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Electro Analysis of Heavy Metals in *Syringodium Isoetifolium*

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Abstract:

To identify the frequency of functional groups in *Syringodium isoetifolium*, FT-IR technique was performed. The main functional groups involved in the sample uptake are ester sulfates, tri substituted alkenes and halides. FT-IR spectra also exhibited the presence of metals such as Pb, Cu, Cd, Ni and Cr. The elemental composition in *Syringodium isoetifolium* by Atomic Absorption Spectroscopy (AAS) is in the order $Co > Pb > Ni > Cr > Fe$. Glassy carbon electrode have been developed in this investigation for the analysis of heavy metals such as copper and arsenic in formulated sample of *Syringodium isoetifolium* by cyclic voltammetry (CV) and linear sweep anodic voltammetry (LSAV). The GC electrode suggested as a suitable matrix for rapid monitoring of these heavy metals at trace levels.

Keywords: FT-IR, AAS, CV, Heavy metals, *Syringodium isoetifolium*.

1. Introduction

Trace metals create several environmental and human health concerns issues when elevated concentrations of metals are present in environment. In this regard, cadmium (Cd), nickel (Ni) and cobalt (Co) are trace metals of prime environmental concern, since they are significant for environmental surveillance, food control, occupational medicine, toxicology and hygiene [1]. The contamination of water with arsenic is a serious worldwide threat to human health especially in Asian countries including Bangladesh, Pakistan, China, along with and eastern parts of India, which generally found due to human activities like mining, combustion of fossil fuels, use of arsenic pesticides, herbicides and crop etc. The World Health Organization's arsenic guideline value for drinking water is 10 ppb [2]. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, geno toxic, mutagenic and carcinogenic effects.

Lead (Pb) is another metal that is constantly monitored in natural and drinking water due to the harmful effects that are often manifested in young children [3]. It is also known that several trace metals are regarded as essential micro-nutrients and play an integral role in the life processes of living organisms. In contrast, metals such as aluminium, silver, cadmium, gold, lead and mercury play no biological role in living organisms and lead to toxicity when present [4-6]. At present there are number of methods available for As detection in laboratory viz. Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption (GFAA), Hydride Generation Atomic Absorption Spectroscopy (HGAAS) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). However, these instruments are bulky, expensive to operate and maintain, as well as require fully equipped laboratories.

Electrochemical methods are preferred over analytical methods discussed above due to number of advantages like ease of portability, low cost instrumentation, less time consuming, longer life time, can monitor large number of sample etc. Seaweeds are multicellular macroalgae used as potential renewable resource in the field of medical and commercial environment [7]. Now a days seaweeds are used as dietary food supplements in daily life and it regulates the human health [8]. In this paper, the use of a GCE as a transducer for the voltammetric analysis of heavy metals in *Syringodium isoetifolium* is reported.

2. Materials and Methods

2.1. Collection and Preparation of Sample Powder

Syringodium isoetifolium was collected from V.O.C Port Trust, Tuticorin coast of Tamil Nadu, India. Collected sample was washed thoroughly with seawater to remove all the unwanted impurities, adhering sand particles and epiphytes. Then the sample was washed thoroughly using tap water to remove all the salt on the surface. The water was drained off and the sample was spread on blotting paper to remove excess water. The sample was shade dried and ground to make powder.

2.2. Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR analysis was performed using a Fourier Transform Infrared (FT-IR) spectrometer (Thermo Scientific Nicolet iS5) iD1 transmission accessory system. FT-IR spectra was recorded in the wave number range from 4000 to 400 cm^{-1} using 16 scans.

2.3. Ultraviolet-Diffuse Reflectance Spectroscopy (UV-DRS)

UV-Visible Spectrophotometer model JASCO V-530 with diffuse reflectance accessory was used to carry out ultraviolet visible-diffuse reflectance spectroscopic analysis in the wavelength region 200 to 900 nm.

2.4. Atomic Absorption Spectroscopy (AAS)

Elemental analysis was carried out on Thermoscientific iCE 3000 series Atomic Absorption Spectrophotometer. The process of atomic absorption spectroscopy (AAS) involves two steps: 1. Atomization of the sample. The absorption of radiation from a light source by the free atoms.

2.5. Atomic Force Microscopy (AFM)

The surface morphology was studied by Nanosurf Easy scan 2 controlled AFM. AFM provides a 3D profile of the surface on a nanoscale, by measuring forces between a sharp probe (<10 nm) and surface at very short distance (0.2-10nm probe-sample separation).

2.6. Electrochemical Methods

Cyclic Voltammetry (CV) and linear sweep anodic voltammetry (LSAV) are performed with a CHI 650C electrochemical workstation. The working electrode is a glassy carbon electrode (GC). An Ag/AgCl 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

3.1. Fourier Transform Infrared (FT-IR) Spectroscopic Analysis

FTIR study was carried out to identify the functional groups present in *Syringodium isoetifolium* which was collected in three different months in the 4000-400 cm^{-1} range (Fig. 1). The characteristic wave numbers of specific functional groups identified in the sample were as follows: OH group (3419.98 cm^{-1}), C-H stretch (2925.58 cm^{-1}), CH_2 stretch (1575.83 cm^{-1}), geminal methyl (1384.72 cm^{-1}), C-O acetate ($1320.59, 1251.57 \text{ cm}^{-1}$), and trans-distributed $-\text{C}=\text{C}-$ (1059.71 cm^{-1}), which agreed well with the reported data [9, 10]. The most important bands were assigned 915.53 cm^{-1} and 885.97 cm^{-1} corresponding respectively to ester sulfates, the asymmetric stretching of S=O [11]. 819.24 cm^{-1} indicates the presence of C-H deformation of tri substituted alkenes. C-Cl stretching vibration of halides appeared at 601.12 cm^{-1} .

The spectra also exhibited a stretching of band appearing at $1073.78, 1070.59, 1061.89, 1059.21$ and 1039.71 cm^{-1} which was assigned to the presence of metals such as Pb, Cu, Cd, Ni and Cr respectively. Numerous workers (Sar et al., 1999; Norton et al., 2004; Lodeiro et al., 2006; Tunalı et al., 2006; Gabr et al., 2008; Giotta et al., 2011) has been reported the same results [12-17].

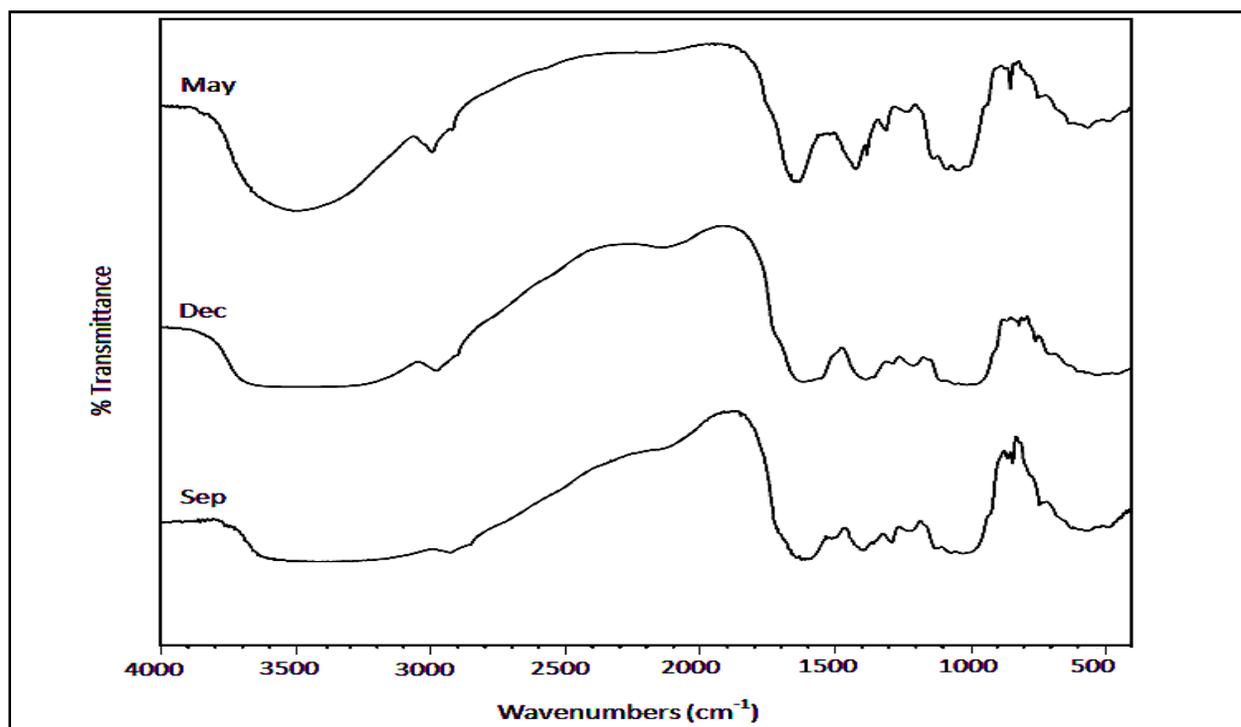


Figure 1: FTIR spectra of *Syringodium isoetifolium* in three different months

3.2. Ultraviolet - Diffuse Reflectance Spectroscopic (UV-DRS) Analysis

The UV spectra was studied for the *Syngodium isoetifolium* collected in three different months (Figure 2). There were no significant differences between the three spectra. All the three spectra show similar bands with slight variation in the absorbance. The peak corresponding to 238 nm may be due primarily to Cu^+ [18]. The absorbance band at 286 nm may be responsible for Cu [19]. The absorption peak at 350 nm may be due to the presence of Cd [20]. The peak at 415 nm may also be due to the presence of Ni. The absorbance band at 508 and 535 nm may be present for Cu. The absorbance measured at 620 nm may be primarily to d-d transitions in Cu^{2+} ions.

Only one broad band was obtained at 669 nm for all the three samples. The absorbance band at 669 nm may be due to the presence of heavy metal of Cu [21]. 0.515601, 0.597201 and 0.604571 are the absorbance values of *Syngodium isoetifolium* corresponding to the months of December, September and May respectively.

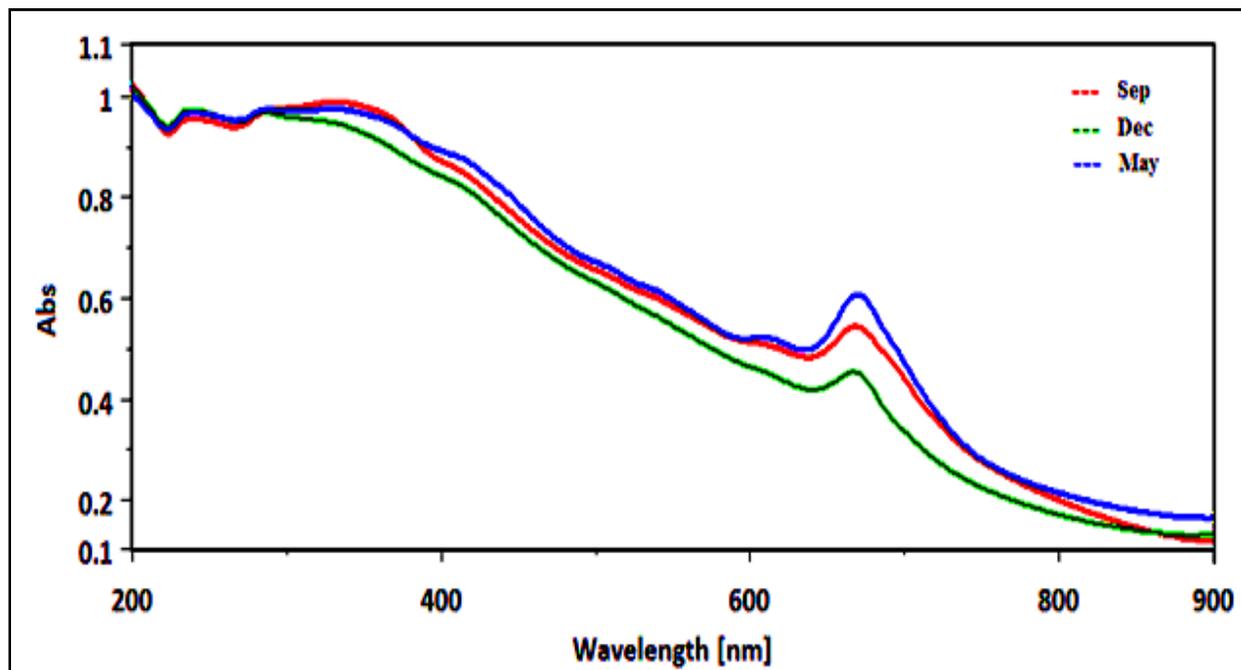


Figure 2: UV (DRS) spectra of *Syngodium isoetifolium* from autumn (Sep), winter (Dec) and spring (May) season

3.3. Atomic Absorption Spectroscopic (AAS) Analysis

In the present study, the concentrations of heavy metals in *Syngodium isoetifolium* were determined. The recoveries of 5 heavy metals were between 0.51 and 74 ppm. According to average value, the heavy metal concentrations in the sample were in the order of Co (0.51 ppm) > Pb (0.9 ppm) > Ni (1.5 ppm) > Cr (4.2 ppm) > Fe (74 ppm).

WHO (1990) highest permissible concentration of chromium in drinking water was mentioned as 0.1 ppm [22]. The permissible limit set by FAO/WHO for lead, nickel and iron in edible plants were 0.43, 1.63, and 20 ppm. The results implied that only the concentration of nickel in *Syngodium isoetifolium* was within the permissible limit. All the other metals showed higher than their respective permissible limit.

3.4. Atomic Force Microscopic (AFM) Studies

The morphology of thin film of *Syngodium isoetifolium* revealed nearly cloudy and snow zone structures in acid and aqueous medium respectively. Fig. 3(a) shows a three dimensional view of sample in acid with the line fit of 177 nm. Fig. 3(b) exhibits 3-D image of *Syngodium isoetifolium* in water with a height of 41.3 nm data scale. In both the structures, the particles are polydispersed with agglomeration. The size of the cloudy structure was found to be 3.44 μm . The snow zone structure revealed the size of 1.56 μm . The difference in the structures was mainly due to their difference in the solvent medium. The cloudy and snow zone structures could be due to the presence of some heavy metals in the seaweed.

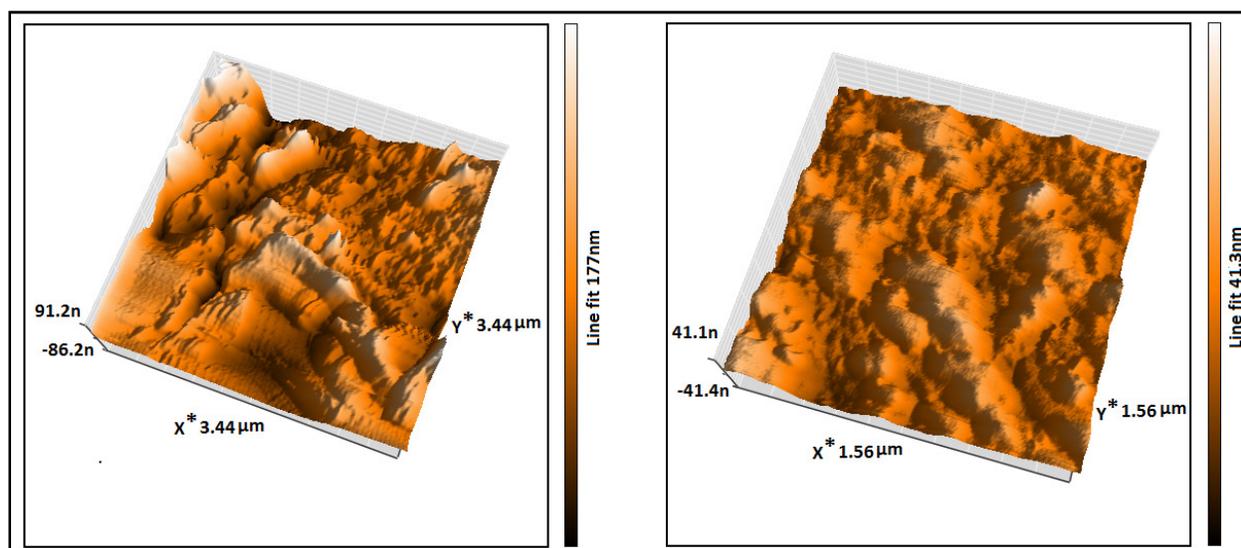


Figure 3(a): Topographic image of thin film of *Syringodium isoetifolium* in acid

Figure 3(b): Topographic image of thin film of *Syringodium isoetifolium* in water

3.5. Electrochemical Analysis

3.5.1. Cyclic Voltammetric Studies

The cyclic voltammogram of *Syringodium isoetifolium* was carried out at pH 7.0 on GCE. It exhibits two well defined anodic peaks representing Cu and as were observed around potential 0.119 V and 0.9584 V for 3125 ppm of *Syringodium isoetifolium* (Fig. 3). The current obtained for Cu and As at 50 mV/s was found to be 15.97 and 12.38 μA . From the plot of peak current against concentration (Fig. 4) it was represented that the peak current increased with increases in concentration.

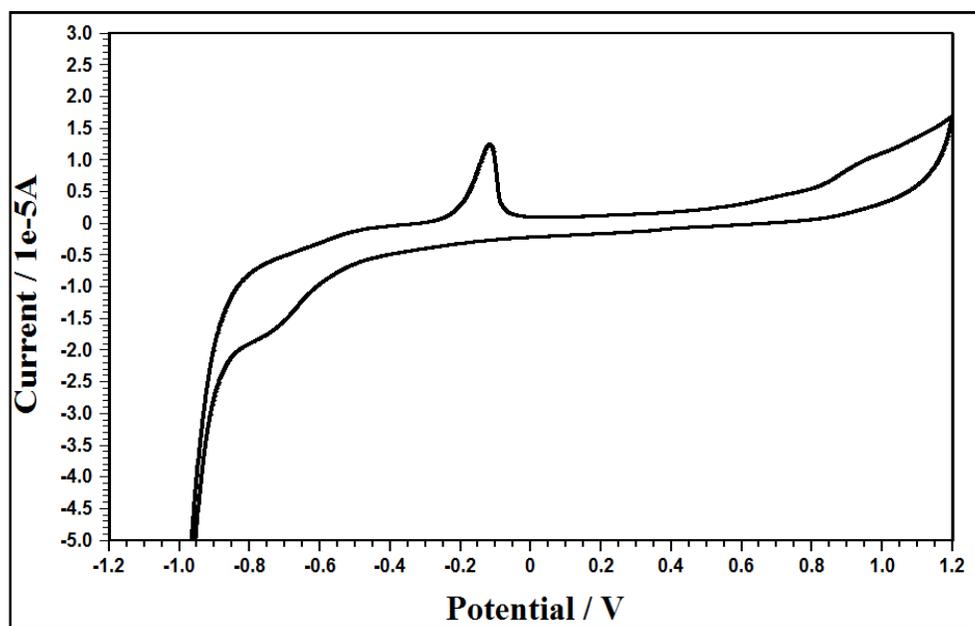


Figure 4: Cyclic voltammogram of 3125ppm *Syringodium isoetifolium* on GCE at pH 7.0; scan rate 50mV/s

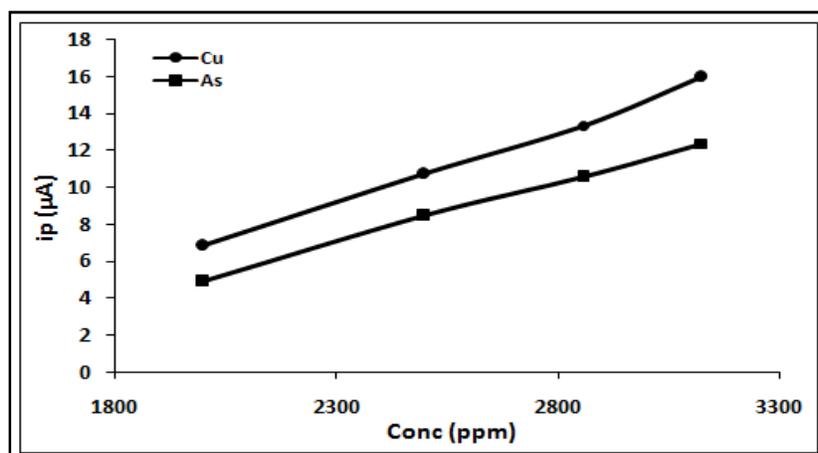


Figure 5: Plot of peak current vs. concentration at pH 7.0; scan rate 50mV/s (CV)

3.5.2. Linear Sweep Anodic Voltammetric Studies

At an optimized pH 7.0, linear sweep voltammetric behaviour of heavy metals were studied on GCE and presented in Figure 6. Two anodic peaks were noticed around 0.0982 V (Cu) and 0.9645 V (As) in the forward scan. Effect of concentration was studied with the constant scan rate of 50 mV/s. Peak current versus concentration plot is given in Figure 6 suggest the increase of peak current with concentration.

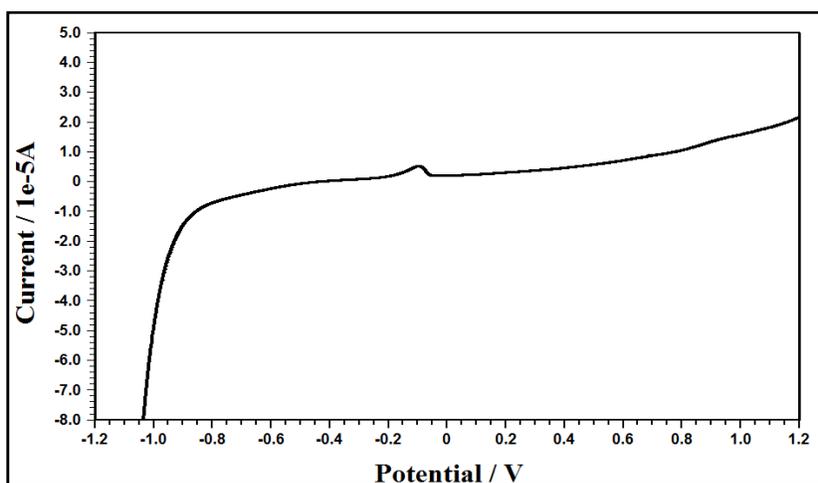


Figure 6: Linear sweep anodic voltammogram of 3125ppm Syringodium isoetifolium on GCE at pH 7.0; scan rate 50mV/s

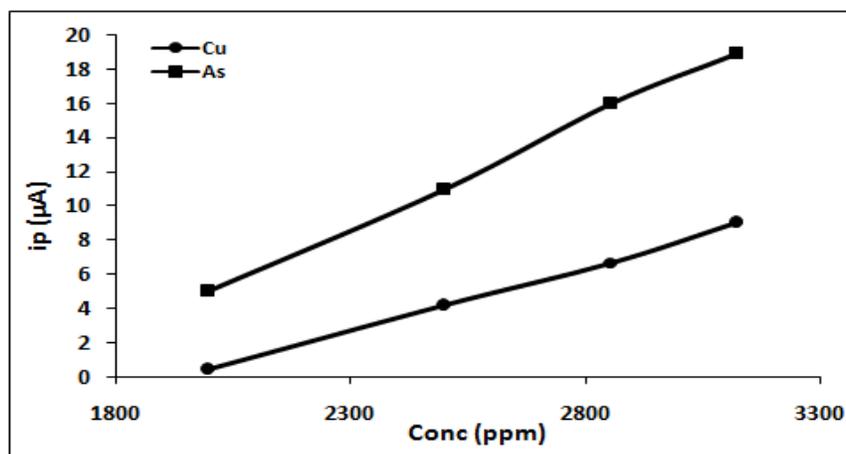


Figure 7: Plot of peak current vs. concentration at pH 7.0; scan rate 50mV/s (LSV)

4. Conclusions

The characteristic wave numbers of specific functional groups were identified from the FTIR study. From the UV-DRS analysis, only one broad band was obtained at 669nm representing the heavy metal of Cu. Five heavy metals (Co, Pb, Ni, Cr and Fe) between 0.51 and 74ppm were analysed from the AAS study. AFM studies revealed both the cloudy and snow zone structures, the particles were polydispersed with agglomeration. CV and LSAV studies concluded that the peak current was increased with increase in the scan rate as well as concentration.

5. Acknowledgements

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