimal ligand (dithiocarbamates) and supporting electrolyte concentrations at fixed pHs. The obtained curves shows that the wave height increased linearly with the Iron(II) concentration in the range of 0.1 to 6.0 ppm with ADMM-DTC/AMP-DTC as shown in Figure 7. The Iron(II) reduction wave increased with increase in metal concentration without any shift in peak potential and interestingly the CHW's also increases linearly with Iron(II) concentration.

3.3. Computational discussion

3.3.1. HOMO-LUMO calculations

It is well known that the electron correlation is important for the transition metal complexes and the motion of the electrons are governed by their instantaneous positions rather than the average positions of other electrons. For DFT calculations, a mathematical representation of the molecular orbitals of the molecule or the basis set is specified which restricts the position of an electron in a particular region. Larger basis set leads to accurate approximations of the molecular orbitals. For the HOMO-LUMO calculations of the ligands and complexes discussed in the present study, 6-31g(d) basis set was chosen. The spatial distribution of the orbitals of the ligands, ADMM-DTC and AMP-DTC calculated using DFT/6-31g(d) have been illustrated in Figure 8.

The presence of electronegative oxygen atom in AMD-DTC is responsible for high band gap energy as compared to ADMM-DTC ligand. Figures 8c-d represents the HOMO and LUMO of geometrically optimized AMP-DTC ligand. In this case, HOMO has electron density on sulphur atoms whereas, in LUMOs, the electron density is high on nitrogen, sulphur as well as the hydrogen atoms of the ring. The band gap energy was found to be 4.12 eV. For the DFT calculated orbitals, the HOMOs are located on the metal atoms i.e. sulphur atoms (Figure 9b) whereas LUMOs are spread on the nitrogen atom of the ADMM-DTC ligand and showing 2pz shape (Figure 9c). It was observed that HOMO has more energy value as compared to LUMO. The band gap energy as calculated from the obtained values of HOMO and LUMO found to be 4.17 eV. Figure 9 represents HOMO-LUMO orbitals and energies of Iron(II)-ADMM-DTC complex molecule where Iron atom has bound with two sulphur atoms thereby forming a complex. In the case of LUMO, the electron density is located on Iron atom showing a dz^2 shape. The calculated band gap energy for the complex is 0.60 eV (see Figure 9a-b).

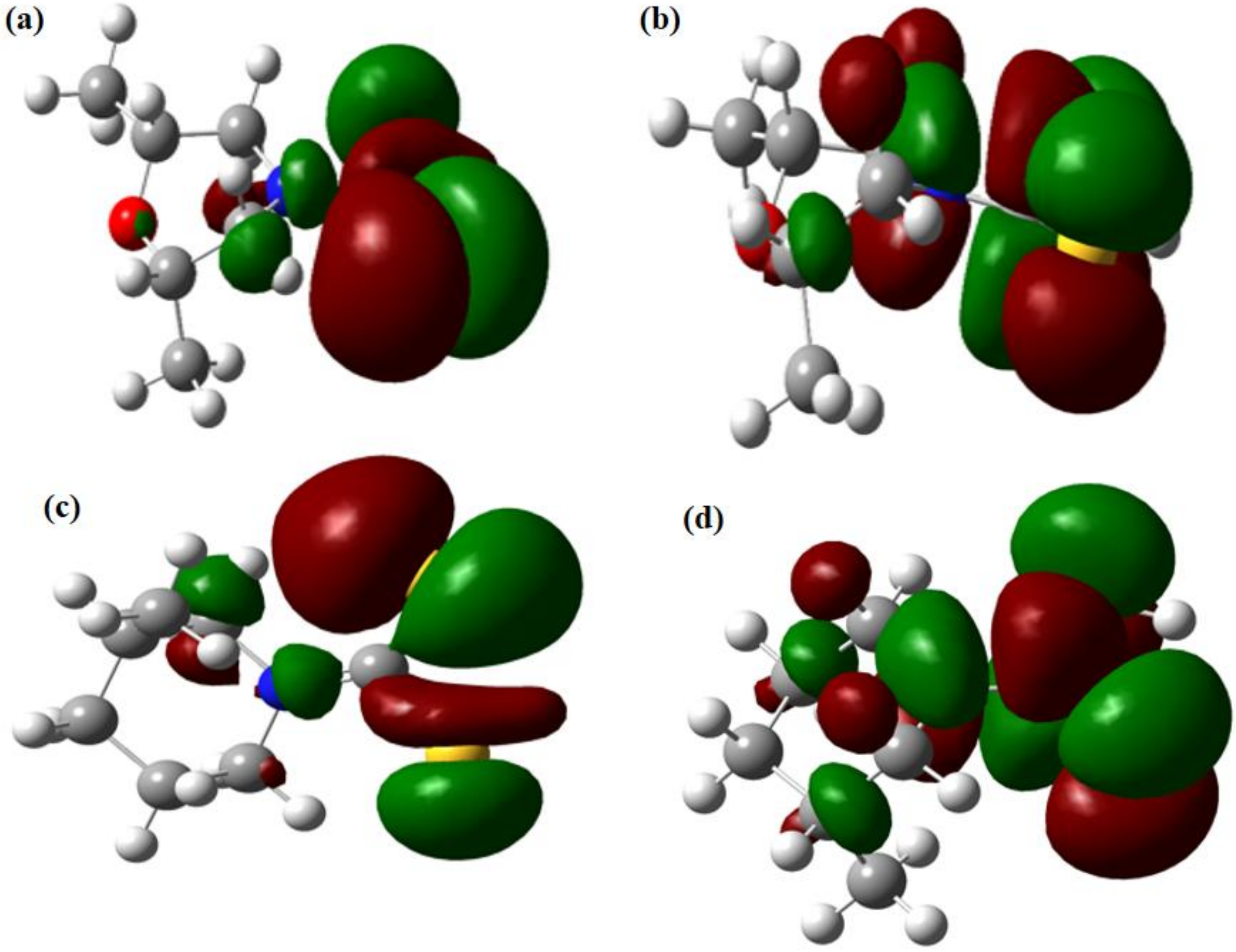


Figure 8. HOMO and LUMO images of (**a**) ADMM-DTC (**b**) ADMM-DTC (**c**) AMP-DTC and (**d**) AMP-DTC LUMO as calculated from DFT/6-31g(d)

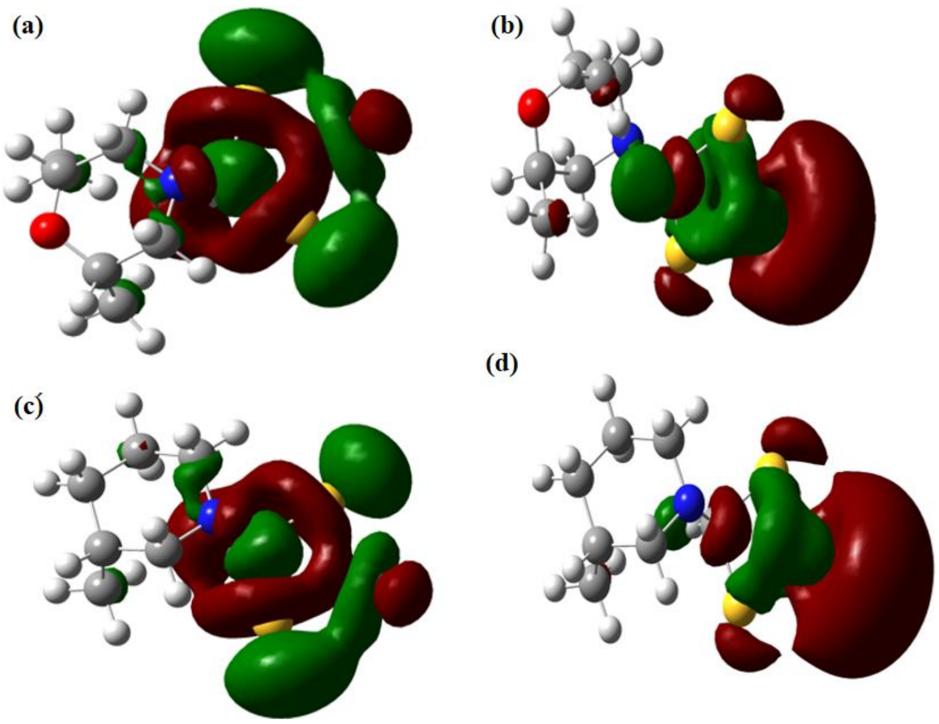


Figure 9. HOMO and LUMO images of (**a**) Iron(II)- ADMM-DTC (**b**)Iron(II)-ADMM-DTC (**c**) Iron(II)-AMP-DTC and (**d**) Iron(II)-AMP-DTC LUMO as calculated from DFT/6-31g(d)

In the Iron (II)-AMP-DTC complex, HOMOs are located spatially on the Iron, sulphur and nitrogen atoms whereas LUMOs are located more on Iron atom. The band gap energy for this complex is 0.54 eV (see Figure 9c-d).

The obtained DFT results from this study suggest that there was a good correlation between experimental and computational data. When compared to ADMM-DTC, the polarogram obtained by AMP-DTC has a more current signal (see Figure 1(B)) which was evident by HOMO-LUMO studies, indicating that the band gap of AMP-DTC is less than ADMM-DTC. This facilitates electrons transfer from Iron(II) to AMP-DTC. On the other hand, stability studies of Iron(II)-ADMM-DTC/AMP-DTC complexes were complemented by DFT calculations which followed the similar trend reported in the . literature [41]. The obtained experimental data (see Table 2) reveals that Iron(II)-AMP-DTC complex was more stable than Iron(II)-ADMM-DTC which were supported by HOMO-LUMO studies.

3.4. Effect of interference studies

To test the selectivity of this method, the impact of interference ions on the CHW of the Iron(II)-ADMM-DTC/AMP-DTC systems were investigated on 0.1 µg mL^{-1}. The tolerance limit was measured as the concentration of an interference ion, resulted in ± 2 % variation in current signals of Iron(II)-ADMM-DTC/AMP-DTC systems. Most of the common anions and cations with relatively high concentration up to 100-fold do not interfere with the Iron(II)- Iron(II)-ADMM-DTC/AMP-DTC systems. However, some of the cations such as Fe^{3+}, Sr^{2+} and La^{3+} ions does interfere, but their effect could be avoided using 5 % citric acid as a masking agent. The results due ion interference were shown in Table 4.

Table 4. Effect of interference ions on the Iron(II)-ADMM-DTC/AMP-DTC systems at 0.1 µg mL^{-1} of Iron(II).

Interference ions	Tolerance limit (µg mL^{-1})	Interference ions	Tolerance limit (µg mL^{-1})
Ba^{2+}	10.0	Co^{2+}	5.0
Mn^{2+}	5.0	Fe^{3+}	1.0
Pb^{2+}	15.0	Cu^{2+}	10.0
Y^{3+}	10.0	NO_3^-	NI
Cu^{2+}	5.0	SO_4^{2-}	NI
Sm^{3+}	1.0	Br^-	NI
Al^{2+}	5.0	SCN^-	NI

NI: No Interference effect

3.5. Analytical applications

Aliquots of the sample solutions (prepared as described under experimental section) were analysed quantitatively with polarography under the optimum conditions. The standard addition method was adapted for the analysis of Iron (II) in both water and leafy vegetable samples. The corresponding curve results obtained by this method are further supported by differential pulse polarography and its curves are shown in Figures 9a-b.

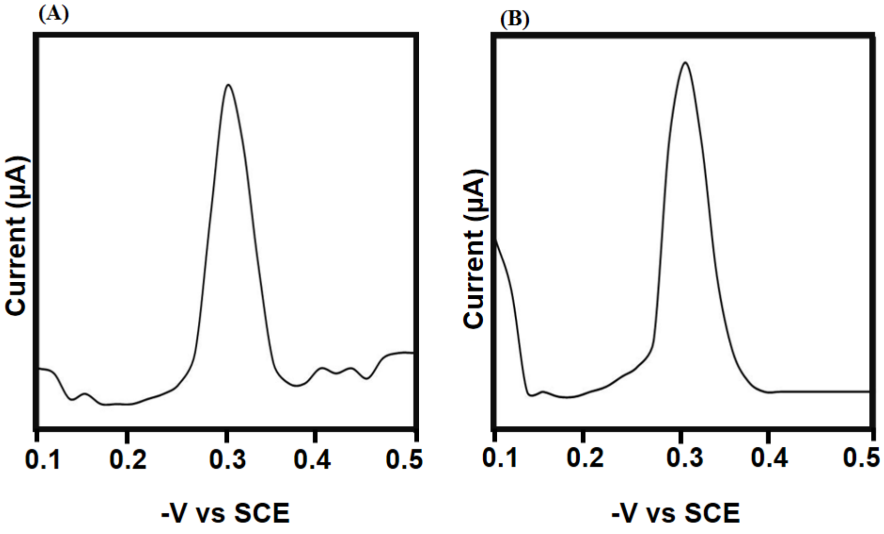


Figure 10. DPP curves for the determination of Iron(II) with (**A**) ADMM-DTC (**B**) AMP-DTC in presence of NH_4Cl-NH_4OH medium (Conditions: Current Range: 100 µA Scan Rate: 6 mV S^{-1}, Pulse Amplitude: 50 mV, Drop time: 1 Sec, Iron(II) : 1.0 ppb)

The present method was compared with the DPP method. The analytical data summarized in Tables 5-8 suggest that the percentage recovery of Iron (II) from water and vegetable samples ranges from 97.0 to 100.0 % with R.S.D (%) = 2.15 which is a facile, sensitive and more reliable method.

Table 5. Determination of Iron(II) with ADMM-DTC in water samples collected from Renigunta Industrial Estate, Tirupati, INDIA using CHW method.

Sample[a]	Iron(II) Added, ppm	Catalytic hydrogen current method(DC)		DPP method	
		AMP-DTC		AMP-DTC	
		Iron(II) Found, ppm	Recovery(%)±R.S.D[b]	Iron(II) Found, ppm	Recovery(%)±R.S.D[b]
I	0.2	0.297	98.50±2.39	0.298	99.00±2.55
	0.4	0.544	98.50±2.37	0.546	99.00±2.54
	0.6	0.673	98.33±2.35	0.675	99.16±2.51
	0.8	0.810	95.00±2.06	0.830	97.50±2.31
	1.0	1.070	96.00±2.17	1.090	98.00±2.30
II	0.2	0.264	97.00±2.26	0.266	98.00±2.55
	0.4	0.526	99.00±2.55	0.528	99.50±2.55
	0.6	0.654	99.00±2.54	0.657	99.50±2.29
	0.8	0.832	99.00±2.54	0.835	99.37±2.53
	1.0	1.080	96.00±2.17	1.100	98.00±2.31

[a] 5 mL of the concentrated sample was used, [b]Relative Standard Deviation(n=6)

Table 6. Determination of Iron(II) with AMP-DTC in water samples collected from Renigunta Industrial Estate, Tirupati, INDIA using CHW method.

Sample[a]	Iron(II) Added, ppm	Catalytic hydrogen current method(DC)		DPP method	
		ADMM-DTC		ADMM-DTC	
		Iron(II) Found, ppm	Recovery(%)±RSD[b]	Iron(II) Found, ppm	Recovery(%)±RSD[b]
I	0.2	0.248	99.00±2.54	0.249	99.50±2.55
	0.4	0.480	99.00±2.55	0.488	99.50±2.54
	0.6	0.715	99.16±2.51	0.718	99.66±2.61
	0.8	0.960	100.00±2.96	0.960	100.00±2.96
	1.0	1.060	98.00±2.31	1.100	100.00±2.96
II	0.2	0.236	98.00±2.30	0.238	99.00±2.42
	0.4	0.457	99.25±2.48	0.459	99.75±2.73
	0.6	0.706	99.33±2.52	0.708	99.66±2.61
	0.8	0.964	99.25±2.48	0.963	99.12±2.50
	1.0	1.090	98.00±2.31	1.100	99.00±2.42

[a] 5 mL of the concentrated sample was used, [b]Relative Standard Deviation (n=6)

Table 7. Determination of Iron(II) with ADMM-DTC in leafy vegetable samples collected from nearby villages of Tirupati, INDIA using CHW method.

Sample[a] Scientific / Local name	Fe(II) added, ppm	CHC method (DC polarography)		DPP method	
		Amm 3-methyl Pip-DTC		Amm 3-methyl Pip-DTC	
Leafy Vegetables		Fe(II) found, ppm	Recovery(%) ± RSD[b]	Fe(II) found, ppm	Recovery(%) ± RSD[b]
Amaranth Viridis (Kuppa Keerai)	0.5	1.412	99.32±2.15	1.410	98.36±2.45
Amaranth polygonoides (Siri keerai)	0.5	1.842	99.15±2.85	1.839	98.75±2.55
Mentha spicata (Mint leaves)	0.5	1.973	97.15±2.35	1.975	98.13±2.45
Piper betle (Betle leaves)	0.5	1.485	98.25±2.15	1.481	97.92±2.35
Murraya Koenigii (Curry leaves)	0.5	1.329	97.85±2.55	1.331	98.95±2.90

[a] 5 mL of the concentrated sample was used, [b]Relative Standard Deviation(n=6)

Table 8. Determination of Iron(II) with AMP-DTC in leafy vegetable samples collected from nearby villages of Tirupati, INDIA using CHW method.

Sample[a] Scientific / Local name	Fe(II) added, ppm	CHC method (DC polarography)		DPP method	
		ADMM-DTC		ADMM-DTC	
Leafy Vegetables		Fe(II) found, ppm	Recovery(%) ± RSD[b]	Fe(II) found, ppm	Recovery(%) ± RSD[b]
Amaranth Viridis(Kuppa Keerai)	0.5	1.413	99.62±2.55	1.411	98.56±2.35
Amaranth polygonoides (Siri keerai)	0.5	1.840	98.65±2.35	1.838	98.15±2.55
Mentha spicata (Mint leaves)	0.5	1.975	97.28±2.05	1.976	98.59±2.45
Piper betle (Betle leaves)	0.5	1.483	97.89±2.15	1.480	97.12±2.85
Murraya Koenigii (Curry leaves)	0.5	1.330	98.15±2.55	1.331	98.65±2.70

[a] 5 mL of the concentrated sample was used, [b]Relative Standard Deviation(n=6)

3.6. Comparison of present method over reported literature methods for the detection of Iron (II)

The present method was compared with the reported literature methods in terms of detection limits and selectivity of ligand towards the targeted analyte. In this study, due to the limited number of studies on Iron (II) determination using DC polarography couple to CHW technique, anodic stripping voltammetry was also considered for comparison. The reported ligands such as 1-amine-2-naphthol-4-sulphonic acid [45] and 1-nitroso-2-naphthol [46] are sensitive with fair LOD's for the detection of Iron (II), however the buffer system is highly complicated and ligands are expensive when compared with the present buffer system (NH_4Cl-NH_4OH) and ligands (ADMM-DTC and AMP-DTC). In the other reports [42, 43, 44], traditional methodologies were employed which leads to the lack of sensitivity and selectivity when compared to the present method. Therefore, the present method was found to be facile, rapid, sensitive and selective for the determination of Iron(II) in different samples of environmental importance. The compared data was presented in Table 9.

Table 9. Comparison of present method over reported literature methods for the determination of Iron(II)

Ligands	pH/Buffer	Samples	LOD's	Citation
EDTA	4.0/Acetate	-	-	[16]
2-Mercapto benzimidazole	7.2/Phosphate	Agricultural and Drugs	0.1 ppm	[39]
-	5.4 to 8.2/Ammonium tartrate	-	-	[42]
-	3.0/ Sodium carbonate-oxalic acid	Coal mine waste waters	10 ppm	[43]
-	6.0/ Sodium Citrate (in presence of 0.005 % gelatin) 2 and 11/Sodium Citrate (in absence of 0.005 % gelatin	-	-	[44]
1-amine-2-naphthol-4-sulphonic acid	6.9/ piperazine-N, N'-bis-2-ethane sulphonic acid), (N-2-hydroxyethylpiperazine-N'-Zethane sulphonic acid	Sea waters	0.36 ppt	[45]
1-nitroso-2-naphthol	6.8/ piperazine-NN1-bis-2-ethane sulfonic acid, monosodium salt	Sea waters	0.2 nM	[46]
Imines	7.8/ Ammonium chloride-ammonium hydroxide	Drinking waters, agricultural materials and pharmaceutical samples.	0.1 ppm	[47]
-	4.35/Acetate buffer		0.02 µg mL^{-1}	[48]
ADMM-DTC AMP-DTC	6.6 6.4/ Ammonium chloride-ammonium hydroxide	Waters Leafy vegetable samples	0.1 ppm	Present study

4. CONCLUSIONS

The CHW based polarographic method is facile, sensitive, selective and reliable for the determination of Iron(II). The two dithiocarbamate (ADMM-DTC/AMP-DTC) employed in this study are cost-effective, selective and fairly soluble in water. The present method is environmental friendly without usage of any hazardous materials, the mercury used in this investigation can be purified and re-used for further experiments. The effect of pH and ammonium chloride concentration clearly indicated the characteristic property of catalytic surface reactions between Iron(II) and dithiocarbamates. The height of the catalytic wave was found to vary linearly with the concentration of dithiocarbamates with parabolic shape. The non-linear portion has the shape of a curve resembling a Langmuir adsorption isotherm and therefore the plot of [(Dithiocarbamate)/i_p] vs [Dithiocarbamate] was straight lines. Lastly, the electron donating ability of ADMM-DTC/AMP-DTC was evaluated in terms of their HOMO-LUMO energy gaps measured at DFT level. These results were experimentally supported by DC and DP polarographic data. Based on this interpretation, AMP-DTC is having more electron donating capacity and Iron(II)-AMP-DTC complex is stable than Iron (II)-ADMM-DTC complex.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial assistance from Durban University of Technology, South Africa. The authors would like to express their acknowledgment to the Centre for High Performance Computing, an initiative supported by the Department of Science and Technology of South Africa.

References

1. M.A. Akl, Y. Mori, K. Sawada, *Anal. Sci.*, 22(9)(2006)1169.
2. R.G. Anderson, G. Nickless, *Anal. Chim. Acta.*, 39(1967)469.
3. R.G. Anderson, G. Nickless, *Analyst*, 93(1968)13.
4. T.H. Bothwell, R.W. Charlton, J.D. Cook, C.A. Finch, Iron metabolism in man., Black well, Oxford, 1979.
5. C. Reilly, “Metal Contamination of Food”, Applied Science Publisher Ltd., London, 156(1980).
6. E.J. Underwood, “Trace Elements in Human and Animal Nutrition”, Academic Press, New York, 25(1977).
7. McGraw-Hill, “Encyclopedia of Science & Technology”, 5th Edition, McGraw-Hill Book Company, New York, 369, 1982.
8. C. Michaelis, N.S. Tarlano, J. Clune, R. Yolles, *Anal. Chem.*, 34(11)(1962)1425-1426.
9. K.W. Cha, K.W. Park, *Talanta*, 46(1998)1567–1571.
10. E. Gundersen, E. Steinnes, *Talanta*, 18(11)(1971)1167-1169.
11. R. Armila, A. Anjala, R. Sanjeev Das, *IJPBA*, 4(3)(2013) 435-438.
12. T. Stasys, S. Laura, K. Rolandas, *J.Serb.Chem.Soc.*, 69(5) (2004)393-402.
13. L.S. Huang, K.C. Lin, *SpectroChim. Acta, part B.*, 56(2001)123-128.
14. Y.S. Milyanskii, S.I, Sinyokova, *Zh. Analyst. Chem.*, 23(1968)1103-1107.
15. Tsuyoshi Nomura, *J. Electroanal. Chem.*, 124(1981)213-219.
16. G. Visalakshi, S.V. Narasimhan, K.S. Venkateswarlu, *Anal. Chim. Acta*, 212(1988)335-339.
17. A.M. Bond, B.V. Pfund, O.M.G. Newman, *Anal. Chim. Acta*, 277(1993)145-151.
18. O.E. Ravinskii, A.K. Neverova, A.V. Kabatskii, *Zh. Anal. Khim.* 30(1975)2409-2413.
19. V.F. Toropova, C.K. Nudnikov, V.P. Frolova, N.A. Ulakhovich, *Ibid*, 32(1977)1850-1855.

20. A.G. Fogg, J.E. Lewis, *Talanta*, 25(1978)461-467.
21. İlknur Durukan, Çiğdem Arpa Şahin, Nuray Şatıroğlu, Sema Bektaş, *Microchem. J.*, 99 (2011)159-163.
22. Tamer Awad Ali, Ahmed A. Farag, Gehad G. Mohamed, *J. Ind. Eng. Chem.*, 20 (2014) 2394–2400.
23. Durali Mendil, Murat Karatas, Mustafa Tuzen, *Food Chem.*, 177(2015)320–324.
24. S. Kanchi, K. Saraswathi, N. Venkatasubba Naidu, *Environ. Monit. Assess.*, 183(2011) 531–543.
25. S. Kanchi, M. Sulochana, K. Babu Naidu, K. Saraswathi, Nuttalapati Venkatasubba Naidu, *Food Anal. Methods*, 4(2011)453-464.
26. N. Venkatasubba Naidu, S. Kanchi, T. Niranjan, K. Saraswathi, *Anal. Chem.: An Ind. J.*, 10(4)(2011)231-238.
27. N. Venkatasubba Naidu, S. Kanchi, P. Krishnamurthy, K. Saraswathi, *Chem. Technol: An Ind. J.*, 6(1)(2011)6-12.
28. S. Kanchi, K. Saraswathi, N. Venkatasubba Naidu, *Food Anal. Methods*, 5(2012) 69-81.
29. S. Kanchi, P. Singh, M.I. Sabela, K. Bisetty, N. Venkatasubba Naidu, *Int. J. Electrochem. Sci.*, 8(2013)4260-4282.
30. S. Kanchi, M.I. Sabela, P. Singh, K. Bisetty, *Arabian J. Chem.*, (2013), http://dx.doi.org/10.1016/j.arabjc.2013.07.061 (Inpress)
31. Myalowenkosi I. Sabela, Suvardhan Kanchi, Bathinapatla Ayyappa, Krishna Bisetty, *Int. J. Electrochem. Sci.*, 9 (2014) 6751-6764.
32. S. Kanchi, P. Singh, K. Bisetty, *Arabian J. Chem.*, 7(2014)11–25.
33. C. Giridhar, S. Kanchi, T. Niranjan, N. Venkatasubba Naidu, *Int. J. Chem. Anal. Sci.*, 5(1)(2014)24-32.
34. Suvardhan Kanchi, Bathinapatla Ayyappa, Myalowenkosi I Sabela, Krishna Bisetty, Nuthalapati Venkatasubba Naidu, *J. Environ. Anal. Chem.*, 1(1)(2014)1-9.
35. Chembeti Giridhar, Suvardhan Kanchi, Thondavada Niranjan, Krishna Bisetty, Nuthalapati Venkatasubba Naidu, *J. Environ. Anal. Chem.*, 1(1)(2014)1-8.
36. C. Giridhar, S. Kanchi, T. Niranjan, N. Venkatasubba Naidu, *Chem. Sci. Trans.*, 3(2)(2014)778-790.
37. Niranjan Thondavada, Suvardhan Kanchi, Krishna Bisetty, Venkatasubba Naidu Nuthalapati, *Int. J. Chem. Anal. Sci.*, 6(1)(2015)1-7.
38. T. Niranjan, Suvardhan Kanchi, Krishna Bisetty, N. Venkatasubba Naidu, *Asian J. Chem.*, 27(10) (2015) 3598-3604.
39. N. Saritha, M. Sulochana, N. VenkatasubbaNaidu, K. Saraswathi, *Int. J. ChemTech Res.*, 4(4), (2012) 1498-1472.
40. Aysegul Golcu, *Tansit. Metal Chem.*, 31 (2006) 405-412.
41. S.A. Beyramabadi, A. Morsali, S.H. Vahidi, *J. Struct. Chem.*, 53(4) (2012) 665-675.
42. Colin D. Kennedy, *Analyst.*, 115 (1990) 1067-1071.
43. L. Stanford, Tackett, Larry F. Wieserman, *Anal. Lett.*, 5(9) (1972) 643-651.
44. Louis Meites, *Anal. Chem.*, 20 (10), 1948, 895–897.
45. M.G. Constant, Vun den Berg, *J. Electroanal. Chem.*, 177 (1984) 269-280.
46. Kunibiko Yokoi, M.G. Constant, vun den Berg, *Electroanal.*, 4 (1992) 65-69.
47. N. Venkatasubba Naidu, N. Saritha, A. Varaprasad, K. Saraswathi, *Anal. Chem.: An Ind. J.*, 8(3)(2009)230-234.
48. I. M. Fitsev, V. F. Toropova, G. K. Budnikov, *J. Anal. Chem.*, 55(11) (2000) 1195-1197.