

# Characterization of *Kappaphycus* sp. and *Padina* sp. as biosorbents for heavy metal ions removal

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## ABSTRACT

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The determination of iron, copper and zinc metal ions removal has been conducted using seaweeds (*Kappaphycus* sp. and *Padina* sp.) as biosorbents. The seaweed was dried using two different drying techniques: oven drying (60 °C, 80 °C and 100 °C) and sun drying. The main functional groups responsible for the metal bindings in seaweed were identified using Fourier transform infrared spectroscopy. It showed that carboxyl, ether, alcoholic, and amino groups participated in the ionic exchange by functional groups on the surface area of metal-treated and untreated seaweed. Phytochemical analysis was conducted to determine the total phenolic content of the samples, as polyphenols are well known for metal binding. In comparison to the other drying techniques, oven-dried (60 °C) for *Padina* sp. (0.2133±0.0125 mg GA/g DS) and *Kappaphycus* sp. (0.0882±0.0071 mg GA/g DS) had the highest phenolic content. Inductively coupled plasma – optical emission spectrometry was also used to measure the reduction of heavy metal concentration in the biosorption process. Sun drying for both biosorbents, *Kappaphycus* sp. (86.08%) and *Padina* sp. (72.75%), achieved high metal adsorption levels for copper ions. According to the results, the rank of metal adsorption abilities of the samples by drying method is oven-dried (60 °C) < oven-dried (80 °C) < oven-dried (100 °C) < sun-dried.

**Keywords:** *Kappaphycus* sp.; *Padina* sp.; drying; biosorbent; heavy metal

## 1. INTRODUCTION

Removing heavy metals from industrial wastewater is necessary as it is carcinogenic. Various methods of heavy metal reduction and removal have been previously studied including alkaline chlorination, sulphide precipitation, electrochemical reduction, reverse osmosis, nanofiltration and ultrafiltration (Kapepula, et al., 2022). This conventional remediation methods are usually expensive or adversely affect the environment. Biosorption processes in organisms involve a synergy of various mechanisms including chemisorption, complexation, surface adsorption, ion exchange and adsorption-complexation on surfaces and pores (Brown et al., 2000). Heavy metals are highly

poisonous and can harm nerves and organs, such as the liver, kidneys, and bones, while also blocking functional groups of essential enzymes (Carson et al., 1986). The demand for novel technologies to extract metal from wastewater is increasing because of strict environmental legislation and the government authority to enforce these restrictions (Janson et al., 1982). Researchers have been looking for cheaper, more efficient ways to treat heavy metal-contaminated waters and lessen the growing threat to public health hazards for over a decade. Removing metal ions from contaminated solutions using adsorption has been proven to be a cost-effective and ecologically beneficial technology (Volesky, 1990). Adsorption is an attachment of atoms, ions, or molecules to the surface of a biosorbent. It also efficiently

removes metals from dilute solutions, produces less chemical and biological waste, regenerates adsorbents, and allows metal recovery (Kratochvil and Volesky, 1998). The biosorption capability of algae has been attributed mainly to the cell wall, which is composed of a fibre-like structure and an amorphous embedding matrix of various polysaccharides. Red algae also have various binding sites, including carboxyl and amino groups, as stated by Rahman and Sathasivam (2016). Previous studies that have been conducted using seaweed as a biosorbent are shown in Table 1. Seaweed cultivation in Sabah, Malaysia was introduced in 1978. Since then, seaweed played an important role creating employment in Sabah (Ahmad et al., 2006). Cultivation of these photoautotrophic organisms has been widely developed for many usages such as in food industries and cosmetics.

Over the years, applying biotechnology in metal pollution removal has become more prevalent in the metal pollution research field. This is due to its low cost, minimization of toxic

by-products and higher efficiency than conventional techniques (Abbas et al., 2014). Seaweed contains dietary fibers, vitamins, minerals, carotenoids, and fatty acids. High contents of phenolics and flavonoids have also been reported in seaweed (Ling et al., 2013). Phenolic compounds are a diverse group of molecules that cover a wide range of aromatic secondary metabolite families. These phenolic compounds in seaweed are able to combat oxidative stress (Ling et al., 2013). Flavonoids are essential antioxidants as they have a high redox potential. This composition makes seaweed a good antioxidant. Multiple studies have demonstrated the significant antioxidant properties of different types of seaweed (Yap et al., 2019; Belattmania et al., 2016; Ling et al., 2013). The functional groups of these phenolic compounds were demonstrated to attach metals to hydroxyl and carboxylic acid. (Mousavi et al., 2021).

The aims of this study were to characterise Sabah seaweeds *Kappaphycus* sp. and *Padina* sp. as adsorbents for iron ( $\text{Fe}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), and zinc ( $\text{Zn}^{2+}$ ) removal.

**Table 1.** Seaweeds as biosorbents

Seaweed	Heavy metal	Reference
<i>Hydrilla verticillate</i>	Cr(IV)	(Baral et al., 2009)
	Cd, Pb	(Al-Zufri and Al-Tabatai, 2020)
<i>Kappaphycus striatum variety sacol</i>	Pb(II), Cu(II), Zn(II), Cd(II)	(Khan et al., 2013)
<i>Caulerpa serrulate</i>	Cu, Cd, Pb	(Mwangi and Ngila, 2012)
<i>Caulerpa taxifolia</i>	$\text{Zn}^{2+}$	(Mithra et al., 2012)
<i>Kappaphycus alvarezii</i>	Cu(II), Ni(II), Cd(II), Pb(II)	(Praveen and Vijayaraghavan, 2015)
<i>Sargassum</i> sp.	$\text{Co}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	(Asencios et al., 2022)
<i>Padina</i> sp.		
<i>Ulva lactuca</i>		
<i>Sargassum sinicola</i>	Cd, Cu	(Patrón-Prado et al., 2010)
<i>Eucheuma denticulatum</i>	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Zn}^{2+}$	(Rahman and Sathasivam, 2016)
<i>Sargassum lacerifolium</i>	Pb, Cu, Zn, Ni	(Ahmed et al., 2021)
<i>Gracilaria changii</i>	Fe, Cr, Ni	(Arumugam et al., 2020)
<i>Posidonia oceanica</i>	Cu, Pb, Ni, Zn, Cd	(Boulaiche et al., 2019)
<i>Hizikia fusiformis</i>	$\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Cr}^{2072-}$	(Lee and Park, 2012)
<i>Laminaria japonica</i>		
<i>Undaria pinnatifida</i>		
<i>L. japonica</i>	Cr(IV)	(Jia et al., 2014)
<i>U. pinnatifida</i>		
<i>Porphyra haitanensis</i>		
<i>Gracilaria lemaneiformis</i>		
<i>Fucus serratus</i>	$\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Ce}^{2+}$	(Ahmady-Asbchin, 2009)

## 2. MATERIALS AND METHODS

### 2.1 Materials

The seaweeds (*Kappaphycus* sp. and *Padina* sp.) were bought from local sellers in Semporna, Sabah. An electronic blender (Butterfly B-592) was used to crush the dried seaweed into powder. The remaining chemicals were all analytical reagent (AR) which is the purity more than 95 percent, in general.

### 2.2 Collection and sample preparation

The seaweed was sun-dried before being delivered to the researchers. The seaweeds were classified as *Kappaphycus* sp. and *Padina* sp. Upon delivery, the seaweeds were cleaned

and washed twice with tap water, followed by a further washing in distilled water. The washing process eliminates impurities such as rope, sand, foreign biota, and salt from the samples.

### 2.3 Drying process

Two different drying methods were used with four different drying conditions, as shown in Table 2. For the sun-drying procedure, 100 g of seaweed was weighed and spread in a single layer on a tray before being exposed to the sun. Samples were weighed every 4 h until a constant weight was obtained. The same procedure was applied to the oven-drying process using a Memmert heating and drying oven at three different temperatures (60 °C, 80 °C and 100 °C). The

seaweed was only chopped into smaller sizes after drying to prevent a significant loss of bioactive compounds. Finally,

the dried seaweeds were ground into powder using a laboratory blender and stored in zip-lock bags.

**Table 2.** Parameters of drying conditions including temperatures and periods.

Drying method	Drying condition	Time
Sun dry	Direct sunlight	5 days
Oven dry	100 °C	6 h
Oven dry	80 °C	6 h
Oven dry	60 °C	6 h

## 2.4 Characterization of seaweed

### 2.4.1 Determination of heavy metals

Determination of metal in seaweeds was done according to Sudharsan et al., (2012). One gram of powdered dried seaweed was weighed and digested in a 100 mL beaker filled with 20 mL of concentrated nitric acid overnight. The solution was mixed with 10 mL of concentrated nitric acid and perchloric acid at a ratio of 4:1. Then, the acid mixture was evaporated on a hotplate at 120 °C until complete dryness was achieved for rapid digestion. The residue was made up to a 20 mL solution of Milli-Q water with 20% concentrated nitric acid and filtered through No. 1 Whatman filter paper. All metal concentrations were determined using inductively coupled plasma/optical emission spectrometry.

### 2.4.2 Fourier transform infrared (FTIR) analysis

An FTIR spectral analysis was conducted to discover the probable functional groups in dried *Kappaphycus* sp. and *Padina* sp. samples. An FTIR spectrometer (Perkin Elmer) was used to obtain infrared spectra of the raw and metal-loaded biomass. The metal-loaded biomass sample was dried for 4 h at 75 °C in a drying oven to eliminate water molecules before the spectrum was measured.

### 2.4.3 Determination of phenolic compound

One gram of each dried seaweed was extracted for 2 h with 80% v/v methanol with a ratio dried seaweed to solvent of 1:20, w/v at room temperature. The mixture was sonicated at 24 °C in a sonicator bath (Elmasonic S 180 H) for 30 min at 50 kHz, then shaken in an incubator shaker for 2 h at room temperature. The extract was filtered through Whatmann No. 1 filter paper before being stored at -20 °C for further analysis. Total phenolic content (TPC) from dried seaweed was determined using the Folin-Ciocalteu method by Neoh et al., (2021) with modification. Then, 100 µL of seaweed extract was applied to 200 µL of Folin-Ciocalteu reagent. After 5 min, 800 µL of sodium carbonate was applied to the mixture and allowed to stand in a dark room for 2 h. Gallic acid was used as standard. The results were expressed in the equivalent of 1.0 mg gallic acid equivalent per 1.0 g dried seaweed extract (mg GAE/g DS). A microplate spectrophotometer reader (Thermoscientific) was used to read absorbance at 765 nm against a blank solution. All of the measurements were carried out using five replicates.

### 2.5 Preparation of metal stock solution

Stock solutions of Zn, Cu, and Fe at 100 ppm were prepared by dissolving zinc nitrate, copper nitrate, and iron chloride in deionized water, respectively. All metal solutions were preserved in nitrate salt. Then, the stock solutions of heavy metals were diluted using deionized water for the solution of 0.5 ppm concentration.

## 2.6 Biosorption study

All the tests were done in a batch system with 150 mL Erlenmeyer flasks in an orbital shaker at 150 rpm. Each flask was filled with 100 mL of heavy metal solution and 1.0 g of sample. After shaking, the mixture was filtered to separate the solution and the seaweed. The solution was then filtered using a 0.45 µm syringe filter nylon membrane. Following separation, an atomic absorption spectrometer (AAS) was used to determine the amount of metal ions remaining in the solutions. The quantity of metal adsorbed per gram of adsorbent at equilibrium,  $qe$  (mg/g), was determined by calculating the metal concentration in the aqueous phase before and after adsorption using the formula given in Equation 1.

$$qe = \frac{(c_i - c_f)}{m} \times V \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations of metal ions in the solution (mg/L), respectively,  $V$  is the volume of metal solution (mL), and  $m$  is the mass of the dry adsorbent (mg). The percentage of metal removal (% adsorption) from the solution was calculated using Equation 2.

$$\% \text{ adsorption} = \frac{c_i - c_f}{c_i} \times 100 \quad (2)$$

Each experiment was repeated in triplicate, with the data expressed as the average of the results. The statistical data analysis was then performed. The Langmuir isotherm model was used to fit the isotherm curve using Equation 3.

$$\frac{Ce}{qe} = \frac{1}{q_{max}} Ce + \frac{1}{q_{max}K} \quad (3)$$

Where  $q_{max}$  is the maximum adsorption capacity (mmol/g),  $K$  is an equilibrium constant (1m/mol), and  $Ce$  is the concentration of the solution at equilibrium (m/mol).

## 3. RESULTS AND DISCUSSION

### 3.1 Heavy metal content

The presence of heavy metals (Cu, Fe and Zn) in both *Kappaphycus* sp. and *Padina* sp., before the biosorption process, are shown in Table 3. Only small quantities of the heavy metals were present in each of the seaweeds, ranging from 0.0022–0.0086 mg per gram of dried seaweed (mg g<sup>-1</sup>) for Cu, 0.0007–0.2259 mg g<sup>-1</sup> for Fe and 0.0061–0.1751 mg g<sup>-1</sup> for Zn, which are below the toxic limits permitted for human consumption (Gunatilake, 2015). These slight amounts of trace metals can be considered as necessary micronutrients for the growth of these algae (Sudharsan et al., 2012).

**Table 3.** Cu, Fe and Zn content in both *Kappaphycus* sp. and *Padina* sp. before biosorption

Sample	Drying conditions	Concentration (mg/g)		
		Cu	Fe	Zn
<i>Kappaphycus</i>	Sun dried	0.0044±0.0003	0.0781±0.0004	0.0018±0.0003
	Oven dried at 60 °C	0.0056±0.0002	0.1218±0.0006	0.0006±0.0003
	Oven dried at 80 °C	0.0046±0.0001	0.1507±0.0001	0.0061±0.0001
	Oven dried at 100 °C	0.0022±0.0001	0.0505±0.0001	0.0040±0.0003
<i>Padina</i>	Sun dried	0.0065±0.0003	0.2119±0.0003	0.0045±0.0002
	Oven dried at 60 °C	0.0086±0.0001	0.1262±0.0001	0.0032±0.0006
	Oven dried at 80 °C	0.0076±0.0005	0.2259±0.0012	0.0332±0.0001
	Oven dried at 100 °C	0.0033±0.0001	0.0007±0.0002	0.1751±0.0005

### 3.2 Total phenolic compound

Table 4 shows the TPC from 50 mg/ml of *Kappaphycus* sp. ranged from 0.0231–0.0882 mg gallic acid equivalent (GAE) g<sup>-1</sup> dried seaweed (DS), whereas the TPC from 50 mg/ml *Padina* sp. ranged from 0.1301–0.2133 mg GAE/g DS. When comparing drying procedures, oven drying at 60 °C had a higher TPC than sun drying. This data implies that *Padina* sp. has a higher TPC than *Kappaphycus* sp for both species.

The cell wall of *Kappaphycus* sp. contains carrageenan and sulphated polysaccharides (Yuan et al., 2005), which may contribute to its antioxidant capacity (Kumar et al., 2008; Matanjun et al., 2008; Ragan and Glombitza, 1986). *Padina* sp. cell walls are composed of cellulose, alginic acid, and polysaccharides, with alginates and sulphates being the most active groups (Romera et al., 2006). Any type of processing or techniques applied such as high drying

temperatures and extended drying may alter and lower certain phenol compounds in the material (Li et al., 2006). Moreover, in low moisture conditions, all plant cell components adhere to one another and potentially make the extraction more difficult, resulting in a lower TPC. Long drying times also decrease TPC leading to alterations in the color by-product.

The combination of moderate temperature (oven dried at 60 °C) and a short drying period (6 h) used in this process had the least affected TPC. The elevated temperature employed in both seaweeds resulted in a reduction of TPC. Sun-dried samples had the lowest levels of phenolic content. The prolonged drying time (4 to 5 days in direct sunlight) and dehydration during drying also affected the phenolic content. The slower drying rate increased the leaching impact and extended the period that the seaweed was exposed to the air.

**Table 4.** Total phenolic content of seaweeds

Sample	Drying	Total phenolic content (mg GAE/g DS)
<i>Padina</i>	Sun dried	0.1301±0.0054
	Oven dried 100 °C	0.1378±0.0054
	Oven dried 80 °C	0.1611±0.0188
	Oven dried 60 °C	0.2133±0.0125
<i>Kappaphycus</i>	Sun dried	0.0231±0.0027
	Oven dried 100 °C	0.0324±0.0027
	Oven dried 80 °C	0.0526±0.0081
	Oven dried 60 °C	0.0882±0.0071

### 3.3 Fourier transform infrared (FTIR) analysis

Drying is an essential step in seaweed production as it greatly impacts the phytochemical and functional group presence in seaweed (Ling et al., 2015). Among all untreated and metal-treated samples, oven dried (60 °C) for both *Kappaphycus* sp. and *Padina* sp. showed significant functional group shifts. The FTIR spectrum analysis before and after metal sorption for *Kappaphycus* sp. by different drying techniques is shown in Table 5. It lists the predominant adsorption peaks of functional groups on the surface of *Kappaphycus* sp. Great acidic properties were acquired after all oven drying treatments (60 to 100 °C) towards S-O stretching of both sulfonyl and sulfonate groups. It has been reported that this promotes metal sorption in *Kappaphycus* sp. (Mingu et al., 2022). FTIR analysis of *Kappaphycus* sp. suggested that its carboxyl,

ether, alcoholic, and amino groups are responsible for the binding of the metal ions.

The FTIR spectroscopic analysis on oven-dried *Padina* sp. at 60 °C is shown in Table 6. Most changes that occurred on biosorbent after biosorption of the three selected metals are reflected in the presence of a broad band between 3000 and 3300 cm<sup>-1</sup>, which represents –OH and –NH stretching groups of carboxylic and amide, respectively. Oven dried *Padina* sp. at 60 °C shows an insignificant peak in those bands. The occurring band between 1000 and 1050 cm<sup>-1</sup> represented –C–O stretching of ether groups and the –C–O stretching of alcoholic groups. This was observed after sorption of Cu, Fe and Zn, showing both groups play a role in the biosorption process. FTIR spectrum analysis of *Padina* sp. also suggests that its carboxyl, ether, phenolic and amino groups are responsible for metal ions binding.

**Table 5.** Functional groups and wavenumbers observed on *Kappaphycus* sp.

Drying	Wavenumber (cm <sup>-1</sup> )				Functional groups
	Before adsorption	Adsorption of Cu	Adsorption of Fe	Adsorption of Zn	
Oven dried 60 °C	3268.41	3326.00	3368.45	3339.14	–OH and –NH stretching
	-	-	-	2918.86	–CH <sub>3</sub> stretching
	-	-	2161.24	-	S–C≡N stretching
	-	1638.39	1641.77	1634.16	–COO stretching
	-	1219.45	1225.93	1225.85	–S–O stretching
	1151.43	1158.30	1158.03	1157.33	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
	1022.87	1034.70	1035.37	1033.95	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
	934.41	925.91	925.30	922.46	–C=C bending
Oven dried 80 °C	-	845.03	844.95	845.20	–C=C bending
	3349.77	3320.46	3366.38	3377.86	–OH and –NH stretching
	-	2160.93	-	2178.88	S–C≡N stretching
	1638.56	1641.44	1641.58	1633.72	–COO stretching
	1424.02	-	-	1373.13	–SO <sub>3</sub> stretching
	1223.29	1231.57	1220.02	1219.09	–S–O stretching
	-	-	1156.31	1157.14	–C–O stretching
	1031.77	1030.55	1035.47	1036.21	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
Oven dried 100 °C	923.69	927.01	924.05	924.77	–C=C bending
	854.56	846.00	845.29	845.57	–C=C bending
	3352.42	3320.92	3297.79	3293.51	–OH and –NH stretching
	-	-	2917.80	2917.76	–CH stretching (aliphatic)
	1637.29	1633.49	1631.81	1631.87	C=O stretching bond and C–O stretching bond vibrations to carboxylate group
	1224.97	1226.91	1227.82	1222.50	C=O stretching bond and C–O stretching bond vibrations to carboxylate group
	1033.67	1030.92	1031.82	1032.49	–C–O stretching alcoholic groups
	926.88	926.94	925.71	925.88	–S–O stretching
Sun dried	847.07	-	845.02	845.88	–S–O stretching
	3340.46	3339.63	3320.43	3330.80	–OH and –NH stretching
	1637.18	1641.82	1643.43	1640.79	–COO stretching
	1224.30	1223.30	1224.86	1222.41	–S–O stretching
	-	1035.89	1155.01	1156.19	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
	1032.994	-	1034.58	1032.60	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
	925.95	924.97	927.05	924.38	–C=C bending
	845.81	845.05	844.07	845.81	–C=C bending

**Table 6.** Wavenumber and functional groups observed on *Padina* sp.

Drying	Wavenumber (cm <sup>-1</sup> )				Functional groups
	Before adsorption	Adsorption of Cu	Adsorption of Fe	Adsorption of Zn	
Oven dried 60 °C	-	3283.55	3284.60	3294.05	–OH and –NH stretching
	-	2174.20	-	-	
	1446.82	1413.29	1416.47	1412.43	weak symmetrical carboxylate ions stretching
Oven dried 60 °C	-	1034.53	1029.91	1032.40	–C–O stretching of ether groups and –C–O stretching of alcoholic groups
	-	873.27	874.31	873.20	–C=C bending
	854.70	853.98	853.92	854.09	
	-	712.70	-	712.72	



**Table 6.** Wavenumber and functional groups observed on *Padina* sp. (Continued)

Drying	Wavenumber (cm <sup>-1</sup> )				Functional groups
	Before adsorption	Adsorption of Cu	Adsorption of Fe	Adsorption of Zn	
Oven dried 80 °C	-	3320.86	3333.27	3312.84	-OH and -NH stretching
	1460.08	1416.90	1411.49	1419.94	weak symmetrical carboxylate ions stretching
	-	1029.86	1030.50	1082.52	-C-O stretching of ether groups and -C-O stretching of alcoholic groups
	-	874.63	873.67	873.74	-C=C bending
	854.74	853.93	854.09	853.94	
	-	-	712.34	712.70	
Oven dried 100 °C	-	3344.14	3309.83	3325.91	-OH and -NH stretching
	-	-	-	2146.26	
	1447.17	1416.97	1417.99	1414.85	weak symmetrical carboxylate ions stretching
	-	1030.68	1034.96	1030.11	-C-O stretching of ether groups and -C-O stretching of alcoholic groups
	-	873.92		874.55	-C=C bending
	854.60	853.96	854.02	853.71	
	-	-	-	712.39	
	507.39	583.94	583.85	-	
	484.36	-	-	-	
Sun dried	-	3282.61	3331.12	3345.17	-OH and -NH stretching
	-	-	2174.91	-	
	1456.73	1420.19	1445.88	1416.70	weak symmetrical carboxylate ions stretching
	-	1029.94	1027.22	1031.51	-C-O stretching of ether groups and -C-O stretching of alcoholic groups
	854.85	853.60	853.56	874.34	-C=C bending
	-	570.47	557.89	-	
	-	-	461.10	-	

### 3.4 Biosorption study

The percentage of metal uptake by both biosorbents (*Kappaphycus* sp. and *Padina* sp.) is shown in Figure 1. Both seaweeds naturally exhibited the ability to adsorb heavy metals. Following the biosorption process, the amount of metals in the biosorbent increased. The quantity of metals in the biosorbent can be measured by the difference between the initial and final concentration of the heavy metal solution used. The results show that the sun-dried biosorbents had a higher heavy metal uptake, especially with *Kappaphycus* sp. It is due to the sulphate ester group, which is assumed to have binding sites higher than hydroxyl of the polysaccharides in the cell wall as phenolic in *Kappaphycus* sp. According to Rahman and Sathasivam (2016), red algae possess several binding sites, including carboxyl and amino groups.

The parameters in the Langmuir equation were obtained using a least square linear regression analysis on each set of isotherm data and are presented in Table 7. The adsorption capacities of copper (Cu), iron (Fe), and zinc (Zn) by the sample were 33.56 mg/g, 32.47 mg/g, and 38.76 mg/g, respectively. The adsorption capacity of Zn was relatively high compared to Cu and Fe. The high coefficient of determination ( $R^2$ ) obtained by Cu ( $R^2 = 0.9839$ ) indicates that biosorption data fit well with the

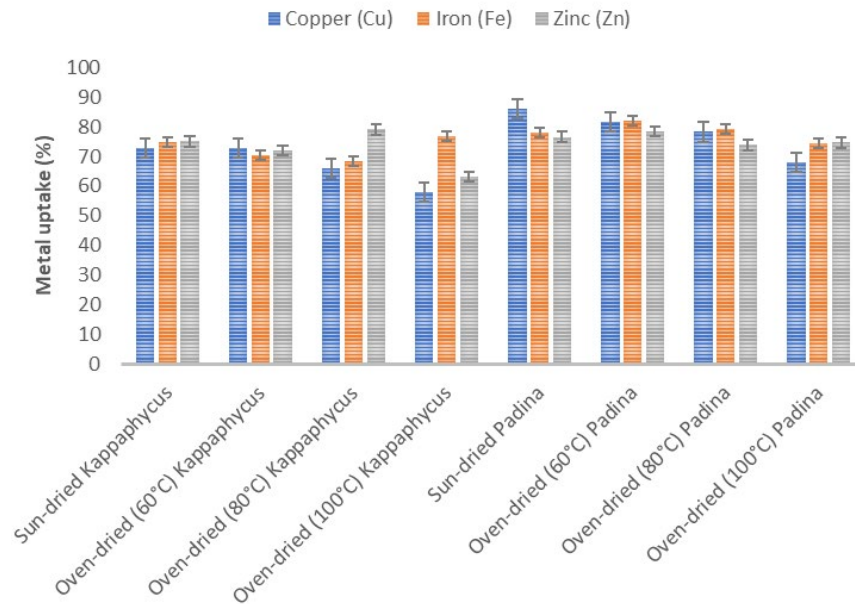
Langmuir isotherm. Therefore, the biosorption of Cu ions can be considered as monolayer biosorption.

## 4. CONCLUSION

This study conveys that *Kappaphycus* sp. and *Padina* sp. could be considered as promising materials to adsorb Cu, Zn and Fe ions from aqueous solutions. The main mechanism implied in heavy metal adsorption may be ionic exchange by functional groups on the surface. However, phenolic content in both seaweeds is not parallel to the of heavy metal uptake, as stated by Mousavi et al. (2021). For further study, a study on the surface morphology of metal-treated and untreated seaweed should be included to determine porosity on the surface of seaweed that may contribute to metal adsorption.

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**Figure 1.** Percentage of metal uptake by biosorbents

**Table 7.** Summary of Langmuir constants

Langmuir	Adsorption capacity, $q_{\max}$ (mg/g)	Equilibrium constant, $K$ (L/mg)	$R^2$
Copper (Cu)	33.56	0.943	0.9839
Iron (Fe)	32.47	0.815	0.9298
Zinc (Zn)	38.76	0.535	0.9056

## REFERENCES

- Abbas, S. H., Ismail, I. M., Mostafa, T. M., and Sulaymon, A. H. (2014). Biosorption of heavy metals: A review. *Journal of Chemical Science and Technology*, 3(4), 74–102.
- Ahemad, S., Ismail, A., and Ariff, M. R. M. (2006). The seaweed industry in Sabah, East Malaysia. *Journal of Southeast Asian Studies*, 11, 97–107.
- Ahmady-Asbchin, S., Andres, Y., Gerente, C., and Le Cloirec, P. (2009). Natural seaweed waste as sorbent for heavy metal removal from solution. *Environmental Technology*, 30(7), 755–762.
- Ahmed, D. A. E.-A., Gheda, S. F., and Ismail, G. A. (2021). Efficacy of two seaweeds dry mass in bioremediation of heavy metal polluted soil and growth of radish (*Raphanus sativus* L.) plant. *Environmental Science and Pollution Research*, 28(10), 12831–12846.
- Al-Zurfi, S. K. L., and Al-Tabatabai, H. H. M. (2020). Aquatic plant (*Hydrilla verticillata*) roles in bioaccumulation of heavy metals. *The Iraqi Journal of Agricultural Science*, 51(2), 574–584.
- Arumugam, N., Chelliapan, S., Thirugnana, S. T., and Jasni, A. B. (2020). Optimisation of heavy metals uptake from Leachate using red seaweed *Gracilaria changii*. *Journal of Environment Treatment Techniques*, 8(3), 1089–1092.
- Asencios, Y. J. O., Parreira, L. M., Perpetuo, E. A., and Rotta, A. L. (2022). Characterisation of seaweeds collected from Baixada Santista litoral, and their potential uses as biosorbents of heavy metal cations. *Revista Mexicana De Ingeniería Química*, 21(1), 1A2600.
- Baral, S. S., Das, N., Chaudhury, G. R., and Das, S. N. (2009). A preliminary study on the adsorptive removal of Cr(VI) using seaweed, *Hydrilla verticillata*. *Journal of Hazardous Materials*, 171(1–3), 358–369.
- Belattmania, Z., Engelen, A. H., Pereira, H., Serrão, E. A., Barakate, M., Elatouani, S., Zrid, R., Bentiss, F., Chahboun, N., Reani, A., and Sabour, B. (2016). Potential uses of the brown seaweed *Cystoseira humilis* biomass: 2- Fatty acid composition, antioxidant and antibacterial activities. *Journal of Materials and Environmental Science*, 7(6), 2074–2081.
- Boulaiche, W., Belhamdi, B., Hamdi, B., and Trari, M. (2019). Kinetic and equilibrium studies of biosorption of M (II) (M= Cu, Pb, Ni, Zn and Cd) onto seaweed *Posidonia oceanica* fibers. *Applied Water Science*, 9, 173.
- Brown, P. A., Gill, S. A., and Allen, S. J. (2000). Metal removal from wastewater using peat. *Water Research*, 34(16), 3907–3916.
- Carson, B. L., Ellis III, H. V., and McCann, J. L. (1986). *Toxicology and biological monitoring of metals in humans: Including feasibility and need*, Boca Raton, FL: CRC Press, pp. 1–15.
- Gunatilake, S. K. (2015). Methods of removing heavy metals from industrial wastewater. *Methods*, 1(1), 12–18.
- Janson, C. E., Kenson, R. E., and Tucker, L. H. (1982). Treatment of heavy metals in wastewaters. What wastewater-treatment method is most cost-effective for electroplating and finishing operations? Here are the alternatives. *Environmental Progress*, 1(3), 212–216.
- Jia, C.-G., Zhang, Y.-P., Wang, H., Ou, G.-N., Liu, Q.-M., and Lin, J.-M. (2014). Rapid biosorption and reduction

- removal of Cr(VI) from aqueous solution by dried seaweeds. *Journal of Central South University*, 21, 2801–2809.
- Kapepula, L. V., Alvarez, M. G., Sefidi, V. S., Tamungang, E. B. N., Ndikumana, T., Musibono, D.-D., van Der Bruggen, B., and Luis, P. (2022). Evaluation of commercial reverse osmosis and nanofiltration membranes for the removal of heavy metals in water sources from the Democratic Republic of Congo. *Clean Technologies*, 4(4), 1300–1316.
- Khan, M. U., Malik, R. N., and Muhammad, S. (2013). Human health risk from heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. *Chemosphere*, 93(10), 2230–2238.
- Kratochvil, D., and Volesky, B. (1998). Advances in the biosorption of heavy metals. *Trends in Biotechnology*, 16(7), 291–300.
- Kumar, K. S., Ganesan, K., and Rao, P. V. S. (2008). Antioxidant potential of solvent extracts of *Kappaphycus alvarezii* (Doty) Doty – An edible seaweed. *Food chemistry*, 107(1), 289–295.
- Lee, S.-H., and Park, C.-H. (2012). Biosorption of heavy metal ions by brown seaweeds from southern coast of Korea. *Biotechnology and Bioprocess Engineering*, 17, 853–861.
- Li, B. B., Smith, B., and Hossain, M. M. (2006). Extraction of phenolics from citrus peels: I. Solvent extraction method. *Separation and Purification Technology*, 48(2), 182–188.
- Ling, A. L. M., Yasir, S., Matanjun, P., and Abu Bakar, M. F. (2013). Antioxidant activity, total phenolic and flavonoid contents of selected commercial seaweeds of Sabah, Malaysia. *International Journal of Pharmaceutical and Phytopharmacological Research*, 3(3), 234–238.
- Ling, A. L. M., Yasir, S., Matanjun, P., and Abu Bakar, M. F. (2015). Effect of different drying techniques on the phytochemical content and antioxidant activity of *Kappaphycus alvarezii*. *Journal of Applied Phycology*, 27(4), 1717–1723.
- Matanjun, P., Mohamed, S., Mustapha, N. M., Muhammad, K., and Ming, C. H. (2008). Antioxidant activities and phenolics content of eight species of seaweeds from north Borneo. *Journal of Applied Phycology*, 20(4), 367–373.
- Mingu, N., Aziz, S. A., Stidi, E. Y., Majid, M. H. A., Idris, J., and Sarjadi, M. S. (2022). Study of composition and surface morphology of seaweed as biosorbent: A review. *Journal of Physics: Conference Series*, 2314(1), 012029.
- Mithra, R., Sivaramakrishnan, S., Santhanam, P., Dinesh Kumar, S., and Nandakumar, R. (2012). Investigation on nutrients and heavy metal removal efficacy of seaweeds, *Caulerpa taxifolia* and *Kappaphycus alvarezii* for wastewater remediation. *Journal of Algal Biomass Utilization*, 3(1), 21–27.
- Mousavi, A., Pourakbar, L., Moghaddam, S. S., and Popović-Djordjević, J. (2021). The effect of the exogenous application of EDTA and maleic acid on tolerance, phenolic compounds, and cadmium phytoremediation by okra (*Abelmoschus esculentus* L.) exposed to Cd stress. *Journal of Environmental Chemical Engineering*, 9(4), 105456.
- Mwangi, I. W., and Ngila, J. C. (2012). Removal of heavy metals from contaminated water using ethylenediamine-modified green seaweed (*Caulerpa serrulata*). *Physics and Chemistry of the Earth, Parts A/B/C*, 50–52, 111–120.
- Neoh, Y. Y., Matanjun, P., and Lee, J. S. (2021). Effects of various drying processes on Malaysian Brown Seaweed, *Sargassum polycystum* pertaining to antioxidants content and activity. *Transactions on Science and Technology*, 8(1), 25–37.
- Patrón-Prado, M., Acosta-Vargas, B., Serviere-Zaragoza, E., and Méndez-Rodríguez, L. C. (2010). Copper and cadmium biosorption by dried seaweed *Sargassum sinicola* in saline wastewater. *Water, Air, & Soil Pollution*, 210(1), 197–202.
- Praveen, R. S., and Vijayaraghavan, K. (2015). Optimisation of Cu(II), Ni(II), Cd(II) and Pb(II) biosorption by red marine alga *Kappaphycus alvarezii*. *Desalination and Water Treatment*, 55(7), 1816–1824.
- Ragan, M. A., and Glombitza, K.-W. (1986). Phlorotannins, brown algal polyphenols. *Progress in Phycological Research*, 4, 129–241.
- Rahman, M. S., and Sathasivam, K. V. (2016). Heavy metal biosorption potential of a Malaysian Rhodophyte (*Eucheuma denticulatum*) from aqueous solutions. *International Journal of Environmental Science and Technology*, 13, 1973–1988.
- Romera, E., González, F., Ballester, A., Blázquez, M. L., and Muñoz, J. A. (2006). Biosorption with algae: A statistical review. *Critical Reviews in Biotechnology*, 26(4), 223–235.
- Sudharsan, S., Seedeve, P., Ramasamy, P., Subhapradha, N., Vairamani, S., and Shanmugam, A. (2012). Heavy metal accumulation in seaweeds and sea grasses along southeast coast of India. *Journal of Chemical and Pharmaceutical Research*, 4(9), 4240–4244.
- Volesky, B. (Ed.) (1990). Biosorption and biosorbents. In *Biosorption of Heavy Metals*, pp. 3–5. Boca Raton, FL: CRC Press.
- Yap, W.-F., Tay, V., Tan, S.-H., Yow, Y.-Y., and Chew, J. (2019). Decoding antioxidant and antibacterial potentials of Malaysian green seaweeds: *Caulerpa racemosa* and *Caulerpa lentillifera*. *Antibiotics*, 8(3), 152.
- Yuan, H., Zhang, W., Li, X., Lü, X., Li, N., Gao, X., and Song, J. (2005). Preparation and in vitro antioxidant activity of κ-carrageenan oligosaccharides and their oversulfated, acetylated, and phosphorylated derivatives. *Carbohydrate Research*, 340(4), 685–692.