

## Optimization of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> determination in the coastal water by using voltammetry

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Received: 7 December 2021 / Accepted: 5 January 2022 / Published: 2 February 2022

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This study was conducted to optimize the use of Anodic Stripping Voltammetry (ASV) for the determination of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> ions concentration in the coastal water. Firstly, different UV irradiation periods were applied to the acidic samples (pH 2), natural seawater (pH 8), and coastal water samples so that the metal ions from the natural organic substances could be completely liberated prior to the voltammetry analysis. Undetected metal ions in the samples that did not go through this UV irradiation indicated the presence of natural organic substances that bind to these metal ions. Hence, the distribution of these organic substances plays a crucial role in the binding of trace metals found in coastal water. The results showed that a 5 minutes UV irradiation period was required for the optimal determination of dissolved Pb<sup>2+</sup> and Cu<sup>2+</sup> concentrations in the sample, while a 30 minutes period was required for dissolved Zn<sup>2+</sup> and Cd<sup>2+</sup> determination. The different UV irradiation periods required to free different types of metal ions in the same sample suggested the existence of a natural organic-metal complex with different architectures that have different binding strengths for different types of metal ions. Compared to the other existing methods, the optimised voltammetry analysis developed in this study can provide a reliable and effective alternative in analysing seawater samples, especially due to the relatively low costs and high sensitivity of this method.

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**Keywords:** Zinc(II), Cadmium(II), Lead(II), Copper(II), coastal water, voltammetry, speciation, organic ligands

### 1. INTRODUCTION

Most trace metals are found naturally in the seawater as organic complexes [1]. For example, humic substances (HS) are known as a type of natural organic substance that exists as a complex binding with the trace metals in the seawater. HS is one of the main components of dissolved organic matters (DOM) that are mostly present in freshwaters, estuaries and coastal waters. This substance is also known

to strongly interact with trace metals through co-precipitation and complexation and [2]. It could bind with a large number of trace metals, such as Aluminium (Al), Copper (Cu) and Iron (Fe), in seawater [3].

The concentration of this HS in natural waters is not exactly known due to the variability in their composition and the lack of a convenient analytical method to quantify it. In addition, its quantification in natural waters is difficult because of analytical uncertainties. A few electrochemical methods can be used to determine HS in the natural waters. An intensive identification study has been carried out during the last decades to understand the character of complexes that formed between HS and major trace metals. The analysis of trace metals and the organic substance could explain the character of their binding with the natural organic substances and their role in the biogeochemistry cycle of the environment. Since the trace metals have different binding strengths to these natural organic substances in the seawater, their optimum concentrations (free ions) were determined after completely breaking down these metal-organic complexes through UV irradiation. After that, more information on their binding strength can be obtained indirectly from the UV digestion periods of each element. It is believed that these trace metal ions have strong binding strength to the natural organic substances, thus needing more time to free the ions from the organic complexes completely. In addition, a digestion time of 275 seconds was required to completely release the  $\text{Cu}^{2+}$  ions, whereas only 150 seconds were needed to completely release the  $\text{Ni}^{2+}$  ions from the natural organic ligands [1]. Thus, it is crucial to identify the optimum UV irradiation period needed to completely free the metal ions from the natural organic substances to correctly and accurately determine the concentrations of trace metals in coastal water.

This traditional UV-irradiation procedure was applied to break down the trace metal-organic ligands complexes prior to a voltammetry analysis. The destruction of natural organic substance is necessary to free the trace metals that are organically complexed and remove interfering organic surfactants since these complexes could interfere with the voltammetry analysis, in addition to the physical electrochemical processes occurring at the electrode surface and within its material. The nature of dissolved organic substances in the seawater is complex, but is thought to include humic acids, fulvic acids, glycollic acid, peptides, proteins, amino-acids, lipids and polysaccharides. Moreover, the coastal water samples may also include EDTA, NTA, citric acid, tartaric acid and surfactants from anthropogenic sources [4].

According to [5], this voltammetry analysis is the only electrochemical method that has enough high sensitivity for the in-situ identification and detection of trace metal ions in the seawater samples. However, its sensitivity decreases due to the presence of organic substances that acts as a surfactant in the sample. This subsequently causes interferences to occur. Hence, in this study, the optimum of UV irradiation as a photochemical process was applied to breakdown the metals from the organic substance so that the concentration could be measured directly. These organic ligands are polydisperse molecules that could emit a significant portion of fluoresces, meaning that upon excitation this compound emits light at different wavelength (approximately between 420 to 460 nm). In addition, this UV irradiation is a clean and effective sample preparation method that does not require any addition of oxidants into the sample. Furthermore, it can be readily incorporated into the voltammetry analysis [6].

The objective of this study was to optimize the use of voltammetry analysis for the determination of dissolved  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  concentrations found in the coastal water samples in order to understand the role of natural organic substances on their biogeochemistry cycle.

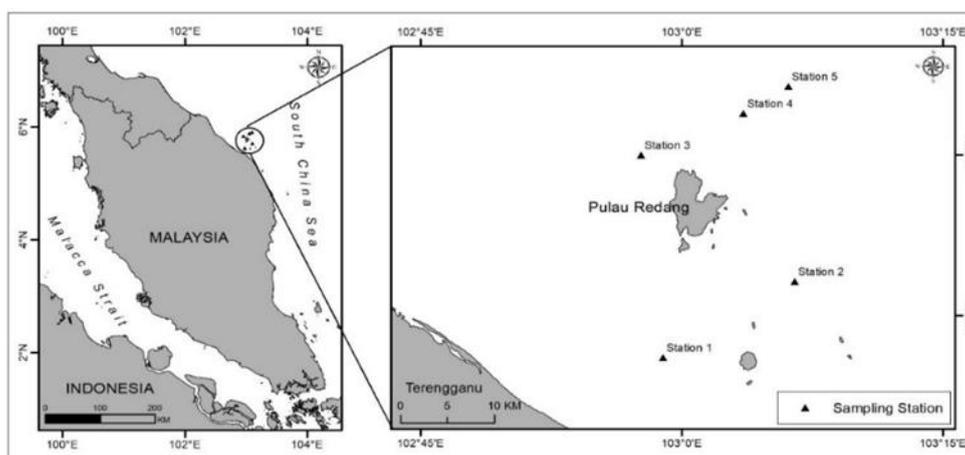
## 2. MATERIALS AND METHOD

### 2.1 Cleaning procedure

All the bottle samples used for seawater sample collection and storage are made of polytetrafluoroethylene (PTFE) (Nalgene). First, the bottles were soaked in Decon 90 (2% v/v) for 24 hours to remove any residual organic materials, followed by rinsing three times with reverse osmosis (Milli-RO; Millipore systems) water. The bottles were then soaked in hydrochloric acid (HCl) for a week before rinsing them for three times with Milli-Q water ( $>18.2\text{ M}\Omega\text{ cm}^{-1}$ ; Millipore Systems). Following these similar pre-treatment steps, the bottles were submerged in a nitric acid ( $HNO_3$ ) bath for another week. After that, they were again rinsed three times with Mili-Q water and dried at room temperature. Finally, the treated bottles were tightly capped, bagged and stored in double plastic bags until they were required for use [5].

### 2.2 Seawater samples

Seawater samples used for optimisation analysis were collected from Pulau Redang, Terengganu, located at the east coast of Peninsular Malaysia (Fig. 1). These samples were collected by using a 5.0 L van dorn water sampler. The in-situ parameters, including dissolved oxygen (DO), temperature, pH, conductivity, total dissolved solid (TDS) and salinity for the collected samples, were recorded with YSI Professional Plus Multi-Parameters (603190 Pro Plus multi-prop). Approximately 1L of seawater samples were filtered through  $0.45\ \mu\text{m}$  cellulose nitrate membrane (Whatman) set. Then, all the filtered samples were kept in PTFE bottles and froze for further analysis.



**Figure 1.** The sampling locations at east coast of Peninsular Malaysia (Pulau Redang, Terengganu). [7]

The seawater profile samples were collected at five selected stations with 4 to 5 different depths. The coordinates for each sampling station were recorded by using Garmin GPSMAP 64s. These samples were analysed to determine the trace metals concentrations throughout the water column at Pulau Redang.

### 2.3 Chemical preparations

The ammonium acetate solution was prepared by adding 1.0 M of ammonia solution (Merck) into 2.0 M of acetic acid (Bendosen). The pH of this buffer solution was measured as pH 4.6, as suggested by [8]. Then, the 1.0 mgL<sup>-1</sup> standard solutions of Zn, Cd, Pb and Cu were prepared from a stock solutions of 1000 mgL<sup>-1</sup> (Sigma-Aldrich) for the voltammetry analysis. These individual standard solutions were used to calibrate the peak of metal ions during the concentration determination by standard addition method step.

### 2.4 UV Irradiation procedure

The digestion of natural organic substances found in the coastal seawater sample was conducted by using 125W medium pressure Hg amps that were positioned in a built housing lamp [7, 8]. The lamp supply was switched from a high output for the initiation of Hg arc lamp, to a reduced output for continuous operation. The housing must be light-tight to prevent the exposure of harmful radiation of UV and so that the power supply to the UV lamp can be cut automatically upon the digestion unit. The experiment was carried out by placing the seawater samples in quartz glass UV digestion tubes (30.0 ml) that were then fitted with PTFE caps. The center-to-center distance between the light source and the tubes was measured at 5 cm.

A different UV irradiation period (ranged from 0 to 120 minutes) was applied to the samples to free the metal ions from the organic complex in the samples prior to the voltammetry analysis. The concentrations of free metal ions in the samples undergoing UV irradiation at 2 different pH of 8.0 (natural pH of seawater) and 2.0 (acidic condition) were also determined.

### 2.5 Anodic stripping voltammetry (ASV) Analysis

Anodic stripping voltammetry (ASV) analysis for dissolved Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> concentrations determination was performed simultaneously by combining Trace Metal Analyzer (797 VA Computrace Metrohm AG Ltd, Switzerland) with three- electrode system that consisted of hanging mercury drop electrode (HMDE) as working electrode, Platinum (Pt) as the auxiliary electrode and Ag/AgCl/ KCl (3.0 mol/L) as reference electrode [8].

A 10.0 ml of UV irradiated seawater sample was cooled down and brought back to the natural pH of 8.0 by adding ammonium hydroxide (Sigma-Aldrich) since the sample was previously buffered to the pH of 6.4 by adding with 1.0 ml of ammonium acetate solution before the voltammetry analysis. The peaks for each metal ion determined in the samples were calibrated by standard addition method.

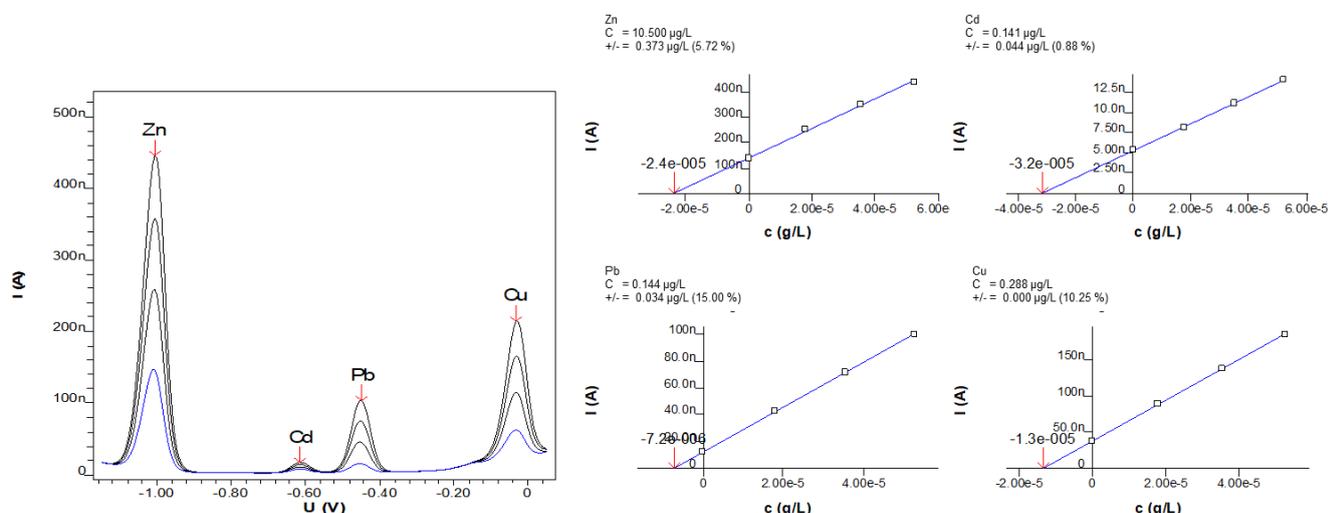
The sweep rate (scan rate) of 59.5 mV/s and pulse amplitude 50 mV were set according to the parameters used in previous study [8].

The analysis stated above was performed in ten replicates to the same sample in order to estimate the accuracy and precision of the voltammetry analysis. The samples were analysed before and after they were spiked with the standard solutions. The recovery percentages were calculated by using a formula  $[(X_s - X)/X_{add} \times 100 \%$ ; where  $X_s$  is concentration of spiked samples,  $x$  is concentration of without spiked samples, and  $X_{add}$  is concentration of spike standard solution]. The recoveries of each element were measured for  $Zn^{2+}$  (95%-105%),  $Cd^{2+}$  (98%-100%),  $Pb^{2+}$  (90%-110%) and  $Cu^{2+}$  (99%-108%), respectively. A relative deviation (RD) was calculated and a low value of standard deviation (0.002) indicated that high sample precision was obtained, thus the methodology developed is considered as reliable to be used for the analysis of coastal seawater samples. The detection limit ( $3\sigma$  of blank) analysis, as calculated from repeated measurements of Mili-Q water, was 0.52 pM. Meanwhile, the blank values, including from the reagents and sample handling, were less than 0.52 pM for Mili-Q.

### 3. RESULTS AND DISCUSSION

#### 3.1 Optimization of UV irradiation

The purpose of performing this UV irradiation procedure was to destroy the organic metal complexes and completely free the metal ions that are presence in the seawater samples prior to the concentration determination by voltammetry. The adsorption of electro-inactive surface-active compounds could reduce the sensitivity of voltammetry analysis [6]. Thus, to decompose these types of organic compounds, we applied the low-pressure mercury (L-Hg) lamp [9, 10]. The optimum condition was referred to the optimum concentration of each metal ion detected by voltammetry after undergoing certain UV digestion periods.



**Figure 2.** The voltammogram of trace metals in the seawater samples and the calibration graphs for the  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  concentration determination.

In this analysis, the coastal seawater samples were irradiated by using UV light at pH 2 and pH 8 solutions prior to the voltammetry analysis. The presence of organic substances that bind to the metal ions in the samples was digested by UV irradiation for between 0 to 120 minutes. The free metal ions concentration in the samples were determined by using voltammetry analysis simultaneously and represented by the peaks in the voltammogram (Fig. 2). The peaks for  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  appeared at -0.90 V, -0.60 V, -0.40 V and -0.10 V, respectively. Then, the concentration for each metal ion was determined by standard addition method.

**Table 1.** Concentration of dissolved  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  in seawater sample at the different UV irradiation periods and pH.

UV periods (min)	Zn ( $\mu\text{g/L}$ )		Cd ( $\mu\text{g/L}$ )		Pb ( $\mu\text{g/L}$ )		Cu ( $\mu\text{g/L}$ )	
	pH 2	pH 8	pH 2	pH 8	pH 2	pH 8	pH 2	pH 8
0	-	-	-	-	-	-	-	-
2	-	-	0.002 $\pm$	-	-	-	0.012 $\pm$	-
5	9.084 $\pm$	6.060 $\pm$	0.104	-	0.174 $\pm$	0.090 $\pm$	0.468 $\pm$	0.241 $\pm$
15	1.027	2.251	0.045 $\pm$	-	0.037	0.001	0.034	0.236
30	9.800 $\pm$	6.060 $\pm$	0.073	-	0.150 $\pm$	0.094 $\pm$	0.308 $\pm$	0.304 $\pm$
60	0.746	2.251	0.082 $\pm$	0.060 $\pm$	0.007	0.025	0.033	0.163
120	10.550 $\pm$	8.620 $\pm$	0.147 $\pm$	0.085 $\pm$	0.144 $\pm$	0.075 $\pm$	0.308 $\pm$	0.321 $\pm$
	0.464	1.194	0.098	0.156	0.028	0.003	0.033	0.525
	10.533 $\pm$	10.739 $\pm$	0.145 $\pm$	0.090 $\pm$	0.143 $\pm$	0.108 $\pm$	0.364 $\pm$	0.376 $\pm$
	0.150	1.305	0.053	0.131	0.024	0.001	0.023	0.220
	10.500 $\pm$	9.880 $\pm$	0.141 $\pm$	0.085 $\pm$	0.144 $\pm$	0.090 $\pm$	0.288 $\pm$	0.352 $\pm$
	0.370	1.3963	0.044	0.222	0.034	0.022	0.000	0.135

No metal ion peaks were detected in the samples without UV irradiation, neither in the acidified sample (pH 2) nor in the natural seawater sample (pH 8). Most of the metal ions (the presence of peaks) were detected only after 5 minutes of UV irradiation, and this indicated that all the metal ions in the coastal water were complexed to the natural organic substances. These natural organic complexes were suggested to play an ecological role in buffering free-metal ion concentrations in the natural systems [3, 2, 11]. In natural waters, the complexing organic substances are present in combination with terrestrial sources and are usually generated in situ. Therefore, any natural water is expected to contain a diverse range of these potential metal-complexing organic substances [12]. According to Buffle [4], these natural organic substances might be EDTA, NTA, citric acid, tartaric acid and surfactants from anthropogenic sources in the coastal water.

The findings of this study showed that most of the metal ions were determined at higher concentration in the acidified samples (pH 2) as compared to the natural seawater samples (pH 8). The concentration of dissolved  $Pb^{2+}$  was ranged from between 0.143  $\pm$  0.024 to 0.174  $\pm$  0.037  $\mu\text{g/L}$  in the acidify samples and between 0.075  $\pm$  3.293 to 0.108  $\pm$  0.001  $\mu\text{g/L}$  in the natural seawater sample (Table 1) at different UV irradiation periods. The results are possibly due to the losses of metal ions into the quartz tubes and foil in non-acidified sample. This could suggest that the optimum digestion process for

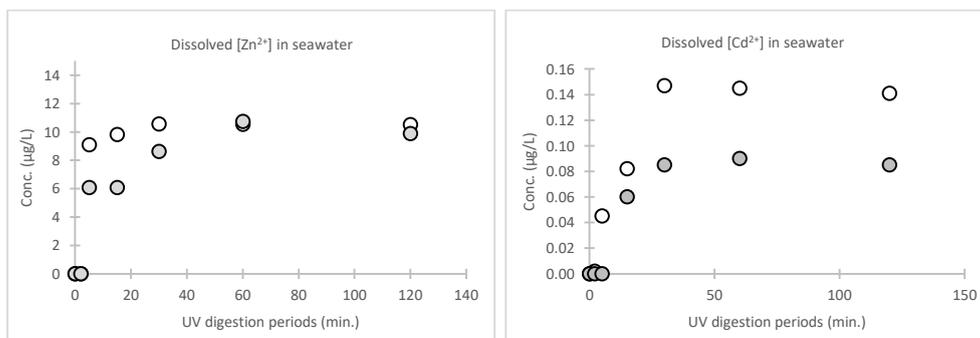
the natural organic substances in the seawater sample using this UV irradiation procedure was the acidified sample (pH 2).

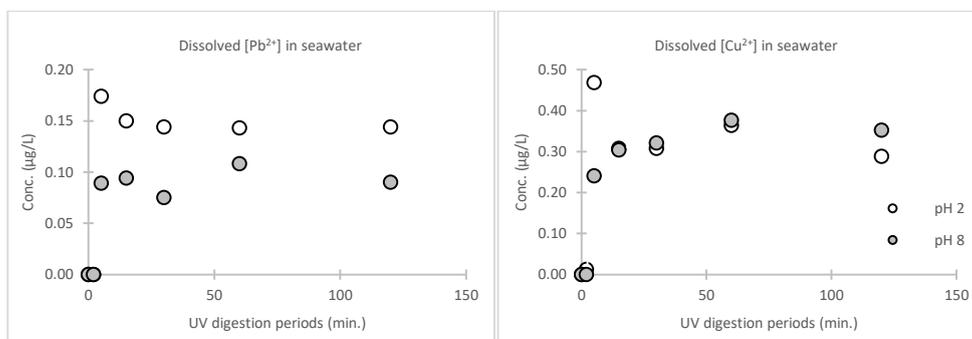
In the acidified sample, the concentration of dissolved  $Zn^{2+}$  increased with the increasing UV irradiation period, with its optimum concentration was determined after 30 minutes of UV irradiation ( $10.550 \pm 0.464 \mu\text{g/L}$ , Table 1). After this period, its concentration was determined to be quite consistent and constant at  $\approx 10.50 \mu\text{g/L}$  (Fig. 3). On the other hand, the concentration of dissolved  $Zn^{2+}$  also increased with the increasing UV irradiation period in the natural seawater pH, but its optimum concentration was determined to occur after 60 minutes of digestion ( $10.739 \pm 1.305 \mu\text{g/L}$ , Table 1). Therefore, the optimum concentration of dissolved  $Zn^{2+}$  in the natural seawater pH was higher than in the acidified sample (Fig. 3). However, after that period (60 minutes), its concentration was decreased to  $9.880 \pm 1.3963 \mu\text{g/L}$ . It showed inconsistent concentration of  $Zn^{2+}$  in the natural seawater pH that undergo UV irradiation (Fig. 3).

An optimum concentration of dissolved  $Cd^{2+}$  ( $0.147 \pm 0.098 \mu\text{g/L}$ , Table 1) was determined in the samples undergoing 30 minutes of UV irradiation in the acidified sample. It showed that the concentration increased with the UV irradiation period after 30 minutes, and then decreased after the optimum UV irradiation period. After 120 minutes of UV irradiation, its concentration was  $0.031 \pm 0.044 \mu\text{g/L}$  (Table 1). However, in the natural seawater pH, its concentration was optimum after 60 minutes UV irradiation ( $0.090 \pm 0.131 \mu\text{g/L}$ , Table 1) and decreased with the increase of irradiation period.

For the dissolved  $Pb^{2+}$  concentration, the optimum concentration was determined after 5 minutes (for the acidified sample with pH of 2) and 60 minutes (for natural seawater with a pH of 8) of the UV irradiation procedure. The optimum concentrations were measured at  $0.174 \pm 0.037 \mu\text{g/L}$  in the acidified sample and  $0.108 \pm 0.001 \mu\text{g/L}$  in natural seawater pH (Table 1). However, the measured concentrations were slightly consistent in both of the samples, similar to the dissolved  $Zn^{2+}$ .

An optimum dissolved  $Cu^{2+}$  concentration ( $0.468 \pm 0.034 \mu\text{g/L}$ , Table 1) was determined in the acidified sample after 5 minutes UV irradiation. It was the shortest time required to completely break down the natural organic  $Cu^{2+}$  complex in seawater sample by using this UV irradiation procedure. However, in the natural seawater pH, the optimum concentration of dissolved  $Cu^{2+}$  ( $0.376 \pm 0.220 \mu\text{g/L}$ , Table 1) was determined after 60 minutes of UV irradiation.





**Figure 3.** An optimum concentration of dissolved Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> in seawater sample at the different UV irradiation periods.

Our analysis on the effects of the UV irradiation period on the optimum determination of dissolved metal ions concentration was in line with the findings of the previous study reported by Town and Filella [12]. They revealed that the divalent trace metals (such as Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup>) are dominated by strong metal-specific organic substances that play important roles in the biogeochemistry cycle. The behaviour of metal ions in the natural waters can be explained by the presence of many different types of binding sites with different complexation strengths and concentrations. In addition, the organic Cu<sup>2+</sup> and Pb<sup>2+</sup> complexes were reported to exist as a deprotonated tetradentate complex [13]. On the other hand, the organic Zn<sup>2+</sup> complex was reported to exist as a hexadentate complex in the seawater [14]. Interestingly, the organic Cd<sup>2+</sup> complex is much stronger, as compared to the other organic metal complexes, due to different functional groups, such as thiol functional groups [15].

The binding strength of the metal-organic complex increases as the metal ion concentration is decreased [12]. This is in agreement with the fact that the stronger sites will be saturated first. This could be used to explain why the concentration of dissolved Cd<sup>2+</sup> ions were the lowest among the selected elements (Table 1). Furthermore, Cd<sup>2+</sup> is generally not thought to have a biological function, but there was evidence that showed that it could fulfil the biochemical role of Zn<sup>2+</sup> [16]. In this present study, we found that a long UV irradiation period (30 minutes) was needed to free the Cd<sup>2+</sup> ions completely from the organic complex, even though its binding strength was less than that of Pb<sup>2+</sup> and Cu<sup>2+</sup> organic complexes. The natural organic Cd<sup>2+</sup> complex binding strength was measured at between 9.82 to 10.93 [17, 18] and consistent with the presence of a stable single class of organic substance in the soluble phase throughout the water column [19]. Moreover, there was a suggestion of the existence of thiol functional groups on these organic complexes. Normally, it was determined simultaneously with Zn<sup>2+</sup> by using voltammetry analysis in most of the seawater samples [17, 15].

Ellwood [18] suggested that Cd<sup>2+</sup> and Zn<sup>2+</sup> ions bind to a similar natural organic complex (thiol functional groups) in the seawater. However, the organic complex that binds to the Zn<sup>2+</sup> ion has a higher metal specificity than Cd<sup>2+</sup>. Thus, the extent of organic complexation of Zn<sup>2+</sup> is substantially more than that of Cd<sup>2+</sup>. Therefore, the percentage of Zn<sup>2+</sup> complexed with the organic substance was measured on an average of 98% compared to only 67% for Cd<sup>2+</sup> [20]. However, the complexation binding strength of organic Zn<sup>2+</sup> complex was ranged from between 9.75 to 10.28, which was less than the binding strength of organic Cd<sup>2+</sup> complex. Additionally, it exists in truly dissolved molecules [21, 18].

In this present study, it was clearly demonstrated that the natural organic substances that bind to the  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  ions in this coastal water have broadly different architectures, therefore contributing to different complexation of binding strengths. The similar period of UV irradiation (5 minutes) used to optimise the concentration of free  $Pb^{2+}$  and  $Cu^{2+}$  ions suggested that these metal ions might be bonded by a similar type of natural organic substance. Similarly, Kozelka and Bruland [22] suggested that even though these metal ions are influenced by multiple classes of organic metal binding complexes, but only one class of organic metal-binding complex binds to the  $Zn^{2+}$  and  $Cd^{2+}$  ions. Wells et al. [21] reported that the strong organic  $Cu^{2+}$  complex ( $L_1$ ) exists largely in the soluble phase (<1kDa), while its weak organic complex ( $L_2$ ) is found in the colloidal phase, at around 24% to 70% of total dissolved concentration. Meanwhile, the strong organic  $Pb^{2+}$  complex ( $L_1$ ) resides in the colloidal phase, while its weaker class ( $L_2$ ) occurs predominantly in the soluble phase. On the other hands, both  $Zn^{2+}$  and  $Cd^{2+}$  organic complexes are found predominantly in the soluble phase only. This again highlighted that  $Pb^{2+}$  and  $Cu^{2+}$  ions were controlled by both soluble and colloidal-sized natural organic complexes, with only the soluble organic complex is responsible for the binding of  $Cd^{2+}$  and  $Zn^{2+}$  ions. There could be a good reason to explain why both soluble and colloidal organic substance phases present in our samples (0.45  $\mu m$  filtered sample) have varying UV irradiation periods during the optimum metal ions concentration determination analysis. In conclusion, these complexes play an important role in controlling the distribution of these metal ions in our study area.

### 3.2 Concentration of dissolved metals at Pulau Redang

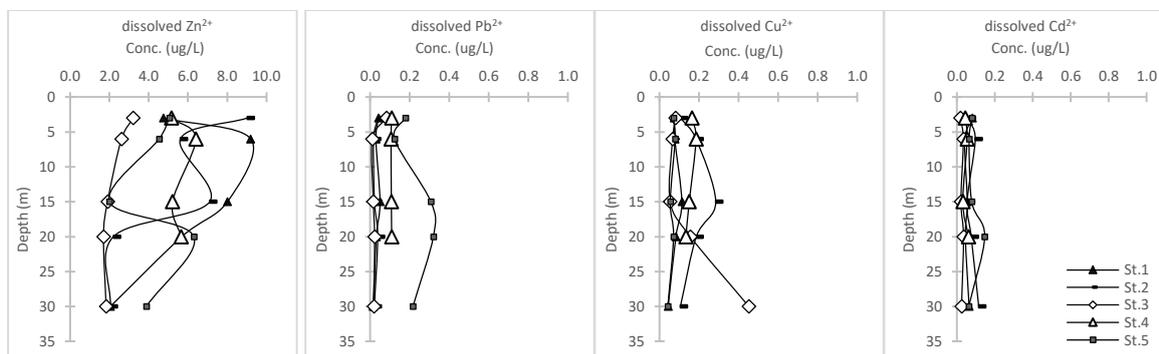
The profile concentrations of dissolved  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  from five selected stations at Pulau Redang (Fig. 1) were determined by applying the procedure mentioned above. Our data were compared to the previous studies in order to validate the results obtained from analysis determination. The concentrations of each dissolved metal ion were as presented in Table 2. All the dissolved metal ions concentrations were in Class I, according to Malaysia Marine Water Quality Criteria and Standard (IMWQS) [23]. The profiles of dissolved metal ions concentrations were divided into two layers, the surface layer (above 15 m depth) and bottom layer (below 15 m depth).

**Table 2.** Concentration dissolved  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  at Malaysia coastal water (Pulau Redang) in April 2019. depth\* is the real depth (m) at each station.

Station	Depth (m)	$Cu^{2+}$ ( $\mu g/L$ )	$Cd^{2+}$ ( $\mu g/L$ )	$Pb^{2+}$ ( $\mu g/L$ )	$Zn^{2+}$ ( $\mu g/L$ )
St.1 (46 m depth*)	3	0.074±0.028	0.081±0.004	0.042±0.001	4.742±0.000
	6	0.077±0.011	0.041±0.000	0.028±0.001	9.194±0.460
	15	0.113±0.049	0.055±0.003	0.049±0.002	8.004±0.000
	20	0.083±0.050	0.045±0.002	0.031±0.001	5.680±0.021
	30	0.043±0.011	0.064±0.001	0.014±0.000	2.040±0.059
St.2 (42 m depth*)	3	0.105±0.023	0.060±0.006	0.038±0.001	9.030±0.044
	6	0.184±0.058	0.097±0.002	0.017±0.001	5.620±0.052
	15	0.284±0.057	0.054±0.006	0.021±0.001	7.110±0.000
	20	0.185±0.057	0.075±0.001	0.037±0.000	2.200±0.328

	30	0.104±0.079	0.115±0.006	0.021±0.001	2.050±0.050
St.3	3	0.081±0.008	0.018±0.002	0.082±0.003	3.205±0.055
(37 m depth*)	6	0.065±0.015	0.034±0.009	0.010±0.000	2.611±0.005
	15	0.053±0.013	0.021±0.005	0.015±0.000	1.905±0.047
	20	0.155±0.018	0.035±0.006	0.021±0.000	1.700±0.000
	30	0.452±0.008	0.024±0.005	0.019±0.001	1.832±0.073
St.4	3	0.164±0.023	0.044±0.007	0.108±0.001	5.150±0.542
(30 m depth*)	6	0.184±0.018	0.053±0.003	0.105±0.001	6.400±0.666
	15	0.149±0.015	0.031±0.001	0.107±0.000	5.210±0.000
	20	0.132±0.023	0.060±0.005	0.109±0.001	5.650±0.000
St.5	3	0.071±0.013	0.079±0.002	0.178±0.001	5.060±0.535
(36 m depth*)	6	0.078±0.016	0.064±0.004	0.122±0.530	4.530±0.054
	15	0.054±0.019	0.078±0.004	0.307±0.014	2.000±0.007
	20	0.070±0.028	0.146±0.001	0.319±0.019	6.300±0.028
	30	0.042±0.012	0.062±0.003	0.216±0.010	3.880±0.063

Dissolved Zn<sup>2+</sup> was shown with the highest concentration among all the selected dissolved metals (Fig. 4). Its concentration ranged from between 1.905±0.047 to 9.194±0.046 µg/L at the surface layer, in comparison to the dissolved Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ions that ranged from between 0.053±0.013 to 0.284±0.057 µg/L, 0.010±0.000 to 0.307±0.014 µg/L and 0.018±0.002 to 0.097±0.002 µg/L (Table 2), respectively. Meanwhile, its concentration at the bottom layer ranged from between 1.700±0.000 to 0.300±0.028 µg/L and the highest concentration among the selected dissolved metals. For the dissolved Cu<sup>2+</sup>, its concentration ranged from between 0.042±0.012 to 0.452±0.008 µg/L (Table 2) at the bottom layer. Besides, the dissolved Pb<sup>2+</sup> and Cd<sup>2+</sup> ions were ranged from between 0.014±0.000 to 0.319±0.019 µg/L and 0.024±0.005 to 0.146±0.001 µg/L (Table 2), respectively. This metal ions concentrations profile (Fig. 4) indicated a slightly consistent concentration of dissolved metal ions between the surface and bottom layers of the study area.



**Figure 4F.** Concentration of dissolved Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> throughout the water column at Malaysia coastal water in April 2019.

The dissolved Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> concentrations measured in this investigation were compared to the previous studies, as listed in Table 3 below. For dissolved Zn<sup>2+</sup> concentration, our recorded concentration was in a wider range than the concentration previously reported by Ariffin et al. [24] at Terengganu coastal water. The previous study reported that the Zn<sup>2+</sup> concentration at surface

layer was ranged from between 3.05 to 7.13 µg/L, but the data was collected in 2007. Furthermore, a wide range of dissolved Zn<sup>2+</sup> concentration (between 4.0 to 112.0 µg/L) at the surface water of Pare Bay had also been reported by Wisna et al. [25]. Another recent study reported that the concentration of dissolved Zn<sup>2+</sup> in Jiuzhen Bay ranged from between 11.5 to 29.2 µg/L [26] (Table 3). However, the concentration of dissolved Zn<sup>2+</sup> at the bottom layer recorded in this study was within the ranges of concentrations reported by all the above previous studies (Table 3).

**Table 3.** Comparison of dissolved metals concentration between present study and previous studies in coastal seawater sample.

Area	Depth (meter)	Concentration range (µg/L)				Period	Station
		Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Cd <sup>2+</sup>		
Pulau Redang	Surface	0.015 - 0.115	0.048 - 0.778	0.010 - 0.655	0.015 - 0.097	Apr-18	Present study
	Bottom	1.700 - 8.180	0.042 - 0.505	0.014 - 0.916	0.018 - 0.115		
Pare Bay, South Sulawesi	Surface	4.0 - 112.0	43.0 - 78.0	111.0 - 2692.0	34.0 - 83.0	Sep-15	[25]
Terengganu water	Surface	3.05 - 7.13	0.50 - 1.91	0.029 - 0.211	0.038 - 0.568	May-07	[24]
	Middle	3.77 - 9.21	0.35 - 1.88	0.042 - 0.286	0.020 - 0.558		
	Bottom	4.57 - 11.2	0.14 - 1.30	0.049 - 0.359	0.016 - 0.520		
Jiuzhen Bay, China	Surface	11.5 - 29.2	3.37 - 5.88	0.25 - 0.45	0.24 - 0.50	May-06	[26]
	Bottom	8.9 - 123.0	4.05 - 6.33	0.25 - 0.54	0.29 - 0.35		

For dissolved Cu<sup>2+</sup>, the concentration recorded in this present data was lower than the concentration recorded from previously reported studies (Table 3). Ariffin et al. [24] reported that the dissolved Cu<sup>2+</sup> concentration that was ranged between 0.50 to 1.91 µg/L at the surface layer (Table 2), meaning that the concentration reported was approximately 10 times higher than our present data. However, the concentration of dissolved Cu<sup>2+</sup> at the bottom layer recorded in this study was similar and still within the range of the concentration reported by Ariffin et al. [24].

Next, the concentration of dissolved Pb<sup>2+</sup> in this study was slightly in line with the concentration that was reported previously (Table 3). However, a high concentration of dissolved Pb<sup>2+</sup> that ranged from between 111.0 to 2692.0 µg/L was determined at Pare Bay (Table 3). It was the highest concentration of dissolved Pb<sup>2+</sup> reported, as compared to the concentration reported in the other studies

listed in Table 3. Meanwhile, the concentrations of dissolved  $\text{Cd}^{2+}$  at the surface and bottom layers in this present study were within the ranges of concentrations measured in the previous reported investigations at Terengganu coastal water (surface: between 0.038 to 0.568  $\mu\text{g/L}$ ; bottom: between 0.016 to 0.520  $\mu\text{g/L}$ ). However, these ranges of concentrations were lower than the dissolved  $\text{Cd}^{2+}$  concentration reported in Pare Bay (between 34.0 to 83.0  $\mu\text{g/L}$ ) and Jiuzhen Bay (between 0.24 to 0.50  $\mu\text{g/L}$ ) (Table 3).

From the comparison, our present data was found to be in line with the previously reported investigation performed by Ariffin et al. [24] in Malaysian coastal water. However, a difference between the ranges of concentrations might be due to the different analytical methods applied since Ariffin et al. [24] applied a chelex-100 resin extraction (sodium form) to their seawater sample in combination with the ICP-MS determination. The results obtained by using ASV in our present study were generally lower than those obtained by using ICP-MS due to the presence of metal organically complex species [27]. These organic substances can act as complexing organic ligands to the metal ions [2], thus interfering with the determination of total metal concentrations. Additionally, the binding also disrupts the adsorption of electro inactive surface-active compounds, thus reducing the sensitivity of voltammetry determination [4]. Even though we have applied the optimum UV irradiation procedure to our samples in order to destroy all the organic substances, but some compositions of aromatic and aliphatic compounds are still difficult to decompose. These compounds can be degraded by the addition of hydrogen peroxide [28], but this oxidising agent could increase the risk of contamination and interfere with reductive voltammetry analysis if it remains after the irradiation. Therefore, the addition of this oxidation agent was not carried out in our analysis.

Furthermore, Buzica et al. [29] suggested that the differences detected between the results of ICP-MS and ASV remained within the requested uncertainties, and this was consistent with the Data Quality Objective (DQO) of the European Directives. Moreover, this voltammetry analysis is increasingly being applied for the analyses of heavy metals (in food, soil, medicinal plants, water, and etc.) since it can be fully automated, can be used for multi-element analysis, needs minimum sample preparation, and requires relatively low investment costs [30, 31, 32].

#### 4. CONCLUSION

The findings of this study demonstrated the optimum determination of dissolved metal ions in the coastal water samples through the use of voltammetry analysis. These low cost yet highly sensitive techniques could be used as an alternative to the ICP-MS in analysing trace metals that are found in high concentrations in organic substance samples. The different UV irradiation periods required for each metal ion determination indicated the existence of natural organic substances that bind naturally to the metal ions at different architectures and with different binding strengths. These organic complexes are believed to play important roles in the bioavailability of dissolved metals. Therefore, further specification studies to identify the organic substances are needed to clearly understand the specific role of dissolved metals in the biogeochemistry cycle at the coastal water.

## ACKNOWLEDGMENT

The authors would like to thank all the members of the Chemical Oceanography Lab from the Department of Environment, Faculty of Forestry and Environment, UPM, for their supports during sampling and analysis. This study was funded by Universiti Putra Malaysia under Grant Putra (Project code: GP/2018/9608500).

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