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# Metal bioaccumulation potential of the seaweed Kappaphycus alvarezii

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Abstract. Kappaphycus alvarezii is one of the two main species of seaweed commodities cultivated in Indonesia. K. alvarezii more popularly known as Eucheuma cottonii, is belongs to the red algae. This seaweed is one of the most important commercial sources of carrageenans, a family of gel-forming, viscosifying polysaccharides. Carrageenans are used as gelling, thickening, and stabilizing agents in a variety of commercial applications, especially in food products such as frozen desserts, chocolate milk, cottage cheese, whipped cream, instant products, yoghurt, jellies, pet foods, and sauces. Aside from these functions, carrageenans are used in pharmaceutical formulations, cosmetics, and industrial applications such as mining. This study aimed to analyse the metal bioaccumulation potential of the seaweed K. alvarezii. This study was conducted in three sea areas around South Sulawesi, namely the Gulf of Bone, Flores Sea and the Makassar Strait. Seaweed samples were collected from seaweed cultivation locations in four locations (Regency of Jeneponto in two locations, Takalar and Pangkep). The metal concentrations analysed were Copper (Cu), Cadmium (Cd), and Lead (Pb). The concentration in Cu, Cd, and Pb in the seaweed K. alvarezii was higher than the concentration in ambient sea water. The seaweed K. alvarezii has a potential as a bioaccumulator, but the accumulation was not consistent. The Cu, Cd, and Pb probably can be accumulated or released back. This is good in terms of food safety because heavy metals can be released during postharvest processing and carrageenan powder processing. The results of this study indicate that K. alvarezii has the potential for bioaccumulation, but not permanent accumulation, so it is safe for human health.

### 1. Introduction

Total world seaweed production in 2014 was around 27.3 million tons, of which Indonesian production reached 10.1 million tons or 37% of total production [1]. This production can be increased if the weaknesses in infrastructure and human resources can be overcome [2]. The development of seaweed cultivation in Indonesia in 1980 was aimed at increasing economic growth in coastal areas [3]. This is supported by Indonesia's location in tropical waters with a relatively stable climate, so that

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it meets the requirements for cultivation of *K. alvarezii* [4]. The seaweed species that are widely cultivated in Indonesia are *Kappaphycus alvarezii*, *Eucheuma spinosum*, *Sargassum* sp, and *Gracilaria* sp. *K. alvarezii* and *E. spinosum* seaweeds are cultivated in the sea along the coast. The centers of seaweed cultivation for *K. alvarezii* and *E. spinosum* are found in South Sulawesi, Central Sulawesi, East Nusa Tenggara, Bali, East Java, Southeast Sulawesi and West Nusa Tenggara [5].

Indonesian seaweed production always shows an increase, with the percentage of increase reaching 27.92% between 2010 and 2014. Production in 2010 was 3.9 million tons, 2011 was 5.2 million tons, 2012 was 6.5 million tons. , in 2013 amounted to 9.3 million tons, and in 2014 reached 10.08 million tons [6].

*K. alvarezii* or more popularly known as *Eucheuma cottonii* is the most widely cultivated species in Indonesia. Indonesia and the Philippines are the main producing countries for *Kappaphycus* [7]. *K. alvarezii* is a producer of carrageenan [8-11] and bioethanol [12]. This seaweed is one of the most important commercial sources of carrageenans, a family of gel-forming, viscosifying polysaccharides. Carrageenans are used as gelling, thickening, and stabilizing agents in a variety of commercial applications, especially in food products such as frozen desserts, chocolate milk, cottage cheese, whipped cream, instant products, yoghurt, jellies, pet foods, and sauces. The yield of kappa carrageenan powder from *K. alvarezii* is 23.01-30.63% [13].

The moisture content of dry *K. alvarezii* is less than 35% [14]. Extract material without nitrogen is 43.42-45.42%. The ash content of *K. alvarezii* was 45.93-48.20%. *K. alvarezii* fat content 0.05-0.01%, protein content was 2.40-3.29%, and crude fiber was 3.88-6.06% [5]. Seaweed is known as a source of dietary fiber by 78.94%, and vitamins A (beta carotene), B1, B2, B6, B12, C and niacin, as well as important minerals, such as calcium and iron [15]. Seaweed is known as a source of dietary fiber by 78.94%, and vitamins A (beta carotene), B1, B2, C and niacin, as well as important minerals, such as calcium and iron [15]. C and niacin, as well as important minerals, such as calcium and iron [15]. Seaweed is known as a source of dietary fiber by 78.94%, and vitamins A (beta carotene), B1, B2, B6, B12, C and niacin, as well as important minerals, such as calcium and iron [15].

The reference that is widely used in determining food safety is metal content that is harmful to health. The bioaccumulation content of dangerous metals in *K. alvarezii* in South Sulawesi, Indonesia has never been studied. Therefore, it is necessary to study the dangerous metal content of *K. alvarezii*. The results of this study are necessary to ensure that the *K. alvarezii* produced by Indonesia is safe for health. This study aimed to analyze the metal bioaccumulation potential of the seaweed *K. alvarezii* cultivated at production areas in South Sulawesi, Indonesia.

## 2. Materials and Methods

Study on metal bioaccumulation potential of the seaweed *K. alvarezii* was done in two sea areas around South Sulawesi, namely the Flores Sea and the Makassar Strait. Flores Sea and the Makassar Strait is the centre of K. alvarezii cultivation in the coastal area of South Sulawesi [16-19]. These two waters included in the Fisheries Management Area (FMA) 713 [20]. Seaweed samples were taken from four seaweed cultivation locations, two locations in Jeneponto Regency, and one each at Takalar and Pangkep Regency (Figure 1). Samples were taken at *K. alvarezii* cultivation locations in coastal areas.

Fresh seaweed is taken to the laboratory to be washed and dried. *K. alvarezii* drying was carried out in two stages, the first stage was air drying with a temperature of 32-33°C for two days; the second stage is drying in an oven with a temperature of 50°C for 48 hours. The sample of *K. alvarezii* was crushed and then analyzed for its heavy metal content. The heavy metal concentrations analyzed were Copper (Cu), Cadmium (Cd), and Lead (Pb). Quantitative content of Cu, Cd and Pb metals was analyzed using Atomic Absorption Spectrophotometry techniques [21, 22].

### 3. Results

#### *3.1. Copper* (*Cu*)

Cu content in seawater was <0.001-0.140 with an average of  $0.078 \pm 0.053$ . Meanwhile, the Cu content in *K. alvarezii* was 0.140-3.610 with an average of  $1.077 \pm 1.447$ . This study indicates that Cu

concentrations in the seaweed *K. alvarezii* was greater than in the sea water, and significantly different (P <0.05). All stations showed accumulated Cu concentrations in *K. alvarezii* (Table 1). The correlation curve of Cu concentrations in seawater and *K. alvarezii* shows that the Cu concentration in *K. alvarezii* did not increase consistently with the increase in Cu concentrations in sea water (Figure 2). All correlation curves of Cu concentrations between sea water and *K. alvarezii* did not show any progressive accumulation. The Cu concentrations of *K. alvarezii* at the four-sampling location were still below the safe limit for human health (30 ppm) (SNI 01-2802-1995).

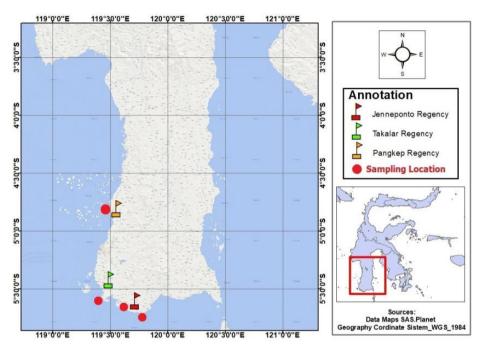
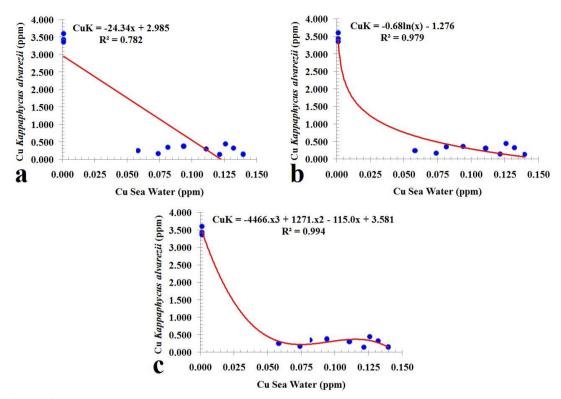


Figure 1. Sampling location of *Kappaphycus alvarezii* at Jeneponto, Takalar and Pangkep Regency.

Table 1. Copper (Cu)	) concentrations at	: Kappaphycus	alvarezii in	Jeneponto,	Takalar and Pangkep
Regency.					

Regency	Cu Sea Water (CuSw)	Cu <i>K. alvarezii</i> (CuKa)	Δ (CuKa-CuSw)	Annotation
Jeneponto 1 (embouchure)	0.059	0.250	0.192	Accumulation
Jeneponto 1 (embouchure)	0.111	0.300	0.189	Accumulation
Jeneponto 1 (embouchure)	0.082	0.350	0.269	Accumulation
Mean±STD	$0.084 \pm 0.026$	$0.300 \pm 0.050$	$0.216 \pm 0.045$	Accumulation
Jeneponto 2 (Punagaya)	0.094	0.370	0.276	Accumulation
Jeneponto 2 (Punagaya)	0.132	0.330	0.198	Accumulation
Jeneponto 2 (Punagaya)	0.126	0.450	0.324	Accumulation
Mean±STD	0.117±0.020	0.383±0.061	$0.266 \pm 0.064$	Accumulation
Takalar (Punaga)	0.140	0.140	0.001	Accumulation
Takalar (Punaga)	0.122	0.150	0.029	Accumulation
Takalar (Punaga)	0.074	0.170	0.096	Accumulation
Mean±STD	0.112±0.034	0.153±0.015	$0.042 \pm 0.049$	Accumulation
Pangkep (Ma'rang)	< 0.001	3.610	3.609	Accumulation
Pangkep (Ma'rang)	< 0.001	3.440	3.439	Accumulation
Pangkep (Ma'rang)	< 0.001	3.360	3.359	Accumulation
Mean±STD	$< 0.001 \pm 0.000$	3.470±0.128	3.469±0.128	Accumulation



**Figure 2.** Relationship curve of Cu concentrations in sea water and *Kappaphycus alvarezii* in Jeneponto, Takalar and Pangkep Regency. Linear Equation (a), Power Equation (b), and Polynomial Equation (c).

# 3.2. Cadmium (Cd)

In general, there is accumulation of Cd in *K. alvarezii*. The Cd content of sea water was <0.001-0.357 with an average of  $0.197 \pm 0.123$ . While the content of Cd *K. alvarezii* was 0.310-1.860 with an average of  $1.022 \pm 0.517$ . This study indicates that Cd concentrations in the seaweed *K. alvarezii* was greater than in the sea water, and significantly different (P<0.05). All stations showed an accumulation of Cd in *K. alvarezii*, except for one replication in Jeneponto Regency (Table 2). Despite the accumulation, the correlation curve of Cd concentration in seawater and *K. alvarezii* shows that the Cd concentration in *K. alvarezii* did not increase consistently with the increase in Cd concentration in seawater (Figure 3). All correlation curves of Cd concentrations between sea water and *K. alvarezii* did not show any progressive accumulation. The Cd concentrations of *K. alvarezii* at the four-sampling location was exceeding the safe limit for health (0.2 ppm) (Indonesian National Standard, SNI: 7383: 2009).

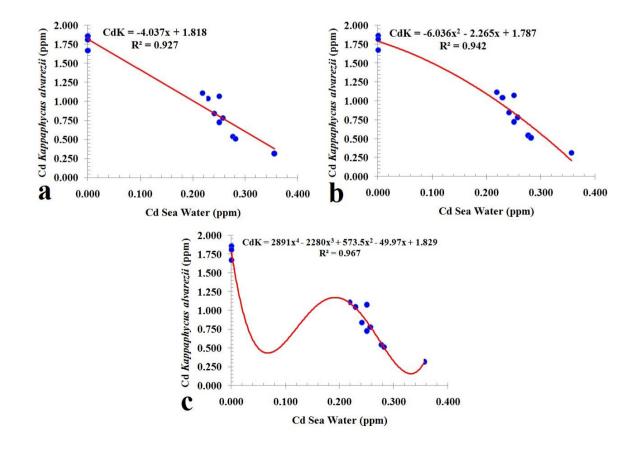
## 3.3. Lead (Pb)

In general, Pb accumulation occurs in *K. alvarezii*. The Pb content in seawater was <0.001-0.996 with an average of  $0.330 \pm 0.375$ . Whereas the Pb content in *K. alvarezii* was <0.001-2.360 with an average of  $0.761 \pm 0.817$ . This study indicates that Pb concentrations in the seaweed *K. alvarezii* were higher than in the sea water, and significantly different (P <0.05). Based on the average Pb content of *K. alvarezii*, all stations show that accumulation has occurred, except for stations in Pangkep Regency (Table 3). The correlation curve of the Pb concentration in seawater and *K. alvarezii* shows that the Pb concentration in *K. alvarezii* did not increase consistently with the increase in the Pb concentration in seawater (Figure 4). All correlation curves of Pb concentrations between sea water and *K. alvarezii* did show non consistent progressive accumulation. The mean Pb concentrations of *K. alvarezii* were not

exceed the safety limit for the health at Pangkep Regency, close to the safety limit at Jeneponto Regency, and exceed the safe limit for health (0.5 ppm) (SNI 7383: 2009) at Takalar Regency.

**Table 2.** Cadmium (Cd) concentrations at *Kappaphycus alvarezii* in Jeneponto, Takalar and Pangkep Regency.

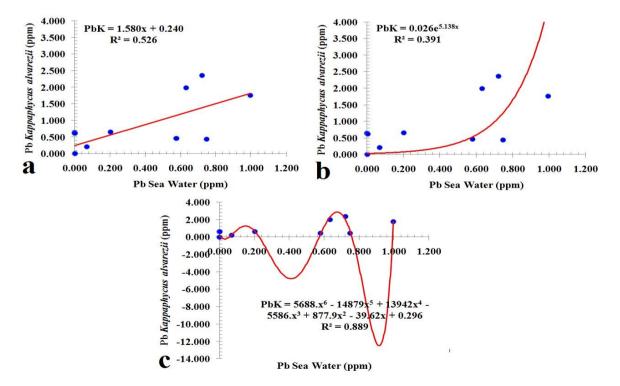
Regency	Cd Sea Water (CdSw)	Cd <i>K. alvarezii</i> (CdKa)	$\Delta$ (CdKa-CdSw)	Annotation
Jeneponto 1 (embouchure)	0.282	0.510	0.228	Accumulation
Jeneponto 1 (embouchure)	0.357	0.310	-0.047	Non accumulation
Jeneponto 1 (embouchure)	0.258	0.780	0.523	Accumulation
Mean±STD	$0.299 \pm 0.052$	$0.533 \pm 0.236$	$0.235 \pm 0.285$	Accumulation
Jeneponto 2 (Punagaya)	0.251	1.070	0.820	Accumulation
Jeneponto 2 (Punagaya)	0.219	1.110	0.891	Accumulation
Jeneponto 2 (Punagaya)	0.230	1.040	0.811	Accumulation
Mean±STD	0.233±0.016	$1.073 \pm 0.035$	$0.840 \pm 0.044$	Accumulation
Takalar (Punaga)	0.251	0.720	0.470	Accumulation
Takalar (Punaga)	0.242	0.840	0.599	Accumulation
Takalar (Punaga)	0.277	0.540	0.263	Accumulation
Mean±STD	$0.256 \pm 0.018$	$0.700 \pm 0.151$	0.444±0.169	Accumulation
Pangkep (Ma'rang)	< 0.001	1.670	1.669	Accumulation
Pangkep (Ma'rang)	< 0.001	1.860	1.859	Accumulation
Pangkep (Ma'rang)	< 0.001	1.810	1.809	Accumulation
Mean±STD	$< 0.001 \pm 0.000$	$1.780 \pm 0.098$	$1.779 \pm 0.98$	Accumulation



**Figure 3.** Relation curve of Cd concentration in sea water and *Kappaphycus alvarezii* in Jeneponto, Takalar and Pangkep Regency. Linear Equation (a), Power Equation (b), and Polynomial Equation (c).

Table 3. Lead (Pb) concentrations at *Kappaphycus alvarezii* in Jeneponto, Takalar and Pangkep Regency.

Regency	Pb Sea Water (PbSw)	Pb K. alvarezii (PbKa)	$\Delta$ (PbKa-PbSw)	Annotation
Jeneponto 1 (embouchure)	0.203	0.650	0.448	Accumulation
Jeneponto 1 (embouchure)	0.070	0.210	0.140	Accumulation
Jeneponto 1 (embouchure)	0.000	0.640	0.640	Accumulation
Mean±STD	0.091±0.103	$0.500 \pm 0.251$	$0.409 \pm 0.252$	Accumulation
Jeneponto 2 (Punagaya)	0.003	0.620	0.617	Accumulation
Jeneponto 2 (Punagaya)	0.748	0.440	-0.308	Non accumulation
Jeneponto 2 (Punagaya)	0.579	0.460	-0.119	Non accumulation
Mean±STD	$0.443 \pm 0.390$	$0.507 \pm 0.099$	$0.064 \pm 0.489$	Accumulation
Takalar (Punaga)	0.633	1.990	1.358	Accumulation
Takalar (Punaga)	0.722	2.360	1.639	Accumulation
Takalar (Punaga)	0.996	1.760	0.765	Accumulation
Mean±STD	$0.783 \pm 0.189$	2.037±0.303	$1.254 \pm 0.446$	Accumulation
Pangkep (Ma'rang)	< 0.001	< 0.001	< 0.001	Non accumulation
Pangkep (Ma'rang)	< 0.001	< 0.001	< 0.001	Non accumulation
Pangkep (Ma'rang)	< 0.001	< 0.001	< 0.001	Non accumulation
Mean±STD	$< 0.001 \pm 0.000$	$< 0.001 \pm 0.000$	<0.001±0.000	Non accumulation



**Figure 4.** Correlation curve of Pb concentration in sea water and *Kappaphycus alvarezii* in Jeneponto, Takalar and Pangkep Regency. Linear Equation (a), Power Equation (b), and Polynomial Equation (c).

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# 4. Discussion

The use of raw seaweed for direct consumption and its extracts in food production continues to increase steadily worldwide. However, the metal absorption ability of seaweed can result in the accumulation of several heavy metals which can harm consumers [23]. This study shows that *K. alvarezii* has the ability to accumulate or absorb metals. This is the same results of previous studies which reported that *K. alvarezii* has the ability to remove Cu, Cd and Pb from aqueous solutions through biosorption. Kinetic studies show that *K. alvarezii* has a high ability to absorb the three metals, *K. alvarezii* can absorb 90% of the metal in 45 minutes [24].

Metal accumulation was not consistently associated with the ability of *K. alvarezii* biosorption [25-27] and desorption [28]. Biosorption causes metal accumulation, and desorption causes metal shedding. Biosorption and desorption probably occur because of the simple cell structure of *K. alvarezii*, so that the metal can be accumulated or released back easily. The same case also happen to other macroalgae [29]. From a food safety perspective, this is a good thing because even though there was metal accumulation, the metal can be released during the processing as food and the product save as food.

Desorption is a mechanism of seaweed adaptation to its poor environmental conditions. Naturally heavy metals are not favorable for any organism life. Biologically, heavy metals can cause a decrease in the ability to absorb solar energy [30]. Ecologically, desorption can reduce the quantity of heavy metal spread to other trophic level organisms such as molluscs, crustaceans and fish [31].

The results of previous studies indicated that there were spatio-temporal variations in macroalgae [32]. *Cystoseira barbata* that lives on the Turkish Coast of the Black Sea shows that there are accumulations with various contents. At Sinop stations in 1998, 1999 and 2000 in these waters, C. barbata contained Cu  $1.70 \pm 0.02$  to  $6.00 \pm 0.01$ . Cd <0.02 to  $0.09 \pm 0.10$  ppm, and Pb <0.01 to  $3.5 \pm 0.40$  [32].

The non-permanent accumulation makes macro algae available as biosorbent agents [29]. The nonpermanent accumulation is possible because Thallus macroalgae has the ability to form selective bonds with metal cations Cu, Cd, and Pb [33]. In addition, the macroalgae cell wall which is rich in polysaccharides and has a functional carboxylic acid group can play an active role in metal binding [34]. The results of this study show that the bioaccumulation in *K. alvarezii* was not permanent, so *K. alvarezii* is safe for human health because heavy metals can be released during post-harvest processing and carrageenan powder processing.

The non-permanent accumulation makes *K. alvarezii* derivative products safe, even though the concentration of metals, for example Pb is much higher  $(0.761 \pm 0.817)$  than other marine organisms. The Pb content in sea cucumber *Holothuria scabra* is only 0.05-0.07 ppm [35], dan sea cucumber *Bohadschia vitiensis* only 0.01 ppm [36]. When compared to Sargassum, the Pb content in *K. alvarezii* was higher, the Pb content of macro algae in *Sargassum* was 0.59 ppm [29]. The greater accumulation ability is thought to be related to the simple macroalgae cell structure so that it is more resistant to higher heavy metal content than higher animals. A Pb concentration of 0.2 ppm has caused hypertrophy in the blue spotted ray gills of *Dasyatis kuhlii* [37].

#### 5. Conclusion

The concentrations in Cu, Cd, and Pb in the seaweed *K. alvarezii* were higher than the concentration in ambient sea water. The seaweed *K. alvarezii* has a potential as a bioaccumulator, but the accumulation was not consistent. The Cu, Cd, and Pb probably can be accumulated or released back. This is good in terms of food safety because heavy metals can be released during post-harvest processing and carrageenan powder processing.

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