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دراسة مقارنة للتراكم الحيوي للعناصر الثقيلة في أنواع مختلفة من الطحالب البحرية بساحل البحر الأحمر السوداني أبوعاقلة يوسف أحمد 1، إسماعيل مختار اوحيده 2، فتحي أحمد صميدة 3. قسم الكيمياء و الأحياء. كلية التربية. جامعة السودان ، السودان قسم الكيمياء. كلية العلوم. جامعة المرقب ، ليبيا 2.3 قسم الكيمياء. كلية العلوم. جامعة المرقب ، ليبيا abubraa2002@gmail.com

A comparative Study of Heavy Metals Bioaccumulation in Different Types of Marine Algae from the Sudanese Red Sea Coast

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تاريخ الاستلام:01-08-2024 تاريخ القبول: 18-08-2024 تاريخ النشر: 04-09-2024

الملخص:

تهدف هذه الدراسة لتحديد تركيز العناصر الثقيلة: الكروم، المانجنيز، النيكل،النحاس، الخارصين، الكادميوم والرصاص في ثلاث مجموعات رئيسية من الطحالب البحرية: الخضراء، البنية والحمراء من مياه الساحل السوداني للبحر الأحمر في سبعة مواقع أساسية. أظهرت نتائج الدراسة إلفه تجاه العناصر الأساسية (المانحنيز، النحاس والخارصين). من بين العناصر الأساسية، التركيز الأعلي وجد لعنصر المانجنيز في كل العينات بصرف النظر عن تصنيفهم (متوسط التركيز من 16.60 الي 172.53 ملجم/جم) واحتوت الطحالب البنية. Cystoseira sp. التركيز الأعلى من المانجنيز (257.32 ملجم/جم) بينما احتوت الطحالب الخضراء .Enteromorpha sp التركيز الأعلى من الكادميوم والرصاص (2.40 و 2.40 ملجم/جم) علي التوالي، هذه العينات اقترحت لتكون ملائمة لرصد تركيز هذه العناصر في بيئة البحر الأحمر.

الكلمات الدالة: عناصر ثقيلة، طحالب بحرية، البحر الأحمر

Abstract

This study aimed to determine the concentrations of heavy metals, Cr, Mn, Ni, Cu, Zn, Cd, and Pb in three main groups of marine algae; green, brown and red from the Sudanese coastal water of the Red Sea at seven main locations. The results of the study showed an affinity towards essential elements

(Manganese, Copper and Zinc). Among the essential elements, highest concentration was exhibited by Mn in all the species, irrespective of their classification, (average range from 16.60 to 172.53 mg/g), where brown algae Cystoseirasp. contains the highest uptake of Mn (257.32 mg/g). However, green algae Enteromorphasp. contains the highest uptake of Cd and Pb (0.25 and 2.40 mg/g) respectively, these species suggesting its suitability for utilization as biomonitor in the Red Sea coastal environment.

Keywords: heavy metals, marine algae, Red Sea

1 - Introduction

Heavy metals discharged into the environment as a result of industrial processes tend to circulate continually and eventually accumulate throughout the food chain, posing a major hazard to the ecosystem. More than 3 billion people live near the world's coastlines. (Kumar et al., 2009) (Peng Z, 2022).

Anthropogenic actions in coastal areas may have an undesirable effect on coastal ecosystems and human health due to the discharge of industrial and household sewage. These effluents often include high quantities of heavy metals, which are known to accumulate in macro algae, which serve as the core of several food chains (Al-Homaidan, 2007).

Trace concentrations of several hazardous and bioaccumulative contaminants are often present in water, and they are frequently discovered at increased levels in sediments. Risk evaluations that solely rely on information from water analysis studies might be deceptive. However, information derived from sediments may not accurately reflect the amounts of pollutants in the water column above it or provide insight into the patterns of contamination at higher trophic levels. (Abuagla Y.A. et al., 2021), (Torres et al., 2008). Around the world, macroalgae have been widely employed to quantify heavy metal contamination in freshwater and marine ecosystems. Their capacity to accumulate metals to an acceptable degree, their lifespan, their prevalence at pollution places, and their ease of identification make them ideal as bioindicators. (Al-Homaidan et al., 2011) (Emin Cadar, et al. 2019). The relation between heavy metals and marine algae has been the subject of several studies. (Anbazhagan. V. et al., 2021). Some marine algae, as Ulva and Enteromorpha (green algae), are employed as biomonitors for heavy metal pollution in marine environments because of their ease of accumulation (Cavas et al., 2009). Marine algae provide a well-known biological significance to the marine environment, serving as the principal productivity in seawater and helping sustain the biological equilibrium. (Aknaf, A., et al 2022). According to their widespread distribution and environmental impact, this paper compares the heavy metal contents of three species of marine algae on the Sudanese Coast of the Red Sea with regard to seven distinct heavy metals: chromium, manganese, nickel, copper, zinc, cadmium, and lead. These are vegetative species that satisfy the criteria to be utilised as bioaccumulative agents in biological monitoring programmes.

2- Species of marine algae in Red Sea coast

The Red Sea is well-known for being the home of several marine tropical species and invertebrates, many of them have more colour than those found in other regions of this world. A novel technique ensures a perfect consistency in the distribution of the heavy metals in the mixture. An enormous and varied group of organisms that have chlorophyll and perform oxygenic photosynthesis are collectively referred to as algae. Their primary home is the marine one, where they present as an intertidal component (Davis et al., 2003). It is likely that within the kingdom of plants, algae do not constitute a homogenous group. They are separated into three distinct evolutionary pathways: the "brown pathway," which contains brown algae (Phaeophyta), the "red pathway," which includes red algae (Rhodophyta), and the "green pathway," which includes green algae (Chlorophyta), mosses, ferns, and other plants. The cell wall, the place where sorption occurs, is primarily where various kinds of algae differ from one another (Romera et al., 2007). These algae have a strong ability to bind metals. This is because several functional groups, including hydroxyl, carboxyl, sulphate, and amino groups, can serve as metal-binding sites (Kumar et al., 2009). High levels of sulfated polysaccharides and alginic acid can be found in brown algae. The purpose of these polysaccharides, that are not found in terrestrial plants, is thought to be to allow marine algae to use ion exchange to preferably absorb metallic ions in a salty water condition (Raize et al., 2004). Researchers have looked at brown algae's ability to biosorb metals widely around the world, with encouraging findings (Kumar et al., 2009). Green algae, or chlorophyta, are primarily responsible for the majority of the primary production occurring in near-shore ecosystems. Because these species should reflect the metal concentrations in the environmental seawater, using algae to monitor metal pollution in the aquatic environment makes sense (Zbikowski et al., 2007). The greatest bioindicator of nutrient and heavy metal pollution of aquatic bodies is widely thought to be green algae, especially Cladophora species. (Medvel and Chmielewiska, 2002).

3- Common species of marine algae in Sudanese Red Sea coast

Table (1) shows three kinds of the common species of algae across Sudanese coast of the Red Sea.

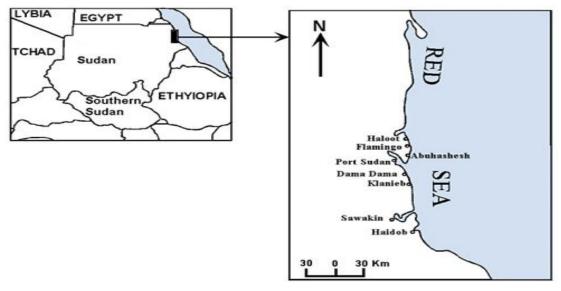
Table 1. Common species of algae in Red Sea coast

Chlorophyta	Phaeophyta	Rhodophyta		
(Green algae)	(Brown algae)	(Red algae)		
Cladophora	Sargassum	Laurencia		
Halimeda	Turbinaria	Gracilaria		
Caulerpa	Padina	Hypnea		
Enteromorpha	Cystoseira	Jania		
Ulva	Dictyota	Corallina		

4- The study area and sampling

The Red Sea coast of Sudan is situated in the east of the country, with a longitude of almost 750 km, as shown in Fig. (1). Port Sudan and Sawakin, two significant year-round trade exchange centres, are situated in this region. As seen in Fig. (1), the region under study covers approximately 100 km of coast that stretches from Haidob, which is approximately 75 km south, and Haloot, which is approximately 25 km north, through seven significant areas. The research's samples have been collected from several study locations at various places. The samples were divided into three primary categories in accordance with (Irvine and Price, 1978) and (Abdel Aleem, 1993). Samples were collected at intervals of around 50 metres along the transect across the region of bordering reefs and into the open sea at a depth of between 0.5 and 1.5 metres. The water samples' salinity, pH, and temperature were noted. After being collected, the samples were sealed in plastic bags and brought to the laboratory in one to three hours. Samples were properly cleaned in a lab using filtered sea water that was taken at the sampling site in order to remove any adhesive foreign particles. Tap water was then used to rinse the samples in order to remove any remaining adhering salts, and finally, distilled water was used many times. Where appropriate, the soft portions were divided, oven-dried, and the dry samples were ground into a fine powder. When manipulating the samples, extensive care was applied to prevent any possible causes of contamination.

Fig. 1. Map showing samples location at Sudanese Red Sea Coast



5 - Sample preparation and instrumental analyses

The usual method of preparing sample for Atomic Absorption Spectrophotometer (AAS) analyses is to treat the solid sample by acid digestion (wet digestion). For this work, 1gram of dried homogenous powder sample was weighted and placed in 100 ml beaker, 7 ml of concentrated nitric acid was added, the mixture was allowed to stand until whole of the sample was dissolved and the evaporation of NO2 was ceased. The solution was cooled; 2 ml of perchloric acid was added and gently heated at about 70 Co to evaporate the excess acid near dryness. Product was resulted, and then transferred to 50 ml double distilled water, the solution was then filtered. The obtained solution was used in the analysis of heavy metals by Atomic Absorption Spectroscopy (AAS).

6- Statistical approach

Statistical methods applied were two– way analysis of variance (ANOVA) for testing the significance of the 2 way differences: differences between elements and differences betweenlocations. No significant differences were shownbetween the samples studied, (P.Value >0.05), Table (2).

7- pH and salinity measurements

pH measurements and salinity were recorded in Table (1), for water of each location using pH-meter (Hanna HI 8314) calibrated continuously and salinometer (Hand-Held Refractometer S/Mile). The pH ranged from (8.11 - 8.82), the range of salinity as estimated was (38 - 41). The result showed the alkaline nature of the red sea water where, evaporation exceeds

precipitation, and this combined with the very restricted exchange of water with the open sea leads to the production of the dense (Sam et al., 1998), (Ency. Britanica, 1976).

Table 1. Descriptive statistic of pH and salinity of the sample sites

3- Site	2- pH	1- Salinity % pps
6- Haloot	5- 8.11	4- 38
9– Flamingo	8- 8.57	7- 41
12- Abuhashesh	11- 8.82	10- 40
15- Dama Dama	14- 8.76	13- 41
18- Klanieb	17- 8.74	16- 39
21- Sawakin (1)	20- 8.73	19- 39
24- Sawakin (2)	23- 8.64	22- 39
27- Haidob	26- 8.71	25- 39
30- Average	29- 8.64	28- 39.5
33- STD	32- 0.23	31- 1.07
36- Min	35- 8.11	34- 38
39- Max	38- 8.82	37- 41

pps ≡ part per thousand

8- Results and discussion

Samples of marine algae collected at random distances near shore environment of the samples locations were analyzed for their heavy metal content (Cr, Mn, Ni, Cu, Zn, Cd, and Pb). The results of the study showedthat marine algae collected from the Red Sea coast were able to accumulate metals from their environment. Among the elements, highest concentration was exhibited by Mn in all the species irrespective of their classification, lower concentration was recognized for Pb and Cd respectively for all kinds of species. The average concentration of heavy metals at samples locations as measured by AAS was shown in Table (3) and figures (2 to 9). The general order of accumulation was Mn>Cr>Zn>Cu>Ni>Pb>Cd. A higher concentration of heavy metals of algae species were presented in Table (4), among the species selected, the accumulation of different metals was comparatively different in different algal

species at the different locations. The highest concentration of Cr (16.95mg/g) was found in brown algae Padinasp. at Haloot and green algae Halimeda sp. at Sawakin (2). For Mn the highest concentration (257.00mg/g) was found in brown algae Cystoseira sp. at Haloot. For Ni three species of marine algae showed high concentration (9.45mg/g), green algae Enteromorpha sp., red algae Corallina sp. at Dama Dama, and green algae Halimeda sp. at Klanieb. For Cu high concentration, (14.10mg/g) was found in brown algae Padina sp. at Haloot.For Zn (22.60mg/g) was found in red algae Jania sp. at Sawakin(2). Cd and Pb which are known as pollutant elements was higher in Sawakin (2) which was suggested as a pollutant area. For Cd the concentration (0.25mg/g) and for Pb (2.40mg/g) was found in green algae Enteromorpha sp.

Table 3. Average concentration of algae groups (mg/g) at various locations.

Location	Algae	Cr	Mn	Ni	Cu	Zn	Cd	Pb	P-value	
Haloot	Green	10.56	148.97	7.20	7.48	9.60	0.10	1.90		
	Brown	11.36	128.95	4.19	7.79	10.31	0.11	1.03	0.985	
	Red	10.97	161.39	6.25	7.67	9.99	0.08	1.19		
Flamingo	Green	9.70	25.60	4.08	5.79	10.54	0.07	1.50		
	Brown	8.20	91.12	4.17	6.65	14.65	0.06	1.22	0.722	
	Red	11.22	62.47	4.73	5.81	20.89	0.08	1.35		
	Green	8.97	16.60	4.50	3.02	6.57	0.06	1.57		
Abuhashesh	Brown	7.97	27.17	5.07	2.69	12.25	0.05	1.09	0.614	
	Red	NA	NA	NA	NA	NA	NA	NA		
	Green	9.70	27.00	5.54	3.47	7.58	0.07	1.69	0.795	
Dama Dama	Brown	8.72	45.45	5.07	2.73	9.97	0.06	1.19		
	Red	11.22	62.08	6.58	5.18	9.83	0.08	1.73		
	Green	8.78	97.32	6.08	3.47	5.93	0.07	1.62	0.914	
Klanieb	Brown	10.33	172.53	4.95	5.53	6.90	0.08	1.93		
	Red	11.98	127.94	4.84	4.33	5.89	0.09	1.63		
	Green	13.30	22.00	5.18	3.30	7.63	0.10	1.85		
Sawakin (1)	Brown	9.65	54.37	4.73	4.40	15.38	0.07	1.53	0.511	
	Red	NA	NA	NA	NA	NA	NA	NA		
Sawakin (2)	Green	15.20	32.86	6.30	4.68	9.35	0.17	1.75	0.784	
	Brown	12.98	53.87	6.08	8.33	19.13	0.09	1.85		
	Red	13.95	52.87	7.43	11.63	22.65	0.13	2.18		
	Green	11.74	59.54	6.25	3.92	5.37	0.90	1.71		
Haidob	Brown	9.25	102.19	5.06	4.13	6.49	0.07	1.81	0.920	
	Red	12.98	105.11	7.09	4.13	5.37	0.10	1.55		

NA: Not Available

Table 4. higher concentration (mg/g) of heavy metals of marine algae species at various locations

Location	Element	Cr	Mn	Ni	Cu	Zn	Cd	Pb
	Concentration	16.95	257.32	8.10	14.10	15.08	0.15	2.10
Haloot	Algae species	B .Padina	B. Cystoseira	G. Caulerpa R. Hypnea	B .Padina	B .Padina	G. Halimeda B. Turbinaria	G. Caulerpa
	Concentration	12.45	161.70	5.87	9.15	20.48	0.09	1.88
Flamingo	Algae species	R. Laurencia	B. Padina	G. Halimeda	R. Laurencia	R. Laurencia	R. Jania	B. Cystoseira
	Concentration	10.95	58.50	8.10	4.13	16.58	0.08	2.10
Abuhashesh	Algae species	G. Halimeda	B. Padina	G. Halimeda	B. Padina	B. Turbinaria	G. Halimeda	G. Halimeda
	Concentration	13.95	109.8	9.45	9.15	17.70	0.11	2.18
Dama	Algae	R. Corallina	B. Padina	R. Corallina	R. Corallina	B. Cystoseira	R. Corallina	G.Enteromorpha
Dama	species			G.Enteromorpha				
	Concentration	15.00	208.00	9.45	6.60	7.95	0.11	2.33
Klanieb	Algae	R. Jania	B. Padina	G. Halimeda	R. Hypnea	B. Cystoseira	R. Jania	R. Hypnea
	species					G.Dictosphyria		
	Concentration	13.95	77.92	6.75	5.78	15.90	0.11	1.95
Sawakin (1)	Algae species	G. Enteromorpha	B. Padina	B. Turbinaria	B. Padina	B. Padina	G. Enteromorpha	G. Enteromorpha
		G. Halimeda		G. Enteromorpha			G. Halimeda	G. Halimeda
Sawakin (2)	Concentration	16.65	53.87	7.43	11.63	22.60	0.25	2.40
	Algae species	G. Halimeda	B. Padina	G. Halimeda	R. Jania	R. Jania	G. Enteromorpha	G. Enteromorpha
				R. Jania				
Haidob	Concentration	13.95	157.35	8.78	6.60	9.15	0.11	2.33
	Algae species	G. Halimeda	B. Padina	G. Enteromorpha	B. Cystoseira	B. Cystoseira	G. Halimeda	G. Halimeda
		R. Jania			G. Enteromorpha		R. Jania	

G= green algae, B= brown algae, R= red algae

Fig.(2) Haloot

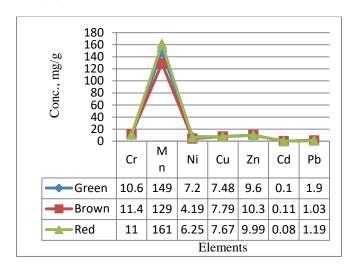


Fig.(4) Abuhashesh

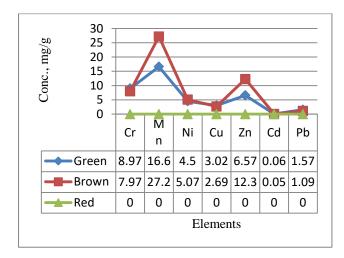


Fig.(6) Klanieb

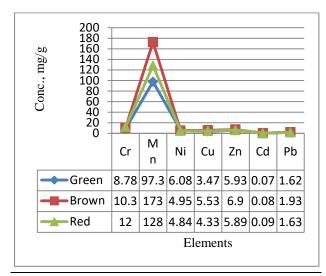


Fig.(3) Flamingo

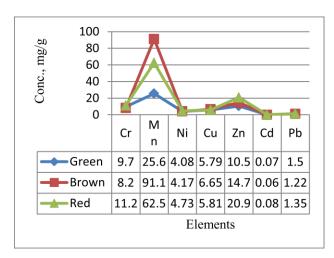


Fig.(5) Dama Dama

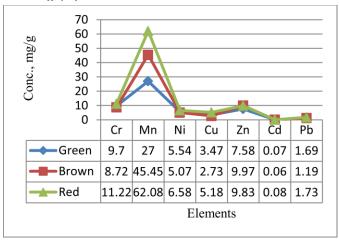


Fig.(7) Sawakin (1)

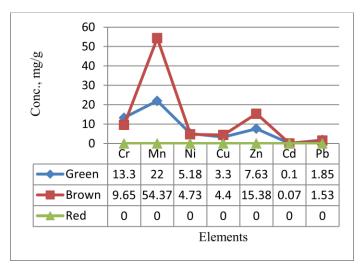


Fig.(8) Sawakin (2)

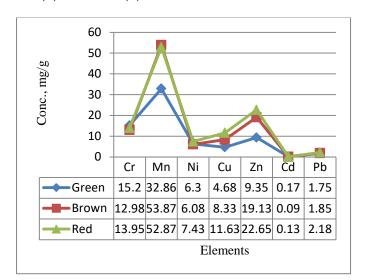
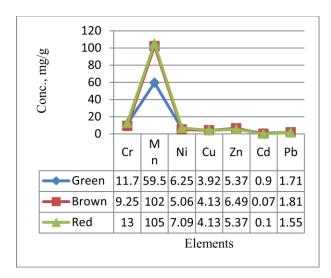


Fig.(9) Haidob



9- Conclusion

In the light of this study, the data obtained may be useful in assessment of the content of heavy metals of marine algae species in Red Sea coast. Padina sp can be used as biomonitors of Cr and Cu content, Cystoseira sp. can be used for monitoring Mn, Enteromorpha sp.can be used to monitor Ni, Cd and Pb, where Jania sp. can be used for monitoring Zn content because of their ability to accumulate high metals concentration from their environment, these species could be considered as biomonitors of heavy metal pollution in Red Sea coast.

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