

Article

Removal of Heavy Metals (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+}) from Aqueous Solution Using *Hizikia fusiformis* as an Algae-Based Bioadsorbent

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Abstract: This study investigated the applicability of algae (*Hizikia fusiformis*, *Green gracilaria*, and *Codium fragile*) for removing heavy metals (Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+}) from aqueous solutions. Among the algae, *H. fusiformis* was chosen as a bioadsorbent and modified with NaOH and HCl. The results showed that the biosorption capacity of *H. fusiformis* improved significantly after treatment with NaOH; however, *H. fusiformis* modified with HCl did not achieve the expected value. The NaOH treatment enhanced the biosorption of metals on the treated *H. fusiformis* because of the hydrolysis reaction producing carboxylic ($-\text{COOH}$) and hydroxyl groups ($-\text{OH}$). The kinetics for Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} biosorption well fitted to pseudo-first-order, pseudo-second-order, and Elovich models, with R^2 of >0.994 . The Freundlich model provided a good fit for the equilibrium biosorption of Cd^{2+} , Cu^{2+} , and Ni^{2+} by both algae and the Langmuir model for Pb^{2+} . The maximum biosorption of metals was in the order $\text{Pb}^{2+} \gg \text{Cu}^{2+} \approx \text{Ni}^{2+} > \text{Cd}^{2+}$, with q_{max} of 167.73, 45.09, 44.38, and 42.08 mg/g, respectively. With an increase in the solution pH, metal biosorption was enhanced, and considerable enhancement was observed in the pH range of 2–4. Thus, *H. fusiformis* is expected to be considered a superior candidate for metal biosorption.

Keywords: heavy metals; biosorption; modification; algae; *Hizikia fusiformis*



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1. Introduction

A large amount and high concentration of heavy metals in industrial wastewater, mainly from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber, and wood products, has been discharged into water bodies without adequate treatment [1]. Heavy metal concentrations exceeding the permissible standards in drinking water and wastewater have often been observed in many countries [2]. Heavy metals are toxic to humans and other animal predators because they accumulate in the body through the food chain [3,4]. These can, accumulated in the body, cause toxic effects such as cancer and gastrointestinal disease, as well as neurological and renal disturbances [5–7]. Therefore, it is vital to develop methods and technologies to remove heavy metals before being discharged into the aquatic environment [8].

Various methods, including ion exchange [9], coagulation/precipitation [10], membrane separation [11], adsorption/filtration [12,13], and electrochemical treatment [14], have been applied to industrial wastewater contaminated with heavy metals. However, most of these methods have limitations for use in the field because of the generation of large amounts of sludge from the chemical process as well as the cost for build-up and management, and low technical maturity [15–17]. For these reasons, the attraction for environmentally friendly technologies as low cost, effective, and easy-to-apply alternatives has been increased by many researchers [18–20]. The adsorption process is preferable for

heavy metal removal because of the relatively low cost for build-up and maintenance, simple implementation, easy operations, availability of a number of adsorbents, environment friendly, high removal efficiency, and ability to remove a variety of pollutants present in wastewater [8,21,22].

The use of living or dead biomass has been considered one of the most effective, economical, and promising bioadsorbents for removing toxic metals from contaminated water [23,24]. Biomass from bacteria, fungi, and algae is also considered a promising adsorbent for removing heavy metals from wastewater because of the abundance of this biomass in nature and its rapid growth, and ease of cultivation [25–27]. Among the types of naturally occurring biomass, marine algae, in particular, are a renewable source and easily obtainable in large quantities [28,29]. A statistical review on biosorption [5] reported that algae had been widely used as raw material for biosorbents 15.3% more than other types of biomass (activated carbon or activated sludge) and 84.6% more than fungi and bacteria. Marine algae also have a high affinity for metals because the polysaccharides, proteins, or lipids on the outer cell wall of the algae provide adsorption sites for the metals via complex formation and ion exchange [30]. Both live and dead algae can be used as adsorbents for heavy metals, and dead algae have several advantages over living algae in terms of utilization. Dead marine algae may be even more cost-effective than living algae because inactive algae require neither food nor essential elements for biological growth [5]. Moreover, dead biomass is not affected by the toxicity of metal ions, and the chemical and physical modification of the biomass can be applied to enhance the adsorption capacity [5,31]. Acid or base modification is the most common method of enhancing the bioadsorption of heavy metals to algae, which results from exposure of active metal-binding sites contained in the cell wall or chemical modification of cell wall components [32].

Therefore, in this study, we evaluated the feasibility of marine algae as bioadsorbents for removing heavy metals from contaminated water. As harvested dead biomass, *Hizikia fusiformis*, *Green gracilaria*, and *Codium fragile* purchased from a local market were tested in this study, and to the best of our knowledge, the heavy metals (Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+}) bioadsorption capacity of these species had never been compared together under identical experimental conditions. In addition, the effects of acid or base treatment on the biosorption capacity of *H. fusiformis* was explored, and the morphology and functional group analyses of untreated and modified biosorbents were performed using field emission-scanning electron microscopy (FE-SEM) and Fourier transform infrared spectroscopy (FTIR). The removal efficiency according to reaction time and initial heavy metal concentration were compared, and experimental data were analyzed using kinetic adsorption models and isotherms to quantify the biosorption characteristics. The effect of solution pH on metal bioadsorption capacity was also evaluated.

2. Materials and Methods

2.1. Bioadsorbent Preparation

As harvested dead biomass, brown marine algae, *Hizikia fusiformis*, *Green gracilaria*, and *Codium fragile* were purchased from a local seafood market in South Korea. The algae samples were washed with deionized water to remove salts and sand until there was no change in the effluent, and then dried at 70 °C for one week. The dried samples of *H. fusiformis*, *G. gracilaria*, and *C. fragile* were ground and sieved to a size of 200–430 μm using US standard sieves (Humboldt Manufacturing Co., Elgin, IL, USA). The algae with a high capacity for heavy metal removal was chosen (*H. fusiformis*), with the goal of modifying the biomass to enhance the biosorption capacity. HCl (Duksan Chemical, Ansan, Korea, 35–37%) and NaOH (Duksan Chemicals, Ansan, Korea, 93%) were selected as reagents for acid and base treatment, respectively. Different concentrations of acid or base were applied to the chosen algae, as shown in Table 1. For acid treatment, the dried algae were soaked in two different concentrations (0.1 M and 1 M) of HCl for 1 h, and the treated algae were washed with deionized water until the pH of the rinsed water was above 4.5.

In the case of base treatment, 0.1 M and 1 M NaOH solutions were employed, and the dried algae were allowed to react for 1 h. The base-treated samples were also washed with deionized water until the rinsing water was below pH 10. The chemically modified algae were dried at 60 °C for 24 h and then stored in a desiccator before use.

Table 1. Conditions for modifying *H. fusiformis* using HCl and NaOH.

Biomass	Untreated	NaOH 0.1 M	NaOH 1 M	HCl 0.1 M	HCl 1 M
<i>H. fusiformis</i>	HR	HN_0.1 M	HN_1 M	HH_0.1 M	HH_1 M

2.2. Characterizations

The morphologies of the untreated and modified algae were investigated using a field-emission scanning electron microscope (FE-SEM; S-4700, Hitachi, Japan). Gold sputtering on the sample was performed at 30 mA for 120 s to prevent overcharging the sample. The specimens of untreated *H. fusiformis* and *H. fusiformis* treated with 1 M NaOH were observed at $\times 3000$ magnification at an accelerating voltage of 5 kV. The functional groups present on the surface of the algae were analyzed using Fourier transform infrared spectroscopy (FTIR; Nicolet iS10, Thermo Scientific, Madison, WI, USA). For the FTIR analysis, the algae were mixed with KBr and formed into pellets, and the spectra in the range of 4000–650 cm^{-1} were recorded at an average of 200 scans and a spectral resolution of 2 cm^{-1} .

2.3. Batch Biosorption Experiments

Batch biosorption experiments were conducted under different initial concentrations to observe the effects of algae species, acid/base treatment, initial metal concentration, reaction time, and pH on the removal of heavy metals. All batch biosorption experiments were performed by reacting a bioadsorbent (0.05 g) with 30 mL of metal solution at 25 ± 0.5 °C with agitation at 100 rpm in a shaking incubator (SJ-808SF, Sejong Scientific Co., Bucheon, Korea) unless otherwise stated. The stock metal solution (1000 mg/L) was prepared by dissolving $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ (Samchun Chemical Co., Pyeongtaek, Korea) in deionized water. The initial pH was adjusted to 4 using 0.1 M NaOH and 0.1 M HNO_3 .

For the comparison of different algal species, including *H. fusiformis*, *G. gracilaria*, and *C. fragile*, 0.05 g of each dried algae was reacted with 30 mL of 100 mg/L of mixed-metal solution at pH 4 for 24 h. The biosorption experiments for *H. fusiformis* treated with different concentrations of HCl or NaOH were performed under the same conditions as the algae comparison experiments.

The biosorption characteristics of 1 M NaOH-treated *H. fusiformis* (HN_1M) were analyzed by varying the reaction time (30–1440 min), initial heavy metal concentrations (10–1000 mg/L), and solution pH (2–9). Kinetic biosorption experiments were performed with pH 4 and 10 mg/L of metal solution and 0.05 g of bioadsorbent under different reaction times (30, 60, 120, 180, 360, and 1440 min). Equilibrium biosorption experiments were conducted with different initial metal concentrations (10, 50, 100, 300, 500, 700, and 1000 mg/L) for a fixed reaction time of 1440 min. The influence of pH on heavy metal biosorption was investigated under different pH values from 2.0 to 9.0 at 10 mg/L of initial metal concentration for 1440 min of reaction time.

After biosorption experiments, the heavy metal solution was separated from the bio adsorbent using filter paper (0.45- μm polypropylene filter; Whatman, Clifton, NJ, USA). HNO_3 (2%) was applied in drops to the filter solution, to prevent the precipitation of heavy metals prior to analysis. The metal concentration in the solution was measured using an inductively coupled plasma spectrometer (ICP-OES 5100 Series, Agilent Technologies Inc., Carpinteria, CA, USA). The amount of metal absorbed was calculated from its initial and final concentrations. The removal percentage was obtained from the ratio of the removed amount to the initial concentration.

2.4. Data Analysis

Kinetic data for the study were obtained using the following pseudo-first-order (PFO, Equation (1)) [33], pseudo-second-order (PSO, Equation (2)) [34], and Elovich (Equation (3)) [35] models:

$$q_t = q_e[1 - \exp(-k_1t)] \quad (1)$$

$$q_t = \frac{k_2q_e^2t}{1 + k_2q_et} \quad (2)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad (3)$$

where q_t (mg/g) is the adsorbed amount of heavy metal at time t , q_e (mg/g) is the adsorbed amount of heavy metal at equilibrium, k_1 (1/min) is the PFO rate constant, k_2 (g/mg·min) is the PSO rate constant, α is the initial rate constant (mg/g·min), and β is the desorption constant (g/mg). Kinetic adsorption data within 180 min were used to analyze PFO, PSO, and Elovich models. The intraparticle diffusion (IPD, Equation (4)) [36] model was also used to analyze kinetic experimental data from 0 to 1440 min:

$$q_t = k_it^{0.5} + C \quad (4)$$

where k_i is the IPD rate constant (g/mg/h^{0.5}), and C is the intercept that reflects the boundary-layer effect or surface adsorption (mg/g).

The equilibrium data were analyzed using the Langmuir isotherm model (Equation (5)) and Freundlich isotherm models (Equation (6)) [37]:

$$q_e = \frac{q_0bC_e}{1 + bC_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

where q_0 (mg/g) is the maximum biosorption capacity, b (L/mg) is the Langmuir constant, C_e (mg/L) is the metal concentration in solution at equilibrium, K_F ((mg/g)·(L/mg)^{1/n}) is the distribution coefficient, and n is the Freundlich constant. The variable was determined by fitting the Langmuir and Freundlich models to the observed data.

All parameters of the kinetic and equilibrium models were estimated by non-linear regression using the Dynamic Fit Wizard function of Sigma-Plot 10.0 (SPSS INC, Chicago, IL, USA). The goodness of model fit was expressed by the determination coefficient (R^2) and the sum of squared errors (SSE).

3. Results and Discussion

3.1. Comparison of Heavy Metal Uptake by Different Algae

The removal efficiency of dried marine algae, *Hizikia fusiformis*, *Green gracilaria*, and *Codium fragile* for Cd²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ were shown in Figure 1 (initial metal concentration: 100 mg/L; pH: 4.0; adsorbent dosage: 1.67 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25 ± 0.5 °C). The Cd²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ metal ion removal performances were 14.9%, 31.6%, 10.9%, and 10.9%, respectively, for *H. fusiformis*. *H. fusiformis* had the highest removal efficiency, followed by *C. fragile*, and *G. gracilaria*. Biomass from different algal species exhibited different metal-binding capacities under these experimental conditions (pH 4 and 25 °C). Differences between algal species in the magnitude of metal-binding capacity may have been due to the properties of the algae such as structure, functional groups, and surface area, depending on the algal division, genera, and species [38]. Based on these experimental results, *H. fusiformis* was selected for further experiments.

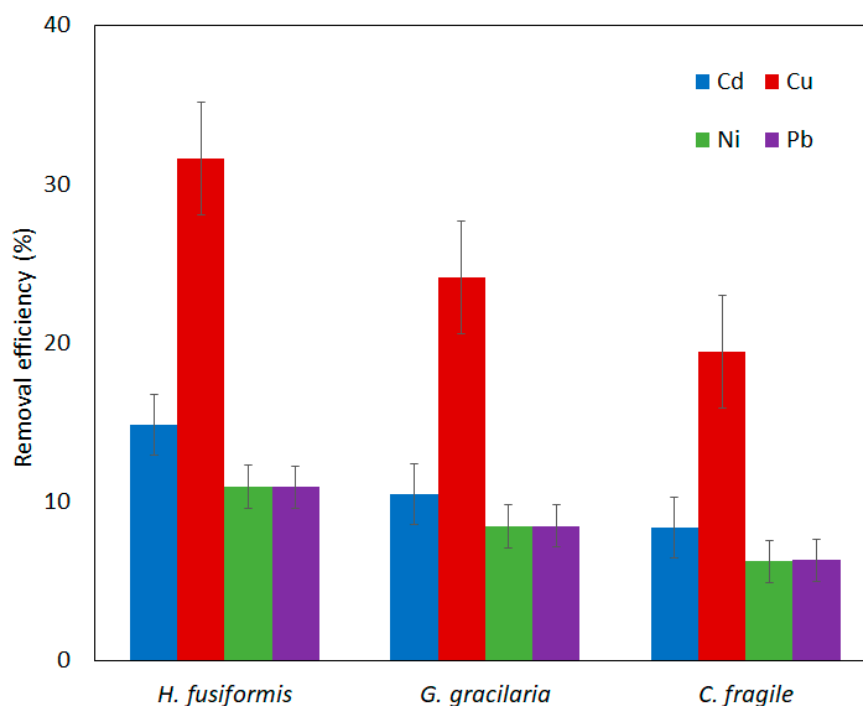


Figure 1. Comparison of metal removal capacity of biomass from different species of algae.

3.2. Effect of Acid and Base Treatment on Heavy Metal Removal by *H. fusiformis*

The biomass from *H. fusiformis* was treated with acid (0.1 M and 1 M HCl) and base (0.1 M and 1 M NaOH) to investigate the effect of chemical treatment on heavy metal uptake capacity, and the effects were compared in Figure 2 (initial metal concentration: 100 mg/L; pH: 4.0; adsorbent dosage: 1.67 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25 ± 0.5 °C). The treatment of *H. fusiformis* with NaOH was effective in increasing the Cu^{2+} uptake capacity, from 35.5 to 58.65 mg/g, whereas *H. fusiformis* modified by acid did not show such an effectiveness. In addition to Cu^{2+} uptake, the uptake of other metals, namely, Cd^{2+} , Ni^{2+} , and Pb^{2+} , were also higher in NaOH-modified *H. fusiformis* than in untreated *H. fusiformis*. Galun, et al. [39], reported that NaOH-treated biomass of *Penicillium digitatum* also showed enhancement of Cd^{2+} biosorption. This could be explained by the change in the cell wall structure and functional groups on the cell wall by chemical modification, which generally enhances the biosorption characteristics of biological materials, mainly due to hydrolysis reactions [40]. The hydrolysis reaction can produce more carboxylic ($-\text{COOH}$) and hydroxyl groups ($-\text{OH}$) on the surface of the cell wall, leading to enhanced metal-binding properties of algal biomass [41].

3.3. Changes in Characteristics of *H. fusiformis* after Base Treatment

FE-SEM micrographs of (a) untreated *H. fusiformis* and (b) after treatment with 1 M NaOH are shown in Figure 3. The crystal precipitates disappeared after NaOH treatment, but the surface of treated *H. fusiformis* was degraded, showing more cracks and greater porosity. This led to improvements in surface area and pore volume, which indicated the potential higher adsorption capacity of the adsorbents [5]. After NaOH treatment, the more active sites absorbed more heavy metals.

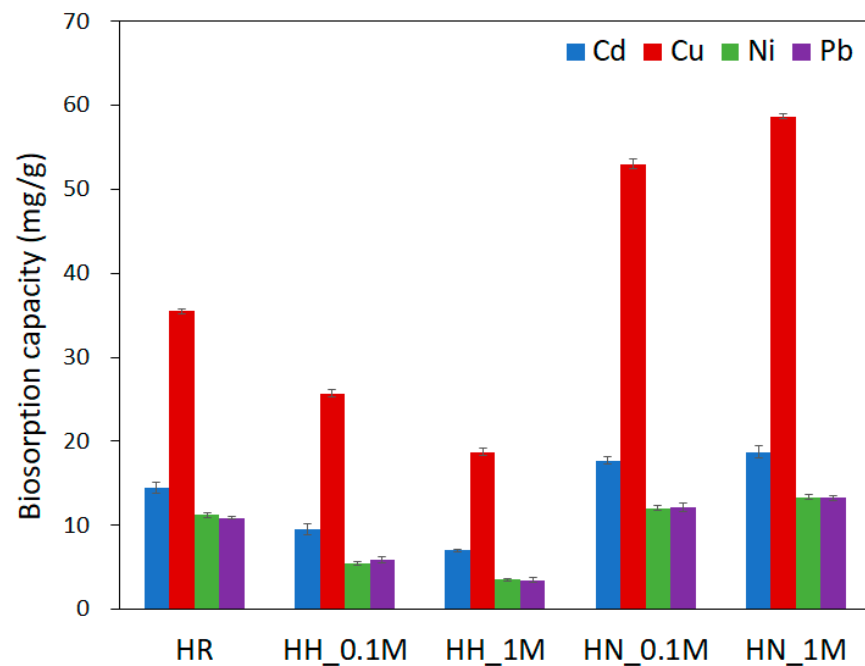


Figure 2. Effect of HCl and NaOH treatment on the pretreatment on *H. fusiformis* (HR: raw *H. fusiformis* without treatment; HH_0.1M and HH_1M: 0.1 M and 1 M HCl-treated *H. fusiformis*; HN_0.1M and HN_1M: 0.1 M and 1 M NaOH-treated *H. fusiformis*).

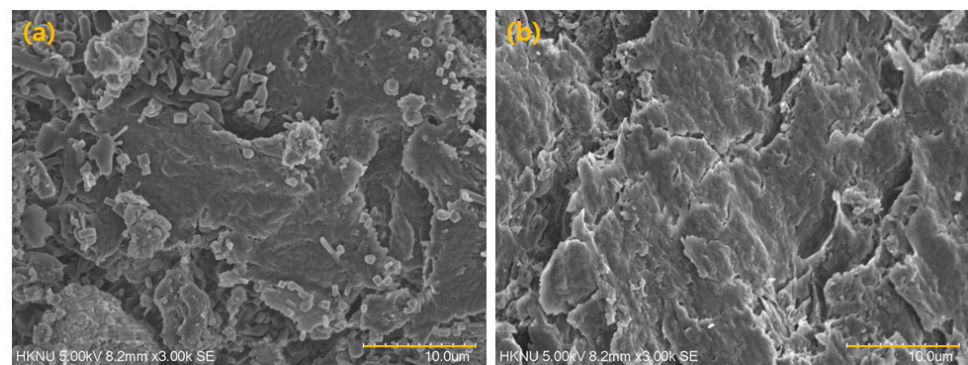


Figure 3. FE-SEM image of (a) untreated *H. fusiformis* and (b) *H. fusiformis* treated with 1 M NaOH (Scale bar: 10 μ m).

FTIR was used to identify the functional groups on the surface of untreated and treated algae and to investigate the contribution of functional groups to the biosorption of metals by algae. The FTIR spectra of *H. fusiformis* is shown in Figure 4. The broad and intense absorption peaks at 3249–3292 cm^{-1} corresponded to the O–H stretching vibrations present in cellulose, pectin, absorbed water, hemicellulose, and lignin [42]. The small bands in the range of 2920–2935 cm^{-1} are attributable to the C–H stretching vibrations of methyl, methylene, and methoxy groups [43]. The peaks at 1604–1618 cm^{-1} corresponded to the ester carbonyl (C = O) groups and carboxylate ion (COO⁻) stretching band of pectin [25,44]. The vibrations at 1430–1455 cm^{-1} are attributable to aliphatic and aromatic (C–H) groups in the plane deformation vibrations of methyl, methylene, and methoxy groups. The bands in the range of 1000–1300 cm^{-1} were assigned to the C–O stretching vibration of R–COOH and R–OH [2]. The change in the vibrational frequency of functional groups after treatment showed that treatment with NaOH could increase the number of ester (1160 cm^{-1}) and carboxylic groups (1419 cm^{-1}), effectively absorbing heavy metals in an aqueous solution [45]. The peaks of *H. fusiformis* at 1082 cm^{-1} and 890 cm^{-1} represent C–O stretching and C = C bending.

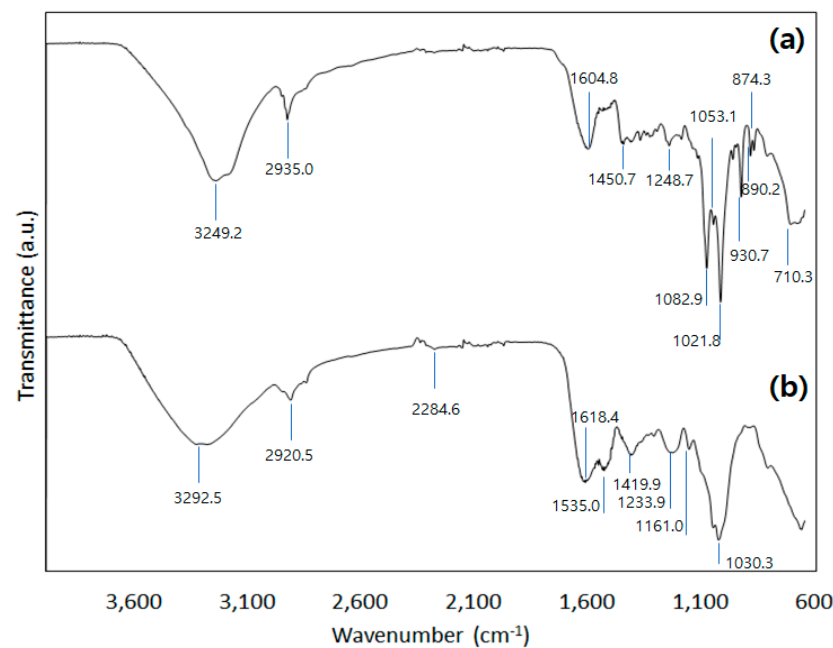


Figure 4. FTIR spectra of (a) *H. fusiformis* and (b) 1 M NaOH-treated *H. fusiformis*.

3.4. Biosorption Characteristics of 1 M NaOH-Treated *H. fusiformis*

3.4.1. Effect of Reaction Time

The biosorption data for the uptake of metal ions versus contact time at pH 4 are shown in Figure 5 (initial metal concentration: 10 mg/L; pH: 4.0; adsorbent dosage: 1.67 g/L; reaction time: 30–1440 min; agitation speed: 100 rpm; temperature: 25 ± 0.5 °C). The adsorbed amount of metal ions increased rapidly within the first 30 min, and equilibrium was reached after 180 min. After this equilibrium period, the amount of metal biosorption remained constant. The removal efficiencies of Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} ions at 180 min were 97.7%, 88.9%, 79.8%, and 61.5%, respectively. High biosorption at the beginning of experiments was also found in other studies: *Chlorella vulgaris* and the freshwater alga *Scenedesmus quadricauda* took up 90–95% of Cu^{2+} within the first 15 min of the experiment and reached equilibrium biosorption after about 2 h [46]; *Ecklonia radiata* took up 90% of Cu^{2+} and Pb^{2+} ions within 30 min and reached equilibrium biosorption after approximately 1 h [47]. This phenomenon can be explained by the fact that the active sites on the surface of algal materials were not occupied at the initial times, resulting in a high biosorption rate of heavy metals without competition with unadsorbed metals and replacement of adsorbed metals [41,43].

The parameters for the PFO, PSO, and Elovich models obtained from the kinetic experimental data from 0 to 180 min are listed in Table 2. For *H. fusiformis*, it can be concluded that the data fitted well with all three models applied in this study with a high correlation ($R^2 > 0.994$). Figure 5a shows that PFO and PSO models seemed to fit better to the experimental data than Elovich models. The good prediction of kinetic data by PFO and PSO models indicates that two or more steps influence the biosorption process [48,49]. The reaction rates of the PFO and PSO models followed the decreasing order of $\text{Cd}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$. Pb^{2+} showed a lower reaction rate but higher equilibrium sorption than Ni^{2+} .

Figure 5b presents that the biosorption process of heavy metals by 1 M NaOH-treated *H. fusiformis* involved two stages of diffusion processes. The parameters for the IPD model obtained from the kinetic experimental data from 0 to 1440 min are listed in Table 3. The first step for the diffusion of heavy metals to the external surface of the bioadsorbents was faster than the second step for the diffusion of metals internal pores of the bioadsorbents [50]. Two straight lines in Figure 5b are observed not to pass through the origin, indicating

that the biosorption rate of the heavy metals was not only controlled by intraparticle diffusion [51].

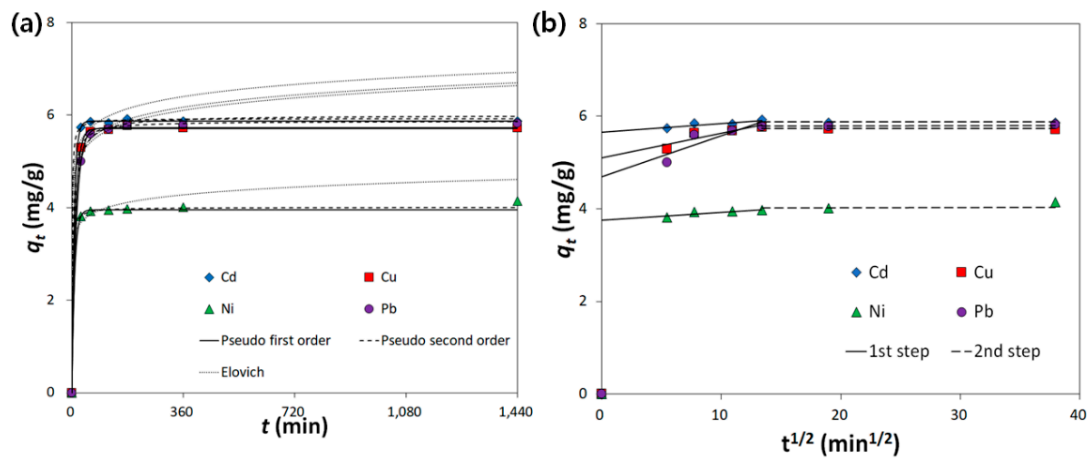


Figure 5. Kinetic sorption of Cd²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ by 1 M NaOH-treated *H. fusiformis*: (a) pseudo-first-order, pseudo-second-order, and Elovich models, and; (b) intraparticle diffusion model.

Table 2. Pseudo-first-order, pseudo-second-order, and Elovich model parameters for heavy metal biosorption on 1 M NaOH-treated *H. fusiformis*.

Metals	Pseudo-First-Order Model				Pseudo-Second-Order Model				Elovich Model			
	q_e (mg/g)	k_1 (1/min)	R^2	SSE	q_e (mg/g)	k_2 (g/mg·min)	R^2	SSE	α (mg/g/min)	β (g/mg)	R^2	SSE
Cd ²⁺	5.869	0.126	1.000	0.004	5.924	0.175	1.000	0.004	2.30×10^4	2.640	0.994	0.164
Cu ²⁺	5.709	0.087	1.000	0.006	5.870	0.055	1.000	0.004	1.15×10^4	2.625	0.998	0.049
Ni ²⁺	3.952	0.112	1.000	0.001	4.005	0.173	1.000	0.000	4.05×10^4	4.191	0.996	0.048
Pb ²⁺	5.726	0.069	1.000	0.006	5.996	0.030	0.999	0.016	8.21×10^3	2.598	0.998	0.056

Table 3. Intraparticle diffusion model parameters for heavy metal biosorption on 1 M NaOH-treated *H. fusiformis*.

Metals	Intraparticle Diffusion Model–1st Step				Intraparticle Diffusion Model–2nd Step			
	k_i (g/mg/min ^{0.5})	C (mg/g)	R^2	SSE	k_i (g/mg/min ^{0.5})	C (mg/g)	R^2	SSE
Cd ²⁺	0.0490	5.816	0.999	0.019	0.0001	6.401	1.000	0.001
Cu ²⁺	0.0573	5.923	1.000	0.011	0.0001	6.657	1.000	0.000
Ni ²⁺	0.0147	5.737	1.000	0.001	0.0001	5.889	0.997	0.006
Pb ²⁺	0.0276	2.352	0.988	0.285	0.0001	5.810	1.000	0.002

3.4.2. Effect of Initial Heavy Metal Concentration

Equilibrium biosorption experiments were performed to quantify the maximum biosorption capacity of 1 M NaOH-treated *H. fusiformis* (initial metal concentration: 10–1000 mg/L; pH: 4.0; adsorbent dosage: 1.67 g/L; reaction time: 1440 min; agitation speed: 100 rpm; temperature: 25 ± 0.5 °C). Figure 6 shows that the biosorption of different metal ions increased with an increase in the initial heavy metal concentration and reached the maximum adsorbed amount at >300 mg/L of initial heavy metal concentration. The equilibrium parameters derived from the fitting of the Langmuir and Freundlich models to the experimental data are presented in Table 4. The Freundlich model provided a good fit for the equilibrium data of biosorption with a high correlation coefficient ($R^2 = 0.965$ for Cd²⁺, $R^2 = 0.956$ for Cu²⁺, and $R^2 = 0.970$ for Ni²⁺). Similar results were obtained by Hong and Park [52], who reported that Cd²⁺, Cu²⁺, and Ni²⁺ biosorption by sepiolite was

well fitted to the Freundlich model. In contrast, the fit of the equilibrium data for Pb^{2+} ion biosorption by the Langmuir model was better ($R^2 = 0.967$, $SSE = 1054.9$) than the Freundlich model. These results indicate that the biosorption of Cd^{2+} , Cu^{2+} , and Ni^{2+} adsorbed on the 1 M NaOH-treated *H. fusiformis* via the formation of a multilayer but Pb^{2+} via monolayer [21].

The maximum biosorption of the treated *H. fusiformis*, obtained from the Langmuir model, was in the order of $\text{Pb}^{2+} \gg \text{Cu}^{2+} \approx \text{Ni}^{2+} > \text{Cd}^{2+}$. The affinity of these heavy metals for *H. fusiformis* can be explained by the electronegativity of metals, the hydrolysis constant, and the charge-to-radius ratio [21,53]. Among them, electronegativity was most suitable to explain our experimental data. The electronegativities of the four heavy metals, in decreasing order, were Pb^{2+} (2.33) $>$ Ni^{2+} (1.91) $>$ Cu^{2+} (1.90) $>$ Cd^{2+} (1.69) [54,55]. Electronegativity can influence heavy metal adsorption because metals with higher electronegativities can build stronger covalent bonds with O atoms present on the surface of the adsorbent [54]. Pb^{2+} , which had the highest electronegative value, showed the highest biosorption, whereas Cd^{2+} , which had the lowest electronegative value, presented the lowest biosorption. Ni^{2+} and Cu^{2+} had similar electronegativity and biosorption amounts similar to those of treated *H. fusiformis*. This relatively superior Pb^{2+} adsorption derived from electronegativity has also been reported similarly in other algae (*Codium vermilara*, *Spirogyra insignis*, *Asparagopsis armata*, *Chondrus crispus*, *Fucus spiralis*, *Ascophyllum nodosum*) [56].

The adsorption of metals onto adsorbents increased as the hydrolysis constant (pK) decreased. The pK values of the metals, in increasing order, were Cu^{2+} (pK = 7.7) = Pb^{2+} (pK = 7.7) $<$ Ni^{2+} (pK = 9.9) $<$ Cd^{2+} (pK = 10.1) [57]. The least amount of Cd^{2+} with pKa was removed by *H. fusiformis*, but the hydrolysis constants for other metals were not consistent with their uptake by *H. fusiformis*. The larger ionic radius led to the lower charge density and coulombic attraction between ions and the surface of adsorbents, and the ionic radius of metals, in decreasing order, was Pb^{2+} (1.20 Å) $>$ Cd^{2+} (0.97 Å) $>$ Cu^{2+} (0.73 Å) $>$ Ni^{2+} (0.69 Å) [58]. Pb^{2+} , which had a larger ionic radius and lower charge density, was taken up by *H. fusiformis*, indicating that electrostatic attraction was not a critical factor for the uptake of heavy metals by *H. fusiformis*.

The removal of heavy metals by biosorption using algae has many advantages: high removal efficiency, low-cost material, reduction of chemical and hazardous sludge, regeneration of biosorbent, and metal recovery [59]. The Langmuir maximum biosorption capacities of 1 M NaOH-treated *H. fusiformis* was compared to that of various algae such as red, green, and brown algae (Table 5), which was comparable to that of other biomass.

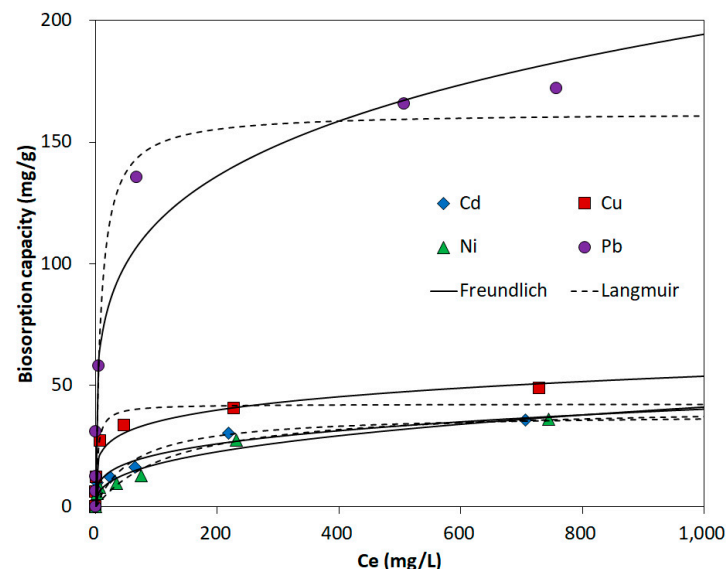


Figure 6. Equilibrium sorption of Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} by 1 M NaOH-treated *H. fusiformis*.

Table 4. Langmuir and Freundlich model parameter of Cd²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ sorption by 1 M NaOH-treated *H. fusiformis*.

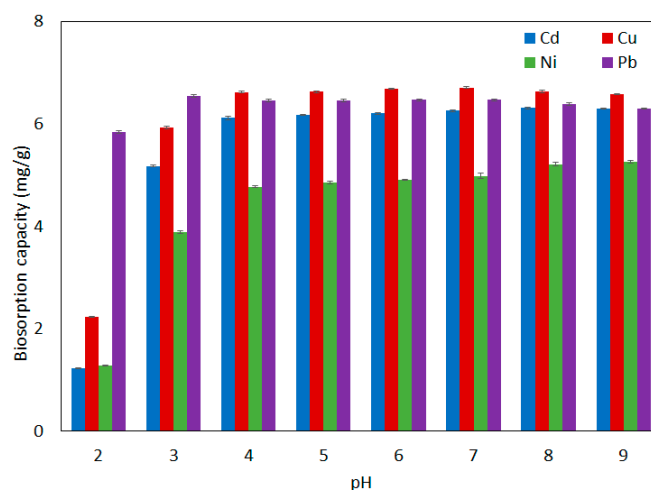
Metals	Langmuir Model				Freundlich Model			
	q_m (mg/g)	K_L (L/mg)	R^2	SSE	K_F ((mg/g)·(L/mg) ^{1/n})	1/n	R^2	SSE
Cd ²⁺	38.390	0.0158	0.882	118.0	6.127	0.272	0.965	34.5
Cu ²⁺	42.250	0.2879	0.952	96.0	14.844	0.186	0.956	88.3
Ni ²⁺	41.872	0.0079	0.933	66.0	3.198	0.369	0.970	29.5
Pb ²⁺	162.201	0.1127	0.967	1054.9	42.060	0.222	0.950	1382.9

Table 5. Comparison of Langmuir maximum biosorption capacities of pretreated *H. fusiformis* with other materials.

Adsorbents	Pb ²⁺ (mg/g)	Cu ²⁺ (mg/g)	Cd ²⁺ (mg/g)	Ni ²⁺ (mg/g)	References
<i>Asparagopsis armata</i>	63.7	21.3	32.3	17.1	[56]
<i>Spirogyra insignis</i>	51.5	19.3	22.9	17.5	[56]
<i>Fucus spiralis</i>	204.1	70.9	114.9	50.0	[56]
<i>Codium vermilara</i>	63.3	16.9	21.8	13.2	[60]
<i>Chondrus crispus</i>	204.1	40.5	75.2	37.2	[60]
<i>Ascophyllum nodosum</i>	178.6	58.8	87.7	43.3	[60]
<i>Caulerpa lentillifera</i>	28.98	8.26	4.70	-	[61]
<i>P. palmata</i>	15.17	6.65	-	-	[62]
<i>H. fusiformis</i>	162.20	42.25	38.39	41.87	This study

3.4.3. Effect of Solution pH

The effect of solution pH (2–9) on the removal of heavy metals by pretreated *H. fusiformis* was also studied (initial metal concentration: 10 mg/L; pH: 2.0–9.0; adsorbent dosage: 1.67 g/L; reaction time: 1440 min; agitation speed: 100 rpm; temperature: 25 ± 0.5 °C). The results show that the uptake of heavy metals significantly increased in the pH range of 2–4 (Figure 7). The biosorption of Cd²⁺, Cu²⁺, and Pb²⁺ plateaued above pH 4, and the Ni²⁺ biosorption continued to increase until pH 9. In acidic pH conditions (pH < 4), the active surface sites of the adsorbent were protonated [63], lowering the biosorption of heavy metals at these pH values [25]. However, as the pH increased, the adsorption of heavy metals increased as the competition between H⁺ ions and heavy metals decreased [64]. Furthermore, at pH > 6, these metal ions can be adsorbed to negatively charged surfaces of pretreated *H. fusiformis* via electrostatic interaction because the point of zero charges of algae has been reported in the range of pH 4–6.1 [65–68].

**Figure 7.** Effect of pH on Cd²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ sorption capacity of 1 M NaOH-treated *H. fusiformis*.

4. Conclusions

This study investigated the removal efficiency of different algae, namely, *H. fusiformis*, *G. gracilaria*, and *C. fragile*, in removing heavy metals (Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+}) from contaminated water. *H. fusiformis* was selected for further studies to improve their biosorption capacity using acid and base treatments. The enhancement of the biosorption capacity of *H. fusiformis* by modification with a base was due to the carboxylate and ester functional groups on the base-treated algae. The equilibrium data fitted well in the Freundlich model (except for Pb^{2+}). The reaction rates obtained from the kinetic models for 1 M NaOH-treated *H. fusiformis* followed the decreasing order of $\text{Cd}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$. The maximum biosorption of metals was in the order $\text{Pb}^{2+} \gg \text{Cu}^{2+} \approx \text{Ni}^{2+} > \text{Cd}^{2+}$, which was consistent with their electronegativity values rather than the hydrolysis constant and ionic radius. The increase in solution pH, especially in the range of pH 2–4, enhanced the metal biosorption by 1 M NaOH-treated *H. fusiformis* because of feasible precipitation and less protonation of the adsorbent surface under the high concentration of OH^- ions. Algal biomass can be easily obtained in large quantities, and these features will enable this biomass to be a biosorbent material for heavy metal removal in the future.

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