[Hadhramout University Journal of Natural & Applied Sciences](https://digitalcommons.aaru.edu.jo/huj_nas)

Volume 18
Issue 1 *6/1/2021*

Article 5

2021

Removal of Lead (II) from Polluted Seawater in Mukalla Coast, Hadhramout Using Biotechnology of Dried Biomass of Macroalgae, Gracilaria sp and Sargassum sp

Abdullah Salem Bawazir
Department of Marine Biology, Faculty of Environmental Sciences & Marine Biology, Hadhramout University

Eman Hassan Ba Othman
Department of Environmental Sciences, Faculty of Environmental Sciences & Marine Biology, Hadhramout University

NAS journal Hadhramout University

Contents lists available at https://digitalcommons.aaru.edu.jo/huj_nas/.

Hadhramout University Journal of Natural & Applied Science

Article

Digital Object Identifier:
Received 7 September 2020,
Accepted 4 January 2021,
Available online 13 December 2021

Removal of Lead (II) from Polluted Seawater in Mukalla Coast, Hadhramout Using Biotechnology of Dried Biomass of *Macroalgae*, *Gracilaria sp* and *Sargassum sp*

Abdullah Salem Bawazir[1*], Eman Hassan Ba Othman[2]

[1] Department of Marine Biology, Faculty of Environmental Sciences & Marine Biology, Hadhramout University
[2] Department of Environmental Sciences, Faculty of Environmental Sciences & Marine Biology, Hadhramout University

Abstract: This study aimed to remove lead ions (Pb^{2+}) from seawater mixed with wastewater that discharged to Mukalla coast. Water samples were collected from points near the sewage discharging sampling station. *Macroalgae* samples, *Gracilaria sp* and *Sargassum sp* were used for bio-sorption of Pb^{2+} from seawater in the study area. Besides, this study aimed to assess the removal efficiency of lead-heavy metal ions (Pb^{2+}) from polluted seawaters in Mukalla coast by *Macroalgae* biomass. The effect of pH values (4.5 –7.5 ± 0.5) and different adsorbent dosages were used on the adsorption process through Winter and Summer seasons. The removal percentage of Pb^{2+} was applied to describe the bio-sorption capacity in polluted water. This method is an eco-friendly technology for reducing heavy metals from polluted seawaters as an effect of functional groups of macro-algae cell walls. The results of lead bio sorption percentages were found to vary from 80.00 % to 90.00% in pH value of 4.5 and from 76.82% to 89.4% in pH value of 7.5 at 20B sampling station through Winter and Summer seasons, respectively. The FT-IR analysis indicated that possible functional groups involved in metal adsorption by macro-algae were C–O, O–H and N–H stretching. FT-IR technique has been proved for detecting probable binding sites of Pb^{2+} induced by the presence of active groups including carboxyl and hydroxyl groups in both *Gracilaria sp* and *Sargassum sp* algae biomass that are of the components of the structure of algae cell walls.

Keywords: Bio-sorption; pb (II); Removal; *Macroalgae*; Ecofriendly Technique; Functional Groups.

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. One of the major reasons of environmental pollution is the rapid growth of human populations and the increased urbanization and industrialization throughout the world that results in a release of toxic metals from its effluents [7,9]. These pollutants usually reached into seas from different sources; domestic and industrial drainage, hospitals, and water used in workshops inside towns, which have a substantial impact on the coastal environments [3,7]. Fear amounts of industrial product elements lie in the discharged wastewater into marine coasts, either directly or indirectly [6,10]. Domestic wastewater was considered as one of the most significant threats to the coastal environment worldwide. Excessive levels of these wastes in the marine environment cause risks to aquatic organisms and consequently consumers [4,32].

Bio-sorption of toxic heavy metals was considered as one of the alternative processes for pretreatment for wastewater in the chemical industry[30]. The equilibrium among all heavy metals is interchangeable and depends on an environmental factor such as temperature, pH value as well as biota bloom in waters [21]. The practical use of bio-sorption technology for controlling heavy metals in the environment as the first industrial applications have been reported in Britain at the end of the eighteenth century[15]. The ability to assess the accumulation of cadmium and lead was evaluated by green macro-algae at different contact periods [14,29]. The bio-sorption of minerals by brown algae was also published [12]. Compared to other algae biomass, brown algae showed the highest capacity of bio sorption for binding with metal ions [27,1].

The coastal environment of Red Sea and the Gulf of Aden is directly suffered by sewage discharges where coastal waters affected with organic nutrients around some population centers in the area [28].

The municipal sewage in Mukalla city is discharged to the coastal waters without treatment. The daily amounts discharged was about 3000 m^3. These sewages contain an organic and non-organic substances that mostly come from domestic uses [4]. The coastal area of Mukalla and other coastal cities of Hadhramout were affected by wastewater effluents which cause an environmental problem. The presence of heavy metals in these coasts may reach dangerous levels to the marine habitat which might affect the human health through its transition across fish consumptions. To ensure a safe and healthy environment, pretreatment of discharged sewage to the area must be applied using macro-algae bio sorption ecofriendly technology. The removal of heavy metal pollutants from the sewages will keep the coasts area harmless to the marine organisms and human being.

This study aimed to evaluate the bio-sorption technique using macro-algae (*Gracilaria sp* and *Sargassum sp*) biomass as an ecofriendly method for removing lead ions from the polluted seawaters at the study area.

2. Materials and Methods

Fuwwah is one of the largest areas of Mukalla city-Hadhramout governorate. Its coast is characterized as sandy rocky beaches. This area is connected with one of the municipality project in the seacoasts, including 20B sewage station (Fig.1) which discharging a considerable amounts of untreated sewages to the coasts of the area. The algae samples (*Gracilaria sp* and *Sargassum sp*) were collected from clean marine habitat, transferred to the laboratory, cleaned by tap water and dried at 80-90 ºC for 24 h. The algae samples were crushed and ground in a blender to granules of 1-2mm [34]. Polluted seawater was sampled from a point near sampling sewage discharge (20B station) at Fuwwah area.

Figure 1. Shows Sampling site (20 Bstation) at Mukalla coastal zone. https://www.google.com/maps (2018).

The study was conducted in the period from November 2017 to December 2018.The contaminated water was sampled in December 2017 (represented Winter season) and in May 2018 (represented Summer season). This sampling pattern was followed because the quantities of untreated sewages discharged in Mukalla coasts were varied in these seasons due to human activity. An experiment was conducted to study the removal of Pb^{2+} from polluted sea water in Winter and Summer. Water temperature in the area was in the range of 24 & 29 ± 2 °C in both Winter and Summer seasons respectively [31]. Water samples were placed in 250 ml glass flasks by adding 100 ml of polluted sea water sample. The solution was then adjusted to the required pH value using (HNO_3 or NaOH, 0.1M) solution. Depending on the pH value of the sample taken from the study area, the pH value measured in the laboratory is adjusted to 7.5 ±0.5 as alkaline solution and modified to 4.5± 0.5 as acidic solution [33]. Four biomass dosages (0.4, 0.6, 0.8, and 1gm) of each marine algae, *Gracilaria sp* and *Sargassum sp* were used. The mixtures (analyzed solution) were steered slowly in a rotary shaker (Hedolph, Unimax 2010) at a vibrating speed of 100 rpm for two hours. The precipitate was separated by Whatman filter paper and the analysis was determined by atomic absorption spectrophotometer [5]. The percentage of removal value of (Pb^{2}+) was calculated by applying the following formula:

Bio-sorption % = (Ci− Cf)/ Ci ×100 [33]

Where Ci is the value of initial metal concentration (mg/L), Cf is the concentration of the final metal ions value.

Detection of the effective groups in algae biomass:

To detect the effective groups through the experiment, the Pb^{2}+ solutions were prepared as standard solution (1000 mg/l) (by dissolving $Cd(NO_3)_2.4H_2O$ in deionized water) [18]. The solution used in the experiment (10 mg/l) was prepared on the basis of the standard solution and considered as the initial concentration. One gram of algae biomass powder for both algae types was used in the experiment. The

Fourier Transformation Infrared (FT-IR) analysis was conducted, before and after bio-sorption process using spectroscopy device. The technique was conducted to determine the vibration frequency changes and effective groups in the adsorbent [22]. About six slices were put within the spectra device. Each sample was recorded alone within the range 400 - 4000 cm-1.

The kinetic models by *Gracilaria sp* and *Sargassum sp* biomass:

The kinetic models of adsorption of Pb^{2+} have been studied using pseudo-first and pseudo-second order reaction [22] which expressed as a model based on linear regression correlation coefficient (R^2). Through the experiment, about 50 ml samples were taken in different times (15, 30, 60, 90 and 120 min). The samples were filtered and measured remaining concentration at each time with determined the efficiency of contact time that reached the equilibrium of the bio-sorption ofPb^{2+}[33].

The linear equation for both models is expressed as follows:

The pseudo-first-order adsorption kinetic modeling is expressed as:

$$\mathbf{Log(qe\text{-}qt) = Log(qe) - (K_1/2.303)t}$$

qe & qt : The amounts of metal ions adsorbed (mg/g) at equilibrium at time (t).

K1 : The bio-sorption rate constant (l/min).

The pseudo-second-order adsorption kinetic modeling is expressed as:

$$\mathbf{t/qt = 1/(K_2.qe^2) + (1/qe)t}$$

K_2: The bio-sorption rate constant of (g/mg/min), qe and R^2 were determined by plot t/qt versus t. The kinetic technique allow great experimental points to be obtained easily and fast. The time needed to achieve the adsorption equilibrium was determined accurately [19].

3. Results:

Analyses of algae and polluted seawater samples:

The initial concentrations of Pb^{2+} in the algae samples were found to be 0.033 and 0.031 mg/l in *Gracilaria sp* and *Sargassum sp* biomass respectively. The initial concentration of Pb^{2+} ions in polluted sea water samples was 2.5 mg/l in winter and 4.4 mg/l in summer season. The results show that, this area was highly contaminated by Pb^{2+} in summer season (Table 1).

Table 1. The initial concentration of Pb^{2+} (mg/l) in algae biomass (one gm) sample and in polluted seawater sampled from the study station

Algae samples		Polluted seawater samples	
Algae species	Conc. of Pb^{2+} (mg/l)	Season	Conc. of Pb^{2+} (mg/L)
Gracilaria sp	0.033	Winter	2.5
Sargassum sp	0.031	Summer	4.4
Control	0		

Bio-sorption of Pb^{2+} from polluted seawater:

Tables 2&3 show that the initial concentration of Pb^{2+} in polluted seawaters was decreased by both *Gracilaria sp* and *Sargassum sp* biomass in both seasons. In winter season, using *Gracilaria sp* biomass, the Pb^{2+} ions was decreased with removal value varied from 82.12 to 87.48% in 4.5 pH value, and from 77.48 to 89.4% in 7.5 pH

value. For *Sargassum sp* biomass, the removal value was varied from 82.48 to 90% in pH value 4.5 whereas, in pH 7.5, the removal values was varied from 77.48 to 87.48%. The best removal rate of Pb^{2+} was obtained by *Sargassum sp* biomass (90% in pH 4.5 and biomass dose of one gram) (Figs 2 & 3; and Table 2).

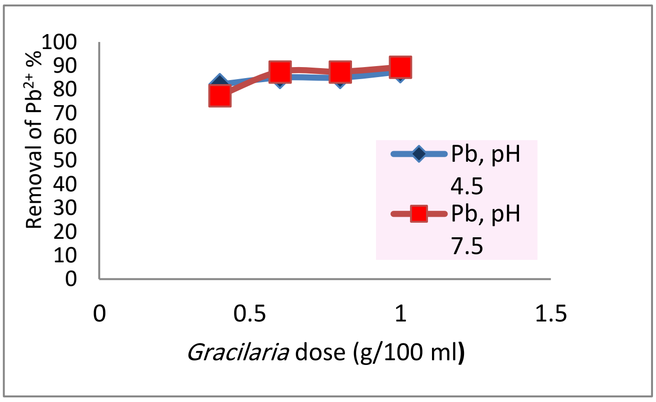

Figure 2. The removal values of Pb^{2+} (%) using *Gracilaria* sp biomass when pH value was 4.5 and 7.5 at station 20B study area in Winter season.

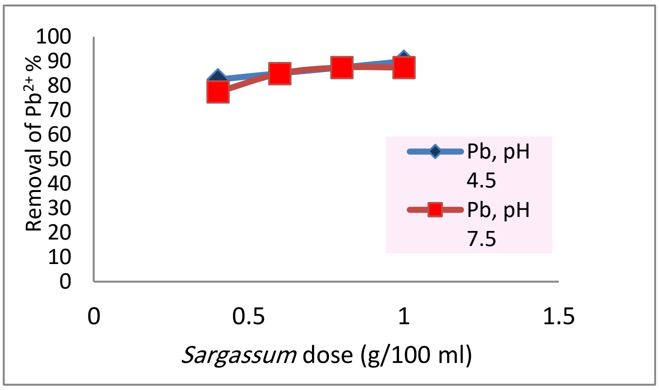

Figure 3. The removal values of Pb^{2+} (%) using Sargassum sp biomass when pH value was 4.5 and 7.5 at station 20B study area in Winter season.

In Summer season, using *Gracilaria* sp biomass, the bio-sorption removal value of Pb^{2+} was varied from 80 to 85.46% in pH value of 4.5 whereas in the pH value of 7.5, the removal rate of Pb^{2+} was varied from 81.82 to 87.27%. When applied *Sargassum* sp biomass, the removal value of Pb^{2+} was varied from 81.82 to 89.09% in pH value 4.5

whereas in pH value 7.5, the removal value was varied from 76.82 to 87.27%.The best removal rate of Pb^{2+}in Summer season was obtained by *Sargassum* sp biomass(89.09% when pH value was 4.5 and 87.27% when pH value was 7.5 at biomass dose of 0.8 g) (Figs 4.& 5; and Table 3).

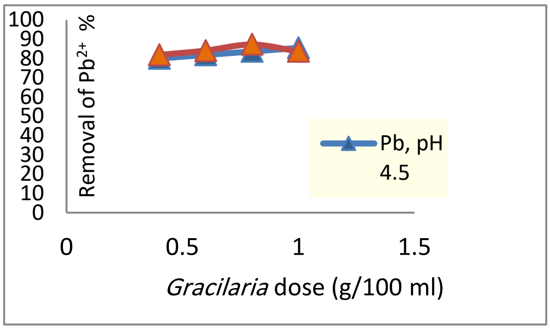

Figure 4. The removal values of Pb^{2+} (%) using *Gracilaria* sp biomass when pH value was 4.5 and 7.5 at station 20B study area in summer season

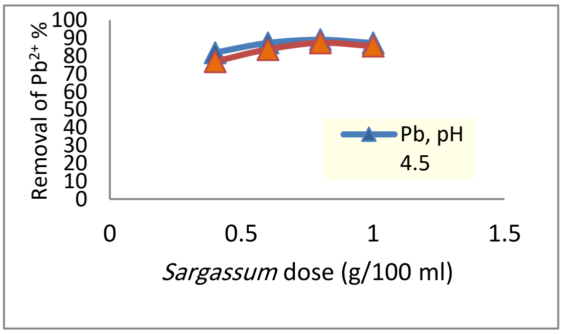

Figure 5. The removal values of Pb^{2+} (%) using *Sargassum* sp biomass when pH value was 4.5 and 7.5 at station 20B study area in summer season

Table 2. The removal values (%) of Pb^{2+} using *Gracilaria* sp & *Sargassum* sp biomass (pH= 4.5 and 7.5) at station 20B study area in Winter season**.**

Biomass	Initial conc. of Pb^{2+}	pH	Dosage of algae biomass (g)	Final conc. of Pb^{2+} (mg/L)	Removal of Pb^{2+} (%)
Gracilaria sp	4.4 (mg/L)	4.5 ± 0.5	0.4	0.88	80
			0.6	0.8	81.82
			0.8	0.72	83.64
			1	0.64	85.46
		7.5 ± 0.5	0.4	0.8	81.82
			0.6	0.7	84.09
			0.8	0.56	87.27
			1	0.72	83.64
Sargassum sp		4.5 ± 0.5	0.4	0.80	81.82
			0.6	0.56	87.27
			0.8	0.48	89.09
			1	0.56	87.27
		7.5 ± 0.5	0.4	1.02	76.82
			0.6	0.72	83.64
			0.8	0.56	87.27
			1	0.64	85.46

Table 3. The removal value (%) of Pb^{2+} using *Gracilaria sp* & *Sargassum sp* biomass (pH= 4.5 and7.5) at station 20B study area in Summer season.

Biomass	Initial conc. of Pb^{2+}	pH	Dosage of algae biomass (g)	Final conc. of Pb^{2+} (mg/L)	Removal of Pb^{2+} (%)
Gracilaria sp	2.5 (mg/L)	4.5 ± 0.5	0.4	0.447	82.12
			0.6	0.375	85
			0.8	0.375	85
			1	0.313	87.48
		7.5 ± 0.5	0.4	0.563	77.48
			0.6	0.313	87.48
			0.8	0.313	87.48
			1	0.265	89.4
Sargassum sp		4.5 ± 0.5	0.4	0.438	82.48
			0.6	0.373	85.08
			0.8	0.313	87.48
			1	0.250	90
		7.5 ± 0.5	0.4	0.563	77.48
			0.6	0.375	85
			0.8	0.313	87.48
			1	0.313	87.48

The contact time and kinetic models for Pb^{2+} removal by both algae:

In both seasons, the contact time of Pb^{2+} bio-sorption by both *Gracilaria sp* and *Sargassum sp* biomass was decreased to become almost constant at 60 minutes.

In winter season, the best removal value was occurred in pH value 7.5 at 120 minutes by *Gracilaria* sp biomass and 90 minutes by *Sargassum* sp biomass (Figs 6, 7 and Table 4). The R^2 value for removal process of Pb^{2+} by *Gracilaria* sp biomass, was varied from 0.9269 to 0.983 by pseudo first order and from 0.9998 to0.9997 by pseudo second order. When using *Sargassum* sp biomass, the R^2 value was varied from 0.9999 to 1 in pseudo first order and from 0.9993 to 1 in pseudo second order modal (Fig. 6 and Table.4). The calculated qe value was varied from 111 to 111.75 mg/g by *Gracilaria* sp biomass when compared with that on the graph value (109.89 to 113.64 mg/g). In the case of *Sargassum sp* biomass, the calculated qe values range was varied from 109.35 to 112.36 mg/g when compared with that obtained on the graph (112.36 - 113.636 mg/g) (Fig. 7 and Table 4).

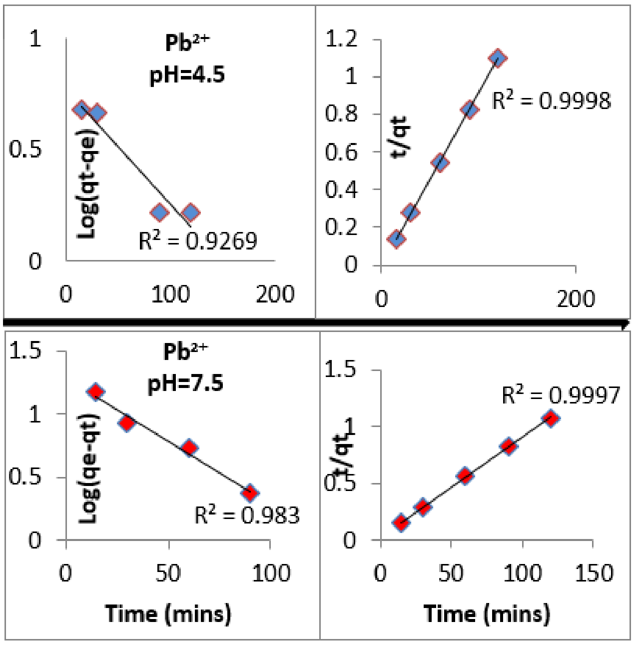

Figure 6. Kinetic models for Pb^{2+} removal and efficiency of contact time by *Gracilaria* sp in pH value 4.5 and 7.5 at 20B station in winter season.

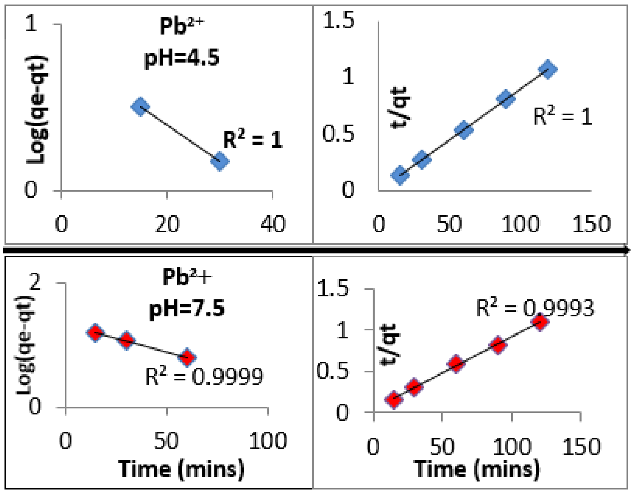

Figure 7. The kinetic models for Pb^{2+} removal and efficiency of contact time by *Sargassum* sp in pH value 4.5 and 7.5 at 20B station in winter season

In summer season, the bio-sorption equilibrium of Pb^{2+} was occurred in 90 minutes at pH value 7.5 using both algae (Figs 8 & 9 and Table 5). In the case of *Gracilaria* sp biomass, the R^2 values obtained were varied from 0.6136 to 0.6583 when applying pseudo first order and from 0.9997 to 0.999 in the pseudo second order in both pH values. By using *Sargassum* sp biomass, the R^2 values were varied from 0.6845 to 0.893 in pseudo first order and from 0.9985 to 0.9994 by pseudo second order modal (Fig.8 and Table 5).

Table 4. The kinetic models for Pb^{2+} removal by using *Gracilaria* sp and *Sargassum* sp biomass in pH values 4.5 and 7.5 at 20B station in winter season**.**

Samples	qe (mg/g)	Pseudo first-order kinetic			Pseudo second-order kinetic		
		qe (mg/g)	K_1 (min1)	R^2	qe (mg/g)	K_2(g/mg/min)	R^2
Gracilaria sp		pH=4.5					
	111	0.7699	0.0118	0.9269	109.890	0.019	0.9998
	111.75	pH= 7.5					
		1.294	0.023	0.983	113.636	0.003	0.9997
Sargassum sp		pH= 4.5					
	112.36	0.821	0.050	1	112.36	0.0240	1
		pH=7.5					
	109.35	1.3362	0.0207	0.9999	113.636	0.0021	0.9993

The calculated qe values for Pb^{2+} as removal value by *Gracilaria* sp biomass was varied from 188 to 192 mg/g in both pH values compared to that on the graph results (188.679 mg/g). In the case of *Sargassum* sp biomass, the calculated qe ranges were varied from 192 to 200 mg/g as compared to that obtained on the graph results(196.078 to 192.308 mg/g) (Fig. 9 and Table 5).

In different pH values, the R^2 values showed that pseudo second order model was better when apply the Lagrange equations for Pb^{2+} removal in both seasons at 20B station sampling area (Figs 6 to 9 and Tables 4 and 5).

4. Discussion

The seasonality of bio-sorption of Pb^{2+}:

Polluted seawater at the study area (20B station) contains high concentration of lead as one of heavy metals (Table 1) that exceed the allowable Yemeni standard values (0.05 mg/l)[36]. The concentration of Pb^{2+} in the study station was low in winter season (2.5 mg/l) than summer (4.4 mg/l) season. These are due to the seasonal increase of polluted water discharged in the study area [13]. The high level of heavy metals in the study area was associated with the increase of discharging polluted water in summer season which responsibly affected the rise of bio-sorption rate on the surface of adsorbents that increases the removal rates of Pb^{2+} metal ions [1,11,35].

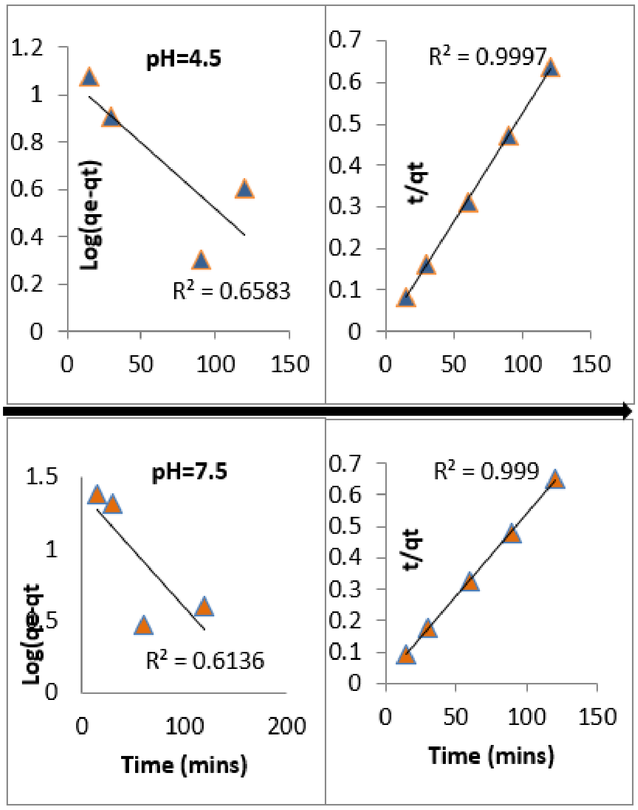

Figure 8. The kinetic models for Pb^{2+} removal and efficiency of contact time by *Gracilaria* sp in pH 4.5 and 7.5 at 20B station in summer season**.**

By using different biomass dosages of *Gracilaria* sp and *Sargassum* sp algae (at pH values of 4.5 and 7.5), the variation of removal rate of Pb^{2+},in the study station was related to the initial concentration in polluted water until the adsorbents biomass is saturated with metal ions (23 and 13). This might occurred due to increases in the surface area of the algae biomass and bonding with the effective groups through the bio-sorption process. Consequently, when removal rate of Pb^{2+} increases, the concentration of elements in polluted water was reduced [33].

The best removal rate of Pb^{2+} obtained in one gram of *Gracilaria* sp biomass was 89.4% in pH 7.5 in Winter whereas in Summer it was 90% in pH value of 4.5 and in one gram of *Sargassum* sp biomass. These results to a certain instance are coincided with that reported by (31 and 20).The brown algae, *Sargassum* sp was the best in removal of Pb^{2+} ions in pH values lower than 7.5 (in one gm biomass) when compared with *Gracilaria* sp (red algae). The results obtained in this study were in agreement with that reported by other researchers (8 and 31).

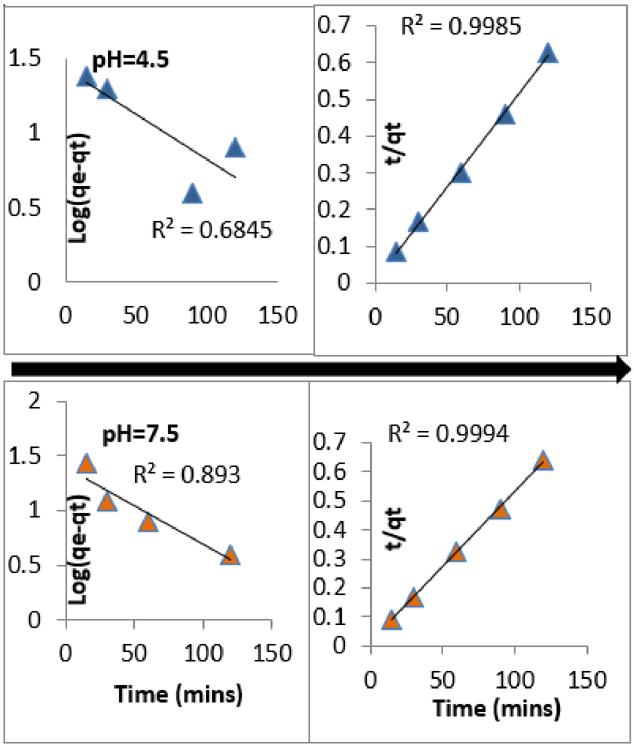

Figure 9. The kinetic models, for Pb^{2+} removal and efficiency of contact time by *Sargassum* sp in pH value 4.5 and 7.5 at 20B station in summer season**.**

Table 5. Kinetic models for Pb^{2+} removal by *Gracilaria* sp and *Sargassum* sp biomass in pH values 4.5 and 7.5 at 20B station in summer season

Samples	qe (mg/g)	Pseudo first-order kinetic			Pseudo second-order kinetic		
		qe (mg/g)	K_1(min1)	R^2	qe (mg/g)	K_2(g/mg/min)	R^2
Gracilaria sp		pH= 4.5					
	192	1.0788	0.0129	0.6583	188.679	0.0011	0.9997
		pH= 7.5					
	188	0.3873	0.0182	0.6136	188.679	0.0021	0.999
Sargassum sp		pH= 4.5					
	200	1.4324	0.0141	0.6864	196.078	0.0038	0.9985
		pH= 7.5					
	192	1.401	0.0161	0.893	192.308	0.0052	0.9994

The effect of pH value:

In the present study, the functional groups of brown algae (*Sargassum sp*) have a high removal rate of Pb^{2+} during Summer season in pH value of 4.5 than red algae (*Gracilaria sp*). Bio-sorption of Pb^{2+} may be affected by distinct pH values as well as chemical composition of adsorbents surface. It is found out that the reduction in pH value up to about 4.5 is a direct reason for an increase in adsorption capacity of Pb^{2+}removal to a certain level [20].

The low pH value decreases Pb^{2+} bio-sorption capacity through the influence of functional sites on adsorbent algae surfaces. This situation might be due to the competition between metal cations and hydrogen positive ions (H^+) which inhibit the binding of metals through bio sorption process. The findings of the present study were in agreement with that reported by other researchers (25 and 20).They pointed out that heavy metals adsorption is pH dependent through the impact on adsorbents surface charge with different structure of adsorbents and degree of ionization of metals.

When pH values are equal or higher than 7, the functional sites on adsorbent surfaces are exposed to enhance electrostatic attraction with heavy metal ions due to a negative charge. Increase in pH value leads to formation of hydroxides anionic complexes which may cause a slight decrease in adsorption forces (33 and 25). Due to the Pb^{2+} that interacts with hydroxide ion (OH^-), the deposition of these ions occurred which widely available in basal solutions [25]. So the hydroxides of these elements formed in pH value are equal to six values and more which affect the deposition and efficiency of bio-sorption, where the Pb^{2+} metal remains soluble in pH value less than seven (Tables 2 and 3). This phenomenon may cause a slight decrease in adsorption forces. So that the removal rate of Pb^{2+} ions in basal solution (pH 7.5) was low compared with that at pH value of 4.5.The results of the present study were coincided with that obtained by [2].

The effect of adsorbent biomass:

The biomass doses are an important factor which has a great influence on the bio-sorption process of pollutants. The possibility of metal ion removals from wastewater by adsorbent structure were due to availability of metal binding sites present on the adsorbent surfaces (26 and 33).

In this study, the best removal value of Pb^{2+} for the absorption process was found to be in biomass value between 0.8gm and one gm for *Gracilaria sp* and *Sargassum sp* through Winter and Summer seasons. The initial concentrations for Pb^{2+} in the study area are affected by biomass values and the removal rate increases with increasing of algae biomass (Tables 4 and 5). The remain value of the initial concentrations of Pb^{2+} ions in polluted water from the study station decreased related to increasing of bio-sorption capacity on the surface area of *Gracilaria sp* and *Sargassum sp* biomass. This situation allowed the entry of Pb^{2+} and their association with effective groups in biomass particularly during bio-sorption in summer season for polluted water [16]. These findings indicated that the absorption characteristic leads to surface saturation of adsorbents which depend on the initial concentrations of metal ions (26 and 35).

The efficiency of contact time on bio-sorption:

The efficiency of contact time for Pb^{2+} removal in pH value 4.5 shows that the initial phase lasted for 15 minutes followed by slower phases until reached the equilibrium state at 60 minutes by *Sargassum sp* and *Gracilaria sp* biomass through the concentration gradient between the liquid phase and the solid surface. As contact time increased, intra-particle diffusion became predominant which makes the solute took more time to diffuse into internal sorption sites through the pores[17]. After attaining equilibrium, the process of bio-sorption is very slow and bio-sorption reduced. The efficiency of contact time in pH value 7.5 to remove high value of Pb^{2+} was 90 minutes in one gram dose by *Sargassum* sp and 90-120 minutes by *Gracilaria sp* in both seasons. Similar results were reported by other researchers in removal of Pb^{2+} ions from polluted waters (17,18 and 35).

The kinetic modeling of bio-sorption by *Gracilaria* sp and *Sargassum* sp :

The correlation coefficients (R2) obtained from the pseudo-second order rate kinetic model were greater than 0.99 for all of the initial Pb2+ ion concentrations (Tables 4&5). The bio-sorption of Pb^{2+} by *Gracilaria sp* and *Sargassum* sp biomass in the present study follows the pseudo-second order kinetic model. The (R_2) for the pseudo-second order is more suitable for different pH values in both seasons and for both algae species (Table 3 and 4). The values of the present study are in agreement with that reported by other researchers in other sudy areas (24 and 26).

References

[1] S. H. Abbas, I. M. Ismail, T. M. Mostafa, and A. H. Sulaymon, "Biosorption of heavy metals: a review," *J Chem Sci Technol*, vol. 3, pp. 74-102, 2014.

[2] S. Ahmady-Asbchin, Y. Andres, C. Gérente, and P. Le Cloirec, "Biosorption of Cu (II) from aqueous solution by Fucus serratus: surface characterization and sorption mechanisms," *Bioresource Technology*, vol. 99, pp. 6150-6155, 2008.

[3] M. Ajmal, A. H. Khan, S. Ahmad, and A. Ahmad, "Role of sawdust in the removal of copper (II) from industrial wastes," *Water research*, vol. 32, pp. 3085-3091, 1998.

[4] M. Al-Eryani, Minister of water and environment. Environment Protection Authority (EPA). Yemen's national program of action for the protection of the marine environment. From Land-Based activities (NPA). Yemen, p.1-144. 2006.

[5] E. A. D. A. W. W. A. W. E. F. American Public Health Association, *Standard methods for the examination of water and wastewater*. Washington, D.C.: APHA-AWWA-WEF, 2005.

[6] K. Andersson, *Sanitation, wastewater management and sustainability: from waste disposal to resource recovery*: UN Environmental Programme Global Programme of Action for the protection of …, 2016.

[7] M. E. Argun, S. Dursun, C. Ozdemir, and M. Karatas, "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics," *Journal of hazardous materials*, vol. 141, pp. 77-85, 2007.

[8] Y. G. Bermúdez, I. L. R. Rico, O. G. Bermúdez, and E. Guibal, "Nickel biosorption using Gracilaria caudata and Sargassum muticum," *Chemical Engineering Journal,* vol. 166, pp. 122-131, 2011.
[9] A. Buasri, N. Chaiyut, K. Tapang, S. Jaroensin, and S. Panphrom, "Removal of Cu2+ from aqueous solution by biosorption on rice straw-an agricultural waste biomass," *International Journal of Environmental Science and Development,* vol. 3, p. 10, 2012.
[10] S. Clearwater, S. Baskin, C. Wood, and D. McDonald, "Gastrointestinal uptake and distribution of copper in rainbow trout," *Journal of Experimental Biology,* vol. 203, pp. 2455-2466, 2000.
[11] J. Cullinane, T. Doyle, and P. Whelan, "Uses of seaweeds as biomonitors of zinc levels in Cork Harbour, Ireland," in *Twelfth International Seaweed Symposium*, pp. 285-290, 1987.
[12] T. A. Davis, F. Llanes, B. Volesky, G. Diaz-Pulido, L. McCook, and A. Mucci, "1 H-NMR study of Na alginates extracted from Sargassum spp. in relation to metal biosorption," *Applied biochemistry and biotechnology,* vol. 110, pp. 75-90, 2003.
[13] A. M. El-Sabbagh, M. I. Ibrahim, A. R. Mostafa, N. O. Al-Habshi, and M. R. Abdel Kireem, "Benthic foraminiferal proxies for pollution monitoring in Al-Mukalla coastal area, Hadramout Governate, Republic of Yemen," *The Journal of Foraminiferal Research,* vol. 46, pp. 369-392, 2016.
[14] S. Farías, S. P. Arisnabarreta, C. Vodopivez, and P. Smichowski, "Levels of essential and potentially toxic trace metals in Antarctic macro algae," *Spectrochimica Acta Part B: Atomic Spectroscopy,* vol. 57, pp. 2133-2140, 2002.
[15] G. T. Goodman and T. Roberts, "Plants and soils as indicators of metals in the air," *Nature,* vol. 231, pp. 287-292, 1971.
[16] M. A. Hanif, R. Nadeem, H. N. Bhatti, N. R. Ahmad, and T. M. Ansari, "Ni (II) biosorption by Cassia fistula (Golden Shower) biomass," *Journal of Hazardous Materials,* vol. 139, pp. 345-355, 2007.
[17] W. M. Ibrahim, "Biosorption of heavy metal ions from aqueous solution by red macroalgae," *Journal of Hazardous Materials,* vol. 192, pp. 1827-1835, 2011.
[18] I. WM, S. Yasmeen, M. Soha, and S. Nahed, "Comparative Study for Biosorption of Heavy Metals from Synthetic Wastewater by Different Types of Marine Algae," *J Bioremediat Biodegrad,* vol. 9, p. 2, 2018.
[19] J. Igwe and A. Abia, "Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co (II), Fe (II) and Cu (II) ions from waste water using modified and unmodified maize cob," *International Journal of Physical Sciences,* vol. 2, pp. 119-127, 2007.
[20] V. Jayakumar and S. Govindaradjane, "Biosorption of cadmium by green algae–a review," *Journal of Advanced Chemical Sciences,* pp. 480-484, 2017.
[21] D. Kaplan, "Absorption and adsorption of heavy metals by microalgae," *Handbook of microalgal culture: applied phycology and biotechnology,* vol. 2, pp. 602-611, 2013.
[22] S. K. Lagergren, "About the theory of so-called adsorption of soluble substances," *Sven. Vetenskapsakad. Handingarl,* vol. 24, pp. 1-39, 1898.
[23] S. Mehta and J. Gaur, "Use of algae for removing heavy metal ions from wastewater: progress and prospects," *Critical reviews in biotechnology,* vol. 25, pp. 113-152, 2005.
[24] R. Nabizadeh, K. Naddafi, and R. Saeedi, "Biosorption of lead (II) and cadmium (II) from aqueous solutions by protonated Sargassum sp. biomass," *Biotechnology,* vol. 5, pp. 21-26, 2005.
[25] S. M. H. Nasab, A. Naji, and M. Yousefzadi, "Kinetic and equilibrium studies on biosorption of cadmium (II) from aqueous solution by Gracilaria corticata and agar extraction algal waste," *Journal of Applied Phycology,* vol. 29, pp. 2107-2116, 2017.
[26] M. Niad, L. Rasoolzadeh, and F. Zarei, "Biosorption of copper (II) on Sargassum angostifolium C. Agardh phaeophyceae biomass," *Chemical Speciation & Bioavailability,* vol. 26, pp. 176-183, 2014.
[27] R. Ofer, A. Yerachmiel, and Y. Shmuel, "Marine macroalgae as biosorbents for cadmium and nickel in water," *Water Environment Research,* vol. 75, pp. 246-253, 2003.
[28] Protocol Concerning the Protection of the Environment from Land-Based Activities in the Red Sea and Gulf of Aden. (Sep 25. 2005). Treaty: Multilateral .Saudi Arabia .Jeddah .(Source: IUCN (ID: TRE-160049).
[29] A. Sarı and M. Tuzen, "Biosorption of Pb (II) and Cd (II) from aqueous solution using green alga (Ulva lactuca) biomass," *Journal of Hazardous Materials,* vol. 152, pp. 302-308, 2008.
[30] M. Stasiak, "Application of biosorption process for renovation of waste waters at chemical industry," *Przemysl Chemiczny,* vol. 48, pp. 426-&, 1969.
[31] D. J. Sweetly, K. Sangeetha, and B. Suganthi, "Biosorption of heavy metal lead from aqueous solution by non living biomass of Sargassum myriocystum," *Inter. Journal of Appl or Inno. in Eng. and Management,* vol. 3, p. 4, 2014.
[32] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, "Heavy metal toxicity and the environment," *Molecular, clinical and environmental toxicology,* pp. 133-164, 2012.
[33] L. A. Thijar, A. A. Al-Hussieny, H. S. Naji, and R. M. Talib, "Biosorption of lead, cadmium and nickle from industrial wast water by using dried macroalgae," *Baghdad Science Journal,* vol. 11, 2014.
[34] H. D. Utomo, K. X. D. Tan, Z. Y. D. Choong, J. J. Yu, J. J. Ong, and Z. B. Lim, "Biosorption of heavy metal by algae biomass in surface water," *Journal of Environmental Protection,* vol. 7, pp. 1547-1560, 2016.
[35] F. Vendruscolo, G. L. da Rocha Ferreira, and N. R. Antoniosi Filho, "Biosorption of hexavalent chromium by microorganisms," *International Biodeterioration & Biodegradation,* vol. 119, pp. 87-95, 2017.
[36] World Health Organization (WHO) (1984). Water Quality Indicators (vol. 1,2,3). Websites: https://www.google.com/maps/place/\@14.4885724,49.0574339, 2018.

إزالة الرصاص (II) من المياه البحرية الملوثة في سواحل مدينة المكلا– حضرموت باستخدام تقنية الكتلة الجافة من مسحوق الطحالب البحرية الكبيرة؛ *Gracilaria sp* و*Sargassum sp*

عبدالله سالم باوزير وإيمان حسن باعثمان

الملخص: يتناول هذ البحث, دراسة إزالة أيونات الرصاص (Pb^{2+}) كأحد المعادن الثقيلة في المياه البحرية من سواحل مدينة المكلا الملوثة بمياه الصرف الصحي باستخدام تقنية الكتلة الجافة من الطحالب البحرية الكبيرة. جمعت عينات من المياه الملوثة من منطقة بجانب إحدى محطات الصرف الصحي (B20) في ساحل المكلا. استخدم مسحوق الطحالب الكبيرة الجافة لكل من النوع *Gracilaria sp* والنوع *Sargassum sp* , لدراسة امتزاز أيون معدن الرصاص من المياه البحرية الملوثة في منطقة الدراسة. ترمي هذه الدراسة إلى تقويم خاصية الإزالة لأيونات المعدن الثقيل ,الرصاص من المياه البحرية الساحلية لمدينة المكلا الملوثة بمياه الصرف الصحي باستخدام الطحالب البحرية الكبيرة . تمت دراسة تأثير قيم مختلفة من pH (0.5 ± 7.5 & 4.5) وكميات مختلفة من مسحوق الطحالب على خاصية الامتزاز في فصلي الصيف والشتاء، حيث استخدمت نسبة الإزالة لأيون معدن الرصاص لتوصيف هذه الخاصية وتأثيرها في إزالة المعادن الثقيلة من المياه الملوثة. تعرف هذه التقنية بأنها إحدى التقنيات الصديقة للبيئة حيث تعمل على إزالة الملوثات بتأثير المجاميع الفعالة في جدران الطحالب البحرية دون إحداث أية تأثيرات بيئية عرضية أخرى . أظهرت النتائج في منطقة الدراسة أن نسب الإزالة لأيون الرصاص (Pb^{2+}) تراوحت ما بين80.00% إلى % 90.00 عند قيمة pH 4.5 وكذلك تراوحت نسبة الإزالة ما بين 76.82% إلى 89.4%عند قيمة pH 7.5 خلال فصلي الشتاء والصيف على التوالي. استخدمت تقنية التحليل الطيفي للكتلة الحيوية للطحالب (FTIR) للكشف عن المجاميع الفعالة على أسطح جدران الطحالب من خلال الأطوال الموجية المعبرة عن تغاير ترددات هذه الموجات لعينات الطحالب المستخدمة , حيث بينت أن المجاميع الفعالة المحتملة في عملية امتزاز العناصر الثقيلة باستخدام الطحالب البحرية هي C–O, O–H و , N–H كما أظهرت هذه التقنية المواقع المحتملة لارتباط أيون الرصاص (Pb^{2+}) وذلك بوجود المجاميع الفعالة التي تشمل مجاميع الكاربوكسيل والهيدروكسيل في مسحوق كل من الطحالب البحرية (*Gracilaria sp* و *Sargassum sp*) التي توجد في ضمن تركيب جدران الخلايا الطحلبية .

كلمات مفتاحية: امتزاز, إزالة, طحالب كبيرة, تقنية صديقة للبيئة, مجاميع فعالة