BCR Sequential Leaching for Geochemical Fractions and Assessment of Fe, Ni, and Mn in the Coastal Sediments Sendang Biru Port, East Java, Indonesia

Anugrah Ricky Wijaya¹, Ida Farida¹, Surjani Wonorahardjo¹, Yudhi Utomo¹, Hasan Daupor², Md. Sazzad Hossain³, Tatsuya Kunisue⁴

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
²Chemistry Major, Faculty of Science Technology and Agriculture, Yala Rajabhat University, Thailand
³Department of Aquaculture, Faculty of Fisheries, Bangladesh Agricultural University (BAU), Bangladesh
⁴Environmental Chemistry and Ecotoxicology, Center for Marine Environmental Studies (CMES), Ehime University, Japan

*Corresponding author’s email: anugrah.ricky.fmipa@um.ac.id

Abstract. The changes in the aquatic environment by either natural or anthropogenic sources may affect the presence of heavy metals in the sediment of Sendang Biru Port. Heavy metals such as Fe, Ni, and Mn possibly give a negative impact on ecological and biological systems in the sea water. To monitor the status of sediment of the Port Sendang Biru, we investigated the geochemical fraction of Fe, Ni, and Mn in sediment using the BCR (European Community Bureau of Reference) sequential leaching method. The precision test of BCR method showed that Fe, Ni, and Mn has 4.82; 3.73; and 3.16 Relative Standard Deviation (RSD), respectively. The accuracy test of BCR method showed that percentage recovery for Fe, Ni, and Mn were 85.5%; 96.2%; and 63.0%, respectively. The fracti

1. Introduction
Sendang Biru Port is one of the major ports in East Java. This Port has about 3000 fishermen in Sendang Biru with fish catch reached 11500 tons per year. Some human’s activities (anthropogenic) that occurred surrounding Sendang Biru Port are possibly contributed by fishing boat activities, waste disposal from the fish market and domestic waste disposal causing the heavy metal contamination in sediment.
Sediment is the final site of an accumulated heavy metal compound in the aquatic environments [1]. Heavy metals (Fe, Ni, and Mn) in dominant sediment may have a toxic effect on the human being.

Some researchers used the method of partial leaching to assess Fe, Ni, and Mn in sediment and coral [1–4]. This method is only for the first assessment of that metals and cannot explain their concentrations in their sediment fraction. The fraction of metal binding in sediment is very important to understand metals mobility which can affect ecological and biological systems in the aquatic environment surrounding the Port. To understand the geochemical fractions, we used sequential leaching for Fe, Ni, and Mn in sediment to know each of fraction mobility which can influence environmental systems.

One of sequential leaching methods that is commonly used is the BCR (European Community Bureau of Reference) method. The BCR method fractionates metals into four fractions comprising exchangeable and easily soluble fraction (F1), easily reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4). F1, F2, and F3 easily indicate heavy metal mobility in the sediment or non-residual fractions, whereas F4 represents a difficult fraction mobilized [5]. Here, we report and assess using BCR method to leach Fe, Ni, and Mn in port sediment fractions.

2. Experimental Methods

2.1. Sample Collection and Pretreatment for Analysis

Figure 1 shows the collected samples of sediment in the center of Sendang Biru Port. The samples were collected on November 12, 2016 using a stainless-steel grab, put in the plastic bag, and then transferred to the Analytical Chemistry Laboratory.

The sediment samples are fine grains and composed of mud and silt. The samples were separated from rock, bone, corals, and wood. The sediment samples were homogenized and then dried in an oven at 60 °C [3]. The qualitative metal composition of representative sediment samples was determined using X-ray Fluorescence. The samples were powdered by hand using an agate mortar and pestle. The instrument used was a PANalytical, Minipal 4. The chemical substances in sediment are listed in Table 1.
Table 1. Chemical substances in sediment

| Metal | Concentration (%) |
|-------|-------------------|
| Al    | 6+/−0.6           |
| Si    | 5.8+/−0.3         |
| K     | 0.3+/−0.2         |
| S     | 0.2+/−0.6         |
| Ca    | 57.9+/−0.003      |
| Ti    | 1.1+/−0.6         |
| V     | 0.05+/−0.009      |
| Cr    | 0.079+/−0.004     |
| Mn    | 0.17+/−0.004      |
| Fe    | 18.8+/−0.2        |
| Ni    | 0.21+/−0.004      |
| Cu    | 0.15+/−0.005      |
| Zn    | 0.02+/−0.005      |
| Br    | 0.21+/−0.01       |
| Sr    | 4.60+/−0.12       |
| Zr    | 0.2+/−0.2         |
| Mo    | 3.28+/−0.94       |
| In    | 0.8+/−1.0         |
| Ba    | 0.1+/−0.03        |
| Yb    | 0.08+/−0.007      |
| Re    | 0.38+/−0.04       |

2.2. The Sequential Leaching Experiment

The sample sediments from Sendang Biru Port and reference sediment of Geochemical Survey of Japan (JSD-1) were analyzed for Fe, Ni, and Mn contents in fraction sediment using BCR method. The determination of metal concentration in the reference sediment was used to control the quality of data through precision and accuracy tests, while the determination of metal concentration in Sendang Biru Port’s sediment was aimed to find out the concentration of its geochemical fraction and status of Fe, Ni, and Mn.

Analysis of Fe, Ni, and Mn in the sediment consisted of four stages: (1) exchangeable and easily soluble fractions. 0.5 grams of sediment samples were leached with 20 mL of acetic acid solution (0.11 M) for 16 hours; (2) the easily reducible fraction. The residue of the exchangeable and easily soluble fraction was leached with 20 mL of hydroxylamine hydrochloride solution (0.1 M; pH 2) for 16 hours; (3) the oxidizable fraction. The residue from the easily reducible fraction was leached using 5 mL of hot hydrogen peroxide (30%) to nearly dry twice, then leaching followed by 25 mL of ammonium acetate solution (1.0 M; pH 2) for 16 hours; (4) the residual fraction. The residue from the oxidized fraction was leached with 5 mL of concentrated nitric acid for 24 hours, then put in a sonic bath for 30 min and heated to 110 °C. After drying, the residue was added with 20 drops of concentrated nitric acid and 10 drops of fluoride acid, then heated until dry. Finally, the residue was dissolved and diluted with 2 mL of 1% HNO₃ five times [3,6]. The leached sample was then analyzed using an AAS (PerkinElmer A Analyst 700) to determine the concentration of Fe, Ni, and Mn of each fraction in sediment.

3. Results and Discussion

3.1. The BCR Method for Leaching Fe, Ni, and Mn in Sediment

The effectiveness of BCR method in leaching Fe, Ni, and Mn in sediment was tested. This test aimed to ensure that the method is able to produce the correct data which are in accordance with its designation. Testing parameters of the effectiveness of this method are the precision and accuracy.
The results of precision test of BCR method for leaching Fe, Ni, and Mn using RSD are listed in Table 2. The leached Fe, Ni, and Mn has relative standard deviation (RSD) of 4.82, 3.73, and 3.16, respectively. The test of BCR method indicated high precision for leaching Fe, Ni, and Mn which has RSD less than 5%. Therefore, it can be stated that the BCR is a precision method for leaching Fe, Ni, and Mn in Sendang Biru Port sediment.

The accuracy test of BCR method for leaching Fe, Ni, and Mn showed the percentage recovery for Fe (85.5%), Ni (96.2%), and Mn (63.0%) (Table 2). The range of percentage recovery for standard accuracy was 85-110%. This suggests that the applied BCR method is accurate for leaching Fe and Ni, but is less accurate for leaching manganese in sediments.

The low accuracy of Mn obtained using BCR method indicated that Mn was not able to be perfectly leached by this method. According to [7], the low Mn accuracy is due to the inability of the solvent used in the second fraction (F2) of the BCR method for leaching MnO. The low Mn accuracy can also be affected by disturbance of sedimentary matrices such as Cu, Ni, Ca, and Fe [8].

| Metal  | RSD  | Percentage Recovery (%) |
|--------|------|--------------------------|
| Fe     | 4.82 | 85.4                     |
| Ni     | 3.73 | 96.2                     |
| Mn     | 3.16 | 62.3                     |

The precision and accuracy tests of BCR method (Table 2) showed that the BCR method is capable of leaching Fe and Ni precisely and accurately, but it is not effective for leaching Mn accurately. This suggests that the BCR method is feasible to be used for leaching Fe and Ni, but less feasible to be used for leaching Mn in Sendang Biru Port sediment.

3.2. Fractionations of Fe, Ni, and Mn Concentrations in Sediment

Metal fractionation in sediments reflects the mechanism of metal binding in sediments. The difference of metal binding in these sediments shows the difference of metal source. Generally, anthropogenic metals are presented in non-residual fractions, whereas metals derived from natural sedimentary materials are in residual fractions [9]. BCR method breaks metals binding in the sediment into four fractions, namely (1) exchangeable and easily soluble fraction (F1), (2) easily reducible fraction (F2), (3) oxidizable fraction (F3), and (4) residual fraction (F4). F1, F2, and F3 are referred to non-residual fraction.

Three dominant metals are suspected to be anthropogenic contaminants surrounding the port (Table 1). The results of Fe, Ni, and Mn fractionation are illustrated in Figure 2. Based on the Figure, it is known that Fe is dominant in the residual fraction while Ni and Mn are dominant in the non-residual fraction.

As shown in Figure 2 and Table 3, the contents of Fe in ion exchangeable and soluble, easily reducible, and oxidizable fractions are 26.2(104) mg/Kg (1.51%), 25.0(104) mg/Kg (1.44%), and 110(104) mg/Kg (6.33%), respectively. The total contents of Fe in this three fractions indicated the Fe binding in the non-residual fraction in sediment. These fractions may be contributed from anthropogenic source surrounding Sendang Biru Port.

| Metal | Metal Contents (mg/kg) |
|-------|------------------------|
|       | Fe (104) | Ni | Mn |
| F1    | 26.2      | 23.6| 69.8|
| F2    | 25.0      | 22.4| 58.1|
| F3    | 110       | 22.9| 58.6|
| F4    | 1572      | 18.5| 55.3|
The concentration of Fe in residual fraction was 1572 (104) mg/Kg (90.7%) (Table 3; Figure 2). The high concentration of Fe in the residual fraction indicated that the sediment was relatively uncontaminated by Fe and it was not harmful to the ecological and biological systems in the waters. The possible chemical reaction in this fraction can be written as follow [3]:

\[
\text{Sediment–SiO}_2–\text{Al}_2\text{O}_3–\text{Fe(III)}(s) + \text{HNO}_3(aq) + HF(aq) \rightarrow \text{Fe(NO}_3)_3(aq) + \text{Al(NO}_3)_3(aq) + \text{SiF}_4(g) + \text{H}_2\text{O}(l) + \text{H}_2\text{O}(g)
\]

\[
\text{Sediment–SiO}_2–\text{Al}_2\text{O}_3–\text{Fe(II)}(s) + \text{HNO}_3(aq) + HF(aq) \rightarrow \text{Fe(NO}_3)_2(aq) + \text{Al(NO}_3)_3(aq) + \text{SiF}_4(g) + \text{H}_2\text{O}(l) + \text{H}_2\text{O}(g)
\]

Fractionation of Ni and Mn in the sediment of Sendang Biru Port shows that both metals are dominant in non-residual fractions (Figure 2). The high concentrations of Ni and Mn in non-residual fractions suggested that Ni and Mn were contributed from anthropogenic process surrounding Sendang Biru Port. Ni and Mn in non-residual fractions may be released from sediment when there is a change in the aquatic environment so that it affects the ecological and biological systems in Sendang Biru Port.

The high concentrations of Ni and Mn in exchangeable and easily soluble fraction were 23.6 and 69.8 mg/kg, respectively (Table 3). The high concentration of Ni and Mn at the most unstable fraction is due to the input of the resident's waste surrounding Sendang Biru Port. Metals in this fraction can impact on ecological and biological systems. These metals are very weakly associated with negative organic or inorganic binding site in the sediment. The presence of a decrease in pH in the aquatic environment can cause Ni and Mn in this fraction dissolved into the surface water so that it can cause the negative impact on the environment.

The high concentrations of Ni and Mn were also found in the oxidizable fraction (22.9 and 58.6 mg/kg) (Table 3). Ni and Mn in this fraction form a stable complex with humic acid (HA) derived from organic matter. The high concentrations of Ni and Mn in this fraction may be contributed from anthropogenic inputs around Sendang Biru Port such as the disposal of fish market waste or domestic waste. This study supports previous similar studies reported by Passos et al. 2010 [9] for suggesting input of human’s activity surrounding the site. Ni and Mn can be released into waters when the process degradation of organic matter occurs.

The concentrations of Ni and Mn were found in the easily reducible fraction (22.4 and 58.1 mg/kg) (Table 3). The presence of Ni in this fraction is bound to Fe-Mn oxide, whereas Mn in this fraction is
derived from Mn bound to Fe and Mn oxides in its oxidant form [11]. Ni and Mn at a reduced fraction may be due to the activity of fishing vessels and discharges from industry [3]. Ni and Mn contained in this fraction can be released into the waters when the aquatic environment becomes anoxic [12].

The possible chemical reaction of Ni and Mn in non-residual fraction can be written as follows, (which Me = Ni or Mn) [3]:

1. **Ion exchangeable and soluble fraction**
   
   \[
   \text{Sediment–Me}^{2+}(s) + \text{CH}_3\text{COOH}(aq) \Rightarrow \text{Sediment–}(\text{H}_2(s) + (\text{CH}_3\text{COO})_2\text{Me}(aq))
   \]
   \[
   \text{Sediment–MeCO}_3(s) + \text{CH}_3\text{COOH}(aq) \Rightarrow \text{Sediment(s) +} (\text{CH}_3\text{COO})_2\text{Me}(aq) + \text{H}_2\text{CO}_3(aq)
   \]

2. **Easily reducible fraction**
   
   \[
   \text{Sediment–MnO}_2–\text{Me}(s) + \text{NH}_3\text{OH.HCl}(aq) \rightarrow \text{Sediment(s) + MnCl}_2(aq) + \text{MeCl}_2(aq) + \text{NH}_3(g) + \text{H}_2\text{O}(l) + \text{O}_2(g)
   \]

3. **Oxidizable fraction**
   
   \[
   \text{Sediment–HA–Me}(s) + \text{H}_2\text{O}_2(aq) + \text{CH}_3\text{COONH}_4(aq) \rightarrow \text{Sediment–HA(s) + (CH}_3\text{COO})_3\text{Fe}(aq) + \text{NH}_3(g) + \text{H}_2\text{O}(l) + \text{O}_2(g)
   \]

The lowest concentration of Ni and Mn were in residual fraction 18.5 mg/kg and 55.3 mg/kg, respectively (Table 3). This is probably related to the abundance of Ni and Mn in the earth’s crust, including sediment in Sendang Biru Port. Metals in the residual fraction are strongly bound to natural minerals and resistant components of the solid matrix in sediment so that they are difficult to mobilize into pore-waters through dissociation. The possible chemical reaction in this fraction can be written as follow, (where Me = Ni or Mn) [3]:

\[
\text{Sediment–SiO}_2–\text{Al}_2\text{O}_3–\text{Me}(s) + \text{HNO}_3(aq) + \text{HF}(aq) \rightarrow \text{Me(NO}_3)_2(aq) + \text{Al(NO}_3)_3(aq) + \text{SiF}_4(g) + \text{H}_2\text{O}(l) + \text{H}_2\text{O}(g)
\]

### 3.3. Assessment of Fe, Ni, and Mn in Sediment

Assessment of sediment status of Sendang Biru Port is used to know the level of contamination of Fe, Ni, and Mn in the sediment associated with water pollution. The determination of this status is based on the calculation of the contamination factor (CF), Geo-accumulation Index (Igeo), and Pollution Load Index (PLI) [2,13]. The calculations of CF, Igeo, and PLI values are respectively based on the mathematical equations expressed by some researchers. CF and Igeo are used to determine the level of contamination of each heavy metal (Fe, Ni, or Mn) in sediment, whereas PLI is used to determine the level of total heavy metal contamination (Fe, Ni, and Mn) in sediment [13–15].

**Table 4. Assessment of Fe and Mn in Sediment**

| Sampling site | CF | Igeo |
|---------------|----|------|
|               | Fe | Mn   | Fe  | Mn  |
| 1             | 1.94 | 1.52 | 0.18 | 0.02 |
| 2             | 1.74 | 1.08 | 0.16 | -0.32 |
| 3             | 1.38 | 1.57 | -0.13 | 0.07 |
| 4             | 2.12 | 1.36 | 0.28 | -0.10 |
| 5             | 0.36 | 3.37 | -2.06 | 1.17 |
| 6             | 0.65 | 1.13 | -1.21 | -0.17 |
| 7             | 1.00 | 1.00 | -1.69 | -0.18 |
| 8             | 1.87 | 1.42 | 0.51 | -0.06 |

As listed in Table 4, CF calculations showed that the sediment of Sendang Biru Port has been contaminated by Fe, Ni, and Mn with a moderate category for Ni and low category for Fe and Mn. In case of Igeo calculation, the sediment was contaminated in the low to moderate category by Ni, whereas
Fe and Mn were contaminated in low category low (Table 4). Based on the calculation, the PLI value was 0.95 (Table 4). These results indicated that the sediment of Sendang Biru Port was low contaminated by Fe, Ni, and Mn. The low contaminated sediment can improve the quality of seawater and its productivity such as increasing fish, lobster, and shrimp (Chitosan) [16].

4. Conclusion
The BCR method was effective for leaching Fe and Ni but was less effective for leaching Mn in sediments. The BCR method was capable of leaching Fe and Ni precisely and accurately but was not effective for leaching Mn accurately. Fe dominant was in residual fraction, while Ni and Mn were dominant in a non-residual fraction. The dominance of Fe in the residual fraction indicated Fe was strongly binding with silicates and alumina in the natural minerals of the sediment. Ni and Mn were dominant in the non-residual fraction indicating that they were contributed from anthropogenic around the Sendang Biru Port. Assessment from the index calculation of sediment had a moderate category contaminated by Ni and a low category contaminated by Fe and Mn.

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