Effective removal of mercury (Hg) from sediment by acid extraction

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Abstract. Mercury (Hg) is a hazardous and toxic substance that is resistant to decomposition and can accumulate in sediment and enter the living organisms via food chain. Due to the status of level mercury in Indonesia has reached the warning level, the action should be taken to avoid any negative impact on the environment and human health. The purpose of this study to developed a simple, fast, and effective sediment washing method for Hg removal using acid extraction. The results showed that pollution level of sediment in Ciujung watershed and its tributaries was high, especially the pollution of Hg and Cd, according to geoaccumulation index ($I_{geo}$) and potential ecological risk index (PERI). By the proposed method, Hg-contaminated sediment can be extracted within 21 minutes with 99.5% of extraction rate. CRM ERM CCS80 (estuarine sediment) was used for validating the results. The optimal conditions such as vortex time, acid concentration, sonication time were evaluated according to analytical parameters. The method is valuable for designing a remediation protocol for sediment washing in developing countries.

1. Introduction

Contamination of sediment is a deliberate, global-environmental issue. Even though anthropogenic emissions to the aquatic environment have decreased significantly in recent years, sediments continue to be a sink for many contaminants because of poor environmental management, diffuse sources, and accidental spills [1]. Agency for Toxic and Substance and Disease Register (ATSRD) of United State of America states that one of priority hazardous substance in sediment is mercury [2]. It can enter human body through anthropogenic and natural sources. In Indonesia, there are around 250,000 small-scale gold miners operating at approximately 1,000 location and over a million people use Hg to extract and concentrate gold in amalgamation process making this country the world’s third-largest Hg emitter [3]. From these activities, more than 75% of Hg used in amalgamation processes is discharged directly into environment without treatment and contaminating soil, fish, soil, sediment, and worker themselves [4].

Mercury from Artisanal and small-scale gold mining (ASGM) activities can contaminate the environment through the oxidation process from elemental Hg to Hg\textsuperscript{2+} which is the general form of Hg in aquatic environments, redeposition of Hg\textsuperscript{0} vapor in the local rain during amalgam smelting, and erosion of contaminated soil during storms and seasonal runoff [4,5]. One of the biggest hot spots of
ASGM in Indonesia, located in Cisitu Village, Lebak Regency, Banten Province, has becoming a national interest since almost 50% of the population are working as miners in gold mining and processing, and within the last decade the gold extraction has been rapidly growing in the residential areas [6].

Several studies reported the pollution caused by ASGM activities in Cisitu-Lebak has been spreading to the surrounding environments (soil, sediment, fish) and has been detected in hair and blood of the local people, in which the Hg concentration exceeded the normal limit [7,8]. Health disorders are found to the people who live nearby ASGM areas, for instance congenital deformity (labiognatopalatoschizis), deaf-mute, deafness, neuron disorder, hypersalivation [6]. There is high probability the mercury has been deposited in the sediment of Ciu Jung watershed and tributaries. Therefore, the mercury contamination in the sediment should be evaluated and remediation efforts should be taken immediately.

Several remediation methods were already reported by using physical and chemical, biological, and thermal techniques. However, the physical and chemical (acid extraction) is the most used for mercury remediation [9]. The technique is easy for application and no need of specific requirement as in the biological technique, hence low cost compared to thermal technique [10].

A combination technique of mechanical and ultrasonic processes was already reported by [11] for removal of heavy metals such as Cu, Pb and Zn by soil washing with recovery rate 71-76% within 30 min. In this research, the distributions and evaluation of heavy metals in sediment from Ciu Jung watershed and its tributaries, for instance As, Cd, Cr, Cu, Hg, Pb and Zn, were studied and an effective technique for the removal of mercury from the sediment was performed with a rapid, simple, and organic solvent free method by combining vortex agitation and ultrasonic irradiation using hydrobromic acid as liquid washing. The evaluation of hydrobromic acid, vortex time, and sonication time were also studied.

2. Method

2.1. Study site

Ciujung is the longest river in Banten Province with a length of approximately 84.8 km and 1,858 km² of area, has significant importance in fulfilling the needs of the community, e.g. irrigation, sanitation, and agriculture. The river is an integration of small rivers, including Ciberang with 305 km² of area and Cisimeut with 458 km² of area, and the upstream of these rivers were derived from Cisitu Village, Lebak Regency [12]. Recently, the degradation of the Ciujung river water quality raises protests and restlessness from communities around the Ciujung watershed [12].

2.2. Sample collection

Seven surface sediments (0-10 cm depth) were collected randomly in January 2020 in rainy season from the mainstream of Ciujung watershed at (6°21’ 13.093” E to 6°9’ 4.878” E and 106° 13’ 56.95” S to 106° 18’ 31.734” S) as much as three samples, and from tributaries namely Ciberang river (6°24’ 14.796” E to 6°23’ 50.91” E and 106° 17’ 25.314” S to 106° 15’ 14.58” S) as much as two samples, and Cisimeut river (6° 30’ 49.982” E to 6° 22’ 27.455” E and 1106° 11’ 37.136” E to 106° 14’ 43.58” S) as much as two samples. Sediment collected at a depth of 0 to 10 cm can provide information about the characteristic of the sediment, the distribution of contaminants, and the most recently deposited sedimentary material [13]. The sediment samples were stored in plastic bag and kept at low temperature in the cool box and immediately transported to the laboratory for the analysis.

2.3. Sample digestion

The sediment samples were air-dried at room temperature and meshed using pestle and mortar followed by sieving through a 150 mm sieve for further analyses. The modified EPA method 3050B (SW-846) was used for heavy metals (As, Cd, Cr, Cu, Hg, Pb, and P) analysis. A Flame-Atomic Absorption Spectrometry (AAS), Graphite furnace-AAS and Hydride Generator-AAS (Hitachi, Japan), and Direct Mercury Analyzer (MA3000, NIC Japan) were used as a main analytical tool for heavy metals measurement. All other acid chemicals, pure standard either ultra-pure or supra-pure were purchased.
from Merck Germany or Wako Japan. Water used for all experiment was ultra-pure with resistivity 18.2 MΩ cm⁻¹.

Figure 1. Location site of surface sediment from Ciujung watershed and its tributaries.

2.4. Pollution indicator

A number of approaches were applied for environmental assessment, including geo-accumulation index [14] and potential ecological risk index [15], which are commonly used for environmental pollution assessment.

2.4.1 Geo-accumulation index (Igeo). The geo-accumulation index (Igeo) is a common criterion for evaluating heavy metal by comparing current concentrations with pre-industrial levels. The pollution in sediments can be calculated using the following equation:

\[ I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right) \]  

where, \( C_n \) is the concentration of element ‘n’ in the enriched sample and the \( B_n \) is the geochemical background value. In this study, \( B_n \) was considered as background concentration of element in sediment of Ciujung watershed and Banten Bay [16,17]. The factor 1.5 was incorporated to minimize possible variation in background data due to lithogenic effect [18]. Based on \( I_{\text{geo}} \), the pollution status were determined as unpolluted, unpolluted to moderately polluted, moderately polluted, moderately to strongly, strongly, strongly to extremely, and extremely contaminated, and extremely contaminated.
status with respective ranges of class 0 (<0), class 1(0–1), class 2(1–2), class 3 (2–3), class 4 (3–4), class 5(4–5), and class 6 (5<).

2.4.2. Potential ecological risk index (PERI). The potential ecological risk index (PERI) is one of methods in the evaluation of heavy metal pollution and the associated ecological risk. The method proposed by Hakanson (1980) is calculated according the following equation:

\[ \text{PERI} = \sum(E_{ir}^i) = \sum(T_{ir}^i) \times \left( \frac{C_{ir}^i}{C_{ir}^{bn}} \right) \]  

where \( C_{ir}^i \) and \( C_{ir}^{bn} \) are the measured concentrations of metal i in the sediment and its background reference value (mg kg\(^{-1}\)), respectively; \( T_{ir}^i \) is biological toxicity factor of an individual element (As=10; Cd= 30; Cr=2; Cu=5; Hg=40; Pb=5; Zn=1); \( E_{ir}^i \) represents the potential ecological risk factor of metal i. In this study, the background values of heavy metals in the sediments of Ciujung watershed and Banten bay were used as reference values [15,16]. Based on PERI values, the pollution status were determined as low potential ecological risk (<40), moderate potential ecological risk (40≤Er<80), considerable potential ecological risk (80≤Er<160), high ecological risk (160≤Er<320), and very high ecological risk (320<).

2.5. Sediment washing

0.5 g of sample was weighed and put into 50 mL of polypropylene tube and added with 10 mL of 15-48% of HBr and vortexed for 5 min. and sonicated at 20°C for 6 min. 0.5 mL of solution was transferred into 2 mL of centrifuge tube and centrifuged at 20°C for 10 min with 12,000 rpm. Afterward, 0.1 mL of supernatant was transferred into 2 mL of centrifuge tube and diluted by 1% v/v of HBr to obtain 1 mL of final solution. The solution were directly measured by Direct Mercury Analyzer and the optimal conditions of method, such as effect of acid, vortex time, sonication time and acid concentration, were studied for quantitative extraction of total mercury in solid sample. A certified reference material ERM CCS80 (estuarine sediment) and CRM NMIJ 7302-a (marine sediment) were analyzed for validating the accuracy of the results.

3. Results and discussion

3.1. Heavy metals distribution

Table 1 shows the range concentration of As, Cd, Cr, Cu, Hg, Pb and Zn (d.w.) in the surface sediment from Ciujung watershed and its tributaries namely Ciberang and Cisimeut river. Except Hg, concentration of the other six heavy metals in these rivers were lower than the threshold of ANZECC and Hong Kong sediment quality guidelines [21]. The lowest concentrations of most heavy metals were in Ciberang river except As and Cd, meanwhile the concentration of Cd in Ciujung watershed was much higher than the threshold limit. The highest concentrations of Cd, Cu, Hg, Pb and Zn appeared in Ciujung watershed because this watershed is surrounded by industrial activities producing untreated waste which was directly discharged into the environment and due to the pollution from agricultural processes. Interestingly, Hg concentrations found in these rivers were higher than the threshold limit, and the highest concentration of Hg was observed in Ciujung watershed followed by Cisimeut and Ciberang river. It can be assumed that sediment in Ciujung river was contaminated by Hg from illegal ASGM activities in the upstream of Ciberang and Cisimeut river, Cisitu Regency, Lebak District. The mean of heavy metals concentrations existed in the following order of Zn>Cu>Pb>Cr>As>Cd>Hg in Ciujung
watershed and its tributaries. The similar trend was found in Korean coast sediment where the concentration of Zn is highest, and Hg was the lowest than the other metals [19]. In overall, the heavy metals concentrations in the mainstream were relatively higher than those in the sediment of tributaries, which is consistent with [20].

**Table 1.** Heavy metals concentration in sediment from Ciberang river, Cisumeut river and Ciujung watershed.

| Location sites          | As     | Cd     | Cr     | Cu     | Hg     | Pb     | Zn     |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|
| Ciberang river (n=2)    | 1.6-2.5| 0.46-0.97| 2.83-4.84| 11-23 | 0.52-0.62| 7.7-22| 51-56  |
| Cisumeut river (n=2)    | 1.4-3.1| 0.77-0.83| 4.67-4.69| 20.0-25.0| 0.77-0.83| 22-23| 59-68  |
| Ciujung watershed (n=3) | 1.0-1.8| 0.06-3.23| 4.24-4.44| 20-27 | 0.65-0.91| 15-30| 54-147 |
| Mean ± S.D              | 1.9±0.77| 1.1±1.11| 4.3±0.74| 21.0±5.62| 0.7±0.15| 20.0±7.7| 72.5±36.96|

Threshold of sediment quality for heavy metals (mg kg⁻¹)

|             | As | Cd | Cr | Cu | Hg | Pb | Zn |
|-------------|----|----|----|----|----|----|----|
| ANZECC⁴      | 20 | 1.5| 80 | 65 | 0.15| 50 | 200|
| ISQG-low⁵    | 8.2| 1.5| 80 | 65 | 0.15| 75 | 200|

³ANZECC, Australian and New Zealand Environment and Conservation Council; ⁴ISQG, Interim Sediment Quality Guidelines

### 3.2. Assessment of heavy metals pollution

The geoaccumulation index, the potential ecological risk index, the enrichment factor, pollution loading index, contaminant factor and other methods have been employed, as reported in several literatures, to assess heavy metal pollution in sediment [14-16]. In this study, we employed Igeo and potential ecological risk index to assess heavy metal pollution in the sediment of the Ciujung watershed and tributaries, using the concentration of Ciujung watershed sediment for As, Cd, Cr, Cu, Pb, Zn and Ciberang sediment and Banten bay sediment for Hg as a baseline.

**3.2.1 Assessment of geoaccumulation index (Igeo).** The Igeo value for seven heavy metals are shown in Figure 2. The pollution levels of the heavy metals are divided into 6 classes according to the Igeo values (Table 2). Igeo values of heavy metals in Cisumeut river can be ranked in ascending order as follows: Cr (-3.3), As (-2.6), Pb (-1.0), Zn (-0.9), Cu (0.6), Hg (1.9) and Cd (3.0); in Ciberang river as follow: Cr (-3.0), As (-2.4), Zn (-0.6), Pb (-0.4), Cu (1.0), Hg (2.4), and Cd (2.7); and in Ciujung watershed as follows: As (-3.2), Cr (-3.1), Pb (-0.4), Zn (-0.2), Cu (1.1), Hg (2.4), and Cd (3.7). In overall, almost all of the investigated rivers is practically unpolluted by Pb, As, Cr and Zn (Class 0), unpolluted to moderately polluted to moderately polluted by Cu (Class 1 and 2), moderate polluted to moderately to strongly polluted by Hg (Class 2 and 3), and moderate to strongly polluted to strongly polluted by Cd (Class 4). Meanwhile, tributaries are mostly contaminated by Hg and Cd.

**3.2.2 Assessment of potential ecological risk index (PERI).** The risks of heavy metals in the sediments were evaluated using the potential ecological risk index to assess the potential risk of the studied element. PERI was determined for As, Cd, Cr, Cu, Hg, Pb and Zn and the obtained results are presented in Figure 3. According to the results, Hg is potentially creating high to very high ecological risk to the sediment in almost all of the rivers and low potential to very high ecological risk was created by Cd, and other heavy metals (As, Cr, Cu Pb, Zn) have low potential to moderate potential ecological risk in all sediment. It can be implied that pollution of Hg and Cd in Ciujung watershed and tributaries was a serious problem.
3.3 Hg remediation using acid extraction

Variety of technologies have been reported for heavy metals remediation in sediment for instance physical (soil/sediment washing, selective catalytic reduction and wet flue gas desulphurization, thermal treatment), chemical (stabilization, electro-remediation, and adsorption) and biological methods (microbial treatment, phytoremediation) to remove toxic metal(loid)s from polluted soil, water, and sediment [22]. The physical technique is regarded to be the best and most successful approach for removing toxic metal(loid)s from sediment among all remediation procedures [23]. In this study, we focused on Hg remediation by using acid extraction due to the sediments in Ciujung watershed and tributaries were highly polluted by Hg according to environmental assessment and the optimization study of acid extraction was studied in laboratory scale.

Figure 2. $I_{geo}$ values of heavy metals in the sediment of Ciberang river, Cisimeut river and Ciujung watershed.

Figure 3. PERI values of heavy metals in the sediment of Ciberang river, Cisimeut river and Ciujung watershed.
3.3.1. Effect of vortex time. Figure 4a presents the optimization of extraction time, with the assistance of vortex agitation, was initially carried out with 10 mL 10% v/v of HBr and 6 min. of sonication time by analyzing CRM NMII 7302-a (marine sediment). The vortex time varied from 2, 5, 10, 15, and 20 min. The concentration of Hg was analyzed in supernatants. The removal efficiency increased by the increasing of vortex time. The maximal removal of Hg was obtained at the 5 min with 70.13±2.3% of extraction rate and gradually stable. It can be inferred that the influence of violent mixing and turbulence at the macroscale contributes to more physical contact between contaminated sediment and washing liquid. The same result reported by [11] where the high efficiency for removing heavy metals in soil was obtained by applying mechanical process.

3.3.2. Effect of HBr concentration. In this study, the removal efficiency was evaluated to be insufficiently high to extract Hg in sediment. Therefore, the next approach carried out in this research was HBr concentration optimization. The sediment was washed with solution of 5%, 10%, 15%, 20%, 30%, and 48% (v/v) of HBr. The extraction conditions of vortex time and sonication time were 5 min and 6 min, respectively. The results are presented in Figure 4b. Removal rate for Hg increased in a linear by increasing the concentration of HBr, in which high removal efficiencies were obtained ranging 15% to 48% v/v with 76.4%±2.6% to 95.02±3.4% of Hg extraction rate. As a result, the optimal concentration of hydrobromic acid can be applied, ranging 15% to 48%. It was discovered that increasing the concentration of hydrobromic acid might extract more heavy metals from sediment. However, the cost and difficulty of pH adjustment for sediment composting should be properly considered.

3.3.3. Effect of sonication time. The optimization of extraction time with the assistance of sonication time was evaluated with 48% v/v of HBr, 5 min of vortex time. and the sonication time varied from 0, 1, 3 and 6 min by analyzing CRM ERM CC580 (estuarine sediment). The results are shown in Figure 4c. As shown in Fig. 4c, higher removal efficiencies were observed at 6 min with 101.14±3.47% of extraction rate due to acoustic cavitation causing microscale turbulence in heterogeneous systems. It reveals that sonication time enhances transfer of Hg species in sediment to liquid washing. Thus, ultrasound demonstrated synergistic effect with hydrobromic acid in extracting Hg from the sediment [24].
Figure 4. Effect of vortex time (a), effect of HBr concentration (b), and effect of sonication time (c).

3.3.4. Quality control. Quality control was performed by measuring certified reference materials, and to evaluate the analytical precision, all samples were determined in triplicate with relative standard deviation <0.67 of CV Horwitz. The accuracy of the total analysis was ensured by using standard reference materials (ERM CC580 and NMIJ 7302-a), with recoveries of 99.5% and 94.2%, respectively.

3.3.5. Method application. The method was also applied to remove selected Hg-contaminated sediment from the Ciberang river, Cisimeut river, and Ciujung watershed, as shown in Table 2. We compared the Hg concentration in supernatant after sediment washing with hydrobromic acid to the Hg concentration in sediment by direct measurement using a mercury analyzer. Table 2 shows that the removal efficiency in all selected sediments was obtained 95-102% of extraction rate. Indicating, the method was successfully applied for Hg remediation. This method can also be a future prospect bioremediation for reducing heavy metals [25].

Table 2. Hg removal from sediment in Ciberang river, Cisimeut river and Ciujung watershed.

| Matrix  | Location          | Hg sources       | Amount of T-Hg | Amount of T-Hg found by proposed method | Efficiency rate |
|---------|-------------------|------------------|----------------|----------------------------------------|-----------------|
| Sediment| Ciberang river    | ASGM             | 0.73 ± 0.14    | 0.69 ± 0.04                            | 95              |
| Sediment| Cisimeut river    | ASGM             | 0.53 ± 0.02    | 0.54 ± 0.05                            | 102             |
| Sediment| Ciujung river     | ASGM & industrial| 0.906 ± 0.01   | 0.914 ± 0.07                           | 101             |
4. Conclusion
The average concentrations of heavy metals in the surface sediments from the Ciujung watershed and its tributaries is in descending order as follow: Zn>Cu>Pb>Cr>As>Cd>Hg. According to the geo-accumulation index ($I_{geo}$), the sediment quality is in moderate to strongly polluted by Hg (Class 2 and 3), and strongly polluted by Cd (Class 4). Potential ecological risk index (PERI) of heavy metals indicated that Cd and Hg had considerable or high risks meanwhile As, Cr, Cu, Pb and Zn had low risk. Sediment washing using acid liquid with combination vortex agitation and ultrasonic irradiation can remove Hg-contaminated sediment within 21 min with 99.5% of extraction rate. However, the secondary pollution needs to be investigated. Furthermore, in-dept research of this study is highly required.

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