



Electroanalysis of *Caulerpa scalpelliformis* on Glassy Carbon Electrode

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ABSTRACT

Glassy carbon electrode (GCE) have been developed in this investigation for the trace analysis of heavy metals in formulated sample of seaweed by cyclic voltammetry (CV) and linear sweep anodic voltammetry (LSAV). Very good responses have been observed for the metals on glassy carbon electrode. An independent atomic absorption spectroscopic (AAS) analysis of the seaweed was carried out and the results compared with the maximum allowable limits set by the world health organization (WHO). All the metals were present beyond the WHO maximum permissible limit. Ultraviolet-Diffuse Reflectance Spectroscopic (UV-DRS) analysis of three different months *Caulerpa scalpelliformis* were scanned in the wavelength range from 200-900 nm and correlated to assess their spectral bands. A resolved broad UV absorbing band was obtained at the wavelength of 667 nm for all the three spectra.

Introduction

The chemical composition of seaweeds varies due to environmental changes i.e., the seasons, the habitats and depth at which they grow (Rashida Qari and Sardar Alam Siddiqui, 2010). Accumulation of metals in seaweed is related to their concentration present in water (Sharp *et al.*, 1988 ; Carvalho *et al.*, 1997 ; Fuge and James, 1974 ; Morris and Bale, 1975 ; Mykkestad *et al.*, 1978). The metals are concentrated by a factor of 30,000 to 50,000 as compared to their concentration in the ambient environment (Antunes *et al.*, 2003). Industrial discharges and often environmental factors may lead to metal pollution of seawater (Güven *et al.*, 1992). They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders to the nervous, immune, reproductive and gastrointestinal systems (Darwish and Blake, 2002). 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 (Dariusz and Barbara, 1993) and atomic absorption spectrometry (Fernando *et al.*, 1999). 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 (Marichamy and Ramalakshmi, 2013). During the past years, there has been extraordinary acceleration of progress in the discovery, synthesis, sensitive electrochemical analysis (Farghaly and Ghandour, 2005; Farghaly *et al.*, 2008 a; Farghaly *et al.*, 2008 b ; Jonathan *et al.*, 2013 ; Almeida *et al.*, 2013 ; Aaboubi and Housni, 2012 ; Xinfeng Cheng *et al.*, 2012 and Yuzhi Li *et al.*, 2013).

Traditional working electrodes for simultaneously voltammetric determination were generally based on a hanging drop mercury electrode (Shams *et al.*, 2004). 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 (Wang *et al.*, 2000) gold-coated electrode (Zhang and Wang, 2005) carbon paste electrode (Hu *et al.*, 2003) and glassy carbon electrode (Yuan *et al.*, 2004) were applied for sensitive metal determinations. In this study, Glassy Carbon Electrode (GCE) was used for analysis of heavy metal ions in the seaweed and its performances were characterized by electrochemical method in terms of cyclic voltammetry (CV) and linear sweep anodic voltammetry (LSAV).

Materials and Methods

Seaweed collection

The green seaweed *Caulerpa scalpelliformis* (Fig. 1) was collected from Tuticorin coast of Tamil Nadu, South India in three selected months of September, December (2013) and May (2014). The material was washed thoroughly with seawater to remove dirt and other attached material and then rapidly rinsed in deionized water to remove adhered seawater. Seaweed was spread on clean polythene sheet under shade for drying. The dried material was powdered and stored in airtight bottle. 5000ppm of seaweed stock solution was prepared with ultrapure H₂SO₄ (2ml acid is added to 0.5g sample, made upto 100ml) and then used in the analysis.

Chemicals and Preparation of electrolyte

The precursors of H₂SO₄, KH₂PO₄, and NaOH were purchased from Merck AR grade and used as such without further purification. The supporting electrolyte solution (pH 7.0) were prepared with the ultrapure water (SG international, Germany) by checking the pH of the medium using Elico LI 120 pH meter.

Atomic Absorption Spectroscopy

Atomic Absorption Spectrophotometer (Thermoscientific iCE 3000 series) was used for the detection



Fig.1. *Caulerpa scalpelliformis*

of heavy metals. Atomic absorption methods measure the amount of energy (in the form of photons of light and thus a change in the wavelength) absorbed by the sample. Specifically, a detector measures the wavelengths of light transmitted by the sample (the “after” wavelengths) and compares them to the wavelengths, which originally passed through the sample (the “before” wavelengths).

UV-Vis spectroscopy

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. UV-Vis spectroscopy probes the electronic transitions of molecules as they absorb light in the UV and visible regions of the electromagnetic spectrum. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength.

Electrochemical methods

Electrochemical workstation CHI 650C (CH Instruments, USA) was employed for performing cyclic voltammetry and linear sweep anodic voltammetry. The glassy carbon electrode used in the present study whose geometric area of cross section was 0.0314 cm². Freshly polished and cleaned glassy carbon electrode surface contained surface functions that showed reversible redox behaviour. In order to get reproducible results great care was exercised in the electrode pretreatment.

Results and Discussion

Atomic Absorption Spectroscopic studies (AAS)

From the AAS results observed (Table-1), Co and Ni were present in a trace amount, Pb, Cr and Cu were present in minor concentration and Fe was present in a major concentration in the seaweed. The heavy metals content in *Caulerpa scalpelliformis* were in the order of Fe > Cu > Cr > Pb > Ni > Co. Eventhough WHO permissible limit for Co was not available (Bala Chennaiaha *et al.*, 2014), the value of Co content in the seaweed was analysed to be 0.44 ppm. Seaweed was found to contain the Ni concentration of 1.8 ppm. According

Table-1. AAS data showing the concentration of metals in *Caulerpa scalpelliformis*

Metals	Concentration (ppm)
Copper	0.44
Nickel	1.8
Lead	4.7
Chromium	10.4
Copper	14.7
Iron	281

ppm indicate parts per million

to the FAO/WHO (1984), the maximum permissible limit of Ni for edible plants was 1.63 ppm. Thus the seaweed slightly exceeds the permissible limit. WHO (1984) maximum permissible limit of 0.43 ppm for Pb in edible plants was reported by Jabeen *et al.*, (2010). Seaweed was found to contain high concentration of lead than the permissible limit and it was found to be 4.7 ppm. According to the WHO (1990), the maximum permissible limit for Cr in drinking water was 0.1 ppm (Baralkiewicz and Siepak, 1999). Sample contained Cr content above the permissible limit and it was found to be 10.4 ppm. WHO (1984) maximum permissible limit for concentration of Cu in edible plants was 3.0 ppm (Jaya Gupta and Amit Gupta, 2013). Cu present in the seaweed was analysed to be 14.7 ppm and it exceeds the permissible limit. According to the WHO (1984), the permissible limit of iron in edible plants was 20 ppm. The seaweed contained a very high concentration of iron than the permissible limit and it was found to be 281 ppm.

Thus the results of AAS study revealed that all the metals were present beyond the WHO maximum permissible limit.

Ultraviolet - Diffuse Reflectance Spectroscopic (UV-DRS) Analysis

DRS spectra of *Caulerpa scalpelliformis* in three different months of September, December and May were scanned in the wavelength range from 200 – 900 nm and correlated to assess their spectral bands (Fig. 2). There were no significant differences between the three spectra. All the three spectra showed similar bands with slight variation in the absorbance. The absorbance wavelength at 234 nm indicated the presence of Cu^+ (Pestryakov *et al.*, 2004). The band at 282 nm was responsible for Cu (Mahmood Payehghadr *et al.*, 2013). The absorbance measured at 414 and 470 nm may be due to charge transfer band of Cu - O - Cu complex (Pestryakov *et al.*, 2004). The band at 414 nm may also be due to the presence of Ni (Okoye *et al.*, 2013). The peak at 538 nm assigned to the presence of Cu (Pestryakov *et al.*, 2004). The peak

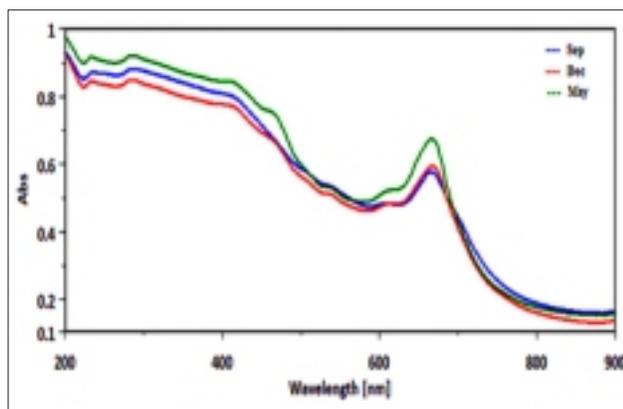


Fig. 2. UV (DRS) spectra of *Caulerpa scalpelliformis* in three selected months (September, December, May)

corresponding to 620 nm is an attribute to d-d transitions in Cu^{2+} ions (Pestryakov *et al.*, 2004). A resolved broad UV absorbing band was obtained at the wavelength of 667 nm for all the three spectra. Only a slight variation occurs in the absorbance. 0.627889, 0.673317 and 0.692318 are the absorbance values obtained for the seaweed corresponding to the month of September, December and May respectively. DRS spectra revealed that the absorption band at 667 nm may be due to the presence of Cu (Kavitha *et al.*, 2013). It is possible to determine qualitatively and quantitatively heavy metals in the seaweed from the preliminary results.

Electroanalysis

Cyclic voltammetry (CV)

Cyclic voltammogram was recorded at a scan rate of 50 mV/s for 3125 ppm of seaweed solution using glassy carbon (GCE) as working electrode. The voltammogram exhibit a very good response at pH 7.0 and is represented in Figure 3. Two anodic peaks representing Cu and As were observed around the peak potential of 0.0733 V and 0.9601 V. The peak current values of Cu and As were measured to be 33.83 and 17.03 μA respectively. The peak was very sharp for Cu than As.

Linear sweep anodic voltammetry (LSAV)

Representative linear voltammogram of *Caulerpa scalpelliformis* was scanned in the forward direction and is given in Figure 4. Here also, two well defined anodic peaks were obtained at the potential 0.1558 V and 0.8328 V. The two peaks corresponding to the oxidation of two metals of Cu and As. The anodic peak representing Cu was very sharp and has higher peak current of 14.98 μA but the peak of As (7.92 μA) was not sharp. This suggests that Cu was present in a large proportion in the studied seaweed sample.

The AAS studies revealed that all the heavy metals found in seaweed exceeds their respective WHO maximum acceptable concentration. UV-DRS analysis showed that the spectra have stronger correlation coefficients with the spectral

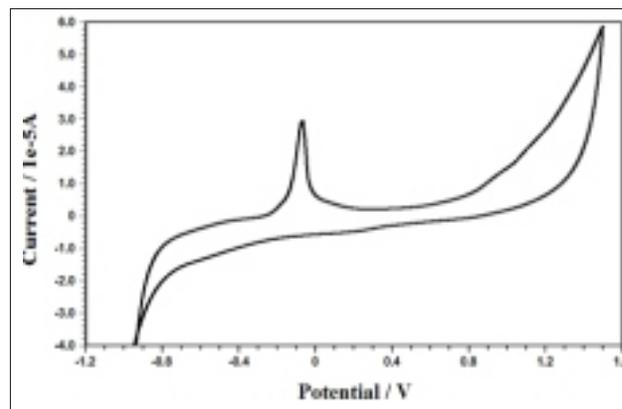


Fig. 2. Cyclic voltammogram of 3125 ppm *Caulerpa scalpelliformis* on GCE at pH 7.0; scan rate 50m V/s

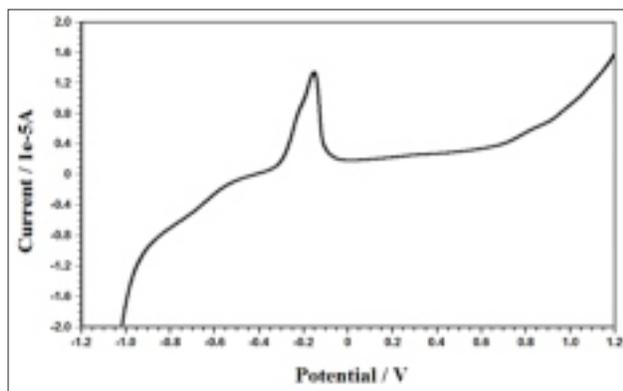


Fig.4. Linear sweep anodic voltammogram of 3125ppm *Caulerpa scalpelliformis* on GCE at pH 7.0; scan rate 50mV/s

bands attributed to the absorption features of heavy metals in the seaweed. A very sharp anodic Cu peak was exhibited from the CV and LSAV characterization. The reproducibility of GCE was said to be an excellent for the studied seaweed sample.

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