Original Article

Assessment of low-cost mercury absorbent to minimize the mercury environmental and health effects in Makassar coastal areas

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ABSTRACT

Mercury contained in waste in public waters is converted by activity of microorganisms into methyl-mercury (Me-Hg) components which have toxic properties and strong binding capacity in addition to their high solubility, especially in the bodies of aquatic animals. This study aims to assess the effectivity Hg absorbent made from sulfur and unsaturated pure cooking in minimizing potential effect of community health and the ecology effect in Makassar coastal areas, Indonesia. This research applied the pre and post-test experimental methods. Results of laboratory tests indicated that two high values of the magnitude of THg before the installment of mercury absorbent on the site study each point was at station 14 and station 15, it is on Paotere Port and SD Negeri Cambayya with values of 1.0019 and 1.3270 mg/l, respectively. Further, the high reduction after the polymer sulfur installment was at the same stations with a magnitude of values 0.9026 and 1.2783, respectively. Furthermore, assessment of ecological risks shows stations with high risks were at SD Negeri Cambayya (13.27), Paotere Port (10.02), and Makassar container terminal with ecological risk of (10.01) unit less, respectively. In addition, the high Hazard Quotient, values were 7.12, 6.48, and 6.23 at the same stations, respectively. There were significant differences in total mercury magnitude between different stations for surface water. The magnitude of total mercury was higher before mercury absorbent application than those and after the application of sulfur polymer. The magnitude concentration of THg reduction reaches up to 100% and some are higher than expected.

Keywords: Sulphur polymer, Mercury absorbent, Health effect, Environmental risks, Target hazard, Low cost

Introduction

Mercury pollutant is a heavy metal correlated to a variety of gold industrial activities, artisanal gold mines, and also gold shops open burning. It is a material and toxic chemical [1, 2] that could lead to skin disease, damage of neurological, and kidney disruption. The coastal area is a zone interaction between the oceans and the land, it covers 15% of the Earth's land area. There are several factors that can affect coastal environmental conditions including population growth, human activities, sedimentation, availability of clean water, and pollution [3-6]. Makassar City is a coastal area filled with various activities in the form of industrial activities, right, ports, hotels, tourism maritime, and households and sufficient water traffic are important. The impact of the activity can directly cause the amount of waste in the aquatic ecosystem one of which is heavy metals such as mercury, chromium, lead, cadmium, etc. In this case, anthropogenic metal concentrations in the environment are increasing rapidly in line with the increasing process of medium and small-scale industrialization in Makassar City [7, 8]. Sulfur in elemental is an amount readily available and not expensive material produced by more than fifty million tonnes yearly as a

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by-product of refining petroleum [9]. Elemental sulfur can capture and stabilize Hg, [10, 11] however it is difficult to apply in remediation directly due to the physical and chemical limitations.

This study is applying Hg sorbent polymers made from a combination of sulfur and pure cooking oils. This Hg sorbent potentially prevents the environment and protects the community from mercury exposure, it is an efficient and low-cost method that is required for its remediation. This mercury sorbent polymer could be applied covered across big areas which are necessary for remediating programs correlated to practices such as the open burning of gold bullion that can generate the contamination of huge land [12-14].

To reduce those problems, here we introduce polymers made from sulfur through the co-polymerization of sulfur and cooking oils that may capture mercury pollution in water and soil. The research herein aimed to evaluate the effectivity of the Hg absorbent made from sulfur and unsaturated pure cooking oil to minimize the potential impact on the community health and the ecological effects because of mercury pollutants in Makassar coastal areas, Indonesia.

Materials and Methods

Study area and study design

Experimental research was undertaken to determine the magnitude of Hg pollutant concentration in water and captures the Hg observant and aquatic media (water) from the Makassar coastal areas. This study was done in 5 districts of the coastal area in Makassar. As shown in the sampling points on the map **(Figure 1)**.

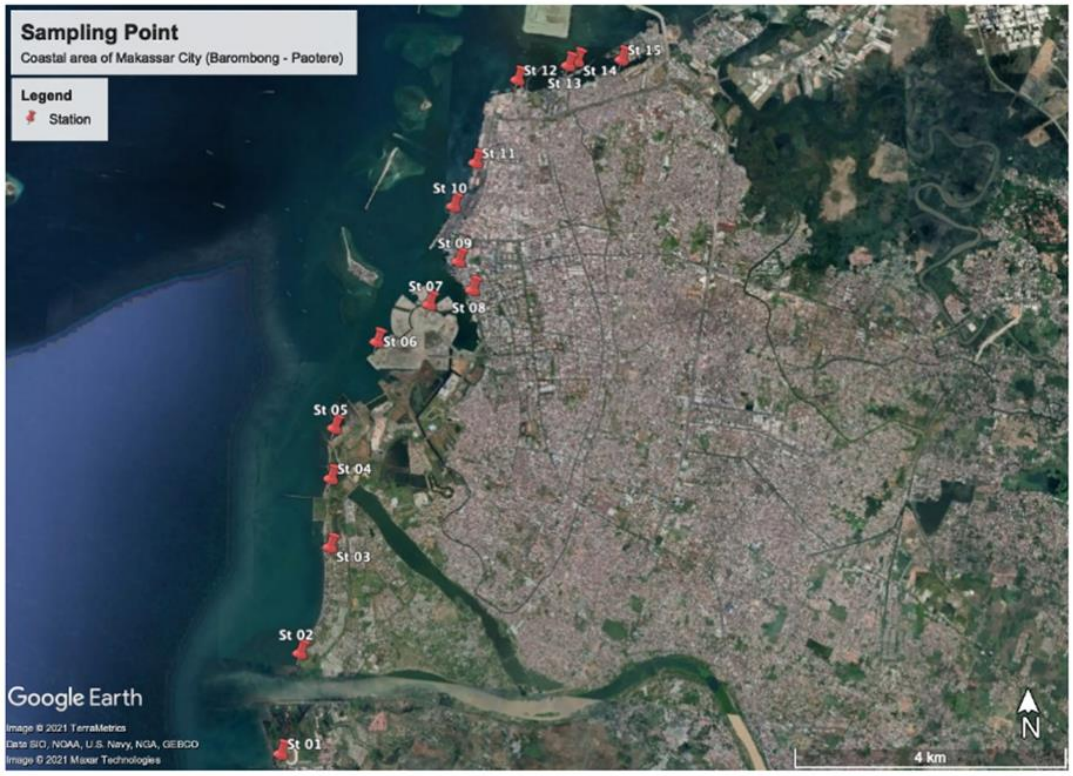

Figure 1. Sampling map location in the coastal area of the city of Makassar, 2021

Manufacturing and benefits of sulfur polymers

The material is made by polymerization of cooking oil and sulfur. Since used cooking oil is suitable for synthesis and sulfur is a by-product of the industry of petroleum, polymers can entirely be made from waste. The polymer is validated in the removal of mercury forms from the air, water, and soil. The result is necessary for the ecology for two reasons: first, the usage of waste as an important starting material in ruling the chemical life cycle, and second, it is not expensive polymers are very effective in capturing various modes of mercury.

In this study, a polymer made entirely of pure and used cooking oil and sulfur was able to remove both inorganic mercury and metallic mercury from water. These materials can be used in detecting or calculating the life of the filter that polymers use to get mercury. Mercury is also insoluble for more than 0.7 ppb as put in water and neither the polymer nor the mercury-bound polymer is toxic for liver cells.

Risks assessment for ecology

The possibility of ecological risk is determined by applying the Hazard Quotient (HQ) approach, especially for quantitative calculations.

i.e. the estimated ecotoxicity (Dose) of the compared exposure dose. while the magnitude of the concentration value in the study background which is about 20 km upstream and downstream from the research location has been determined.

The exposure ratio is regarded to represent a safe ecological magnitude concentration level or to be a screening benchmark as indicated in the formulation;

$$HQ = \frac{EEC}{Filter\ Benchmark} \quad (1)$$

EEC = predicted concentration of environmental pollutants in the study area [15-17];

Target hazard quotient (THQ)

The use of formulas and methodologies to calculate the target hazard quotient (THQ) does not give quantitative results that indicate the probability that the exposed population will experience health effects, but the results of the THQ calculation describe and offer results that indicate the level of risk due to exposure to pollutants that occur in individuals. This method is also recommended for use in the United State Environmental Protection Agency Region III US-EPA health risk-based concentration [18-20], which is shown in the equation below:

$$THQ = \frac{EF \times ED \times FIR \times C}{RFD \times BW \times TA} \times 10^{-3} \quad (2)$$

Formula description:

EF indicates the frequency of exposure (365 days/year); ED is the exposure duration (70 years), similar to a lifetime mean; FIR is the level of meal consumption (fish: 36 g/person/day; shellfish: 9.80 g/person/day; C is the metal level in seafood (µg g_1); RFD indicates the reference dose orally sourced from EPA-IRIS data. (Hg = 0.004 g g_1/day) BW was obtained by direct weighing of the respondent's body weight (60 kg), and TA was the average exposure time for non-carcinogenic substances (365 days/year x ED) [18-21].

Statistical analysis

ANOVA was used to test the difference in the number of pollutants in various locations. This study was applied to assess the hypothesis of variety in the amount of accumulation of THg contaminants and to determine whether there were differences in concentration and accumulation patterns as a function of water in various locations. in this study XLSTAT.4.05 (Windows 2010) is applied. The results indicated a significant difference statistically if the p-value is less (< 0.05).

Results and Discussion

Mercury concentration before and after the installation of sulfur polymer

After 5 weeks of placement, the mercury present and accumulated in the polymer samples were in the range of 1 mg/kg of successfully bound mercury, which was marked in red MEMC observed directly from the sample pouch up to 10 cm where MEMC was applied. as well as polymer bags installed in tailwater pits. Mercury captured and bound to the field-mounted polymer not treated with MEMC was still below the detection limit. furthermore, all soil samples to a depth of 36 cm contained between 0.03-0.04 mg/kg hg after polymer placement for 7 and 10 weeks. After 10 and 15 weeks absorbed THg < 1 mg/kg was detected in the polymer, as shown in the following **Table 1**.

Table 1. The concentration of total mercury on the 15 sites before and after the application of polymer sulfur of Makassar City Coastal Area.

Stations	Description of stations area	Longitude Latitude	Total Mercury Concentration On Water Before PSA (mg/l)	Total Mercury Concentration On Water After PSA (mg/l)	Total Mercury Reduction After PSA (mg/l)
1	Pantai Barombong	119°22'52.6"E 5°12'12.0"S	0.0071	0.0043	0.0028
2	Pantai Tanjung Layar Putih	119°23'01.3"E 5°11'24.7"S	0.0081	0.0032	0.0051
3	Tanjung Biru	119°23'15.3"E 5°08'54.5"S	0.0055	0.0012	0.0043
4	Gowa Development Tourism PT	119°23'15.4"E 5°10'01.1"S	0.0081	0.0023	0.0058
5	Tanjung bunga	119°23'16.9"E 5°09'36.6"S	0.0052	0.0022	0.0030
6	Universitas ciputra Makassar	119°23'37.4"E 5°08'54.5"S	0.0025	0.0003	0.0022
7	Twin tower CPI	119°24'03.0"E 5°08'36.2"S	0.0032	0.0011	0.0021
8	Anjungan Mandar Losari	119°24'24.3"E 5°08'29.0"S	0.0035	0.0012	0.0023

9	Dermaga Kayu Bangkoa	119°24'17.4"E 5°08'14.9"S	0.0095	0.0032	0.0063
10	Makassar Container Terminal	119°24'14.9"E 5°07'47.4"S	1.0013	0.0011	0.0002
11	Pelabuhan Soetta	119°24'25.9"E 5°07'25.7"S	0.0091	0.0043	0.0048
12	Dekat Jetty II TBBM Makassar	119°24'46.7"E 5°06'43.9"S	0.0056	0.0024	0.0032
13	TPI Lelong pattern	119°25'12.0"E 5°06'36.7"S	0.0089	0.0041	0.0045
14	Pelabuhan Paotere	119°25'16.5"E 5°06'34.6"S	1.0019	0.0993	0.9026
15	SD negeri cambaya	119°25'38.7"E 5°06'33.8"S	1.0070	0.0487	1.2783

PSA; Polymer Sulfur Application

Based on the laboratory analysis, two high value of the concentration of total mercury (THg) before the application at the research location was at points 14 and 15, namely at Pelabuhan Paotere and SD Negeri Cambayya with values of 1.0019 and 1.3270 mg/l, respectively. In addition, the high reduction after the polymer sulfur application was at the same stations with a magnitude of values are 0.9026 and 1.2783, respectively.

There is some reduction of THg concentration during the experiment after the installation of this mercury absorbent on water. The results of measuring the level of THg concentration at fifteen stations show results that are mostly influenced by the situation of using the area and also the distance of the pollutant from the pollutant source point. The maximum mean value of the concentration in water after the installation of the mercury absorber was lower than the initial concentration at each station.

Ecological, hazard risks, and target hazard risks

Ecological risks and target Hazard Quotient calculation results from 15 stations are shown in the following **Table 2**.

Table 2. Ecological Risk, Hazard Risks and Target Hazard Risks of Mercury on Water from coastal areas Makassar, South Sulawesi

Stations	Description of stations area	Longitude Latitude	Ecological Risks of Water	HQ of Water	THQ of Water
1	Pantai Barombong	119°22'52.6"E 5°12'12.0"S	7.1	1.28	0.0024
2	Pantai Tanjung Layar Putih	119°23'01.3"E 5°11'24.7"S	8.1	1.84	0.0062
3	Tanjung Biru	119°23'15.3"E 5°08'54.5"S	5.5	1.02	0.0049
4	Go Dev Tourism PT	119°23'15.4"E 5°10'01.1"S	8.1	2.61	0.0088
5	Tanjung bunga	119°23'16.9"E 5°09'36.6"S	5.2	1.76	0.0034
6	Universitas ciputra Makassar	119°23'37.4"E 5°08'54.5"S	2.5	0.78	0.0062
7	Twin tower CPI	119°24'03.0"E 5°08'36.2"S	3.2	0.88	0.0031
8	Anjungan Mandar Losari	119°24'24.3"E 5°08'29.0"S	3.5	0.91	0.0043
9	Dermaga Kayu Bangkoa	119°24'17.4"E 5°08'14.9"S	9.5	2.76	0.0053
10	Makassar Container Terminal	119°24'14.9"E 5°07'47.4"S	10.01	6.48	0.0232
11	Pelabuhan Soetta	119°24'25.9"E 5°07'25.7"S	9.1	4.72	0.0341
12	Dekat Jetty II TBBM Makassar	119°24'46.7"E	5.6	1.55	0.0041

		5°06'43.9"S			
13	TPI Lelong paotere	119°25'12.0"E 5°06'36.7"S	8.9	2.11	0.0075
14	Pelabuhan Paotere	119°25'16.5"E 5°06'34.6"S	10.02	7.12	0.8027
15	SD negeri cambaya	119°25'38.7"E 5°06'33.8"S	13.27	6.23	0.2783

The results of the assessment of ecological risks showed that high risks areas for ecology consisted of, SD Negeri Cambaya (13.27), Pelabuhan Paotere (10.02), and Makassar container terminal with ecological risk of (10.01) unit less, respectively. The results for HQ value indicated that high values were 7.12, 6.48, and 6.23 at the same stations, respectively. In addition, the magnitude of the (THQ) values was 0.0.8027 in station 14, then 0.2783 at station 15, and 0.0075 in station 13, respectively.

The capture of mercury from water possibly occurs since the surface of the polysulfide is rich in sulfur, and an affinity for Hg was anticipated. Exploration of organic lead polysulfide materials has long been carried out to help capture Hg in water, although this material has a short shelf life and is only prepared when needed [22]. Before the supplied oil polysulfide was tested, the polymer was thoroughly washed using a NaOH solution (0.1 m) to ensure that there were no small molecule thiols such as H2S which could interfere with the experiment, especially in binding mercury.

This was done based on reports by Char, and Pyun. at. all found that H2S can be generated in several reverse vulcanization reactions [23]. After being washed with water the material is then dried in the air, then the polymer is tested for mercury bonds. In the preliminary test session, 2.0 g of poly-sulfide canola oil (50% by weight sulfur) was incubated, without stirring, in 5.0 mL of HgCl2 solution (3.5 ppm in Hg2+).

Ecological risks assessment

High risks of ecology were found in SD Negeri Cambaya with a value of 13.27, then followed by Pelabuhan Paotere with 10.02 and Makassar Container Terminal with an ecological risk of 10.01 unit less, respectively. **Table 2** indicated that the level of three values of environmental risks, the water column is more than one, those values state risks on every single site of the sample station. This fact described that the magnitude of THg in these areas due to the tailing waste from the amalgam center was high both in the background and in polluted sites. However, after the those THg observed by the Hg absorbent, the value of the THg has been decreased to a lower level that could be accepted both by environment and human health.

Target hazard quotient (THQ)

If the target Hazard Quotient value < 1 then it indicates the magnitude of the level is still lower than the RFD, and that implies the level of exposure daily does not lead to negative health impact over the whole lifetime of the communities residing at that location [24].

The daily calculation of exposure for Hg relative to intake of water largely being in the ranges of 0.0.8027 at point 14, then followed by 0.2783 at point 15 and 0.0075 at point 13, respectively. As whose values < 1. As it is apparent from these results, the THg health risk exposure correlated with the intake of water analyzed was not considerable. This is similar to the finding by EFSA [25-27]. If mercury values were < 1 for all species analyzed (fish: 0.04–0.80; cephalopods: 0.03–0.09; crustaceans: 0.02–0.05), even results close to 1 that were correlated to the consumption of swordfish (0.80), Atlantic bluefin tuna (0.74), European conger eel (0.70) and black belly rosefish (0.68), those various subjects and media indicated that when the magnitude of pollutant in water high, then it tends to increase also in the aquatic biota, vise versa [28-35].

Conclusion

Results of data analysis indicated significant differences in the magnitude of THg in all various stations of water THg, the magnitude level before and after the installment of Hg sulfur polymer as the THg absorbent.

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Conflict of interest: None

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Ethics statement: This study was approved by the Ethical Committee of Public Health Faculty of Hasanuddin University.

Informed consent was obtained from each participant included in the study.

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