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# Determination of Lead Desorption from *G. fisheri* Seaweed Using Edible Eluents by Voltammetry at the Hanging Mercury Drop Electrode

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**Keywords:** Lead, edible eluent, *G. fisheri* seaweed, DPASV, HMDE.

**Abstract.** A simple, rapid, selective and sensitivity approach for the determination of Pb(II) in *G. fisheri* seaweed is described. The method is based on differential pulse anodic stripping voltammetry (DPASV) at hanging mercury drop electrode (HMDE) vs. Ag/AgCl in 0.2 M ammonium acetate ($NH_4OAc$) pH 7.5. The operating analytical conditions; deposition potential ($E_{dep}$) of -0.4 V, peak potential of -0.78 V, and mercury dropped size of 3 were performed. To see the sensitivity of Pb(II) measurement, the influences of deposition time and stirring speed were investigated. From the findings, the optimal parameters; deposition time of 90 s, and stirring speed of 2000 rpm were obtained. In these conditions, the limit of detection (3σ) of 0.60 $\mu gL^{-1}$ and the linear range extended to 12.50 $\mu gL^{-1}$ ($r^2$=0.9999) were obtained. The relative standard deviation (RSD) of triplicate measurements using 1.8 $\mu gL^{-1}$ of Pb(II) was 1.22%. The method was then applied to measure Pb(II) in real samples. In this study, the desorption efficiency of edible eluents by batch method was determined. The method is based on Pb(II) desorption using different types of edible eluents; acetic acid (HOAc), citric acid (CTA), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), ethylenediaminetetraacetic acid (EDTA), and chitosan (CTS). Batch desorption of Pb(II) from seaweed soaked in individual eluent was performed by shaking at 100 rpm for 2 h at ambient temperature. Results show that the most effective eluent in desorbing the contaminated Pb(II) from *G. fisheri* with up to 82.2% of desorption efficiency for bound Pb(II) was EDTA solution.

## Introduction

With the current trend in the consumption of healthy foods, seaweed is one of the natural materials using for food product processing, especially of *G. fisheri* seaweed due to its high amounts of nutrient elements [1]. Generally, *G. fisheri* is a natural sorbent to act as a biomass for desorption of heavy metals. The previous studies have been reported that *G. fisheri* was contaminated by heavy metals [2-3], such as lead, cadmium, zinc, manganese, arsenic, etc. Particularly of lead, it was found at somewhat higher concentrations in such seaweeds [2]. Because of *G. fisheri* contained significant amounts of nutrient elements, the consumption of seaweed products has increased as hazard to health causing from bound lead contamination [2, 4]. Therefore, the removal of lead from the seaweed prior cooking should be required. Several strong acids such as HCl, $HNO_3$, $H_2SO_4$ and chelating agent such as EDTA demonstrated as high effective eluents for removal of heavy metals from different types of seaweed by batch method [4-7]. However, those inorganic acid are inedible eluents for removal of contaminated heavy metals from edible seaweeds which were further consumed for food products.

The toxicity of lead seriously affects on health and interrupts physical development and nervous system. Therefore, the determination of lead in seaweeds is absolutely required. Many techniques, i.e. spectrometric methods and electroanalytical methods using for Pb(II) measurement have been reviewed [8-10]. Anodic stripping voltammetry (ASV) is electroanalytical technique, which has been applied for determination of Pb(II) due to inexpensive instrument and easy using on-site

analysis with the comparison of spectrometric instruments such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS). In this study, ASV at HMDE has been employed for the determination of Pb(II) in *G. fisheri* seaweed due to its high sensitivity, good selectivity and economically.

## Experimental

**Apparatus.** Votammetric measurement made using a 797 VA-Computrace (Metrohm, Switzerland) connected to an electrode standard, 797 VA-Stand (Metrohm, Switzerland). The three-electrode configuration comprising a Metrohm multi mode electrode (MME) in HMDE state as working electrode, a double junction Ag/AgCl (3 M KCl, saturated Ag/AgCl, and 3 M KCl in the bridge) reference electrode, and a Pt wire auxiliary electrode were used. All the potentials quoted are relative to the Ag/AgCl reference electrode. A rotating Teflon rod stirred the solutions in votammetric cell or measuring vessel. The high pure mercury (99.9999%) was used. All experiments were carried out at ambient temperature. The pH measurements were made with a Mettler Toledo SevenEasy S-20 pH meter (Thailand). Eppendorf reference variable micropipettes (10-100 and 100-1000 μL) were used for pipette micro litre volume of solutions. All glassware and storage bottles were soaked overnight in 2 M $HNO_3$ and thoroughly rinsed with de-ionized (DI) water before using.

**Reagents and solutions.** All chemicals used were of analytical grade and without further purification. High purity DI water obtained from a Milli-Q water purification system was used through-out. The stock solution of 1000 $mgL^{-1}$ Pb(II) was prepared by a careful weighting of solid lead nitrate and dissolving in DI water in 100 mL volumetric flask. Supporting electrolyte of 0.2 M ammonium acetate (pH 7.5) was prepared by dissolving 1.54 g of $CH_3COONH_4$ (Merck) with 100 mL DI water.

**Desorption study by batch method.** In the study of Pb(II) desorption from *G. fisheri* seaweed using different types of edible eluents, i.e. HOAc, CTA, NaCl, $NaHCO_3$, EDTA, and CTS, a 1.0-g of clean dried samples was weighed into conical flask. Six sets of sample were impregnated into 75-mL individual eluent which its concentration was controlled at 0.1 M except for 0.2% (w/v) of CTS. The seaweed-eluent mixtures were left on a shaker at 100 rpm for 2 h at ambient temperature. Each mixture was then filtered using a domestic cotton sieve. Desorption efficiency of eluents for bound Pb was calculated with the following Eq. 1:

$$\%\ \text{Desorption efficiency} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where $C_i$ and $C_f$ were the initial and final concentrations of Pb(II) in seaweed samples, respectively. The initial concentration of Pb(II) was obtained from impregnated dried-seaweed into DI water whereas the final concentration of Pb(II) was obtained from desorbed dried-seaweed with the studied eluents.

**Sample preparation.** A portion of 1.0 g filtered sample was subjected to microwave digestion using a 5.0-mL of conc. $NHO_3$ acid in tightly closed Teflon vessel which was placed in a pressure cooker. Electricity power and time programs used for domestic microwave digestion were carried out at 900 Watt for 5 min. on high power and at 600 Watt for 10 min. on mid-high power, subsequently. Clear solutions were then obtained and subjected to ASV measurement.

**Analytical procedures.** A portion of 1.0 mL clear solution of digested sample mixed with 10 mL DI water was placed into a measuring vessel, subsequently added of 1 mL of 0.2 M ammonium acetate (pH 7.5) as supporting electrolyte solution. The mixture solution of sample was purged with oxygen free nitrogen gas (UHP 99.999%, United Industrial Gases, Thailand) for 300 s to remove oxygen and other gaseous compounds before analysis. The operating analytical conditions, i.e. deposition potential: -0.40 V vs. Ag/AgCl [11], equilibration time: 5 s, end potential:

-0.25 V, voltage step: 5.6 mV, amplitude: 20 mV, frequency: 10 Hz, sweep rate: 140 mV, and mercury dropped size: 3 were performed. A voltammogram and peak potential of -0.78 V vs. Ag/AgCl were recorded to give the sample peak current which was directly proportional to Pb(II) concentration. The method of standard addition was selected to use due to the matrix effects interfering. The experiments were conducted in triplicate and the means of three measurements were calculated. The procedure to evaluate the limit of detection (LOD) for ASV instrument was undertaken using 10-replicate aliquots of DI water to determine its Pb(II) concentration.

To see the sensitivity of Pb(II) measurement, the influence of two parameters, i.e. deposition time and stirring speed was investigated. The sensitivity of Pb(II) was considered from percent deposition efficiency of Pb(II) at mercury surface of electrode. The deposition efficiency was calculated with the following Eq. 2:

$$\%\ \text{Deposition efficiency} = \frac{I_{n+1} - I_n}{I_n} \times 100 \quad (2)$$

where $I_n$ and $I_{n+1}$ were Pb(II) peak currents that correspond to the investigated parameters, i.e. deposition time, and stirring speed at the order of "n" and of "n+1", respectively.

## Results and discussion

**Effects of the variables.** In order to achieve the highest sensitivity for ASV measurement, the experimental variables, i.e. deposition time, and stirring speed were optimized as below.

**Influence of deposition time.** The effect of deposition time on the higher the stripping peak currents for Pb(II) in the range of 60 to 150 s was studied. It is known that the higher the sensitivity for ASV measurement is based on the fact that the longer the deposition time gives the higher the peak currents. However, this fact is not strong enough to consider the highest sensitivity for measurement. Therefore, the sensitivity of Pb(II) was considered from percent deposition efficiency of Pb(II) on to mercury surface. From the investigation, the optimized deposition time obtained from the highest percent deposition efficiency of 36.62% was at 90 s as shown in Fig. 1. However, the decrease in deposition efficiency for deposition of Pb(II) after 90 s was also observed. This is due to the ion saturation at mercury surface of HMDE.

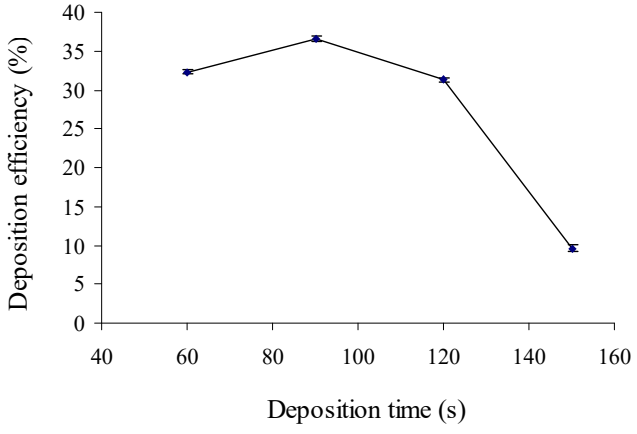


Fig. 1 Effect of deposition time on percent deposition efficiency of Pb(II) at mercury surface of HMDE. The working conditions for detection of 1.8 $\mu gL^{-1}$ Pb(II) in 0.2 M $CH_3COONH_4$ (pH 7.5) are controlled at deposition potential: -0.40 V vs. Ag/AgCl, peak potential: -0.78 V vs. Ag/AgCl, stirring speed: 2000 rpm, and mercury dropped size: 3.

**Influence of stirring speed**. The effect of stirring speed on the increase in transport of Pb(II) to accumulate at the mercury surface in the range of 1600 to 2400 rpm was studied. For high accumulation rate, the solution should be stirred and the deposition potential should be much more negative (-0.2 to -0.4 V) [12]. In this study, the operating deposition potential of -0.40 V vs. Ag/AgCl was used. The transport of Pb(II) to mercury surface taken place by diffusion and was also

supported by convection so that the solution should be stirred during accumulation. From the investigation, the highest percent deposition efficiency of 8.51% achieved from the stirring speed at 2000 rpm was optimized as shown in Fig. 2. However, the ion saturation at mercury surface with corresponding to decrease in deposition efficiency was also observed when the stirring speeds over 2000 rpm were used.

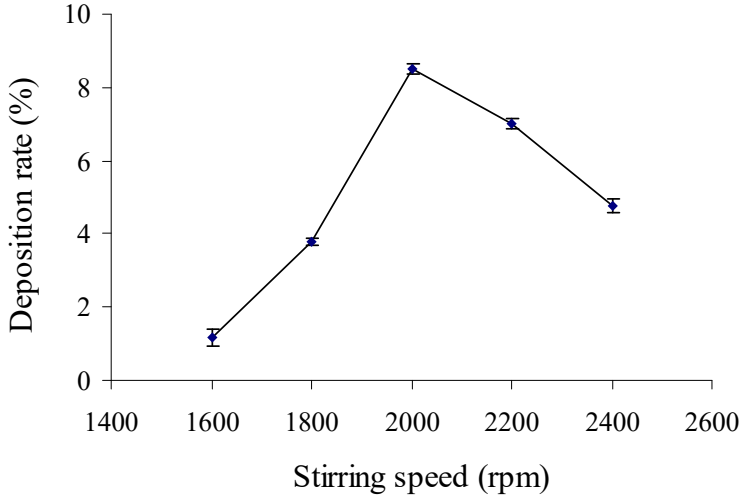


Fig. 2 Effect of stirring speed on percent deposition efficiency of Pb(II) at mercury surface of HMDE. The working conditions for detection of 1.8 $\mu gL^{-1}$ Pb(II) in 0.2 M $CH_3COONH_4$ (pH 7.5) are controlled at deposition potential: -0.40 V vs. Ag/AgCl, deposition time: 90 s, peak potential: -0.78 V vs. Ag/AgCl, and mercury dropped size: 3.

**Linear range, limit of detection and precision.** The optimal parameters obtained from the method and the operating analytical conditions were then applied to real sample. The peak current of Pb(II) was proportional to its concentration. The voltammograms obtained from DPASV system for a portion solution of real samples in supporting electrolyte containing various concentrations of Pb(II), which was supported to compute from the standard addition method were depicted in Fig. 3A. The calibration curve in the range from 0.83 to 12.50 $\mu gL^{-1}$ of Pb(II) was then constructed by plotting peak current against Pb(II) concentration and the plot was depicted in Fig. 3B. The curve linearity with a correlation ($r^2$) of 0.9999 and a slope of 5.6975 was excellent demonstrated. Under this system for triplicate measurements using 1.8 $\mu gL^{-1}$ of Pb(II), the reproducibility was showed the RSD of 1.22%. The LOD (3σ) obtained was found at 0.600 $\mu gL^{-1}$.

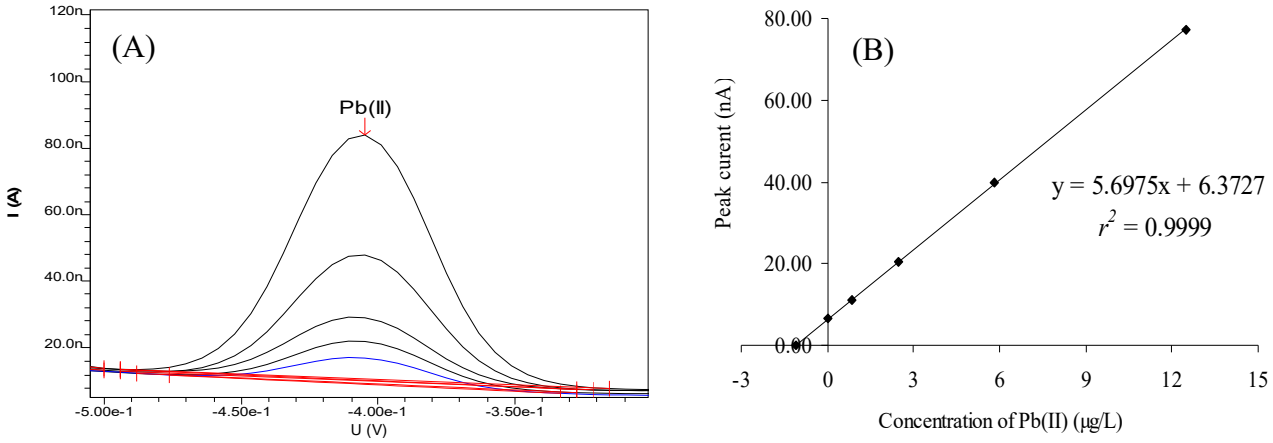


Fig. 3 Voltammograms obtained from DPASV system of *G. fisheri* seaweed in 0.2 M $CH_3COONH_4$ (pH 7.5) containing various Pb(II) concentrations increasing from 0.83 to12.50 $\mu gL^{-1}$ (A), and standard addition calibration curve for the retained amount of Pb(II) computing in *G. fisheri* seaweed (B).

**Effect of edible eluents.** According to desorption of bound Pb from *G. fisheri* seaweed is based on its desorption mechanism by desorbing eluents, the desorption efficiency of different types of edible eluents was determined. It was found that the chelating agent as 0.1 M EDTA solution was the most effective desorption eluent for bound Pb from seaweed with over 82% of desorption efficiency being achieved as shown in Fig. 4. This is due to being formation of Pb-EDTA stable complex [6] for desorption mechanism better than being other Pb-eluent interactions such as being an ion exchange [6] between $H^+$ ion of acid eluents, i.e. HOAc, and CTA and $Pb^{2+}$ ion, being sorption of Pb(II) through the amine functional group [13] of the CTS eluent, and being other complex formations between Pb(II) and bicarbonate or chloride [4] of the salt eluents, i.e. $NaHCO_3$, and NaCl, respectively.

The amounts of Pb(II) in seaweed samples in mg $Kg^{-1}$-dry weight are presented in Table 1. The results show that 0.1 M EDTA solution is the most effective eluent in desorbing contaminated lead from *G. fisheri* seaweed with down to 0.56 mg $Kg^{-1}$ of Pb(II) being retained. The obtained amount of Pb(II) is lower than that of the toxic level of 1 mg $Kg^{-1}$ seaweed product (dry weight) which was noticed from the Thai office of community product standards (CPS-55/247) for food consumption.

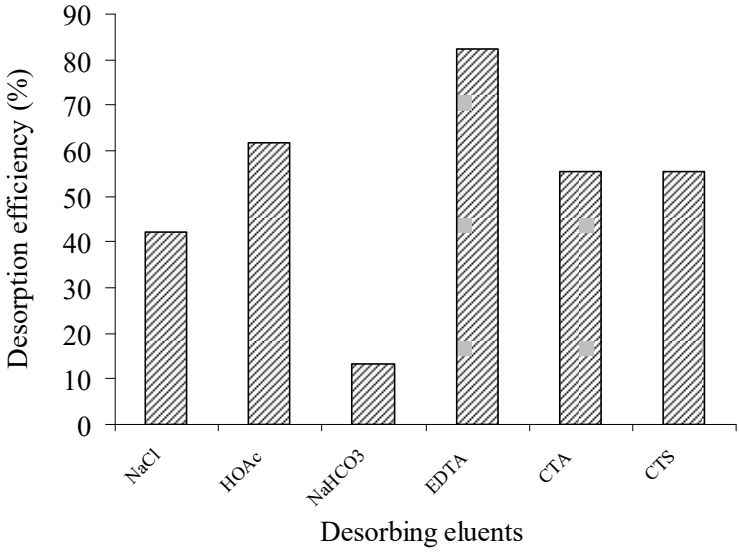


Fig. 4 Effect of desorption eluents on the percent desorption efficiency of edible eluent for bound Pb(II) from seaweed *G. fisheri*.

Table 1 Amounts of Pb(II) found in the real sample and in the desorbed sample after treatment with different types of eluent/

| Real sample* | Desorbed samples* using different eluents (mg $Kg^{-1}$ – dry weight) | | | | | |
|---|---|---|---|---|---|---|
| (mg $Kg^{-1}$-dry weight) | NaCl | HOAc | $NaHCO_3$ | EDTA | CTA | CTS |
| 3.08±0.13 | 1.69±0.09 | 1.15±0.10 | 2.61±0.13 | 0.56±0.05 | 1.32±0.11 | 1.30±0.12 |

* Mean of triplicate measurements ± sd.

## Summary

In this study, the determination of Pb(II) in seaweed was successfully performed by DPASV at HMDE in 0.2 M ammonium acetate (pH 7.5) at deposition time of 90 s and stirring speed of 2000 rpm. The proposed method can be applied to measure Pb(II) for the determination of desorption efficiency of different edible eluents by batch method. The results of the present study conclude that 0.1 M EDTA solution is the most effective edible eluent to remove bound Pb(II) from *G. fisheri* seaweed with regarding as suitable for cooking and further consumed for food products.

## Acknowledgements

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