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Analysis of Fe in Sediment Material using a Modified Tessier Technique for Detection of Fe-Anthropogenic and Fe-Naturals

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Abstract. Monitoring of environmental pollution can be carried out in the leaching process to determine the quality of sediment. This study modified the Tessier method leaching process using an optimized microwave. This study reported the effect of radiation contact time and microwave power in the microwave Tessier method based on their level of accuracy and precision to the analysis of Fe in sediment. After optimizing the microwave Tessier method, we continued using this optimization to determine pollution status using the Contamination Factor (CF) values. The results showed the time of contact of the radiation and microwave power gave an influence in the optimized Tessier analysis of Fe in sediment. The optimized conditions were in the fraction 1 (power radiation: 10%; time: 2 minutes), fraction 2 (power radiation: 30%; time: 3 minutes), fraction 3 (power radiation: 50%; time: 2 minutes), fraction 4 (power radiation: 50%; time: 3 minutes). The microwave Tessier method produced the recovery percentage of 94.11%. Fe concentration in sediments showed in the non-resistant fraction had a range between 537.6 mg/kg - 575.9 mg/kg, whereas Fe concentrations in the resistant fraction ranged from 3161.6 mg/kg - 10067.2 mg/kg. The results of CF values were obtained at 1.933-1.961, indicating the moderate contamination status in the Gulf of Prigi.

Keywords: Fe, sediment, Tessier microwave, Prigi.

1. Introduction

Monitoring the pollution of the aquatic environment can be assessed by the quality of sediment. Wijaya *et al.* reported the sediment quality is very important to understand the level of metal contents, coral, Pb isotopes, and residue of marine natural products as the fingerprint in the status of pollution in the ecosystem [1-5]. The increasing age of the earth's layers reflected the recent sediments and ancient sediments. The high level of metal contents in the recent sediments indicates the modern contaminated in sediment.

Investigating the pollution of heavy metals in sediments requires the selection of appropriate analytical methods. The conventional method of the Tessier method uses the acid destruction method. The weakness of the Tessier method is it takes for 20 hours digestions with 5 fractions indeed to use a water bath. The method of acid destruction using microwaves has been carried out in monitoring heavy metal pollution in sediments and soil [6–8]. The disadvantage of the acid destruction method cannot provide information about the fractionation of heavy metal attachments in the sediment. This causes mobility and the nature of heavy metal resistance cannot be differentiated from their sources.

The microwave technology provides an opportunity to reduce leaching time by calculating the dissociation energy needed to break bonds in sediment using microwave power radiation. The radiation of microwave radiation is absorbed by the atoms in the sediment. The absorption of energy causes the processes of atoms in the sediment to rotate/vibrate of elements inside. The heating process with microwaves added the energy to leach in each of sediment fractions.

We applied the Tessier method combined with the optimization power radiation and contact time of Fe leaching in sediment. The leaching process was carried out using a physical method (microwave) and chemical methods (Fraction 1/$MgCl_2$, fraction 2/NaOAc, fraction 3/$NH_2OH.HCl$, fraction 4/HNO_3, H_2O_2 and NH_4OAc, fraction 5/aqua regia, HF, and HNO_3). The variation of time and microwave power was to determine the influence of microwaves and heat in helping to leach metal bonds in the sediment.

The variation of radiation contact time and microwave power in the Fe analysis was tested for accuracy and precision. The accuracy test was done by comparing Prigi sediment and JMS-1 as a reference sediment. The precision test was carried out by applying radiation contact time and optimal microwave power to test the accuracy in sediment. JMS-1 sediments are obtained from the Geochemical Survey of Japan [9]. They found the relative standard deviations of all four steps were less than 30% using JMS-1 with BCR method.

This study aimed to determine the effect of radiation contact time and microwave power in Fe fractionation using Microwave Tessier method to understand the effectiveness of Microwave Tessier method with accuracy and precision for Fe leaching processes in Prigi sediment samples and to inform the status of distribution of Fe in the Gulf of Prigi sediments.

2. Methods

2.1. Sample Preparation

The position of three groups of sediment samples was collected from the west (WS), north (NS) and east (ES) (-8.311875 LS; 111.748362 BT) in the Gulf of Prigi. The sample was then separated from dead coral reefs, shells, and other marine products. The bulk sample was dried for 7 days in an oven at 60 ^oC. The sample was then weighed about 0.25 grams for treatment.

2.2. Leaching Fe in sediment using Tessier Method with modified microwave.

A total of 0.25 grams of samples were put into polyethylene vials and 4 ml of $MgCl_2$ 1 M were added and adjusted at pH 7.0. The mixture of samples was put in a microwave with variations in power (10, 30, and 50%) and time (1, 2, and 3 minute/s). The samples were centrifuged at a rate of 3500 rpm for 15 minutes. The filtrate was transferred into a glass vial (Fraction 1). The residue was washed with distilled water until a neutral condition. The second fraction was added with 4 ml of NaOAc 1 M with pH 5.0 with variations in power (10, 30, and 50%) and time (1, 2, and 3 minute/s). The mixture was centrifuged at a rate of 3500 rpm for 15 minutes. The filtrate was transferred into a glass vial (Fraction 2). The residue from fraction 2 was washed with distilled water to a neutral condition. The filtrate from the third fraction was added with 10 ml of 0.04 M $NH_2OH.HCl$, then the mixture was put into the microwave with variations in power (10, 30, and 50%) and time (1, 2, and 3 minutes/s). The mixture was centrifuged at a rate of 3500 rpm for 15 minutes. The filtrate was moved into a glass vial (fraction 3). The residue was washed with distilled water until neutral. The fourth fraction of the residue was added with 1.5 ml of 0.02 M HNO_3 and 2.5 mL of 3.2 M NH_4OAc. The mixture of the samples was put in the microwave with variations in power (10, 30, and 50%) and time (1, 2, and 3 minute/s). The filtrate was transferred into a glass vial (Fraction 4). The residue from fraction 4 was placed on Teflon and heated on the hotplate containing sand. The sample was added with 10 mL of the concentrated HF and 6 mL of aqua regia and heated at 185 ^oC until dried then was finally diluted with 10 mL 1% HNO_3. The filtrate was put into a plastic vial (Fraction 5) [10].

All of the filtrates in each of fractions in sediment sample and sediment reference sample were analyzed by atomic absorption spectroscopy (AAS) to determine Fe concentration. The comparison of concentration Fe between sample and reference was continued to calculate the level of accuracy and precision and investigate the level of contamination.

3. Results and Discussion

3.1 The Effectiveness of the Optimized Microwave Tessier Method

As listed in Table 1 and Figure 1, the optimized condition in the contact time and microwave power radiation at each fraction showed the microwave energy's ability to break bonds of Fe in the bulk of sediment. In the fraction 1, the dissociation energy of Fe-H bond was 148 kJ/mol and the concentration of Fe was 107.840 mg/kg (0.0108% wt) with the optimum microwave power and contact time (10% - 1 minute) using a total microwave energy of 1075.20 kJ/mol. In the fraction 2, the dissociation energy of the Fe-C bond was 376.3 kJ/mol and the concentration of Fe was 98.334 mg/kg (0.0098 % wt) with the optimum of microwave power and contact time (30% - 3 minutes) using the microwave energy of 9676.80 kJ/mol. In the fraction 3, the dissociation energy of the Fe-Fe bond was 118 kJ/mol and the concentration of Fe was 3059.46 mg/kg (0.3059 %wt) with the optimum microwave power and contact time (50% - 3 minutes) using microwave energy of 16128.0 kJ/mol. In fraction 4, the dissociation energy of Fe-O bond was 407.0 kJ/mol with the concentration of Fe of 319.467 mg/kg (0.0319 %wt) with the optimum microwave power and contact time (50% - 2 minutes) using totally microwave energy of 10752.0 kJ/mol. The conditions of optimum microwave power showed stronger that released the highest concentrations (the number of Fe bonds) at each fraction (except for fraction 4). The decrease in the microwave energy in the fraction 4 was affected by the low concentration of Fe in sediment.

Table 1. Fe leaching using Tessier microwave

Fraction	Variation	The concentration of Fe (mg/L)			The concentration of Fe (mg/kg)			Average (mg/kg)	%wt
		1	2	3	1	2	3		
F1	10%-1	0.521	0.585	0.530	83.36	93.6	84.8	87.253	0.0087
	10%-2	0.714	0.680	0.628	114.2	108.8	100.48	**107.84**	**0.0108**
	10%-3	0.396	0.467	0.441	63.36	74.72	70.56	69.547	0.0070
	30%-1	0.427	0.457	0.376	68.32	73.12	60.16	67.200	0.0067
	30%-2	0.460	0.500	0.555	87.36	80.0	88.8	85.387	0.0085
	30%-3	0.532	0.475	0.504	85.12	76.0	80.64	80.587	0.0081
	50%-1	0.594	0.539	0.544	95.04	86.24	87.04	89.440	0.0089
	50%-2	0.591	0.601	0.620	94.56	96.16	99.2	96.640	0.0097
	50%-3	0.679	0.673	0.660	108.6	107.68	105.6	107.31	0.0107
F2	10%-1	0.231	0.192	0.255	36.96	30.72	40.8	36.160	0.0036
	10%-2	0.231	0.266	0.225	36.96	42.56	36.0	38.507	0.0039
	10%-3	0.293	0.281	0.24	46.88	44.96	38.4	43.413	0.0043
	30%-1	0.334	0.313	0.328	53.44	50.08	52.48	52.000	0.0052
	30%-2	0.318	0.326	0.329	50.88	52.16	52.64	51.893	0.0052
	30%-3	0.603	0.628	0.613	96.48	100.48	98.08	**98.347**	**0.0098**
	50%-1	0.39	0.383	0.454	62.4	61.28	72.64	65.440	0.0065
	50%-2	0.45	0.458	0.368	72.0	73.28	58.88	68.053	0.0068
	50%-3	0.442	0.444	0.443	70.72	71.04	70.88	70.880	0.0071

Fraction	Variation	The concentration of Fe (mg/L)			The concentration of Fe (mg/kg)			Average (mg/kg)	%wt
		1	2	3	1	2	3		
F3	10%-1	0.499	0.46	0.483	399.2	368	386.4	384.533	0.0385
	10%-2	0.701	0.71	0.699	560.8	568	559.2	562.667	0.0563
	10%-3	0.61	0.617	0.567	488	493.6	453.6	478.400	0.0478
	30%-1	1.144	1.142	1.16	915.2	913.6	928	918.933	0.0919
	30%-2	2.136	2.161	2.173	1708.8	1728.8	1738.4	1725.333	0.1725
	30%-3	2.018	1.98	1.962	1614.4	1584	1569.6	1589.333	0.1589
	50%-1	0.822	0.844	0.786	657.6	675.2	628.8	653.867	0.0654
	50%-2	1.332	1.308	1.335	1065.6	1046.4	1068	1060.000	0.1060
	50%-3	3.789	3.842	3.842	3031.2	3073.6	3073.6	**3059.46**	**0.3059**
F4	10%-1	0.543	0.543	0.547	173.76	173.76	175.04	174.187	0.0174
	10%-2	0.585	0.554	0.584	187.2	177.28	186.88	183.787	0.0184
	10%-3	0.400	0.347	0.382	128	111.04	122.24	120.427	0.0120
	30%-1	0.755	0.767	0.839	241.6	245.4	268.4	251.840	0.0252
	30%-2	0.511	0.472	0.467	163.5	151.1	149.4	154.667	0.0155
	30%-3	0.455	0.403	0.431	145.6	128.9	137.9	137.493	0.0137
	50%-1	0.556	0.528	0.541	177.9	168.9	173.1	173.333	0.0173
	50%-2	1.042	0.995	0.958	333.4	318.4	306.5	**319.467**	**0.0319**
	50%-3	0.941	0.903	0.893	301.1	288.9	285.7	291.947	0.0292
F5	10%-1	31.01	31.06	31.16	32250	32302	32406	32319.73	3.2320
	10%-2	35.73	35.97	35.95	37159	37408	37388	37318.67	3.7319
	10%-3	37.72	37.66	37.62	39228	39166	39124	39173.33	3.9173
	30%-1	0.612	0.674	0.701	636.4	700.9	729.04	688.827	0.0689
	30%-2	35.39	35.44	35.44	36805	36857	36857	36840.27	3.6840
	30%-3	34.34	34.27	34.28	35713	35640	35651	35668.53	3.5669
	50%-1	25.38	25.62	25.7	26395	26644	26728	26589.33	2.6589
	50%-2	0.858	0.884	0.963	892.3	919.3	1001.5	937.733	0.0938
	50%-3	30.28	30.45	30.61	31491	31668	31834	31664.53	3.1665

As listed in Table 1, the range concentrations of Fe (mg/L) and Fe (mg/kg) were compared to detect the interference in the filtrate from AAS measurement of Fe with their Fe concentrations in the bulk sediment. In the fraction 1, 2, 3, 4, and 5, the pattern of Fe in the bulk sediment followed their patterns in the concentration of Fe in the filtrate.

It suggested that there was no interference during the measurement of Fe in the filtrate sediment using Tessier microwave with the variation of power radiation and contact time. The %wt range of Fe in the concentration of fraction 1 to fraction 4 was detected 0.098-0.3059 compared with those in fraction 5 (0.0689-3.9713). We suggested that Fe in the non-residual fraction (F1-F4) can be detected with Tessier microwave with an optimized condition as anthropogenic input only. In the fraction (F5), Fe concentration in the residual fraction can be analyzed by the total leaching using aqua regia as a natural input of Fe in sediment. In addition, the highest portion of Fe in the Gulf of Prigi sediment in F4 compared with those in F1-F4 indicated Fe in the sediment contributed by natural sources.

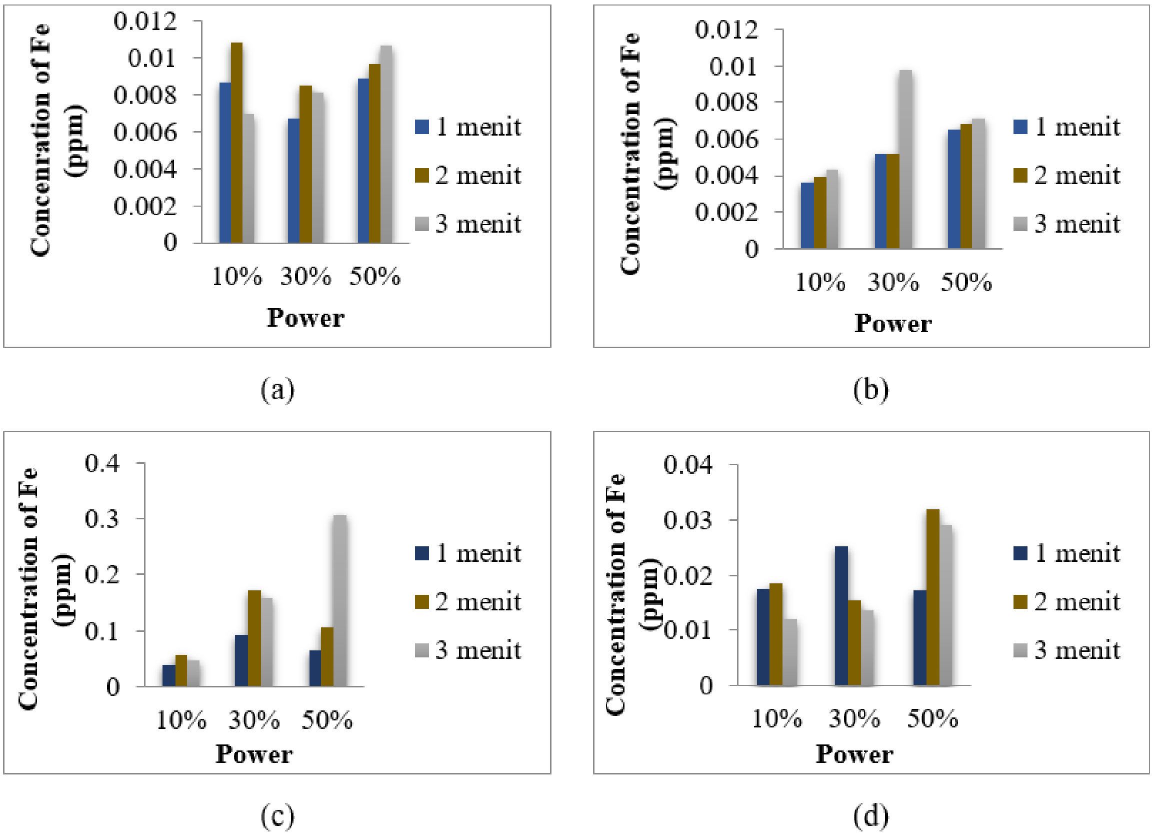

Figure 1. The relationship between Power radiation of Tessier microwave and the concentration of Fe in the variation of time.

3.2. The Test of the Accuracy and Precision for Tessier Microwave Method

The tests of accuracy were carried out on sediment reference with variations in the power of microwave and contact time using Tessier method (Table 1). From this test of sediment reference, we calculated the accuracy of Tessier microwave method based on the maxima leached Fe in the sediment with the contact time shortly. The total concentration of Fe in each of fractions at the optimized power of microwave and contact time was then compared with the results of the sediment reference (Table 2).

Table 2. The test of accuracy of leached Fe in sediment

The leached Fe Tessier microwave (%wt)	***Database of Fe (%wt)** [9]
4.27	6.60
%Recovery	**64.8%**

We detected the accuracy based on the percentage of recovery. The leached Fe using Tessier microwave in the optimized condition in sediment reference was 4.27 %wt. The result of the test of accuracy of JMS-1 reference using Tessier microwave method released the recovery percentage of 64.8%. According to the Association of Analytical Chemists [11], an accurate method has a recovery percentage of 75-120% for the concentration of metal contents (≤ 1 ppm). We suggest the Tessier microwave method has a high accuracy of Fe analysis with an optimized condition. To investigate the precision method, we continued the testing to analyze Fe in the sediment collected from the Gulf of Prigi with the 3 repetitions at each point. The results of the precision test of Fe leached are presented in the Table 3.

Table 3. Precision test in the leached of Fe using Tessier microwave

Fraction	Concentration of Fe (mg/L)			Average	SD	%RSD
	1	2	3			
1	0.71	0.68	0.63	0.67	0.0430	6.38
2	0.60	0.63	0.61	0.62	0.0130	2.11
3	3.78	3.84	3.84	3.82	0.0310	0.81
4	1.04	0.99	0.96	0.99	0.0420	4.21
5	37.7	37.7	37.6	37.7	0.0500	0.133

The range of %RSD in the leached Fe in the sediment was from 0.81 to 6.38 indicating the lowest of RSD with the higher level of precision. A method with good precision is indicated by the acquisition of relative standard deviation (% RSD) ≤8% for analyte concentration (≤ 1 ppm) [11]. As list in Table 3, the percentage of RSD in each fraction in the leached of Fe in sediment has a high level of accuracy for Fe analysis using Tessier Microwave method.

3.3. Analysis of Contamination Factor (CF) in Sediment of the Gulf of Prigi

The level of Fe contents in the optimized Tessier microwave was evaluated using the Contamination Factor (CF). Islam et al. (2015) confirmed CF is less than 1 that indicates the low contamination; CF that is more than equal to 1 and less than 3 means moderate contamination; CF that is more than equal to 3 and less than equal to 6 indicates high contamination and CF that is less than 6 contaminations is very high [12].

The contamination factors were determined by the Fe contaminant in the sediment. The sources of Fe pollutants come from natural or anthropogenic inputs. As listed in Table 4, the values of CF in the three locations were 537.65, 575.84 and 575.84 mg/kg which indicated the level of CF in the Gulf of Prigi has moderate levels of sediment contamination.

Table 4. CF calculation of Fe in sediment

Sample	Non-resistance (mg/kg)	CF	Sediment quality
WS	537.65	1.00	Low contamination
NS	553.44	1.03	Medium contamination
ES	575.84	1.07	Medium contamination

The high level of Fe in the sediments is 15 mg/g or equivalent to 15000mg/kg [13] . The three locations have the values far below the WHO standard, so these three locations can be declared as a natural source and reflected no potential for serious pollution.

4. Conclusion

The optimization of microwave power and contact time used Tessier method to leach Fe in sediment in the fraction 1 (power radiation 10% at 2 minutes), fraction 2 (power radiation 30% at 3 minutes), fraction 3 (power radiation 50% at 3 minutes), and fraction 4 (power radiation 50% at 2 minutes). The effectiveness of optimized microwave Tessier method has a value percent recovery of 64.8%, while the precision of this method has a value of % RSD at the fraction 1 (6.38%), fraction 2 (2.11%), fraction 3 (0.811%), fraction 4 (4.21%), and fraction 5 (0.133%) indicating high precision. The content of Fe in the non-resistant fraction was 34.8% at East of the Gulf of Prigi near to agricultural areas (the sample of ES) with the low-categorized contamination levels. The high level of Fe contents in the non-resistant fraction was 64.4% and with the level of contamination being potential for marine pollution.

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