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BIOSORPTION CAPACITY OF HEAVY METAL LEAD (Pb(II)) USING DRY SEAWEED Eucheuma denticulatum

(Kapasiti Biojerapan Logam Berat Plumbum (Pb(II)) Mengunakan Rumpai Laut Kering Eucheuma denticulatum)

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Abstract

The seaweed industry plays a significant socio-economic role in tropical coastal communities. This study presents the biosorption behaviour of Pb(II) aqueous solution onto seaweed E. denticulatum. The impact of pH contact time, the initial concentration of the metals, and the adsorption-desorption activities were studied. The findings demonstrated that the Pb(II) uptake rate rose with increased concentration and contact time. The Pb(II) uptake reached saturation at 1000 mg/L after 120 min at room temperature. Pb(II) biosorption onto $Eucheuma\ denticulatum$ fitted well to the Langmuir isotherm, with a maximum adsorption capacity (q_{max}) of 416.67 mg/g. The results suggest that this type of seaweed, E. denticulatum, is an effective biosorbent for removing Pb (II) and may control toxic metal pollution in tropical aquatic ecosystems.

Keywords: biosorption, Eucheuma denticulatum, heavy metals, Langmuir and Freundlich models

Abstrak

Industri rumpai laut memainkan peranan sosio-ekonomi yang sangat penting bagi masyarakat pesisir pantai tropika. Kajian ini menunjukkan tingkah laku biojerapan larutan akues Pb(II) ke atas *Eucheuma denticulatum*. Pengaruh hubungan masa pH, kepekatan awal logam, dan kajian penjerapan-penyerapan telah dilakukan. Hasil kajian menunjukkan bahawa kadar pengambilan Pb(II) meningkat dengan peningkatan kepekatan dan masa hubungan. Pengambilan Pb(II) mencapai titik tepu pada 1000 mg/L setelah 120 minit pada suhu bilik. Biojerapan Pb(II) ke atas *E. denticulatum* dipasang dengan baik pada isoterm Langmuir dengan kapasiti penjerapan maksimum (q_{max}) 416.67 mg/g. Hasilnya menunjukkan bahawa rumpai laut *E. denticulatum* adalah biopenjerap yang berkesan untuk menghilangkan Pb(II) dan mungkin boleh digunakan untuk mengawal pencemaran logam toksik di ekosistem perairan tropika.

Kata kunci: biojerapan, Eucheuma denticulatum, logam berat, model Langmuir dan Freundlich

Introduction

Heavy metal pollution is a serious concern due to its profound impact, even at small concentrations. It is caused by enhanced industrialisation and human activities that release various contaminants into the environment [1, 2, 3]. Heavy metals are considered among the most toxic groups reaching the food chain via waste disposal in water bodies and on land [4]. Therefore, eliminating heavy metal ions in wastewater is crucial for public health protection. The conventional methods for treating toxic metals are expensive and difficult to manage. Some methods lead to ineffective metals removal, restricted tolerance to pH change, slight metal selectivity, and the generation of toxic by-product waste that must be appropriately disposed of [5]. Attention has focused on heavy metals biosorption using various biological materials as this enables a higher metal binding capacity than chemical-based methods [6, 7].

Biosorption is a subtraction technique directed at contaminants or pollutants through inactive biomass, which allows the contaminants to be passively concentrated and bound to their cellular structure. Several absorbent materials have previously been used, including algae [8], fungi [9], bacteria [10], seaweeds [11], and some higher plants [12]. Several studies have assessed the efficiency of using different biosorbent materials for treating heavy metals in wastewater. For example, Tabaraki et al. [13] assessed the efficiency of brown seaweed on Pb(II) ions biosorption. At optimal conditions, they found the maximum seaweed uptake for the Pb(II) ions uptake to be 195±3.3 mg/g. The study of peanut shell efficacy on Pb2+ ions was carried out by Taşar et al. [14], and 39 mg/g was the maximum uptake obtained. The biosorption capacities of olive mill solid (OMS) and olive stone (OS) on Pb2+ ions uptake were examined by Blázquez et al. [15] in batch experiments under varied temperatures. The results revealed that the maximum Pb uptake was 6.57 mg/g on OS and 23.69 mg/g on OMS at 25 °C. Gerola et al. [16] investigated the biosorption capacity of the residue of passionfruit skin onto Pb2+ ions and found that the maximum

biosorption capacity was 204 mg/g at pH 4 for 170 min. Senthilkumar et al. [17] evaluated the biosorption functions of ten (10) different seaweed species on Pb²⁺ ions uptake under varied pH environments. The brown seaweed Turbinaria Conoides displayed optimal Pb2+ ions uptake of 439.4 mg/g at pH 4.5 and a temperature of 30 °C. The work of Abdel-Aty et al. [18] presented the applicability of Blue-Green Alga Anabaena Sphaerica as a biosorbent of Cd²⁺ and Pb²⁺ ions from aqueous solutions. The ideal biosorption capacity was 111.1 mg/g and 121.95 mg/g, respectively, at peak conditions. The adsorption capacities of Macroalgae Eucheuma Spinosum, Padina Minor, and Sargassum Crasifollum were assessed by Putri [19] for their Pb²⁺ biosorption. The maximum biosorption capacity (55.56 mg/g) was demonstrated by Sargassum Crasifollum, followed by Padina Minor (40.00 mg/g), while the lowest (32.26 mg/g) was demonstrated by Eucheuma Spinosum. Studies on Pb²⁺ ions adsorption from aqueous solutions using raw and chemically modified green freshwater algae (Scenedesmus Obliquus) were conducted by Abdel Ghafar et al. [20]. The modified biomass was found to have higher biosorption capacity (207.2 mg/g) compared to raw biomass (112.0 mg/g). Therefore, algae have proven to be a more efficient and promising biosorbent to use for heavy metal removal from wastewater. The biosorption method is comparatively inexpensive and it offers elevated efficiency in terms of metal removal, as well as minimum chemical and/or biological sludge production, among others [21].

Algae biosorbent materials are gaining significant attention due to their abundance in the oceanic environment, relative easiness to process, and high accumulated ability of metal content. Algal-like seaweed is sufficient to facilitate a complex solid-liquid separation process, thus making seaweed a suitable form of biomass for heavy metal biosorption in the marine environment [22]. Seaweeds are marine algae found in coastal areas. The red algae *Eucheuma cottonii* and *Eucheuma denticulatum* are grown in eastern Africa's tropical coastal regions [23, 24]. The seaweed industry

in Tanzania employs more than 30,000 people [25]. Approximately 5,000 tons of dry seaweed are exported annually from Tanzania [25]. The high production of seaweed in Tanzania has motivated the authors to propose this substance as a potential biosorption material.

Heavy metal pollution has recently gained scientific attention due to its ubiquity in marine and coastal ecosystems [26]. Heavy metals' pathways into the human body are through food, water, and air. They are absorbed through the skin or by exposure from various agricultural, manufacturing, pharmaceutical, and urbanisation activities. Lead (Pb) is among the heavy metals proving to be the most serious toxic contaminant in Tanzania [27, 28, 29].

Previous studies have demonstrated the high metal-binding abilities of brown and green seaweeds [30, 31, 32]. However, there is a lack of data on the heavy metal biosorption by red seaweed species (*E. denticulatum*) in Tanzania. Therefore, this study discusses the biosorption behaviour of Pb(II) solution onto *E. denticulatum*. The findings from this study on *E. denticulatum* as a potential biosorption material of toxic metals have extensive consequences for the economy and health of farmers engaged in seaweed aquaculture in the coastal areas of Tanzania.

Materials and Methods

Study area

This study was conducted in three locations (Unguja Ukuu, Tumbe, and Kiungoni) along the coastal areas of Zanzibar. Tumbe and Kiungoni are located in the northern part of Pemba Island (Figure 1), while Unguja Ukuu is situated in the southern part of Unguja island (Figure 2). Seaweed farming is mainly found in these areas. Fresh seaweed *E. denticulatum* samples were cleaned carefully on-site with ocean water to eliminate impurities.

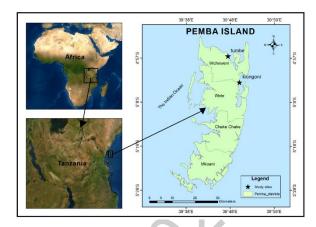


Figure 1. The sampling areas in the Pemba Island coastal region

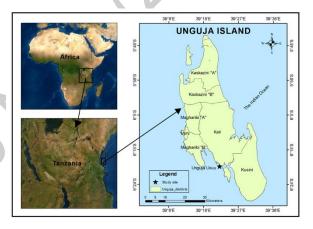


Figure 2. The sampling area in the Unguja Island coastal region

Sample preparation

The seaweed samples were washed with tap water, before being washed again with deionised water to eradicate salts and particulate matter from the surface of samples. The samples were then air-dried for 48 hours and then oven-drying at 80 °C for 24 hrs. The dried samples were ground into a homogeneous powder using a laboratory blender and stored in a desiccator before the biosorption experiments were conducted.

Pb(II) ions solution preparation

Pb(II) ions stock solution was prepared by dissolving 1.60g of Pb (NO)₃ in 1000 ml of deionised water. The different concentrations of Pb(II) solutions (50, 100, 250, 500, 1000, 1500, and 2000 mg/L were prepared by diluting the stock solution. The initial pH of the standard solutions was adjusted to the desired value by adding 0.1 M HCl or 0.1 M NaOH. The analytical grade of chemicals from Merck was used in this study. The concentrations of the standard solutions of 0.20, 1.00, 2.00, 7.00, 10.00, and 20.00 mg/L were precisely prepared.

Preliminary concentration of Pb(II) in E. Denticulatum

The initial Pb(II) ions levels were determined using a modified version of the methods devised by Luis et al. [33] and Rubio et al. [34]. Next, 25 g of *E. denticulatum* was oven-dried at 70 °C for 12 hours. Then, the sample was burned in a furnace at 550 °C for 20 hours to remove the organic matter. The ash of the sample was digested in 2 mL of HNO₃ (v/v) for 18 hours. The digested solution was filtered with a filter paper (Whatman no 2) and transferred into a 50 mL test tube. The solution was meshed up to 30 mL with deionised water. The atomic absorption spectrometer (AAS) Thermo Scientific model iCE 3300 was used to determine the Pb(II) ion concentrations.

Batch biosorption experiments

The batch biosorption experiments were established using a magnetic stirrer (120 - 180 min) at 120 rpm in a 250 mL beaker. Next, 50 mL of the standard solution was introduced into the beaker and biosorbent was added appropriately. The different parameters were organised as follows: solution pH (2-8), contact time (0-150 minutes), initial Pb(II) ion concentration (50-2000 mg/L). The Pb (II) ion biosorption characteristics were evaluated using a biomass weight of 0.5 g. The solution was separated using a Whatman filter paper No 2 or centrifuging and decanting.

Optimum pH for Pb(II) biosorption

The Pb(II) biosorption optimum pH was established by adding 50 mL solutions of 50 mg/L Pb (II) ions into a 100 mL centrifuge tube with 0.5 g of dry seaweed. The samples, which were of varying pH (2.0 to 8.0), were adjusted using 0.1 M NaOH or 0.1 M HNO₃ [35]. The mixtures were stirred for 180 minutes with a magnetic stirrer at room temperature. The supernatant was collected after centrifuging the mixture using the Gallen Kamp Centrifuge 200 at the lowest rate for 10 minutes. The AAS was used to determine the Pb(II) ion concentration in the supernatant. The analysis of each sample was performed in a duplication setting.

Optimum contact time for Pb(II) adsorption

The optimum contact time for Pb(II) adsorption was determined at optimum pH by adding 0.5 g biomass to 50 mL of the 50 mg/L metal solution. The mixture was stirred for 180 min using a magnetic stirrer at moderate speed at room temperature. At 5, 10, 30, 60, 120, and 180 min, the samples were removed, centrifuged, decanted. The supernatant was collected and stored for AAS analysis. The samples were prepared in duplicate.

The effect of Pb(II) ion concentration on biosorption

The effect of Pb(II) ion concentration on biosorption was investigated by mixing 0.5 g of seaweed and 50 mL of solutions of known concentrations at room temperature. The Pb(II) ion concentration levels were 50, 100, 250, 500, 1000, 1500, and 2000 mg/L. The solution mixture was corrected to the required pH with HNO₃ or NaOH solution before it was stirred with a magnetic stirrer at moderate speed and room temperature for 120 minutes. The samples were decanted using a Gallen Kamp Centrifuge 200 centrifuge for 20 minutes. The supernatants were then kept in centrifuge tubes and determined using the Atomic Absorption Spectrometer (AAS). This process was performed in duplicate.

Biosorption models

The Langmuir and Freundlich isotherm models were used to calculate Pb(II) biosorption from the aqueous solutions. The following is a linearised Langmuir equation [36]:

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{b \cdot q_{max} C_f} \tag{1}$$

where q_{max} is the Langmuir adsorption capacity (mg/g) and b is the adsorption energy (l/mg). The intercept and slope from the 1/q Vs 1/C_f graph were used to calculate q_{max} and b.

The following equation represents the Freundlich isotherm linear form [37]:

$$\log q = \log K + \frac{1}{n} \log C_f \tag{2}$$

where K is the Freundlich constant correlated to adsorption capacity, and n is the adsorption intensity. Furthermore, the separation factor R_L describes the essential characteristics of the Langmuir isotherm [38]:

$$R_L = \frac{1}{1 + bq_{max}} \tag{3}$$

Kinetic adsorption study

Adsorption kinetics is a significant aspect of biosorption studies since it presents valuable information concerning adsorption mechanisms and allows the investigation of the controlling biosorption mechanism. The assessment of Pb^{2+} ions adsorption kinetics onto *E denticulatum* was conducted using pseudo-first-order and pseudo-second-order kinetics. The pseudo-first-order equation was devised by Febrianto et al. [39]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}$$

where q_e and q_t (mg/g) are the equilibrium and time t, respectively, of the adsorption capacities. k_1 (min⁻¹) is the pseudo-first-order adsorption rate constant. The linear correlation of $\log(q_e-q_t)$ versus t implies that the reaction fits with the pseudo-first-order reaction. The slope and the model's intercept, respectively, give k_1 and q_e .

According to Ho and Ofomaja [40], the pseudo-second-order reaction is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 (g mg⁻¹min⁻¹) is the rate constant for the pseudo-second-order adsorption model. The linear

relationship from the $\frac{t}{q_t}$ versus t plot gives the values of q_e and k_2 from the slope and intercept, respectively.

Results and Discussion

The initial levels of Pb(II) in seaweed

The initial concentration of Pb (II) detected in E. denticulatum was 0.084 µg/g. The results indicate that only trace amounts of Pb(II) were present in the E. denticulatum samples. The lead levels in Zanzibar's coastal areas range from 228 to 1150 ppm [41]. It was surmised that the trace value might be attributed to the anthropogenic sources and/or the natural background value.

Optimum pH for the biosorption of Pb(II)

The solution pH plays a vital role in controlling the metal ions biosorption of metal ions from aqueous solutions [42]. The findings presented in Figure 3 indicate that the removal of Pb(II) was low in an acidic medium (pH < 4). As pH increased, the metal uptake also increased until pH 4. Afterwards (beyond pH > 4), it showed a rapid decline. At low pH, the biosorption capacity was low due to the competition for binding sites on the biomass surface between the H+ ions and the metal ions [43, 44]. Therefore, repulsive forces between the metal ions and the protonated biomass cell wall prevent the metal ions from approaching the cell wall [38]. However, as pH increased, the concentration of H⁺ ions declined. The biomass became more negatively charged, resulting in the electrostatic attraction of the positive charge metal ions. Therefore, biosorption rose to its maximum point [45, 46, 47] before the precipitation of metal hydroxides occurred at higher pH due to the high OH- ion concentration. This resulted in a decline in uptake capacity [48] and the electrostatic repulsion between the negatively charged anionic species in the solution [49]. This study revealed that the adsorption rate of Pb(II) ions was optimum at pH 4 and with a concentration of 4.7 mg/g. Therefore, the findings suggest that pH 4 is the most effective pH to use for Pb (II) biosorption, based on the range investigated (Figure 3).

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Various biosorption studies employing algal biomass have demonstrated similar results (that pH 4 is the optimum pH). These include the works by Yipmantin et al. [50] using *Chondracanthus* (red alga); Lee and

Park, [51] using brown seaweeds; and Nessim et al. [52] using *Ulva fasciata*, green seaweed and *Sargassum sp.*, brown seaweed.

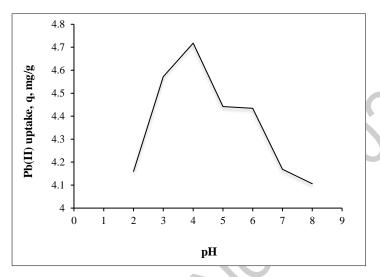


Figure 3. Variation of Pb(II) uptake of E. denticulatum with pH

Optimum contact time for Pb(II) biosorption

The metal ions biosorption in aqueous solutions is highly influenced by contact time, as shown in Figure 4. The results from this research study demonstrated that Pb(II) uptake onto *E. denticulatum* increased with longer contact times. Initially, during the first 20 minutes, there was a rapid Pb (II) uptake and a gradual increase until equilibrium at 120 minutes. Meanwhile, no further changes in biosorption were noticed beyond 120 minutes. Thus, 120 minutes can be considered the ideal contact time in other biosorption experiments.

The sharp increase in biosorption during the early stage was likely due to the high solute concentration gradient [53] and the availability of vacant active sites on the biomass surface. Thus, the adsorption of metal ions took

place on these sites [54, 55]. In the subsequent stages, the metal removal declined because the active sites were gradually occupied [56] and there was difficulty occupying the residual binding spots due to the forces between the solid and bulk phases [57, 58].

Several biosorption studies have demonstrated that metal ions adsorption employing algal biomass attained maximum adsorption in the interval between 60 and 120 min. These include the works of Ibrahim, [59] using *Corallina mediterranea, Galaxaura oblongata, Jania rubens*, and *Pterocladia capillacea* (red macroalgae); Ozudogru, [60] using *Padina pavonica* (brown algae); and Abdel-Aty et al. [18] using *Anabaena sphaerica* (freshwater alga).

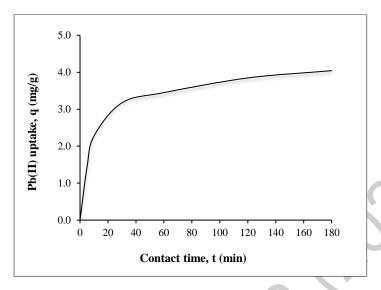


Figure 4. Effect of contact time on Pb(II) adsorption

Effect of initial metal ion concentration on Pb(II) biosorption

The initial metal ion concentration highly affects the biosorption capacity due to a substantial driving force that eliminates the resistance of all the metal ions between the aqueous and solid phases [61]. The present study demonstrated a rapid increase in Pb(II) biosorption with increased metal ion concentration until 1000mg/L, as shown in Figure 5. The metal uptake increased slowly, implying that the biomass had approached the saturation point [62].

The increased Pb(II) uptake during the early stage might be due to the enhanced driving force of metal ions into the biomass surface and the presence of abundant binding spots on the biosorbent surface areas [63, 64]. Consequently, when the Pb(II) ion concentration increases further, the active sites are overburdened by the ions, thereby preventing further metal ions adsorption [64, 65]. Thus, the metal uptake was enhanced with an increase in the initial levels of Pb(II) ions, reaching saturation when Pb(II) concentration attained a threshold value.

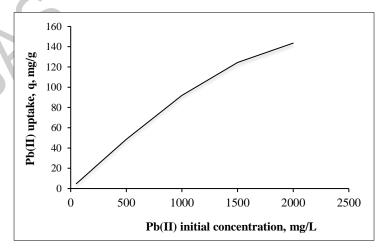


Figure 5. Effect of initial Pb (II) concentration on Pb(II) biosorption onto E. denticula

Biosorption models

The Freundlich and Langmuir models are isotherm models used to present the relation between equilibrium metal biosorption (q) and final concentration (C_f) at equilibrium [66]. Both adsorption models were used to measure the relationship between the Pb (II) uptake capability (q) and equilibrium concentration (C_f) . The constants and correlation coefficients of the adsorption models employed were determined from the respective adsorption isotherms (Table 1). It was found that the Langmuir model ($R^2 = 0.9935$) fitted well, compared with the Freundlich model ($R^2 = 0.9534$). The high Langmuir correlation coefficient suggests conformity of the P(II) adsorption to the model, implying the existence of monolayer adsorption conditions in the Pb (II) – E. denticulatum system [67].

The maximum Langmuir monolayer Pb(II) uptake capacity (q_m) and the Langmuir constant (b) isotherm were 175.13 mg/g and 0.01476 l/mg, respectively, implying the high uptake of Pb(II) by the biomass, which might have been due to its low capability of

forming complex [68]. The presence of carboxylate polysaccharides in seaweed promotes the binding of cations with large ionic areas [69]. Moreover, the range of the Pb(II) ions separation factor, $R_L = 0.2789$, fell between 0 and 1 (0 < R_L < 1), implying that Pb(II) adsorption is favourable at all the concentrations studied [70].

The slopes and intercepts from the linear graphs (Figures 6 and 7) were used to compute the Langmuir and Freundlich isotherm constants, and the results are summarised in Table 1.

The magnitude of the Freundlich constant K suggests the high adsorption capacity of Pb(II) ions on E. denticulatum. The value of n = 1.67 (n > 1) indicates that under the given experimental conditions, the heterogeneity of the biomass surface and the metal ions were adequately and intensively adsorbed by the dried seaweed E. denticulatum.

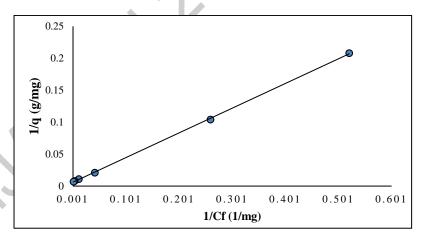


Figure 6. Langmuir isotherm for Pb (II) biosorption by E. denticulatum

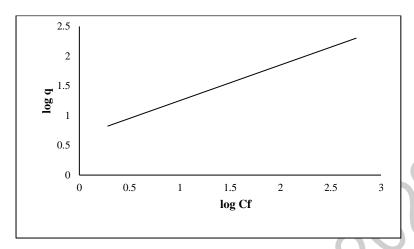


Figure 7. Linearised Freundlich isotherm for Pb(II) biosorption by E. denticulatum

Table 1. The Langmuir and Freundlich parameters and correlation coefficients for the biosorption of Pb (II) onto *E. denticulatum*

Metal	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters			
	q _{max} , mg/g	<i>b</i> , l/mg	R^2	K, mg/g	1/n	n	R^2
Pb	175.13	0.01476	0.9991	4.517	0.632	1.67	0.9272

Kinetic studies

The Pb²⁺ ions adsorption rate onto *E.denticulatum* was estimated for contact times ranging from (0-180) min. The experimental data were interpreted using pseudofirst-order and pseudo-second-order kinetic models. The kinetic parameters and regression coefficients were obtained from their corresponding linear graphs (Figures 8 (a) and (b)) and these are summarised in Table 2. The $\log(q_e-q_t)$ Vs. t plot gives an approximate line, and the rate constant (k_1) and q_e can be estimated from the slope and the intercept, respectively. The k_1 , q_e , and R^2 are shown in Table 2. Even though the plot is linear and the R^2 is 0.911, the

value of q_e does not agree with the experimental q_e value (4.044). Therefore, Pb(II) adsorption does not follow pseudo-first-order kinetics.

The pseudo-second-order kinetic model was employed to find a more trustworthy Pb (II) adsorption kinetics description. The results from the $\frac{t}{q_t}$ Vs. t plot indicates that the pseudo-second-order kinetic model fits the metal adsorption experiment. The regression coefficient (R²) was 0.998, and the q_e equals 4.3802 mg/g, which is close to the experimental q_e (4.044mg/g).

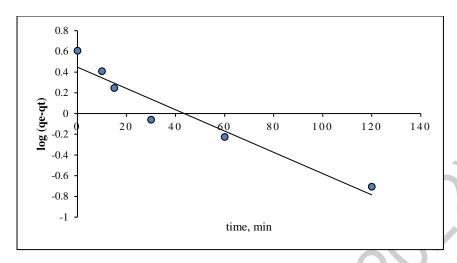


Figure 8(a). Pseudo-first-order for Pb(II) adsorption kinetics onto E. denticulatum

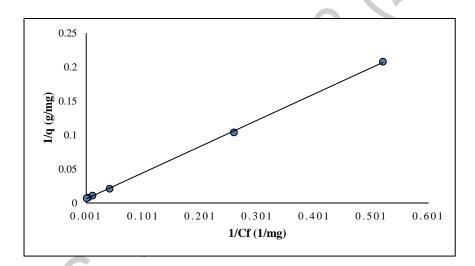


Figure 8(b). Pseudo-second-order for Pb(II) adsorption kinetics onto E. denticulatum

Table 2. The pseudo-first-order and pseudo-second-order kinetics parameters and correlation coefficients for the Pb (II) adsorption kinetics onto *E. denticulatum*

Pseudo-f	ïrst-order kinet	ics	Pseudo-second-order kinetics			
K ₁ (min ⁻¹)	qe (mg g ⁻¹)	\mathbb{R}^2	K ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)	\mathbb{R}^2	
2x20.0237	2.801	0.911	0.0148	4.3802	0.998	

Conclusion

The present study demonstrated that the seaweed E. denticulatum was an effective biosorbent of Pb^{2+} from aqueous solutions. The availability of biomass and its

cost-effectiveness are additional benefits that make it a potential biosorbent for treating heavy metals in the marine environment. The impact of processing constraints - including pH, metal ion concentrations, and

absorption period - significantly affected the equilibrium process. The Pb²⁺ uptake increased with the increase in metal ion concentration. It was also ascertained that the metal uptake increased with the rise in pH until pH 4; thereafter, the metal uptake began to decline. The Langmuir model might better represent the adsorption isotherms compared to the Freundlich model. According to these findings, the seaweed *E. denticulatum* can be considered a potential biosorbent for removing heavy metal from marine and coastal areas due to its high biosorption capability.

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