ICSTSI 2020
Proceeding ICSTSI 2020 : 43 – 50
ISBN : 978-602-53575-1-0

Determination of Fe, Cu, Pb and Cd in seaweed (*Eucheuma cottonii*) and the seawater in Pico Village-Bantaeng District using inductively coupled plasma optical emission spectroscopy (ICP-OES)

N R M Aras

Akademi Komunitas Industri Manufaktur Bantaeng

Email: neny.rasnyanti@gmail.com

Abstract. Bantaeng is located in a coastal area which is quite potential for the development of fisheries and seaweed. The type of seaweed which is widely cultivated is Eucheuma Cottonii. This study aims to determine the existing heavy metals contamination of seaweed and seawater in the Pico Village, Bantaeng, as well as a preliminary study of the potential of seaweed as a metal binder. The sample in this study was seawater as a medium for seaweed growth and seaweed itself. The research method was an experimental method by destructing the sample and were analyzed using ICP-OES. The results showed that the quality of waters for the metal content of Fe, Cu, Pb, and Cd in Location I and location II were still below the permitted threshold according to Ministry of Environment and Forestry No. 51 2004. As for seaweed itself, it had much higher levels of metals than the seawater. Fe, Pb, Cu, and Cd of seaweed in the location I and location II were still in below BPOM regulations, except the Cd metal content obtained has exceeded the allowable threshold (0.05 ppm). Differences in metal content in seaweed and its seawater could be an indication that seaweed absorbs metals in the seawaters.

1. Introduction

One of the districts in South Sulawesi Province that manages seaweed (*Eucheuma Cottonii*) and has a fairly wide and potential coastal area is Bantaeng which covering the west and east coasts. Bantaeng has marine and non-biological potentials that are quite promising to manage. Bantaeng is one of the central locations of seaweed production *Eucheuma Cottonii (E. Cottonii)* in South Sulawesi and one of the main export commodities that plays an important role in improving the welfare of people who cultivate seaweed on a large scale. However, lately, the condition of coastal waters has become increasingly worrisome with the number of industrial discharges through rivers into sea waters suspected of containing heavy metals

The industrial sector is the second choice to be developed in Bantaeng, which has increased year to year. The development of the industrial sector is very likely in the future, but requires very strong investors. With the development of the industrial sector, the impact is very positive because in addition to increasing people's income it also absorbs a lot of labor. But on the other hand, the presence of the industry can have an impact on pollution if the Environmental Impact Analysis (EIA) application is not carried out.

Most of the pollutants found in the ocean come from human activities on land. In general, these pollutants come from industrial, agricultural, and household activities. According to the source, this pollution can be divided into 7 groups, namely: (1) industry, (2) surface liquid waste (sewage), (3) urban waste water (storm water), (4) mining, (5), shipping, (6) agriculture and (7) aquaculture. While the types of pollutants mainly consist of sediment, nutrients, toxic metals, pesticides, exotic organisms, pathogenic organisms, and oxygen depleting substances (substances that cause oxygen to dissolve oxygen in water) [1]. Heavy metals can enter the waters naturally with natural events such as weathering, rock, and soil erosion. The presence of heavy metals in waters can also come from urban runoff, rainwater, household waste, industrial waste, mining operations, atmospheric deposition, and agricultural activities (Haynes and Johnson, 2000) in [2]. This study aims to determine the existing heavy metals contamination of seaweed and seawater in the Pico Village, Bantaeng, as well as to see the potential of seaweed as a metal binder by looking at the relation of metals contained both in seaweed and seawater.

In this research, the heavy metals that measured were Fe, Cu, Pb, and Cd by using ICP-OES because of its ability to identify and measure all elements simultaneously. ICP is suitable for measuring all concentration of elements from ultra-trace to the level of the main component, detection limits are generally low for most of the typical elements until µg / L scale. ICP can complete various readings of elements in a short period of 30 seconds and only use ± 5 ml of the sample.

2. Materials and methods

This research was conducted in October 2019 located in location 2. Samples were taken directly in Pico Village, Bantaeng. The study was conducted at the Bantaeng AK-Manufacturing Chemical Analysis Laboratory Laboratory.

2.1. Tools

Multiparameter, hot plate, beaker glass, beaker flask, stir bar, bulb, funnel, analytical balance, furnace, Buchner.

2.2. Materials

Seaweed (*E. Cottonii*), sea water, multi-element standard solution 1000 ppm, aquabides, HCl 10%, HNO_3 pro analysis, aluminum foil, filter paper.

2.3. Methods

2.3.1. Sampling and preparation of samples One kg of wet seaweed and 500 mL of sea water were taken from Desa Pico. Sea water that was taken was sea water where the sample was taken. A sample of 10 mL of sea water was put into a beaker and added by 0.5 mL of concentrated nitric acid (HNO_3). The mixture was stirred until homogeneous, then heated using a hot plate until the solution almost used up. Then put into a 100 ml measuring flask and was added with distilled water until meniscus mark.

Seaweed samples were cleaned from impurities using aqua dest and dried at 120^{o}C until it turns blackish brown. Then dried seaweed, crushed and homogenized into powder with a mortar and then stored in aluminum foil until analysis was carried out. The sample was weighed as much as 5 grams in a clean porcelain cup, then ashed in a furnace at 400^{o}C for 20 hours (until it turns to ash). Add 20 mL of a concentrated solution of nitric acid (HNO_3) in a beaker glass and heated using a hot plate. The filtrate was cooled at room temperature and placed in a 50 ml volumetric flask and dissolved with 1 N hydrochloric acids (HCl) solution to the meniscus mark. Filter the solution by used Whatman paper 42 so that a clear yellowish solution was obtained and ready to be analyzed.

2.3.2. Made standard solution

Multi-element standard solution series with a concentration of 0.05; 0.10; 0.20; 0.50 and 1.00 ppm

ISBN : 978-602-53575-1-0

made into a 50 mL measuring flask and with 5% nitric acid (HNO_3) to each flask until miniscus mark. Subsequently tested with ICP to analyze metals (Fe/ Cu / Pb /Cd) in seawater.

2.3.3. Measured parameters
Field Parameters is measured by multiparameter (temperature) with a different location. The heavy metal of Seaweed and sea water is analyzed by ICP-OES with the condition operation are in table 1.

Table 1. ICP-OES working condition.

Parameters	Working condition
Exposure time	UV : 15s; Visible : 5s
RF power (W)	UV : 1150 W; Visible : 1150W
Nebulizer gas flow	UV : 0.5 L/min;Visible :0.5 L/min
Coolant gas flow	12 L/min
Auxilary gas flow	0.5 L/min
Pump speed	50 rpm
Flush pump speed	50 rpm
Maximum delays	Uptake: 300 ; Rinse : 300
Miniumum delays	Uptake: 30 ; Rinse : 30
Measure mode	Axial

3. Results and discussion

3.1. Concentration of heavy metal in seaweed and seawater
Pollutants are materials that are foreign to nature or materials originating from nature itself that enter an ecosystem structure so that it disrupts the designation of the ecosystem. The source of pollution that enters the body of water is divided into pollution caused by natural pollutants (natural) and pollution due to human activities or commonly called anthropogenic pollutants. Heavy metals can enter the marine environment naturally through; weathering, rock and soil erosion, or through urban and city runoff, rainwater, sewage, industrial waste, mining operations, atmospheric deposition, and agricultural activities (Batley, 1996; Irvine and Brich, 1998; Haynes and Johnson, 2000) in Govindasamy [2]. This pollutant needs to be analyzed considering the impact caused can be fatal both for the environment and humans.

One of the seaweed commodity-producing regions in South Sulawesi is Bantaeng Regency, which is one of the centers of the seaweed processing industry in South Sulawesi. Sea waters stretching between the Flores Sea of Mount Lompobattang, with an altitude of 0 (zero) to an altitude of more than 1,000 meters above sea level, with a coastline length of 21.5 Km. Seaweed is widely cultivated in waters making it vulnerable to heavy metal pollution.

Based on the results of research in the Pico Village, Bantaeng Regency at different sampling times had different concentrations of metal content as well. This can be seen in table 2 and 3. In general, the results of the study showed the levels (Fe / Cu / Cd / Pb) in location II had lower concentrations than in location I both in sea water samples and seaweed samples. Based on government regulation No. 51 of 2004 [3] concerning Sea Water Quality Standards in Appendix III obtained limits for the content of heavy metals for each (Cu / Cd / Pb) according to the table 4.

The metal content of seaweed both in samples taken in the location I or in location II has the same tendency where the content of heavy metals in seaweed is higher than in waters. Based on the regulation of the Food and Drug Supervisory Agency (BPOM) No 5 2018 [4] concerning the maximum limit of heavy metal contamination in food can be seen in table 4.

Based on the table, the metal content in Pb either in seaweed or in sea water are still below the limit allowed by BPOM. However, the Cd metal content in seaweed taken in location I and II have a that exceeds the content of Cd those are 0.121±0.000363 ppm and 0.160 ± 0.001000 ppm, respectively. Among others, cadmium (Cd) toxicity is caused by its ability to bind to S (sulfur) and COOH groups of protein molecules (amino acids and amides). This heavy metal also has the ability to replace the presence of other metals contained in metalloproteins such as Cu and Zn [5]. In a weak acid condition, cadmium is easily absorbed into the body and is a carcinogen as well as cumulative toxins that can damage organs such as the kidneys, liver, lungs, cardiovascular system, immune system and reproductive system [6,7].

Table 2. Concentration of seaweed in location I and II.

Heavy metals	Concentration Heavy Metals of Seaweed (ppm)	
	Location I	Location II
	x̅ ± SD	x̅ ± SD
Fe	3.434 ±0.033262	2.302 ± 0.010786
Cu	0.107±0.000577	0.100 ± 0.000577
Pb	0.013±0.000577	0.104 ± 0.000577
Cd	0.121±0.000363	0.160 ± 0.001000

Table 3. Concentration of seawater in location I and II.

Heavy metals	Concentration heavy metals of seaweed (ppm)	
	Location I	Location II
	x̅ ± SD	x̅ ± SD
Fe	0.088 ± 0.001000	0.019 ± 0.000577
Cu	0.009 ± 0.000577	0.003 ± 0.000000
Pb	0.003 ± 0.000577	0.003 ± 0.000577
Cd	0.000 ± 0.00000	0.000 ± 0.000000

Table 4. Quality standards of sea water for marine biota.

Heavy metal	Max concentration (mg/L) (a)	Max concentration (mg/L) (b)
Cu	0.008	-
Cd	0.001	0.05
Pb	0.008	0.2

a) Quality standards of sea water for marine biota regulation no. 51 of 2004
b) Maximum limits of heavy metal contamination in processed food for seaweed based on the regulation of the food and drug supervisory agency (BPOM) no. 5 of 2018

Cadmium is a type of heavy metal that when exposed to the human body will bind to albumin and also blood cells and metallothionein in liver and kidney tissue. If oral exposure, it can cause injury to the proximal tubule of the kidney. Symptoms of acute cadmium poisoning include vomiting and diarrhea. While the symptoms of chronic poisoning are the occurrence of nephrotoxicity. The results of cadmium measurements on 3 replications using ICP-OES showed that the three replications had very small absorption values so that it showed that the Cd metal content in the sample was not detected or below the instrument measurement limit. The results of this study are similar to those of Teheni [8] which showed high levels of Cd up to 0.2920 ppm in samples of *E. Cottonii* originating from Takalar seawaters. Cadmium was not detected in seawaters could be an indication that the metal content in the waters were absorbed by seaweed as well as

ISBN : 978-602-53575-1-0

other heavy metals (Fe, Cu, and Pb) were detected smaller in the waters compared to the in seaweed.

In seaweed and other biota, heavy metals content such as cadmium and lead are often found. Lead is everywhere in the environment because it is found in nature and is used in the industry. Lead absorption is mainly through the gastrointestinal tract and the respiratory tract. Direct consumption of large amounts of lead can cause tissue damage especially liver and kidney tissue [9]. This is quite alarming considering that heavy metals have high toxicity [10,11]. Aquatic plants such as algae or Bryophyta have the ability to absorb heavy metals from water so that the levels in plants are higher than those in their environment [12].

Temperature plays an important role in seaweed growth. Seaweed lives and grows in waters with a water temperature range between 20-28^{0}C. Based on the research results the temperature of waters around 25-27^{0}C. The temperature will affect the process of photosynthesis because it will affect the oxygen content dissolved in the waters. Besides sea water sampling had been done in different seasons. This will also affect the solubility of metals in waters. According to Hutagalung [13] in [14], rising temperatures will cause higher levels of bioaccumulation. Strengthened by the opinion of Darmono [15] that the higher the water temperature in water, the power of toxicity increases, so that the content of heavy metals (Fe/Cu/Cd/Pb) is more easily absorbed by seaweed. Rising temperatures in the waters will accelerate the reaction in the formation of heavy metal ions.

The degree of acidity or pH is one of the factors that affect the life of seaweed. The maximum pH range for the life of marine organisms is 6.5 - 8.5 [16]. The composition of dissolved elements and compounds causes sea water to have a pH (acidity) in general between 7.5 - 8.4 with an average pH of 7.8. The degree of acidity will affect the biological activity and chemical reactions that occur. As pH increases, the toxicity of heavy metals decreases. Marine biota that lives in water will experience bioaccumulation if the pH gets lower [17].

Low levels of heavy metals in the waters are estimated because the metal has entered the seaweed. This is consistent with the results of research in which the levels of metals in seaweed are much higher than those in the waters. As explained above the pH of water that tends to be normal influences the stability of the metal solubility [18]. The results showed the levels of metals (Fe / Cu / Cd / Pb) seaweed taken in the location I and II almost the same.

Pb in the air is mainly sourced from motor vehicle exhaust (smoke) which partially forms particulates in the free air and partially attaches and is absorbed by plant leaves [18]. The presence of lead-heavy metal contamination (Pb) found in the waters in Pico Village is most likely derived from the air due to the exhaust gas used by fishermen or boats around the Port. In addition, lead naturally enters water bodies through the crystallization of lead in the air with the help of rainwater [19].

The results of the study of the heavy metal content found in biota from Ling-Ding in Guangdong province are very high examples of pollution that occurs due to economic development [20]. Pollution that occurs in Marine Biota will directly affect human health. The presence of pollutants such as iron for example can come from rust on ships or iron poles in the water. Although it is not regulated in the Ministry of Environment and Forestry Regulation for waters the presence of iron if it is too high it will be dangerous.

High population, port activities and industrialization are real sources of pollution. This activity will produce ecologically damaging pollution which results in the death of marine life and a decline in its economic value [21]. Damage and decline in natural values and the most dangerous is that it can cause poisoning and even death in humans themselves. Water bodies that are contaminated with heavy metals from estuary environments are likely to cause bioaccumulation in the food chain. Usually, this contamination is transported from the source through the river system and deposited downstream. Most pollutants can be mixed through sedimentation and are suspended into solids. The presence of heavy metals in sediments causes greater environmental problems when contamination of aquatic organisms occurs (Morrisey, 2003) in [22].

Some damage caused by toxicity of Pb to health had been identified such as disturbed heme biosynthesis, disorders of the nervous system, reproductive disorders, and even inhibition of growth [13,15]. Lead (Pb) is one of the heavy metals that most pollute the sea waters. It is because lead is one of the decomposition products of fuel used by ships. When the human body is exposed to lead, lead is carried by red blood cells and distributed to the soft tissues (kidneys and liver); redistributed to bones, teeth, and hair usually in the form of phosphate salts. The mechanism of toxicity is because lead can inhibit heme biosynthesis, and can also bind to Sulfhydryl groups in proteins.

4. Conclusion

Seaweed and seawater samples at two sampling locations indicate that the levels of heavy metals other than Cd are still below the standard quality standards set by the Ministry of Environment and Forestry No. 51 of 2004 and regulation of the Food and Drug Supervisory Agency (BPOM) No 5 2018. The metal content in seaweed samples is higher than that in seawater, this indicates that seaweed has the potential as a heavy metal biosorbent.

Acknowledgments
Many thanks to the Director of AK-Manufacturing Bantaeng who have provided financial support and facilities for this research, to the lecturers team of Chemistry Study Program for sharing their knowledge and experience as well as laboratory staff for their willingness to help during research in the laboratory.

References
[1] Dahuri R 2003 *Paradigma Baru Pembangunan Indonesia Berbasis Kelautan: Orasi Ilmiah* (Bogor: IPB Press)
[2] Govindasamy, Chinnavenkataraman, Arulpriya M, Packiasamy, Ruban, Francisca L J and Ilayaraja A 2011 Concentration of heavy metals in seagrasses tissue of the palk strait, Bay of Bengal *Int. J. Environ. Sci.* 2 145-53
[3] Kepmen LH 2004 *Keputusan Menteri Negara Lingkungan Hidup No. 51 Tahun 2004 tentang Baku Mutu Air Laut* (Jakarta: Deputi Menteri Lingkungan Hidup, Bidang Kebijakan dan Kelembagaan L&H)
[4] Food and Drugs (BPOM) Regulation No 5 2018 *Batas Deteksi Logam Berat Maksimum yang Terkandung dalam Makanan* (Jakarta: BPOM Indonesia)
[5] Nath R, Prasad R, Palinal V K and Chopra R K 1984 Basis of cadmium toxicity *J. Prog Food Nutr Sci.* 8(1–2) 109–63
[6] Fowler B A 2009 Monitoring of human populations for early markers of cadmium toxicity: a review *J. Toxicol Appl Pharmacol*. 238(3) 294– 300
[7] Godt J, Scheidig F, Grosse-Siestrup C, Esche V, Brandenburg P and Reich A 2006 The toxicity of cadmium and resulting hazards for human health *J. Occup Med. Toxicol*. 1(1) 22
[8] Teheni M T and Syamsidar H S 2013 Penentuan kadar dan distribusi spasial logam berat kadmium (Cd) pada rumput laut Euchema cottonii asal perairan Kab. Takalar dengan metode spektrofotometer serapan atom (SSA) *J. Al-Kimia*. 1(1) 30–41
[9] Mudipalli A 2007 Lead hepatotoxicity & potential health effects *Indian J. Med Res.* 126(6) 518
[10] Whitton B 1980 *Zinc and Plants in Rivers and Stream, In: Zinc in Environment* (New York: John Wiley & Sons Inc) pp 364–400
[11] Tchounwou P B, Yedjou C G, Patlolla A K and Sutton D J 2012 *Heavy Metal Toxicity and the Environment* (Basel: Springer) 101:133-64 doi: 10.1007/978-3-7643-8340-4_6
[12] Whitton B A, Say P J, Wehr J D 1981 *Use of Plants to Monitor Heavy Metals in Rivers, In: Metals in Northern England: Environmental and Biological Aspects* (Universitas Durham: Departemen Botani) pp 135–45
[13] Hutagalung H P 1984 Logam berat dalam lingkungan laut *J. Oseana.* IX(1) 11-20
[14] Endang S and Hadi E 2015 Kandungan logam berat besi (Fe) pada air, sedimen, dan kerang hijau (*Perna viridis*) di perairan tanjung emas semarang *J. Kelautan Tropis* 18 (1) 38–45

ISBN : 978-602-53575-1-0

[15] Darmono 2001 *Lingkungan Hidup dan Pencemaran* (Jakarta: Universitas Indonesia)
[16] Sumarheni S, Yulica T, Burhanuddin T and Tadjuddin N 2017 Analisis kandungan logam berat As, Cd dan Pb pada *Eucheuma Cottonii* dari perairan takalar serta analisis maximum tolerable intake pada manusia *J. M.F.F.* 21(3) 63-6
[17] Mukhatasor 2007 *Pencemaran Pesisir dan Laut* (Jakarta: Pradyna Paramytha)
[18] Palar and Heryando 2012 *Heavy Metal Pollution and Toxicology* (Jakarta: Rineka Cipta)
[19] Bridiatama 2014 *Sea Water Pollution Index of North Coast of Tuban Regency with Metal Parameters* (Surabaya: Department of Environmental Engineering, Faculty of Civil Engineering and Planning, The Ten November Institute of Technology)
[20] Wang S L, Xu X R, Sun Y X, Liu J L and Li H B 2013 Heavy metal pollution in coastal areas of South China: a review *J. Mar. Pollut. Bull.* 76(1-2) 7-15. doi: 10.1016/j.marpolbul.2013.08.025. Epub 2013 Sep 29. PMID: 24084375
[21] Farid 2007 *Desain Sistem Pengendalian Pencemaran Perairan Kota Makassar* Disertasi Prog. Stud. PSDAL (Bogor: Sekolah Pascasarjana Institut Pertanian Bogor)
[22] Mohd A H *et al*. 2007 Heavy metals (Cd, Cu, Cr, Pb and Zn) in meretrix roding, water and sediment from estuaries in Sabah, North Borneo *Int. J. of Env. & Sci. Education* 2(3) 69-74