International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Determination of Bioavailable Dissolved Fe(III) at Different Fractionation Sizes at Coastal Water by Adsorptive-Cathodic Stripping Voltammetry

Nur Jannati Ramjam and Khairul Nizam Mohamed<sup>\*</sup>

Environmental Science Department, Faculty of Forestry and Environment, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia \*E-mail: <u>k\_nizam@upm.edu.my</u>

Received: 17 May 2022 / Accepted: 16 June 2022 / Published: 17 November 2022

The concentration of Fe(III) was determined at different dissolved fractionation, which is small colloidal Fe(III) (< 0.20  $\mu$ m) and dissolved Fe(III) (< 0.45  $\mu$ m) to identify the phase partitioning of bioavailable Fe(III) at Pulau Redang, Terengganu. The determination was obtained by using a newly developed adsorptive-cathodic stripping voltammetry (AdCSV) method with 2,3-dihydroxynapthalene (DHN) as a binding ligand. The results show an increase in the concentration of dissolved Fe(III) compared to small colloidal Fe(III); however, no significant differences are found between both phases after being tested by statistical analysis. The increased concentration of Fe(III) in the dissolved phase was smaller (mean concentration = 16.64 pM) than previously reported (range concentration = 0.04 – 1.98 nM), suggesting that Fe(III) mainly existed as particulate Fe rather than as dissolved Fe during the period in our study area.

Keywords: dissolved iron, bioavailability, coastal water, voltammetry, organic ligand

# **1. INTRODUCTION**

Phytoplankton growth and nitrogen fixation in the water systems are greatly influenced by iron (Fe) availability [1], which is controlled by the physicochemical speciation of dissolved Fe(III) [2]–[4]. Generally, dissolved Fe (dFe) is the filterable Fe with a fractionation size of  $< 0.4 \mu m$  or  $< 0.2 \mu m$ , but now known to include colloids [5]. However, some studies have categorized dFe into several different fractionation sizes, which are soluble Fe ( $< 0.02 \mu m$ ) [1], colloidal Fe (0.2-0.4  $\mu m$ ) [1], small colloidal Fe ( $< 0.2 \mu m$ ) [6] and dissolved Fe ( $< 0.45 \mu m$ ) [1].

Although Fe(III) is the fourth most abundant element in the earth's crust [7], it is presents extremely low in oxygenated water due to the formation of oxy-hydroxides which decrease its solubility

[8]. To render the problem, dFe(III) tends to form complexes with ligands [9] that are commonly produced by Fe limited phytoplankton or bacteria [8] and by the sediment re-suspension [10] to increase the Fe(III) solubility as well as to extend the residence time of dFe(III) within the euphotic zone [11]. A few studies on determination of dFe(III) in Malaysia water recorded the concentration between 0.70-1.55 mg/L (mean :1.17 mg/L, n=6) at estuarine water of Bagan Pasir, Perak [12], and between 0.04-0.94 ng/L (mean : 0.42 ng/L, n=22) (April 2016) and 0.003-0.025 ng/L (mean : 0.013 ng/L, n=22) (October 2016) at coastal water of Pulau Perhentian, Terengganu [13]. The lower concentration of dFe(III) in the coastal environment was due to the alkaline pH value combined with the oxygenated water in the system.

Fe enters the seawater system through river discharge, aeolian deposition, remobilization and resuspension of marine sediments, and hydrothermal activities [14], [15]. By that, their partitioning between particulate (>  $0.45\mu$ m) and dissolved (<  $0.45\mu$ m) form is controlled by the chemical interaction of surface binding and solution complexation [16]. Both interactions are the basic processes in controlling the cycle of trace elements in seawater [17]. The binding of trace elements to different types of inorganic and biogenic particles (eg; colloidal, suspended, and large, fast-sinking types) affects their removal rates and the composition of seawater [16], [17]. According to [15], particulate Fe (pFe) and dFe interact with each other in numerous processes including biological uptake, re-mineralization, absorptive/desorption and dissolution/precipitation that could result in Fe fractionation. Fractionation is defined as the relative change in solutions or particle composition for a group of trace elements as the effect of geochemical response [17].

Even though dissolved Fe (dFe) is the most biologically accessible fraction, their distribution and reactivity rates are varied among coastal areas, depending on the environmental conditions [17]. Our current study [18], revealed that the concentration of dFe(III) in the coastal water was lower with the concentration more than 6 times smaller than previously reported [19]–[23]. The study suggested the probability of dFe(III) in the study area exists in different phase forms, resulting from the re-suspension of bottom sediment [18]. However, the study provided only the data on the inorganic dFe(III) with a particle size of < 0.20  $\mu$ m which could not describe the overall biogeochemical cycle of Fe. Hence, we extend the analysis by determining the concentration of inorganic dFe(III) at different dissolved fractionation sizes (< 0.45 and < 0.20  $\mu$ m) to evaluate the phase partitioning of dFe(III) in the area. Since particulate Fe (pFe) is considered unavailable to phytoplankton uptake, as it tends to settle down onto the sediment [24] hence the determination of Fe in particulate form was ignored in this study.

The electrochemical approach by using voltammetry is the best approach in determining the concentration of dFe(III) in the seawater in our study area due to its simple machinery equipment, inexpensive, low detection limit, direct seawater analysis, rapid analysis speed and easily automated detection [25]. The electrochemical approach included cathodic stripping voltammetry (CSV), anodic stripping voltammetry (ASV), differential pulse voltammetry (DfPV), square wave voltammetry (SqWV) and adsorptive stripping voltammetry (AdCSV) [26]. In this study, the combination of adsorptive-cathodic stripping voltammetry (AdCSV) was used for the sample analysis [18]. This technique allows the addition of a ligand (2,3-dihydroxynaphthalene, DHN) to form a complex with Fe(III) and adsorb onto the surface of the working electrode, holding them at a specific potential. Then, the complex was pre-concentrated before the reductive stripping of the complex back into the solution

[26]. This technique has better sensitivity performance that capable to determine the analytes in highly diluted samples [27].

Pulau Redang is located about 45 km off the coast of Terengganu [28] and gazetted as a Marine Park which promises protection over special biological and environmental values [29]. It is the largest island over a group of nine protected islands (eg: Pulau Pinang, Pulau Ling, Pulau Ekor Tebu, Pulau Kerengga Besar, Pulau Kerengga Kecil, Pulau Paku Besar and Pulau Lima) dotting the South China Sea [28]. The island is experienced an equatorial climate and is affected by the north-east monsoon (NEM) from November to March resulting in rainstorms, wind storms and tidal waves [30]. The precipitation is recorded at 615 mm in December compared to 120 mm in April after the monsoonal seasons [30]. The influence of NEM in the study area was suggested to cause changes in physicochemical parameters (eg; pH, dissolved oxygen (DO), and salinity) of seawater [31] due to the phenomena of upwelling that were documented by [32], [33]. They found changes in the behaviour of temperature and salinity in Terengganu coastal resulting from the rises of cooler water from the deep layers of seawater. This event was suggested to affect the distribution of dFe(III) throughout the water column. Hence, the objective of this present study was to determine the phase partitioning of bioavailable dFe(III) at Pulau Redang, Terengganu. Therefore, this study will provide information on the fractionation of Fe(III) in the area.

# 2. METHOD AND MATERIALS

#### 2.1. Sampling Activities

The vertical profile of seawater samples was collected in March 2019 at five different selected stations (Figure 1) by using a Van Dorn water sampler. The stations were selected at four different sides of Pulau Redang (Figure 1), which were St.1 (mixing between the freshwater and seawater zone), St.2 and St.3 (near the marine park zone), and St.4 to St.5 (facing the South China Sea). The purpose of this sampling approach was to identify the possible effect of the geological factor of each station on the dissolved Fe(III) fractionation in our study area.

The samples were collected within the depth of 3m, 6m, 15m, and 30 m except for St.1 (3m, 6m, and 15m) due to its shallow depth. The bottom sample for each station was collected above 2 meters from the surface sediment to avoid the sediment inputs from entering the water samples. The seawater was collected into 1 L polytetrafluoroethylene (PTFE) bottles after being rinsed twice with the seawater sample. In-situ parameters for each sample were recorded directly using YSI Professional Plus Multiparameter coupled with multi-sensor probes including salinity, pH, temperature, barometric pressure, DO, electrical conductivity (EC), and total dissolved solids (TDS).

The seawater samples were pressure-filtered on a 0.45  $\mu$ m of cellulose nitrate filter membrane (Whatman) for the dissolved phase sample. The filtered samples were transferred into 250 mL low-density polyethene (LDPE) bottles (Nalgene) that has been proper cleaning according to [8]. The procedure was repeated on the remaining samples over a pore size of 0.20  $\mu$ m (cellulose nitrate filter membrane, Whatman) for a small colloidal phase sample. All the samples were immediately frozen to prevent the biological activities from altering the nature of the samples [34].



Figure 1. Location of seawater sampling stations at Pulau Redang, Terengganu during March 2019 (post-monsoonal season).

#### 2.2. Chemicals and Reagents

All the reagents used in this experiment were prepared using ultrapure water (MQ, Millipore; N 18.2  $\mu\Omega$  cm<sup>-1</sup>), except for the one being mentioned. Ammonium hydroxide (NH<sub>4</sub>OH, MERCK, purity 30%) and nitric acid (HNO<sub>3</sub>, MERCK, purity 65%) were used in sample pH adjustment.

A 0.1 M of HEPES buffer/bromate solution was prepared by combining 5 mL of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), 6.667 mL of 0.4 M potassium bromate (KBrO<sub>3</sub>, Sigma Aldrich), 0.169 mL of NH<sub>4</sub>OH (MERCK, purity 30%), and ultrapure water (MQ, Millipore; N 18.2  $\mu\Omega$  cm<sup>-1</sup>) to a final volume of 50 mL [18]. The pH of this mixture was brought to pH 8.00-pH 8.10 after the addition of 0.5 mL of the mixture to 10 mL of seawater sample [18]. The possible contaminating Fe was removed by overnight equilibration with 100  $\mu$ M manganese oxide (MnO2, MERCK) and was filtered through a nylon syringe filter (pore size 0.20 nm, Whatman) [18].

A stock solution of 0.1 M 2,3-dihydroxynaphthalene (DHN,  $C_{10}H_8O_2$ , Sigma Aldrich) was prepared by dissolving DHN in methanol to a final volume of 30 mL. A series of Fe standards (10 ppm, 20 ppm, 30 ppm, and 50 ppm), a final volume of 20 mL, was obtained by dilution from a stock solution (1000 ppm, Sigma Aldrich). The reagents were chilled at a temperature of ~4°C when not in use.

#### 2.3. Instrument and Equipment

The determination of Fe(III) was carried out using voltammetry (Metrohm Model 797 VA) apparatus which consists of three electrodes named hanging mercury drop electrode (the surface area was 0.45 mm<sup>2</sup>) as a working electrode, Ag/AgCl, saturated AgCl 1 M KCl as a reference electrode, and platinum (Pt) wire as a counter electrode. A rotating PTFE rod was attached to stir the solution throughout the deposition step. The scan obtained for trace metal determination was passed on a Lenovo computer for evaluations of peak height using a software program (797 Computrace).

#### 2.4. Determination of Fe(III)

The determination of Fe(III) in this study was carried out using the adsorptive - cathodic stripping voltammetry (AdCSV) method as described by [18]. A 30 mL of acidified (pH < 2) seawater sample (filtration size of < 0.20  $\mu$ m) was UV irradiated for 2 hours in an acid-clean quartz tube to remove the natural organic content in the sample. A 10 mL aliquot of the acidified sample was pipetted into a quartz voltammetry cell and the pH was brought back to the natural pH (8.00-8.10). A 500  $\mu$ L of HEPES/bromate solution (final concentration 0.005 M, pH: 8.10) and 40  $\mu$ L of 0.1 M DHN (final concentration 400  $\mu$ M) were added, followed by manual addition of 100  $\mu$ M of Fe standard during the standard addition step. The steps above were repeated on the sample filtration size of < 0.45  $\mu$ m.

Dissolved oxygen (DO) in the samples was removed by purging with dry nitrogen gas (purity 99.99%) for 300 s. Subsequently, a new mercury drop was used to adsorb the Fe(III) in the sample at the applied potential of -0.1 V within 60 s, while the sample was stirred. Upon completion, the potential was scanned at the differential pulse from -0.9 V to -0.1 V in 0.04 s. Next, the stripping current from the adsorbed Fe(III) was swept at -0.60 V ( $\pm 0.05$  V) (Figure 2).



**Figure 2.** Example of voltammetric scan for dissolved Fe(III) in our study area. The blue line represents the scan for the sample, and the black lines represent the scan for the added Fe standard. The stripping current was swept at -0.60 V ( $\pm 0.05$  V), and the concentration obtained was 14.334  $\pm$  1.022 pg/L.

# **3. RESULTS AND DISCUSSION**

## 3.1. In-situ parameters and identification of water

Table 1 shows the in-situ parameters (salinity, temperature, pH, DO, EC and TDS) of all sampling locations at Pulau Redang, Terengganu. The salinity was recorded between 31.66 ppt - 32.09 ppt, meanwhile, the temperature ranged from 27.8°C to 28.9 °C (Table 1).

Table	1.	Vertical	in-situ	parameters	of	all	sampling	locations	at	Pulau	Redang,	Terengganu	during
	Μ	arch 201	9										

Station	Depth	Salinity	Temp	pH	DO	Cond.	TDS
(Latitude, Longitude)	(m)	(ppt)	(°C)		(mg/L)	(mS/cm)	(mg/L)
1	3	32.09	28.9	7.45	7.72	52932	32045
(5.623, 102.982)	6	31.84	28.3	7.71	7.57	35295	31785
	15	32.09	28.9	7.81	7.12	52934	32045
2	3	31.68	27.8	8.04	7.54	39757	24169
(5.702, 103.108)	6	31.67	28.5	8.04	7.24	51925	31633
	15	31.68	27.8	8.04	7.19	31655	31655
	30	31.95	28.1	8.03	6.59	51892	31872
3	3	31.97	28.8	8.05	7.06	52666	31915
(5.833, 102.961)	6	31.66	28.8	8.06	7.34	52224	31633
	15	31.83	28.8	8.06	7.08	52438	31763
	30	31.91	28.9	8.05	6.83	52639	31850
4	3	31.78	28.7	8.06	6.92	52243	31742
(5.844, 103.025)	6	31.80	28.7	8.07	7.09	52338	31763
	15	31.91	28.7	8.07	7.16	52463	31850
	30	31.90	28.2	8.05	6.41	52197	31980
5	3	31.71	28.3	8.08	7.35	51226	32500
(5.876, 103.059)	6	31.72	28.6	8.08	6.94	52081	31677
	15	31.69	28.5	8.08	7.26	51982	31655
	30	31.93	28.1	8.07	6.42	51911	31850





**Figure 3.** In-situ parameters of all sampling locations at Pulau Redang, Terengganu during March 2019. The data was plotted by using Ocean Data View (ODV) software. The dashed lines indicated the sampling stations based on their latitudes. And the colours presented the reading of each parameter throughout the vertical profile.

The pH of the samples was measured at 7.45 - 8.08 and DO was varied from 6.41 mg/L - 7.72 mg/L (Table 1). Finally, the EC and TDS lie between 35295 mS/cm - 52934 mS/cm, and were between 24169 mg/L to 31980 mg/L (Table 1), respectively. A profile graph (Figure 3) was plotted using Ocean Data View (ODV) to describe the trend of the parameters throughout the water column and within each station.

Generally, most of the in-situ parameters of the sampling stations recorded inconsistent readings at St. 1 (Identity 1), while being consistent at St. 2-St. 5 (Identity 2). For example, the pH lies between 7.45 - 7.81 (standard deviation =  $\pm 0.19$ ) in Station 1 and lies between 8.04 – 8.08 (standard deviation =  $\pm 0.02$ ) in Station 2 – Station 5. This could indicate the source of the water mass. The water mass in Identity 1 probably was a mixture between freshwater and seawater (well mixed), and Identity 2 was from the seawater source (less mixed). For example, the pH value in Identity 1 was slightly acidic (mean pH: 7.66, *n*=3) compared to the pH value in Identity 2 (mean pH: 8.06, *n*=16). The lower pH was expected to be influenced by the freshwater input as St. 1 is located near the coastal line. Meanwhile, the pH in Identity 2 is alkaline, which compliments the natural seawater pH (pH > 8), which is probably from the South China Sea.

# 3.2. The concentration of small colloidal Fe and dissolved Fe

This study provided the data on the concentration of Fe(III) in two filterable sizes which were  $< 0.20 \ \mu m$  (small colloidal phase) and  $< 0.45 \ \mu m$  (dissolved phase) after being determined by the AdCSV method. The results for the concentrations and its ratio are presented in Table 2.

**Table 2.** Concentration of Fe(III) for the samples in 0.20 μm and 0.45μm filterable size, and the ratio for the dissolved form to the small colloidal form of Fe(III)

Station	Depth (m)		Ratio (Fe0.45/Fe0.20)			
		Fe0.20	±	Fe0.45	±	
	3	21.12	0.00	15.25	1.85	0.72
1	6	26.03	2.60	12.58	3.05	0.48
	15	15.63	1.24	10.00	1.00	0.64
	3	4.51	2.00	11.92	0.82	2.64
2	6	10.82	4.30	18.48	2.99	1.71
	15	20.00	4.00	28.89	0.90	1.44
	30	5.54	0.52	15.00	3.62	2.71
	3	7.97	2.81	18.73	0.87	2.35
3	6	8.20	5.11	14.82	1.52	1.81
	15	23.89	5.45	23.34	4.55	0.98
	30	17.35	2.47	14.09	1.86	0.81
	3	8.11	5.33	9.57	1.75	1.18
4	6	9.67	2.27	6.03	1.38	0.62
	15	13.35	3.00	19.06	2.17	1.43
	30	8.37	5.36	11.99	1.58	1.43
	3	13.27	2.12	27.00	0.82	2.03
5	6	7.86	2.03	23.95	2.20	3.05
	15	16.21	3.04	19.32	0.34	1.19
	30	8.46	2.46	16.23	1.27	1.92

Table 2 shows the data on the concentration of Fe(III) in the small colloidal (< 0.20  $\mu$ m) and dissolved (< 0.45  $\mu$ m) phase in five sampling stations at Pulau Redang, Terengganu in March 2019. The small colloidal Fe(III) (c<sub>s</sub>Fe(III)) recorded the concentration between 4.51–26.03 pM (Table 2). Meanwhile, the dissolved Fe(III) (dFe(III)) was between 6.03–28.89 pM (Table 2). Generally, there is a little change from 1.11 – 1.34 times of concentration between both phases (Table 2). Furthermore, by calculating the ratio between dissolved Fe(III) and small colloidal Fe(III), most Fe(III) was recorded as >1 (Table 2) in the dissolved phase (< 0.45  $\mu$ m) rather than in the small colloidal phase (< 0.20  $\mu$ m). This indicates that most of Fe(III) exists in the form of dissolved fraction in all sampling locations, except for Station 1 (Figure 4).



**Figure 4.** Verticle profile distribution of concentration of dFe(III) in colloidal (0.20 μm) and dissolved (0.45 μm) form at Redang Island, Terengganu during the post-monsoonal seasons (March 2019)

The input of freshwater in Station 1 is probably the key factor that influences the particle size in that area. According to the previous study [35], the rates of aggregation of Fe(III) oxy-hydroxide colloids is much slower in freshwater, and their surface properties are controlled by the interaction between organic matter and calcium. The association of riverine Fe colloids with natural organic matter (NOM) stabilizes the colloid particle-particle interaction through steric effects, thus, inhibiting the aggregation of colloids to form larger particles [36]

However, to make sure that there is a difference between the concentration of Fe(III) in both small colloidal and dissolved phases, a statistical analysis using an independent t-test has been tested using Statistical Package for Social Science (SPSS) Software (IBM SPSS Statistics 22), and the results were presented in Table 3:

dFe(III)	-		-
			Independent Samples Test
		L	

**Table 3.** Independent sample t-test between the size of the filterable sample and the concentration of

		Independent Samples Test					
		Levene's					
		Equility of					
		F	Sig.	t	df	Sig. (2	
						tailed)	
VAR00001	Equal variances	.189	.667	-1.830	36	.076	
	assumed						
	Equal variances not			-1.830	35.919	.076	
	assumed						

The test has been calculated based on a 95% confidence level of different. Based on the data presented in Table 3, the *p*-value was 0.667, which is greater than 0.05. Hence, there is no significant

difference between the size of the filterable sample and the concentration of Fe(III), probably due to the small sample size (n = 19) and the small concentration difference between both phases of filtration. Moreover, Figure 4 shows the same distribution pattern of  $c_sFe(III)$  and dFe(III) with some of them overlapping each other, showing merely the same concentration obtained in both phases.

Even though most of the Fe(III) exists in the dissolved phase (< 0.45  $\mu$ m), we found that the concentration of both forms of Fe(III) is still extremely lower compared to the previous studies [19]–[23]. By comparing the concentration of Fe(III) reported in [18], we have verified the probability of Fe(III) is present as a particulate form during this period (post-monsoonal seasons). It might be due to the process of rapid mixing and the strong turbulence of the water current that occurs during the Northeast monsoon (November-March) [37]. This phenomenon could influence the biogeochemistry cycle of Fe(III) after the monsoonal episode. The suggestion was confirmed by the previous study [38] that found an increasing level of particulate cadmium (Cd), chromium (Cr), lead (Pb) and manganese (Mn) at the southern part of Terengganu during the monsoonal seasons (November 2007). In addition, the latest study by [39] found that 95% of zinc (Zn) is present in the form of particulate Zn (pZn) at Pulau Redang, Terengganu during Mac 2019.

Previous studies [38], [39] have suggested the increased level of particulate trace elements in their study area was due to the re-suspension of bottom sediment during the Northeast monsoon. In sediment, the aquatic system is in an anoxic condition (without oxygen) [40]. Under this condition, Fe exists in the form of ferrous, Fe(II) and is associated with sulfide to form precipitate Fe sulfide mineral [40]. The re-suspension then flushed the dissolved Fe(II) into the oxygenated (oxic) water column [41]. Thus, Fe(II) was rapidly oxidized into Fe(III) and formed a particulate or colloidal Fe(III) hydroxide, Fe(OH)<sub>3</sub> which is insoluble in water [40]. Freshly precipitated Fe(OH)<sub>3</sub> is an effective scavenger of numerous other chemicals in the water [40]. Scavenging is defined as the ability of Fe(OH)<sub>3</sub> to adsorb micro-components from the solution to their gelatinous or finely divided precipitate [42]. This process enhances the transformation of medium and low-molecular-weight Fe (colloid, complex and ionic Fe) into particulate Fe (pFe), hence decreasing the concentration of dissolved Fe throughout the water column [43].

The scavenging Fe might be combined with other colloids and particles [5], precipitate quantitatively into solid form and settle down onto the sediments [24], making it unavailable to phytoplankton uptake [44]. According to [44], Fe is readily available for uptake by phytoplankton in the form of a dissolved fraction, whereas most of it is bound to organic ligands to increase the Fe(III) solubility and to remain the Fe(III) within the euphotic zone [11]. The Fe(III) can form binding with either small or large Fe-chelators such as siderophores, humic substances, exopolymeric substances and transparent exopolymers [45]. Finally, the Fe-organic complex is transported directly onto the phytoplankton cell membrane via the specific carrier protein and Fe is released by the chelating ligands [46]

Even though the concentration of bioavailable Fe(III) is considered low in our study area, with a mean concentration of 12.97 pM (for  $c_s$ Fe(III)) and 16.64 pM (for dFe(III)) (Table 2), however, this concentration is sufficient for the growth of marine phytoplankton. In the marine system, the species of phytoplankton that exist mainly consist of microalgae such as diatoms and dinoflagellates [47], [48]. According to [49] the diatoms (eg: *Thalassiosira spp.*) need approximately 0.7 to 14 pM of Fe(III) to

bloom. This could suggest that the phytoplankton in the study area can undergo photosynthesis, which is the main process in the oxygen generator to the surface ocean [50]. Besides that, the growth of phytoplankton plays an important role in balancing the carbon cycle in the marine ecosystem [51]. They have the ability to uptake the inorganic carbon dioxide ( $CO_2$ ) from the atmosphere and transform the  $CO_2$  into organic carbon inside their cell [51]. When the phytoplankton dies, some of the carbon is transported to the deep ocean and some is released back into different layers of the water column [51].

Our present study has revealed the concentration of bioavailable Fe(III) in both small colloidal and dissolved fraction was low, but sufficient for phytoplankton growth. It was probably due to the absorption of Fe into the particulate resulting in the rapid water mixing and the strong turbulence of the water current. This pFe decreases the solubility of Fe(III) throughout the water column and declines its concentration in the dissolved phase. However, this suggestion was based on the present data obtained during the post-monsoon season only. Therefore, further determination on the distribution of Fe(III) before NEM (pre-monsoonal season) is needed to evaluate the bioavailability of Fe(III) prior to the NEM event. With that, we could better understand the effect of NEM on the biogeochemistry of Fe(III) in the study area.

# 4. CONCLUSION

In conclusion, most Fe(III) in our study area is present in the form of a dissolved phase (<0.45  $\mu$ m) rather than in a small colloidal phase (< 0.20  $\mu$ m). However, the phase partitioning does not affect the concentration of Fe(III) as there is no significant difference between both phases. The low concentration of Fe(III) determined in this study suggested the probability of Fe being formed as a particulate Fe as re-suspension of bottom sediment enhances the production of scavenging Fe that tends to become a particulate and not bioavailable to the phytoplankton uptake. However, its concentration was sufficient for the growth of phytoplankton (eg; diatoms) as it met the minimum Fe requirement for its growth. As our study area is affected by NEM every year, hence further studies need to be carried out in order to evaluate the effect of the monsoon on the distribution of dFe(III) in that area.

#### ACKNOWLEDGEMENT

This research was funded by Universiti Putra Malaysia (UPM) under Putra Grant (GP/2018/9608500). Special thanks to the Department of Marine Park Malaysia, the Ministry of Natural Resources and Environment for the permission in collecting the samples in Pulau Redang, Terengganu. Besides that, we would like to express our gratitude to our sampling team and all the laboratory staff in the Faculty of Forestry and Environment for their assistance during sampling and laboratory activities.

#### References

- 1. J. Wu, E. Boyle, W. Sunda and L S. Wen, Science, 293 (2001) 847.
- 2. K.S. Johnson, R. Michael Gordon and K.H. Coale, Mar. Chem., 57 (1997) 137.
- 3. X. Liu and F.J. Millero, Geochim. Cosmochim. Acta, 63 (1999) 3487.
- 4. Y. Shaked, B.S. Twining, A. Tagliabue and M.T. Maldonado, Global Biogeochem. Cycles, 35

(2021) 1.

- 5. P.W. Boyd and M.J. Ellwood, Nat. Geosci, 3 (2010) 675.
- 6. J. Nishioka, S. Takeda, C.S. Wong and W.K. Johnson, Mar. Chem., 74 (2001) 157.
- 7. P.A. Frey and G.H. Reed, ACS Chem. Biol., 7 (2012) 1477.
- 8. E.P. Achterberg, T.W. Holland, A.R. Bowie, R.F.C. Mantoura and P.J. Worsfold, *Anal. Chim. Acta*, 442 (2001) 1.
- 9. K. Hirose, Anal. Sci., 22 (2006) 1055.
- 10. K.N. Mohamed, N.J. Ramjam, N.I. Azahar, J. Sustain. Sci. Manag., 16 (2021) 256.
- 11. H. Su, R. Yang, A. Zhang and Y. Li, Mar. Chem., 173 (2015) 208.
- 12. S.S.M. Kamel, K.N. Mohamed, F.M. Yusuff and A.M. Amiruddin, *Pertanika J. Sci. Technol.*, 27 (2019) 2317.
- 13. N.I. Azahar and K.N. Mohamed, In-house Semin. Chem. Oceanogr. Lab., 1 (2016) 1.
- 14. M.L. Wells, Biol. Oceanogr., 6 (1988) 463.
- 15. M. Labatut, F. Lacan, C. Pradoux, J. Chmeleff, A. Radic, J.W. Murray, F. Poitrasson, A.M. Johansen and F.Thil, *Global Biogeochem. Cycles*, 28 (2014) 1044.
- 16. E.R. Sholkovitz, W.M. Landing and B.L. Lewis, Geochim. Cosmochim. Acta, 58 (1994) 1567.
- 17. K.N. Mohamed, N.S. Rosli, S.A. Bohari and M. Rahimi, *In-house Semin. Chem. Oceanogr. Lab.*, 1 (2016) 6.
- 18. N.J. Ramjam and K.N. Mohamed, Int. J. Electrochem. Sci., 16 (2021) 1.
- 19. S. Blain, S. Bonet and C. Guieu, Biogeosciences, 5 (2008) 269.
- 20. Y. Kondo, S. Takeda and K. Furuya, Deep Sea Res. II, 54 (2007) 60.
- 21. C.E. Thuróczy, L.J.A. Gerringa, M.B. Klunder, R. Middag, P. Laan, K.R. Timmermans, H.J.W de Baar, *Deep Sea Res. I*, 57 (2010) 1444.
- 22. M.B. Klunder, P. Laan, R. Middag, H.J.W. de Baar and J.C. van Ooijen, *Deep Sea Res. II*, 58 (2011) 2678.
- 23. C.M. Marsay, P.M. Barrett, D.J. McGillicuddy and P.N. Sedwick, J. Geophys. Res. Ocean, 122 (2017) 6371.
- 24. J.N. Fitzsimmons, S.G. John, C.M. Marsay, C.L. Hoffman, S.L. Nicholas, B.M. Toner, C.R. German and R.M. Sherrell, *Nat. Geosci.*, 10 (2017) 195.
- 25. Y. Zhu, X. Hu, D. Pan, H. Han, M. Lin, Y. Lu, C. Wang and R. Zhu, Sci. Rep., 8 (2018) 1.
- 26. M. Lu, N.V. Rees, A.S. Kabakaev and R.G. Compton, *Electroanalysis*, 24 (2012) 1693.
- 27. E.P. Achterberg, M. Gledhill and K. Zhu, *Voltammetry-Cathodic Stripping*, Elsevier, (2018), Waltham, MA.
- 28. M. Nashriyah, M.Y.N. Athiqah, H.S. Amin, N. Norhayati, A.W.M. Azhar and M. Khairil, *Int. J. Nutr. Food Eng.*, 5 (2011) 911.
- 29. M.R. Yacob, A. Radam and A. Shuib, J. Sustain. Dev., 2 (2009) 94.
- 30. E. Pesiu, M.T. Abdullah, J. Salim and M.R. Salam, J. Sustain. Sci. Manag., 11 (2016) 48.
- 31. E. Godon, K.N. Mohamed, M.A. Gani and S. Johan, Orient. J. Chem., 34 (2018) 1858.
- 32. M.F. Akhir, F. Daryabor, M.L. Husain, F. Tangang and F. Qiao, Open J. Mar. Sci., 5 (2015) 273.
- 33. Z. Zainol and M.F. Akhir, J. Teknol., 78 (2016) 11.
- 34. M. Leermakers, W. Baeyens, M.D. Gieter, B. Smedts, C. Meert, H,C.D. Bisschop, R. Morabito, P. Quevauviller, *Trends Anal. Chem.*, 25 (2006) 1.
- 35. A. Gunnars, S. Blomqvist, P. Johansson and C. Andersson, *Geochim. Cosmochim. Acta*, 66 (2002) 745.
- 36. U. Nowostawska, J.P. Kim and K.A. Hunter, Mar. Chem., 110 (2008) 205.
- 37. E. Godon and K.N. Mohamed, In-house Semin. Chem. Oceanogr. Lab., 2 (2016) 12.
- 38. G. Adiana, N.A.M. Shazili, M.A. Marinah and J. Bidai, Environ. Monit. Assess., 186 (2014) 421.
- 39. N. Muhammad, *Determination of Cadmium, Copper, Lead and Zinc in Particulate Phase at Redang Island, Terengganu* (thesis), Universiti Putra Malaysia, (2019), Selangor, Malaysia.
- 40. A.J. Lee and G.F. Lee, *Remediation*, 16 (2005) 33.

- 41. V. Hatje, G.F. Birch and D.M. Hill, Estuar. Coast. Shelf Sci., 53 (2001) 63.
- 42. G.D. Edward, J. Geol., 62 (1954) 249.
- 43. X.F. Pan, B.X. Yan and Y. Muneoki, Sci. China Earth Sci., 54 (2011) 686.
- 44. J.K. Moore, S.C. Doney, D.M. Glover and I.Y. Fung, Deep Sea Res. Part II, 49 (2001) 463.
- 45. M. Gledhill and K.N. Buck, Front. Microbiol., 3 (2012) 1.
- 46. H. Lis, Y. Shaked, C. Kranzler, N. Keren and F.M.M. Morel, ISME J., 9 (2015) 1003.
- 47. S.C. Leterme, L. Seuront and M. Edwards, Mar. Ecol. Prog. Ser., 312 (2006) 57.
- 48. L.S. Zaremba and W.H. Smoleński, Ann. Oper. Res., 97 (2000) 131.
- 49. M.T. Maldonado and N.M. Price, Mar. Ecol. Prog. Ser., 141 (1996) 161.
- 50. K. Richardson and J. Bendtsen, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci., 375 (2017) 1.
- 51. S. Basu and K.R.M. Mackey, Sustainability., 10 (2018) 1

© 2022 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).