CHARACTERIZATION AND FRACTIONATION OF PHOSPHORUS USING SEQUENTIAL EXTRACTION FROM MARINE SEDIMENT OF JAKARTA BAY

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ABSTRACT

Characterization and fractionation of phosphorus (P) in the marine sediment of Jakarta Bay were investigated in this study. IR spectroscopy resulted from the main peaks at the wavenumber were 900 – 1500 cm⁻¹ indicates the minerals, oxide, and phosphates. Physicochemical with pH (5.8-6.7), lost on ignition (11.73-16.03 %), Fe content (8.40-59.12 mg/g), Mn content (0.17-1.38 mg/g), Ca content (0.01-8.25 mg/g) and total phosphorus (8.73-994.72 µg/g). Fractionation of phosphate using sequential extraction resulted in water-soluble P (H₂O-P) of 0.27-0.76 µg/g, loosely bound-P (NH₄Cl-P) of 0.54-2.27 µg/g, exchangeable fraction-P (NaHCO₃-P) of 3.53-9.69 µg/g, P bound to Fe (NaOH-P) of 1.63- 11.23 µg/g and P bound to Ca (HCl-P) of 1.20-2.21 µg/g. The linear correlation between Mn content in sediment to HCl-P fraction with R² = 0.9126 and between calcium content in sediment to HCl-P fraction with R² = 0.8476.

Keywords: Jakarta Bay, Marine Sediment, Phosphorus, Sequential Extraction.

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INTRODUCTION

Phosphorus is an important nutrient in both marine and freshwater ecosystems for the phosphorus cycle in marine environments.¹ Many pollutants are accumulated to sediment in the river, marine, or lake. The phosphorus can pollute the water into the sediment with a chemical reaction such as adsorption and precipitation.² Phosphorus has a strong association with particulate matter in the water system, both inorganic and organic forms which commonly occur. The chemical characterization of sediment is necessary for predicting the phosphorus exchange between water and sediment.³⁻⁷

The method for separation and determination of phosphorus content in marine sediment is the sequential extraction method.⁸ This method has the advantages of simple operation, easily accessible reagent, and less interference between various form.⁹ The concentration of phosphorus fractions from sequential extractions was used to describe different forms of phosphorus in the sediment.¹⁰ Phosphorus in marine sediment was fractionated using a sequential extraction scheme such as extraction using NH₄Cl, NaOH, and HCl.¹¹ Some of the studies about fractionation phosphorus include sediment from river¹² and sediment from lakes.¹³⁻¹⁵ Limited study about characteristics and fractionation phosphorus from marine sediment. The objective of this study is to explore the characteristics and fractionation of phosphorus in marine sediment from Jakarta Bay and to give information about relationships between phosphorus form and sediment characterization in the marine environment.

EXPERIMENTAL

Materials

The reagent used in this research was from Merck with an analytical grade. KH₂PO₄, NH₄Cl (1.0 M), NaHCO₃ (0.5M), NaOH (2M), HCl (0.5M), and aqua distillation.

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Sediment Sampling

Sediment samples were obtained from Jakarta Bay, Indonesia. Location of study with six station were station 1 (106° 32' 17.6" E, 06° 00' 47.3" S), station 2 (106° 33' 29.8" E, 06° 00' 51.0" S) station 3 (106° 34' 32.6" E, 06° 01' 24.2" S), station 4 (106° 34' 45.6" E, 06° 00' 55.2" S), station 5 (106° 35' 48.3" E, 06° 00' 51.6" S) and station 6 (106° 37.6' 44.3" E, 06° 00' 26.6" S).

Fig.-1: Geographical Position of Studied Area in Jakarta Bay

Infra-Red Analysis

Characterization of a functional group from sediment used the infrared analysis method. FTIR analysis was used for the identification of the functional group of sediment including organic and inorganic compounds.

Chemical Characterization.

The measurement of pH was carried out in suspensions formed with distillation water. Nitric acid and perchloric acid were used in the digestion process. The determination of Fe, Mn, and Ca content using atomic absorption spectrometry.

Fractionation of Phosphorus

The phosphorus form in the sample was separated by sequential extraction. The first extraction used H₂O as solvent. The next extraction used NH₄Cl (1.0 M), NaHCO₃ (0.5M), NaOH (2 M), and HCl (0.5 M). The phosphorus concentration was measured using a UV-Vis spectrometer at 891 nm.

RESULTS AND DISCUSSION

Sediment Characterization.

Sediment from six stations (S1, S2, S3, S4, S5, S6) was used in this study. Functional group analysis was done to know the active group of sediment by using spectroscopy infrared spectrum of IR analysis and the peak of wavenumber showed in Fig.-2.

The organic and organic compounds can be identified by FTIR spectroscopy.¹⁷ The wavenumber of the IR spectrum can be seen in Table-1.

Table-1: Wavenumber of IR Spectrum from Marine Sediment of Jakarta Bay

Sediment	Location	Wavenumber (cm ⁻¹)
S1	106° 32' 17.6" E, 06° 00' 47.3" S	1002.7 ; 909.5
S2	106° 33' 29.8" E, 06° 00' 51.0" S	1420 ; 1006
S3	106° 34' 32.6" E, 06° 01' 24.2" S	3693.8 ; 3623 ; 909.5 ; 998.9
S4	106° 34' 45.6" E, 06° 00' 55.2" S	3693.8 ; 3623 ; 1638 ; 909.5 ; 993.9
S5	106° 35' 48.3" E, 06° 00' 51.6" S	3693.8 ; 3623 ; 1636.3 ; 905.5 ; 998.9
S6	106° 37.6' 44.3" E, 06° 00' 26.6" S	3693 ; 3623 ; 3388 ; 1636 ; 909.5 ; 995.2

Fig.-2: Infra-Red Spectrum of Sediment

The sediment at each station was coded as S1, S2, S3, S4, S5, and S6. All spectrum showed the peak at 900-1000 cm^{-1} that indicated fingerprint for metal and minerals. The peak at 1400 cm^{-1} for carbonates and 683 cm^{-1} , 790 cm^{-1} , 1009 cm^{-1} were predicted for silicates and iron-oxide.¹⁸ Phosphates usually at 850-1075 cm^{-1} , PO_4^{3-} at 1005 cm^{-1} , and mineral goethite-phosphate and TiO_2 were present in these peaks. Phosphates as HPO_4^{2-} at peaks of 850 cm^{-1} , H_2PO_4^- at peaks of 875 cm^{-1} , 940 cm^{-1} , 1075 cm^{-1} .¹⁹ The IR spectra of PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- and H_3PO_4 will show the differences peaks.²⁰ The dominant species of phosphorus in the sediment is H_2PO_4^- . The low intensity in 3700-3000 cm^{-1} indicates the presence of clay minerals. The peak at 3623 cm^{-1} referred to the OH stretch of H_2O .²¹

Spectrum with wavenumber at 110-913 cm^{-1} was contributed to Si-O stretching band of kaolinite. Spectrum at a wavenumber of 676-693 cm^{-1} was the deformation of metal oxide.^{22,23}

The physicochemical of marine sediment can be seen in Table-2.

Table-2: Physicochemical Analysis of Marine Sediment from Jakarta Bay

Sediment	pH	LOI (%)	Fe content (mg/g)	Mn content (mg/g)	Ca content (mg/g)	Total P ($\mu\text{g/g}$)
S 1	6.5 $\pm$ 0.1	15.83 $\pm$ 0.24	55.18 $\pm$ 3.57	1.21 $\pm$ 0.11	0.31 $\pm$ 0.26	363.43 $\pm$ 22.20
S 2	6.7 $\pm$ 0.2	12.72 $\pm$ 0.39	8.40 $\pm$ 0.68	0.17 $\pm$ 0.05	8.25 $\pm$ 1.00	21.74 $\pm$ 10.17
S 3	6.0 $\pm$ 0.1	11.76 $\pm$ 0.02	59.12 $\pm$ 1.62	1.51 $\pm$ 0.05	0.01 $\pm$ 0.01	994.72 $\pm$ 13.01
S 4	6.0 $\pm$ 0.1	15.90 $\pm$ 0.06	54.19 $\pm$ 2.62	1.38 $\pm$ 0.02	0.01 $\pm$ 0.00	979.69 $\pm$ 21.36
S 5	5.8 $\pm$ 0.0	11.73 $\pm$ 0.05	57.20 $\pm$ 1.93	1.35 $\pm$ 0.03	0.07 $\pm$ 0.00	24.36 $\pm$ 7.87
S 6	5.9 $\pm$ 0.1	16.03 $\pm$ 0.09	58.33 $\pm$ 0.96	1.36 $\pm$ 0.02	0.04 $\pm$ 0.00	316.70 $\pm$ 31.12

The pH range of sediment was found from 5.8 to 6.7. The effect of pH on total phosphorus showed that the acid condition can increase the total phosphorus. The H_2PO_4^- species at pH 2-7 and HPO_4^{2-} species are present in the pH region between 7 and 11. The pH higher than 12 the concentration of PO_4^{3-} species becomes. Organic matter was measured as a loss of ignition (550°C for 4 hours). The LOI indicated the organic component in the sediment.

The result showed that Fe in sediment ranged from 8.40 to 59.12 mg/g. The highest iron content was found in station 6 and the lowest iron content at station 2 was 8.40 mg/g. Manganese content were 0.17 mg/g -

1.38 mg/g. The highest manganese content was at station 4 was 1.38 and the lowest at station 2. Calcium was analyzed 0.01-8.25 mg/g. The highest calcium content was at station 2.

The total phosphorus concentration of sediment samples was 21.74 – 994.72 $\mu\text{g/g}$ (dry weight). The highest TP was found at station 4 and the lowest Total P was at station 2. Increasing total phosphorus at the sediment has been related to eutrophication.²⁴⁻²⁹

Fractionation of Phosphorus in Marine sediment

Fractionation of phosphorus in marine sediment used a sequential extraction method. The fractionation of phosphorus can be seen in Table-3.

Table-3: Fractionation of Phosphorus

Sediment	H ₂ O-P ($\mu\text{g/g}$)	NH ₄ Cl-P ($\mu\text{g/g}$)	NaHCO ₃ -P ($\mu\text{g/g}$)	NaOH-P ($\mu\text{g/g}$)	HCl-P ($\mu\text{g/g}$)
S 1	0.76 ± 0.43	0.92 ± 0.07	6.49 ± 0.84	3.29 ± 0.09	2.19 ± 0.58
S 2	0.27 ± 0.02	2.27 ± 0.04	9.69 ± 0.12	1.63 ± 0.37	2.21 ± 0.23
S 3	0.45 ± 0.07	0.99 ± 0.20	5.19 ± 0.73	9.78 ± 0.26	1.20 ± 0.07
S 4	0.44 ± 0.20	0.75 ± 0.03	7.36 ± 0.32	6.95 ± 0.95	1.33 ± 0.26
S 5	0.27 ± 0.06	0.62 ± 0.33	3.53 ± 0.09	11.23 ± 0.14	1.91 ± 0.21
S 6	0.30 ± 0.08	0.54 ± 0.10	5.12 ± 0.37	7.92 ± 0.76	1.88 ± 0.03

Speciation of inorganic P was carried out using the method on sequential extraction procedure which divided inorganic P-fraction in a sediment into water-soluble P (H₂O-P), loosely bound-P (NH₄Cl-P), exchangeable fraction-P (NaHCO₃-P), P bound to iron (NaOH-P), P bound to calcium (HCl-P). Phosphorus content in H₂O (0.27-0.76 $\mu\text{g/g}$), NH₄Cl (0.54-2.27 $\mu\text{g/g}$), NaHCO₃ (3.53-9.69 $\mu\text{g/g}$), NaOH (1.63- 11.23 $\mu\text{g/g}$) and HCl (1.20 -2.21 $\mu\text{g/g}$) from six stations. Stations 1, 2, and 4 indicated the highest fraction as P-NaHCO₃ (exchangeable fraction) with content 6.49 $\mu\text{g/g}$, 9.69 $\mu\text{g/g}$, and 7.36 $\mu\text{g/g}$ respectively. Sediment at stations 3, 5, and 6 was the highest component was extracted by NaOH with content were 9.78 $\mu\text{g/g}$, 11.23 $\mu\text{g/g}$, and 7.92 $\mu\text{g/g}$. The knowledge of the chemical speciation of phosphorus is important to know the biogeochemical of phosphorus in the ocean.³⁰ The relationship of Mn content with phosphorus fractionations from sediment of Jakarta Bay can be seen in Fig.-3

Fig.-3: Relationship between Mn Content with Phosphorus Fractionations

Figure-3 showed the relationship between Mn content with phosphorus fractionation in the samples. There was no correlation between Mn content with $\text{H}_2\text{O-P}$ and $\text{NaHCO}_3\text{-P}$. Mn content showed a negative correlation to the $\text{NH}_4\text{Cl-P}$ fraction. This indicated that the greater Mn content in sediment affected the smaller $\text{NH}_4\text{Cl-P}$ fraction. A negative correlation also showed the relationship of Mn content with HCl-P . It showed a linear correlation with an R^2 value was 0.9126 and a regression linear of $0.2189x + 2.5527$. The HCl-P fraction indicated Ca-bound phosphorus but this value is also influenced by Mn content. The larger Mn content affected the smaller calcium-bound phosphorus was found in sediment. The result indicated no correlation between Mn content with $\text{H}_2\text{O-P}$ and $\text{NaHCO}_3\text{-P}$ and a negative correlation between the $\text{NH}_4\text{Cl-P}$ fraction and HCl-P . It happened because the Mn was an unstable ion. Mn can be found as Mn(II) and Mn(IV) . The form of Mn depending on the pH of the solution was generated from each solvent.

The relationship of Fe content with phosphorus fractionations from the sediment of Jakarta Bay can be seen in Fig.-4.

Fig.-4: Relationship of Fe Content with Phosphorus Fractionations

Characteristics of phosphorus can be determined from iron and calcium content. It can predict P behavior and estimate the potential risk for eutrophication and environmental condition. From Fig.-4 it can be seen there is no correlation between Fe Content with the fractionation of phosphorus. It happened because the Fe was an unstable ion. Fe can exchange from Fe(II) to Fe(III) which is influenced by the environmental conditions.

The relationship of Ca content with phosphorus fractionations from the sediment of Jakarta Bay can be seen in Fig.-5.

Linear correlation can be found in the relationship between Ca content with the HCl-P fraction with R^2 value was 0.8476 and regression linear equation was $0.207x + 1.283$. The correlation of Ca content to HCl-P fraction indicated if the sediment has the rich of calcium showed the high HCl-P fraction (calcium bound to phosphate).

CONCLUSION

Characteristics of marine sediment of Jakarta Bay in six stations were characterized by IR spectroscopy, physicochemical properties, and fractionation of phosphorus by sequential extraction. The relationship of metal content to phosphorus fractionation showed that there is no correlation between Fe, Mn and Ca content against total phosphorus in the marine sediment of Jakarta Bay. There was a linear correlation between Mn content in sediment to HCl-P fraction showed by R^2 value was 0.9126 and regression linear

was $0.2189x + 2.5527$. The curve obtained a negative correlation. A linear correlation between calcium content in sediment to the HCl-P fraction with the R^2 value of 0.8476 and regression linear was $0.207x + 1.283$ and the curve showed a positive correlation.

Fig.-5: Relationship Between Ca Content with Phosphorous Fractionations

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