Non-linear Isotherm Models, Cadmium Kinetics, and Biosorption Thermodynamics of Dried Biomass of Native *Aphanothece sp.* in a Batch System

Awalina Satya [1,2,*], Ardiyan Harimawan[1], Gadis Sri Haryani[2] & Tjandra Setiadi[1,3]

[1]Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Jalan. Ganesha No.10, Bandung 40132, Indonesia
[2]Research Centre for Limnology,-The Indonesian Institute of Sciences (P2L-LIPI) Cibinong Science Center, Cibinong-Bogor 16911, Indonesia
[3]Centre for Environmental Studies (PSLH), Institut Teknologi Bandung, Jln. Sangkuriang 42A, Bandung 40135, Indonesia
*E-mail: awalina@limnologi.lipi.go.id

Abstract. Dried biosorbent was prepared from *Aphanothece sp.* cyanobacteria harvested from a photobioreactor system fed with atmospheric carbon dioxide. Cadmium-ion biosorption of the prepared biosorbent from aqueous solution was characterized by non-linear (Langmuir, Freundlich and Dubinin–Radushkevich) isotherms, non-linear kinetics (pseudo first-order and pseudo second-order) and thermodynamic analysis. The optimum conditions were pH 8.0, 30°C, 0.1 g/L biomass, and 60 min contact time. The biosorption efficiencies exceeded 90%. The low-range data (initial Cd concentration C_0 = 1.09–6.23 mg/L) and high-range data (C_0 = 5.41–83.07 mg/L) were best fitted to the Langmuir model, with maximum uptake capacities of 12.01 and 187.5 mg/g (R^2 = 0.995 and 0.996). In the Dubinin–Radushkevich isotherm model, the mean biosorption energy was 12.91 kJ/mol, suggesting that ion exchange was the working mechanism. The biosorption apparently followed pseudo second-order kinetics (R^2 = 0.994–0.999; k_2 = 2.04 E-03 to 3.86 E-02 g/mg min). The biosorption process was energetically feasible (ΔG^0 = −13.47–−8.88 kJ/mol), exothermic (ΔH^0 = −74.82 kJ/mol) and tended to become more ordered (ΔS^0 = −0.204 kJ/mol K) towards the end of the process. The biosorbent was reusable through three adsorption/desorption cycles in 1 M HCl.

Keywords: *Aphanothece sp.; biosorption; cadmium; equilibrium isotherms; non-linear; pseudo first-order; thermodynamic.*

1 Introduction

Aquatic ecosystems play important ecological and economical roles in many human societies. However, these limited resources are susceptible to contamination by persistent toxic heavy metals released by human activities and frequently discarded improperly into aquatic environments, such as cadmium (Cd), lead (Pb) and zinc (Zn). Once these metals enter the aquatic ecosystem,

Received March 21st, 2017, Revised September 28th, 2017, Accepted for publication November 8th, 2017.
 ISSN: 2337-5779, DOI: 10.5614/j.eng.technol.sci.2017.49.5.5

they can be transferred through the aquatic food web and bio-accumulated in the top consumers (humans), causing numerous health problems [1-3]. Among these metallic toxins, Cd is the most toxic metal and frequent found in contaminated aquatic ecosystem. Metal-dependent industries such as metallurgy, electroplating, dyeing, plasticisers and battery manufacturers are becoming major sources of Cd contamination in aquatic ecosystems. To mitigate this problem, metal-borne wastewater treatment is urgently needed [4-8].

Conventional wastewater treatments are mainly based on precipitation, evaporation, ion exchange or oxidation/reduction. Such methods incur high investment and operational costs, especially when removing dilute metal ions from wastewater. Furthermore, environmental regulations have been strictly capping the permissible level of metal ions discharged into open waters at low concentrations (0.05 mg/L).

Unfortunately, conventional wastewater treatments produce several hazardous by-products. Therefore, a more economical and feasible technique for sequestering Cd from aqueous phase or wastewater streams is needed [4, 7-10]. Among the most prospective methods for removing metals in aqueous phase is sorption by non-viable biomaterials known as *biosorption* [4,5,6,8]. Microalgae are especially attractive as biosorbent in metal-borne wastewater treatment installations because they simultaneously adsorb toxins and fix carbon dioxide. To select the most effective freshwater microalgae species for the biosorbent, we must investigate the natural Cd-uptake capability of the living organisms. Many studies show that microalgae readily uptake Cd through their membranes, which comprise lipids, proteins, and polysaccharides. These compounds contain hydroxyl, carboxyl, sulfhydryl, amide, and amine functional groups with high affinity to metal ions under certain conditions. The quantity and quality of these functional groups differ among microalgae, meaning that each algal species has a different metal-binding capability [1,7,11].

Biosorbent made from microalgae biomasses, such as *Spirulina plantesis, Desmodium sp.* and *Oedogonium sp.*, have successfully removed Cd ions from aqueous solutions [12-14]. However, the use of *Aphanothece sp.* as a biosorbent agent seems to not have been reported. This cyanobacterial species, which inhabits Rawa Kalong Lake in Depok City, west of Java, demonstrates excellent natural uptake capacity and bio-accumulation of Cd from its habitat waters, where the Cd concentration in biomass was 4,150 times higher than in the surrounding waters. *Aphanothece sp.* dominate the microalgae community structure in this urban lake and perform well under certain aquatic physico-chemical conditions [15]. From this viewpoint, *Aphanothece* biomass can be feasibly used for Cd biosorption in batch experiments. However, before

performing biosorption experiments, we must cultivate the organism. Awalina, *et al.* grew *Aphanothece sp.* isolates in a photobioreactor system fed with atmospheric carbon dioxide as the inorganic carbon source for growth [16].

Awalina's research [15] confirmed the high cadmium biosorption capability of living *Aphanothece* biomass (concentrated by up to 4,150 times its natural-habitat concentration). Batch biosorption tests of dried biosorbent are technically simpler than investigations of living microalga (which require the addition of nutrients for growth and incur a toxicity risk). Microalga-based biosorbent is also highly selective for the removal and recovery of metal ions and exhibit high affinity to metal ions (reducing residual metals in aqueous solution to parts-per-billion levels) and rapid biosorption kinetics. Therefore, they can treat large volumes of Cd-borne wastewater. Moreover, microalgae are naturally abundant, promising inexpensive production and low operational cost. Nonetheless, microalga-based biosorption systems are hampered by impediment of developing a generic technology. Multiple variables (microalga biomass type, processing methods, contacting environment and wastewater compositions ([7,18]) present major barriers to realising this technology in a sustainable wastewater treatment system.

The present batch study determines the ability of dried *Aphanothece sp.* biomass to eliminate Cd^{2+} ions from aqueous phase. To find the optimum operational conditions, we varied the pH, biomass concentration, solution temperature, contact time and initial Cd^{2+} concentration and observed the consequent effects on Cd^{2+} biosorption. The biosorption process and its probable mechanism (physio sorption or chemisorption) were derived from equilibrium isotherms. For this purpose, the data were fitted to three non-linear isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich (DR)). To deduce the biosorption kinetics, we fitted the data to the non-linear pseudo first-order and pseudo second-order Lagergren equations. The thermodynamic behaviour of this biosorption process was then evaluated by calculating the changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0). Finally, the reusability of the regenerated biosorbent was evaluated in recovery tests of the adsorbed Cd with 1-M HCl eluent.

2 Experimental Procedures

2.1 Biomass Preparation

Aphanothece sp. (a member of the blue–green algae cyanobacteria) was cultivated in a photo-bioreactor system in photoautotrophic mode with BG-11 medium, atmospheric carbon dioxide feeding and ~5700 lux illumination. After 14 days' cultivation, the biomass harvested by centrifugation at 6000 rpm for 15

min at 25°C. The harvested biomass was dried at 60°C for a week and then crushed in a mortar and sieved through a 45-size mesh (Retsch, West Germany). The resulted particles were ~354 μm in diameter. The important functional groups on the surface of the dried biomass were characterised by Fourier transform infrared (FTIR) spectroscopy (Prestige 21, Shimadzu, Japan). The carbon (C), hydrogen (H) and sulphur (S) contents were quantified by an elemental analysis method (Labconco Elemental (CHNS) Analyzer, USA). The surface character of the biosorbent was determined by the Brunauer–Emmet–Teller (BET) method (Quanta chrome Instruments BET Analyzer, USA). The obtained biosorbent was stored in a bottle until required for biosorption experiments.

2.2 Batch Biosorption Procedure

The 1000 mg/L Cd^{2+} stock solution was prepared by mixing 2.0318 g of $CdCl_2.2.5H_2O$ (M&B Chemical, UK) in demineralised water (Kemflo Reverse Osmose, China), followed by 20 mL of 1:1 HCl solution (Merck, Germany). This solution was diluted to 1 L with demineralised water. To vary the Cd^{2+} concentration, we prepared suitable dilutions of the stock solution with known concentration. The initial Cd^{2+} concentrations were organised into two ranges: low (1.08–6.23 mg/L) and high (5.41–83.07 mg/L). To investigate the effect of pH on the biosorption, test solutions were adjusted to pH 3.0 (with buffer KH-phthalate and 0.1 M HCl), pH 5.0 (with buffer KH-phthalate and 0.1 M NaOH), pH 7.0, pH 8.0 (with buffer KH_2PO_4 and 0.1 M NaOH), pH 9.0 (with buffer Na-tetra borate and 0.1 M HCl) and pH 11.0 (with buffer Na-bicarbonate and 0.1 M NaOH). All chemicals for these buffer solutions were produced by Merck, Germany.

Biosorbent was prepared at 0.1 g/L in a series of bottles containing 25 mL of Cd solution (initial Cd^{2+} concentration = 1.3 mg/L) at each pH. The bottles were placed in a 30°C shaking incubator (Daihan Labtech, China) at 120 rpm for 60 min. To explore the effect of biosorbent concentration on the Cd biosorption capacity, we prepared a weighed series of biomass concentrations ranging from 0.1 to 2.0 g/L, maintaining the initial Cd concentration, pH, and temperature at 7.77 mg/L, 8.0 and 30°C. The mixtures were constantly agitated at 120 rpm, and 30°C for 120 minutes. Sample solutions were withdrawn at different time intervals (5-120 minutes). Thermodynamic experiment was conducted in varied temperatures (27–50°C). Biosorption equilibrium isotherm, kinetics, and thermodynamic tests maintaining the biomass concentration at 0.1 g/L and the optimum pH of 8.0. The optimum pH is adjusted with buffer KH_2PO_4 and 0.1 M NaOH solutions. The solution content of the sorption flask was filtrated before and after the biosorption.

The solutions were then analysed for their Cd^{2+} content using a flame atomic absorption spectrophotometer (FAAS; Shimadzu AA-7000) at 226.5 nm. All experiments were conducted in duplicate, and the results were averaged to obtain accurate data. The quantity of adsorbed Cd in the biosorbent over a given contact time was calculated from the mass-balance equation as shown in Eq. (1) as follows:

$$q_t = (C_{initial} - C_t)\frac{V}{W} \quad (1)$$

where $C_{initial}$ and C_t denote the Cd^{2+} concentrations in solution at the initial time and time t, (mg/L), q_t is the amount of adsorbed Cd in the biosorbent (mg/g), V is the volume of Cd in solution (L) and W is the weight of the biosorbent (g). The Cd biosorption efficiency BE (%) was calculated in Eq. (2) as follows:

$$BE\ (\%) = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \quad (2)$$

where $C_{initial}$ and C_{final} denote the initial and final concentrations. The adsorbed Cd ions were withdrawn from the *Aphanothece sp.* dried biomass in 25 mL of 1-M HCl solution over three biosorption/desorption cycles. The Cd content in the 1-M HCl solution was determined by FAAS. Prior to each biosorption, the biomass was twice washed in demineralised water to remove the excess HCl.

For determining the effect of pH on Cd biosorption, the pH was ranged from 3.0 to 11.0, maintaining the other parameters constant (initial Cd concentration = 1.3 mg/L, biosorbent concentration = 0.1 g/L, temperature = 30°C).

3 Results and Discussion

3.1 Dried Biosorbent Characteristics

The moisture content of the dried *Aphanothece sp.* biomass varied from 93.16% to 99.72%. The other characteristics are presented in Table 1.

Table 1 Physical and chemical characteristics of dried Aphanothece sp. biomass as biosorbent.

Dried Biosorbent *)	%C	%H	%N	%S	Diameter size µm	BET surface area (m^2/g)	Average of pore diameter (Å)	Pore volume cm^3/gram
Aphanotheece sp.	42.5	6.43	7.71	0.51	354	0.571	271.55	3.88E-03

*previously cultivated in 0.044% (atmospheric) CO_2 fed photobioreactor

The mass proportions of C, H, N and S in the dried biomass (Table 1) were comparable to those in *Spirullina platensis* (43.10% C, 6.47% H, 9.9% N and

2.89% S, as reported in [12]. But in contrast, the N content was threefold higher in our dried biomass than in *Chlorella vulgaris*, which contains 45.6% C, 6.9% H and 2.7% N [18]. The C, N and S contents of dried *Aphanothece sp.* biomass also exceeded those of red macroalgae *Oedogonium sp.* (reported as 25.4%, 3.06% and 1.77%, respectively [12]. The BET surface area was higher than *Fucus vesiculous* as reported in [19] which only 0.22 m^2/g. In case of average pore diameter and pore volume, this study result showed higher than banana peel based biosorbent (22.59 m^2/g and 8.71Å) as mentioned in [20].

Figure 1(a) shows a microimage of living *Aphanothece sp.* after 10 days' cultivation in the photobioreactor system. It represents cell radius range of 2.51-3.76 µm. The image of final processed dried biosorbent particles (after grinding and sieving) was magnified in 50 times show uneven surface texture (Figure 1(b)).

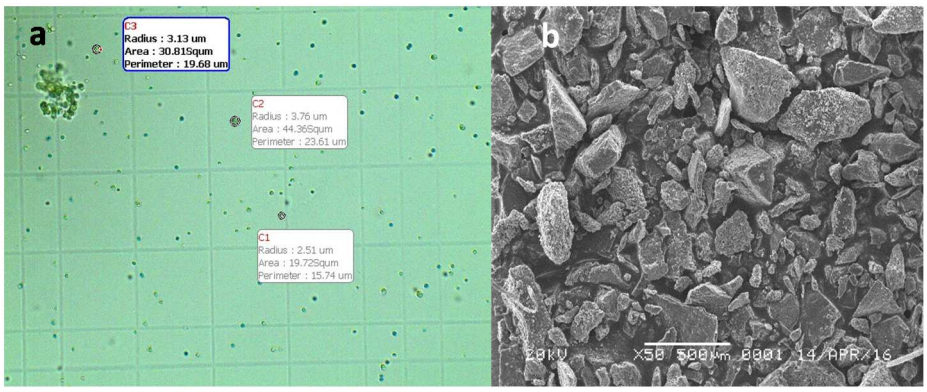

Figure 1 (a) Optical microscope image of living *Aphanotece sp.* cells after 10 days' cultivation (×400) and (b) scanning electron microscopy image (x 50) of dried biomass after grinding and sieving.

3.2 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra revealed the interaction between the biosorbent and Cd^{2+} ions. After recording the spectra of both unloaded and Cd-loaded dried *Aphanothece sp.* biomass at wavenumbers of 500–4500 cm^{-1}, we identified the number of functional groups on the biosorbent surface. The broad, strong bands at 3292–3388 cm^{-1} in Figure 2 are attributable to hydroxyl (–OH) groups bonded to the biomass surface. The peaks at 2854–2926 cm^{-1} represent the stretching vibrations of the $–NH_2^+$, $–NH^+$ and–NH groups of the microalgae. The band peaks at 1388–1651 cm^{-1} arise from the asymmetric and symmetric vibrations of carboxyl (–C=O) groups, and those at 1034–1074 cm^{-1} are contributed by thiocarbonyl (C=S) and sulfoxide (S=O) groups. The band observed at 1153–

1242 cm^{-1} is attributed to C–O stretching of alcohols and carboxylic acids. Some bands in the fingerprint region are assignable to phosphate (P=O), SOR esters and disulphide (S=S) groups.

In the Cd^{2+}-loaded biomass spectra acquired after the biosorption process, the stretching vibration bands of the hydroxyl and amide groups were shifted to 3282–3425 cm^{-1} and 1539–1654 cm^{-1}. Moreover, stretching vibration bands of the carboxyl groups were shifted to 2924, 1655 and 1539 cm^{-1}. The bands assigned to sulfoxide (S=O) and disulphide stretching were shifted to 1039 cm^{-1}. These results indicate that the biosorption involves ion exchanges between the metal ions and the hydrogen atoms of the carboxyl, hydroxyl, amides, and sulfoxide groups in the biomass. Similar FTIR results were reported for the biosorption of Cd(II) from aqueous solution by the red macroalgae *Ceramium virgatum* [21] and the biosorption of Pb(II) from aqueous solution by the green microalga *Spirogyra sp*. [22].

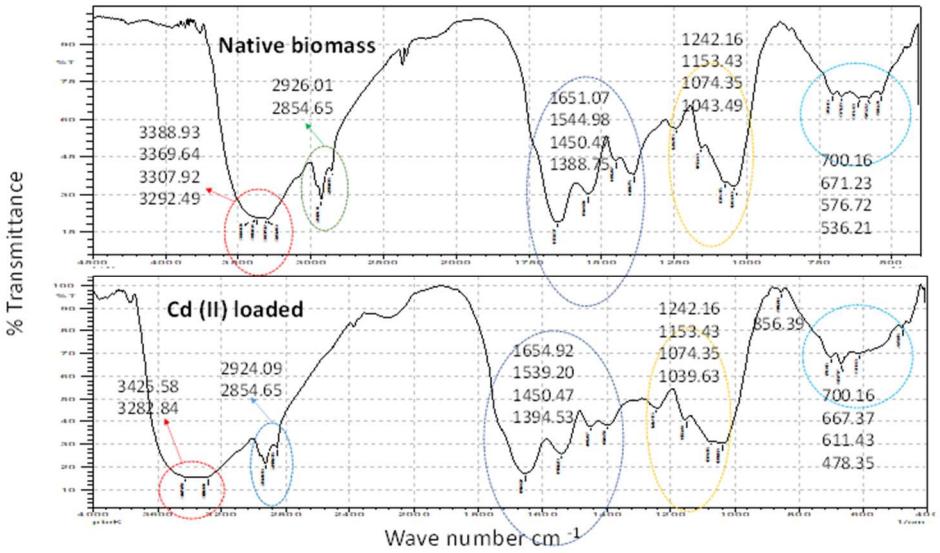

Figure 2 FTIR spectra of native and Cd-loaded dried Aphanothece sp. biomass. Ovals enclose the peaks undergoing wavenumber shifts from the native to the loaded biomass spectra.

3.3 Effect of pH

The pH measures the quantity of hydronium ions in water or solution and hence determines the acidic or alkaline properties of the solution. For a biosorbent immersed in solution, hydrogen ions alter the chemical properties of both the solution and the biosorbent surface. Therefore, pH value becomes the most

important parameter in biosorption process. This measurement must be conducted first before other optimization steps [10, 23-25]. The above-cited reports implied that pH promotes protonation or deprotonation, thereby altering the active sites of sorbate binding. Biosorbent surfaces are commonly rich in carboxylate and hydroxyls groups contributed by the high polysaccharide content. As these groups are sensitive to pH changes, the pH can significantly affect the metal bonding performance.

Here we investigated the effect of pH on Cd biosorption by dried *Aphanothece sp.* biomass. The biosorption capacities at each pH are presented in Figure 3. At pH values below 8.0, the Cd biosorption capacity and Cd removal efficiency significantly dropped. Both the biosorption capacity and removal efficiency were maximised at pH 8.0 and minimised at pH 9.0. We suggest that up to pH 8.0, there is less competition between the Cd ions and protons for active sites on the biosorbent surface. In addition, the net charge of the biosorbent surface is negative at pH 8.0, favouring Cd^{2+} adhesion. However, bulky Hydroxyl-Cd ion complexes ($Cd(OH)_2^+$) formed at pH 9.0, which precipitated out rather than bound to the biomass and resulted lowest biosorption capacity. At pH 11.0, the $Cd(OH)_2^+$ precipitation more hindered the Cd biosorption. Conclusively, pH 8.0 is the optimum pH for the biosorption experiment.

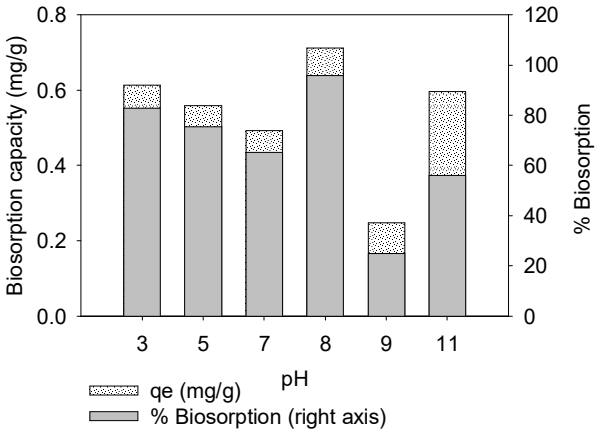

Figure 3 Effect of pH on Cd biosorption by dried Aphanothece sp. biomass in a batch study (initial Cd concentration = 1.3 mg/L; solution temperature = 30°C). The errors in the averaged results are below 1.1%.

3.4 Effect of Biomass Concentration

The biosorption uptake of Cd^{2+} ions were assayed by the biosorption capacity and biosorption efficiency. As shown in Figure 4, both variables decreased with

increasing biosorbent concentration and both were maximised at a biosorbent concentration of 0.1 g/L. The uptake sharply declined at higher biosorbent concentrations. This trend was attributed to partial aggregation, which decreases the effective surface area of the biosorption. Conversely, at lower biosorbent concentrations, the entire active surface of the biosorbent is available for biosorption, enhancing the biosorption capacity. Similar trends were reported by Sari and Tuzen and Rathinam et al. (2009) [25, 26], who conducted biosorption of Cd ions experiment onto dried biomasses of *Hypnea valentinae* and the macro fungus *Amanita rubescens*. Hence, in the following biosorption experiment, the biomass concentration was set to the optimum concentration of 0.1 g/L.

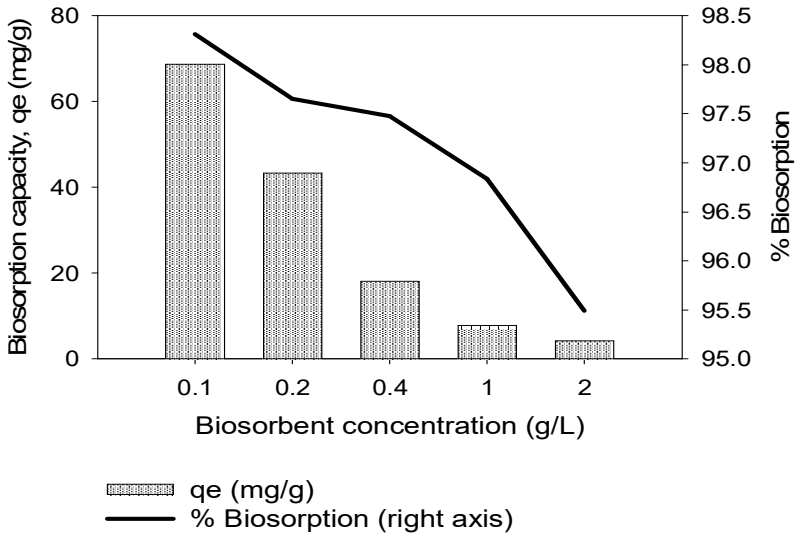

Figure 4 Effect of biosorbent dosage on Cd biosorption by dried Aphanothece sp. biomass in a batch study (initial Cd concentration = 7.9 mg/L, pH = 8.0, solution temperature = 30°C). The errors in the averaged results are below 1.5%.

3.5 Effect of Contact Time and Initial Cd Concentration

In the next biosorption batch experiment, we determined the effect of contact time on the biosorption capacity and efficiency of Cd ions by the dried *Aphanothece sp*. biomass. The results are plotted in Figure 5. Both the biosorption capacity and biosorption efficiency were equilibrated after 60 min of contact. After 120 min, both variables declined and plateaued. Similarly, Sari and Tuzen [27] reported that the Cd^{2+} biosorption efficiency of dried green macroalgae (*Ulva lactuta*) increased up to 60 min contact time and remained constant thereafter.

Dried biomasses of red microalgae (*Ceramium virgatum*) and blue–green microalgae (*Oscillatoria sp.*) also exhibited their highest $Cd^{2+,}$ biosorption efficiencies after 60 min [19, 26].

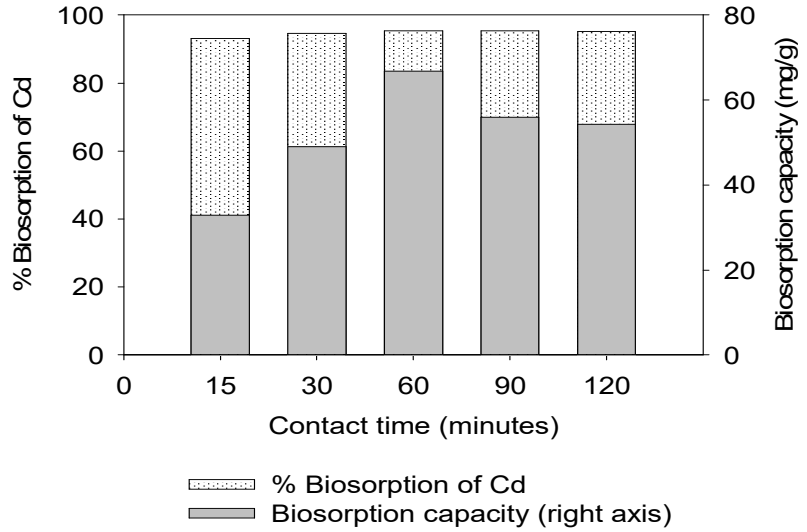

Figure 5 Effect of contact time on the biosorption of Cd(II) ions by dried algal Aphanothece sp. biomass in aqueous solution (temperature = 30°C, initial Cd(II) concentration = 7.7 mg/L, pH = 8.0). The error in the averaged results was below 1.5%.

3.6 Effect of Temperature

The temperature effects on Cd biosorption by the dried *Aphanothece sp.* biomass are presented on Figure 6. It shows that both biosorption capacity and biosorption efficiency were highest at 30°C and lowest at 50°C. This finding suggests the exothermic nature of Cd biosorption from aqueous solution by dried *Aphanothece sp*. However, the biosorption capacity reduced from 66.80 mg/g (at 30°C) to 13.33 mg/g (at 50°C). These trends indicate damages of the active binding sites on the biomass surface, which encourage desorption of the metal ions from the biosorbent surface into the solution.

Similar patterns were observed in Cd-ion biosorption by the blue–green microalga *Spirullina platensis*, the red macroalga *Ceramium virgatum* and the green macroalga *Ulva lactuta* [12,21,27].

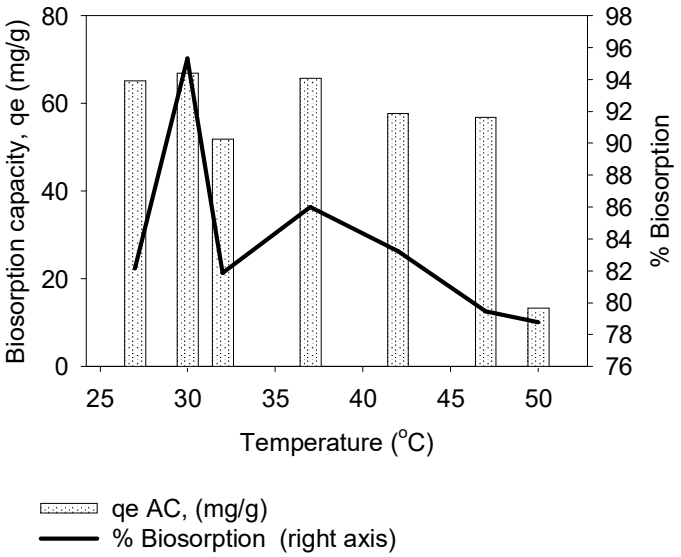

Figure 6 Effects of operational temperature on Cd biosorption by dried Aphanothece sp. biomass in a batch study (pH = 8.0, initial Cd(II) concentration = 2.09 mg/L, biomass concentration = 0.1 g/L and contact time = 60 min). The error in the averaged values is below 1.5%.

3.7 Biosorption Isotherm Models

In previous reports [18,29,30], the biosorption capacities of numerous biosorbents were assessed at fixed values of the experimental parameters, which describe the surface properties of the biosorbents and their affinity to tested metals. In this batch study, the Cd biosorption isotherm was studied in three equilibrium isotherm models: Langmuir, Freundlich and Dubinin-Radushkevich. The model parameters were determined by non-linear regression, as discussed in Tuzen and Sari et al. as well as Apiratikul and Pavasant [31,32]. Their non-linear equations are calculated as Eqs. (3), (4) and (5).

The Langmuir model is given by following Eq. (3):

$$q_e = q_{max} \frac{K_L C_e}{1+K_L C_e} \tag{3}$$

where q_e and q_{max} are the equilibrium and maximum biosorption capacities, (mol/g), K_L is the Langmuir isotherm parameter (L/mg), C_e is the equilibrium Cd concentration in solution and q_m is the monolayer biosorption capacity of the biosorbent (mg/g).

The Freundlich model is shown in following Eq. (4):

$$q_e = K_F C_e{}^n, \tag{4}$$

where K_F and n are the Freundlich sorption capacity (mg/g(L/mg)$^{1/n}$) and the biosorption intensity.

Finally, the DR model is defined by Eq. (5) as follow:

$$q_e = q_{max} exp^{-\beta\left(RTln\left(1+\left(\frac{1}{Ce}\right)\right)\right)^2}, \tag{5}$$

where R is the universal gas constant (8.314 E-03 kJ/mol K), and β is the Polanyi potential representing the activity coefficient in the DR isotherm model (mol^2/J^2). β is related to the mean sorption energy E (kJ/mol) described in Eq. (6) as follows:

$$E = \frac{1}{\sqrt{(-2\beta)}}. \tag{6}$$

The non-linear fittings of the experimental data in the above isotherm models are summarised in Table 2 and plotted in Figure 7. Table 2 provides the correlation coefficient R^2, the residual root means square error and the χ^2 error for non-linear equations.

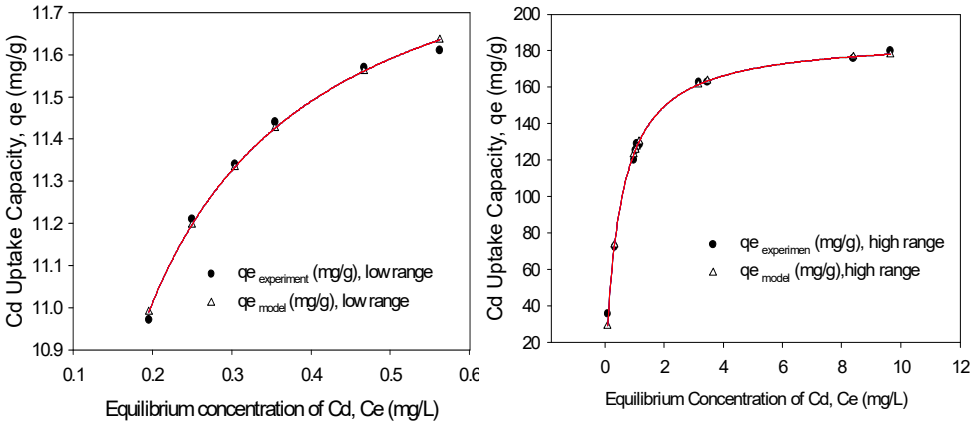

Figure 7 Non-linear equilibrium Langmuir isotherm model fitted to the data of the batch biosorption experiment at low and high ranges of initial Cd concentration ($C_{initial}$ = 1.09–6.23 mg/L and $C_{initial}$ = 5.41–53.47 mg/L). In both ranges, the pH and temperature were 8.0 and 30°C.

Table 2 Non-linear solutions of the three isotherm models of biosorption by dried *Aphanotece sp*. biomass at two ranges of initial Cd concentration.

Initial Cd^{2+} (mg/L)	Non Linear Langmuir isotherm constant				
	q_{max} (mg/g)	K_L(L/mg)	R^2	RMSE	$\chi 2$
A.C_0=1.09-6.23	12.01	5.49E-02	0.995	0.001	0.001
B.C_0=5.41 to 83.07	187.51	1.96E-03	0.996	0.394	1.699
Initial Cd^{2+} (mg/L)	**Non Linear Freundlich isotherm constant**				
	$KF_{(mg/g(L/mg)^{1/n})}$	l/n	R^2	RMSE	$\chi 2$
A.C_0=1.09-6.23	12.27	0.07	0.999	3.24E-05	0.058
B.C_0=5.41 to 83.07	114.13	0.23	0.886	7.31E-01	23.658
Initial Cd^{2+} (mg/L)	**Non Linear Dubinin-Radushkevich isotherm constant**					
	q_{max} (mol/g)	B(mol^2/J^2)	E(kJ/mol)	R^2	RMSE	$\chi 2$
A.C_0=1.09-6.23	1.13E-04	3.00E-09	12.91	0.990	5.838E-07	5.75E-07
B.C_0=5.41 to 83.07	1.17E-02	3.00E-09	12.91	0.991	6.662E-07	9.60E-07

Non-linear regression solved each model parameter. The Langmuir and DR models were better fitted to the experimental data than the Freundlich model. This implies that biosorption by the dried *Aphanothece sp.* biomass was a monolayer process, involving functional groups on the biosorbent surface. The maximum biosorption capacities q_{max} were 12.01 and 187.51 mg/g in the low and high ranges of initial Cd concentration. By partitioning the concentrations into low and high ranges, we can understand the effects of high and low initial concentrations on the biosorption characteristics (maximum biosorption capacity and kinetics constant).

High initial concentrations yielded larger q_{max} than the lower initial concentrations. Moreover, the q_{max} values obtained in the present study exceeded those in earlier reports [12, 23, 29, 34]. In the earlier researches, q_{max} was 98.04 mg/ml in the blue–green microalgae *Scenedesmus platensis* [28], 85.30 mg/g in the green microalgae *Chlorella vulgaris* [34], 88.20 mg/g in the filamentous green microalgae *Oedogonium sp.* [14] and 27.3 mg/g in the macro fungus *Amanita rubescens* [25]. In the present study, the Langmuir biosorption constant (K_L) was 28 orders of magnitude higher in the low range than in the high range of initial concentrations (Table 2). The K_Ls were within the range of K_Ls found in *Oedogonium sp.* reported by Gupta and Rastogi [14].

The biosorption energy (E) was estimated from the DR isotherm (see Table 2), and the fitting result is shown in Figure 7. The value of E determines whether

the sorption mechanism is physical or chemical. Chemisorption occurs between 8 and 16 kJ/mol. The coefficient of determination (R^2) in the non-linear DR isotherm modelling was extremely high, confirming that the dried *Aphanothece sp* biomass adsorbed Cd ions by a chemisorption mechanism (with a biosorption energy of 12.91 kJ/mol).

Similar results were reported by Sari and Tuzen [27], who obtained E = 9.6 kJ/mol in Cd biosorption by the green macroalga *U. lactuta.* They suggested that chemisorption occurs by electron exchange between the Cd ions and functional groups on the biosorbent surface. The biosorption capacity estimated from the DR isotherm (q_{max}) in the low range of initial Cd concentrations was 1.13 E-04 mol/g, comparable with that of *Ulva lactuta* reported by Sari and Tuzen [27] (Figure 8). Meanwhile, in the high range of initial concentrations, the q_{max} increased up to one hundred fold its value at low concentrations (1.17 E-02 mol/g).

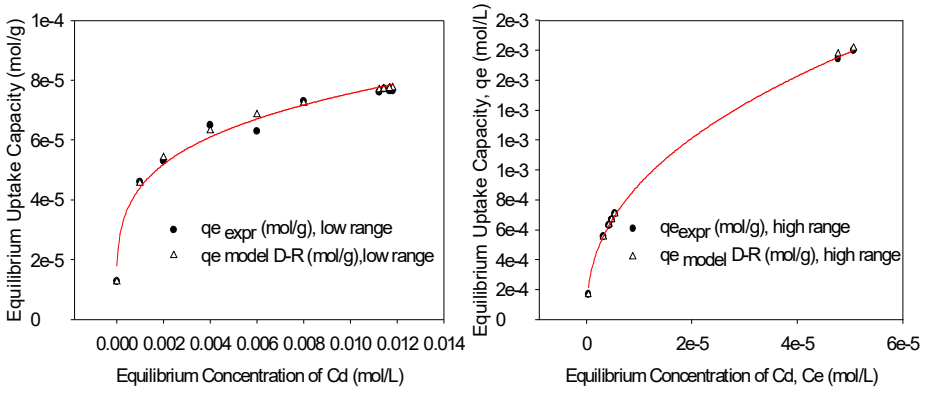

Figure 8 Non-linear equilibrium DR isotherm model fitted to the data of a batch biosorption experiment in the low and high ranges of initial Cd concentrations ($C_{initial}$ = 1.08–6.23 and $C_{initial}$ = 5.41–53.47 mg/L). In both cases, the pH and temperature were 8.0 and 30°C).

3.8 Biosorption Thermodynamics

To understand the thermodynamic behaviour of Cd^{2+} biosorption by the dried *Aphanothece sp*. biomass in this study, we calculated the changes in free energy, enthalpy and entropy (ΔG^0, $\Delta H0$ and ΔS^0, respectively), as described in Sari and Tuzen [27], Aksu [34] and Rathinam et al. [26]. Figure 9 plots ln Kd (the distribution coefficient of Cd between biosorbent and solution, equal to q_e/C_e) as a function of 1/T. The value of ΔG^0 is related to the operational temperature T, here expressed in Kelvin (K). Therefore, ΔG^0 in the 300–323 K range is given by Eq. (7) as follow:

$$\Delta G^0 = -RT \ln K_d. \quad (7)$$

Next, ΔH^0 and ΔS^0 were obtained from the slope and intercept of the ln K_d versus 1/T plot (Figure 9). The results are presented in Table 3.

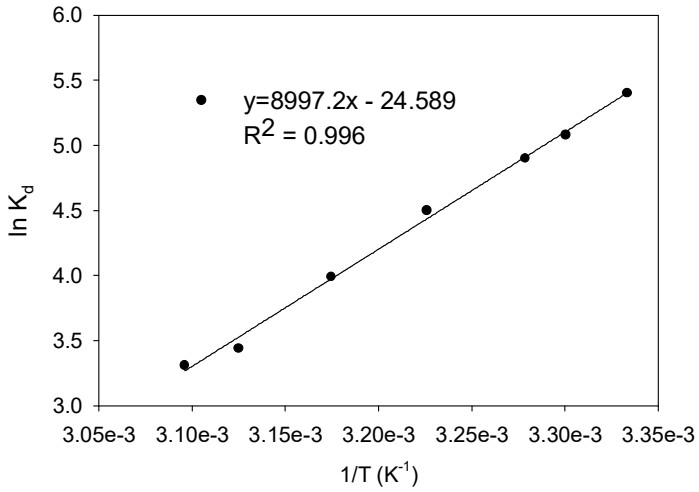

Figure 9 The plot of ln K_d versus 1/T for estimating the thermodynamic parameters of Cd^{2+} biosorption by dried *Aphanothece sp.* biomass (pH = 8.0, biomass concentration = 0.1 g/L, contact time = 60 min and initial concentration = 8.8 mg/L).

The negative ΔG^0 values indicate that Cd biosorption onto the dried *Aphanothece* sp. biomass is spontaneous and energetically feasible. The ΔG^0 increased with increasing temperature, meaning that the spontaneity of the reaction decreased at higher temperatures. The ΔH^0 describes both the nature of the heat reaction (exothermic or endothermic) and the nature of the biosorption (physio sorption or chemisorption). The magnitude of ΔH^0 lies between −20 and 0 kJ/mol for physio sorption and between −80 and −400 kJ/mol for chemisorption [27]. In Table 3, the heat of reaction ΔH^0 is −74.82 kJ/mol (between −20.9 and −418.4 kJ/mol), suggesting that the biosorption process on the dried *Aphanothece sp*. biomass was exothermic and chemisorptive. Chemisorptive biosorption of Cd(II) was likewise observed on dried *Ceramium virgatum* biomass (ΔH^0 = −31.8 kJ/mol) [21] and on dried *Hypnea valentinae* biomass (ΔH^0 = −4.82 kJ/mol) [26].

This result was then confirmed by the DR isotherm model, which analyses the mean biosorption energy. The disorder indicator ΔS^0 was negative (−0.204

kJ/mol; see Table 3), indicating that the interface between the biosorbent surface and solution was less disordered after the biosorption process [27,28].

Table 3 Thermodynamic parameters of Cd biosorption on dried Aphanothece sp. biomass at different temperatures.

Thermodynamics Parameter			
Temperature (K)	**ΔG^0(kJ/mol)**	**ΔH^0(kJ/mol)**	**ΔS^0(kJ/mol K)**
300	-13.47	-74.82	-0.204
303	-12.80		
305	-12.43		
310	-11.60		
315	-10.45		
320	-9.15		
323	-8.88		

3.9 Biosorption Kinetics

To optimise the batch biosorption system, we must predict the biosorption rate. The efficiency of the reaction is strongly correlated with the reaction kinetics. To calculate the rate of reaction, we fitted the experimental data by two kinetic models, Lagergren's pseudo first-order and pseudo second-order models. The non-linear forms of both models are given in Freitas, *et al.* [35]:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{8}$$

$$q_t = \frac{k_2 q_e^2 t}{(1+q_e k_2 t)}, \tag{9}$$

where q_e and q_t denote the amounts of Cd ions adsorbed on the biosorbent at the equilibrium time and at time t, (mg/g), and k_1 and k_2 are the pseudo first- and second-order rate constants. The R^2 of this evaluation and two error functions (the normalised standard deviation (NSD) and the average relative error (ARE)) are presented in Table 4.

The R^2, NSD and ARE values inform that Cd biosorption on the dried *Aphanothece sp.* was better fitted to the pseudo second-order model than to its first-order counterpart. In addition, the values predicted by the pseudo second-order model are much closer to the experimental q_e. Similar results were reported by Freitas, *et al.* [35], who investigated Cd^{2+} removal by the dried biomasses of four macroalgae species (*Laminaria hyperbora, Sargassum muticum, Fucus spiralis and Bifurcaria bifurcate*). The pseudo second-order model best fitted the biosorption of Cd^{2+} on *Fucus spiralis*.

Table 4 Kinetic rate constants in the pseudo first- and second-order models in the low and high ranges of initial Cd concentration during the biosorption of Cd ions from aqueous solution by dried *Aphanothece sp.* biomass.

Initial Cd^{2+}	$qe_{(exp)}$(mg/g)	Pseudo First Order Constant Rate				
		k_1(min^{-1})	$qe_{(cal)}$(mg/g)	R^2	NSD	ARE
C_0=1.59 mg/L (low conc.)	3.24	8.39E-02	3.00	0.990	0.119	0.096
C_0=5.41 mg/L (high conc.)	53.75	9.17E-02	50.49	0.982	0.350	-0.284
Initial Cd^{2+}	**$qe_{(exp)}$(mg/g)**	**Pseudo Second Order Constant Rate**				
		k_2(g/mg.min)	$qe_{(cal)}$(mg/g)	R^2	NSD	ARE
C_0=1.59 mg/L (low conc.)	3.13	3.86E-02	3.33	0.999	0.092	-0.075
C_0=5.41 mg/L (high conc.)	55.56	2.04E-03	56.61	0.994	0.173	-0.140

3.10 Reusability

The repetitive reusability of dried *Aphanothece sp.* as biosorbent was studied under the following operational conditions: initial Cd concentration = 7.2 mg/L, pH = 8.0, biosorbent concentration = 0.1 g/L and 1-M HCl as desorbing eluent. The experiment was conducted over three cycles, and the result is given in Figure 6.

The Cd-uptake capacity slightly reduced after the third cycle (from 63.51 to 58.23 mg/g). Conversely, the uptake capacity declined steeply at the third desorption process (from 48.71 to 15.62 mg/g), suggesting that 1-M HCl is an overly strong desorbing eluent, destroying the important functional groups on the biosorbent surface. This would lower the Cd^{2+} ion uptake and the desorption/biosorption ratio. Cd^{2+} biosorption onto other dried blue–green microalgae species, namely *Oscillatoria sp.*, showed no significant change in biosorption capacity after three cycles (27.5 mg/g after Cycle 1 vs. 27.4 mg/g after Cycle 3) [28].

The discrepancy between this study and their report probably arises from the different concentrations of the desorbing eluent in the two studies (Katircioglu, *et al.* [28] used 0.1-M HCl as the eluent) and from the different properties (structure, functional groups, and surface area) of the *Oscillatoria sp.* and *Aphanotece sp.* dried biosorbents.

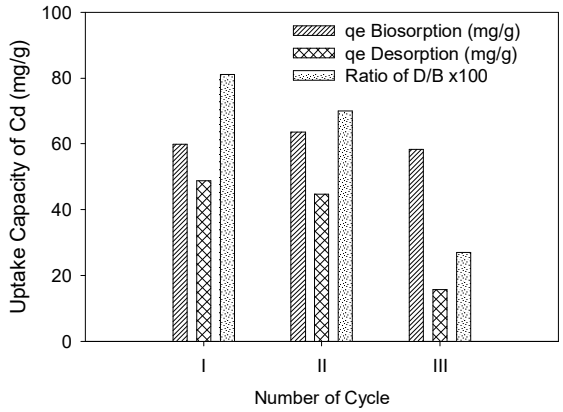

Figure 10 Successive Cd-ion biosorption/desorption cycles. The biosorbent was the dried biomass of *Aphanothece sp.* reared in a batch system (initial Cd concentration = 7.2 mg/L, pH = 8.0, biosorbent concentration = 0.1 g/L, temperature = 30°C and 1-M HCL as desorbing eluent).

4 Conclusion

This study evaluated the equilibrium, thermodynamics, and kinetic aspects of Cd^{2+}ion biosorption from aqueous solution by dried *Aphanothece sp.* biomass. The effective operating parameters (solution pH, biomass concentration, contact time and reaction temperature) were obtained. The biosorption capacity was maximised at 187.51 and 12.01 mg/g in the higher and lower ranges of initial Cd concentrations. The other optimal conditions were pH = 8.0, contact time = 60 min, biomass concentration = 0.1 g/L and temperature = 30°C. The mean free energy calculated from the DR model (12.91 kJ/mol) and the heat of reaction ΔH (−74.82 kJ/mol) indicate that the Cd^{2+} ions were adsorbed to the dried *Aphanothece sp.* biomass through chemical ion-exchange or chemisorption.

The negative values of ΔG^0 and ΔH^0 confirmed that the reaction was spontaneous and exothermic, demonstrating the feasibility of Cd(II) biosorption using dried *Aphanothece sp.* biomass. The ΔS^0 parameter decreased during the binding of Cd^{2+}ions to the active sites of the biosorbent, indicating reduced disorder at the solid–solution interface after binding. The kinetics of the experimental data were best described by a pseudo second-order model (R^2 = 0.994–0.999). The slightly decreased Cd^{2+} biosorption capacity after three adsorption/desorption cycles indicates that the biosorbent retains its removal ability for this metal after three successive runs. Therefore, dried biomass of native *Aphanothece sp.* (cultivated in an atmospheric photobioreactor system) is

a potential alternative biosorbent for wastewater contaminated by Cd^{2+}ions. It demonstrated high biosorption capacity, high biosorption efficiency and good reusability in the present study.

Acknowledgement

We are grateful for the financial and technical support provided by the Department of Chemical Engineering-Faculty of Industrial Technology-Institut Teknologi Bandung, Research Centre for Limnology-The Indonesian Institute of Sciences and Research Centre for Geotechnology- The Indonesian Institute of Sciences.

References

[1] Wang, J. & Chen, C., *Biosorbents for Heavy Metals Removal and Their Future*, Biotechnology Advances, **27**(2), pp. 195-226, 2009.

[2] Flouty, R. & Estephane, G. *Bioaccumulation and Biosorption of Copper and Lead by a Unicellular Algae Chlamydomonas Reinhardtii in Single and Binary Metal Systems: A Comparative Study*, Journal of Environmental Management, **111**, pp. 106-114, 2012.

[3] Dil, E. A., Ghaedi, M. & Asfaram, A., *The Performance of Nanorods Material as Adsorbent for Removal of Azo Dyes and Heavy Metal Ions: Application of Ultrasound Wave, Optimization, and Modeling*, Ultrasonics Sonochemistry, **34**, pp. 792-802, 2017.

[4] Chen, C., Chang, H., Kao, P., Pan, J. & Chang, J., *Biosorption of Cadmium by CO2-fixing Microalga Scenedesmus Obliquus CNW-N*, Bioresource Technology, **105**, pp. 74-80, 2012.

[5] Darmayanti, L., Notodarmodjo, S. & Damanhuri, E., *Removal of Copper (II) Ions in Aqueous Solutions by Sorption onto Fly Ash*, Journal of Engineering and Technological Sciences, **49**(4), pp. 546-559, 2017.

[6] Muslim, A., Ellysa, E. & Said, S.D., *Cu(II) Ions Adsorption Using Activated Carbon Prepared from Pithecellobium Jiringa (Jengkol) Shells with Ultrasonic Assistance: Isotherm, Kinetic and Thermodynamic Studies*, Journal of Engineering and Technological Sciences, **49**(4), pp. 472-490, 2017.

[7] Chojnacka, K., *Biosorption and Bioaccumulation – The Prospects for Practical Applications*, Environment International, **36**(3), pp. 299-307, 2010.

[8] Das, N., *Recovery of Precious Metals through Biosorption — A Review*, Hydrometallurgy, **103**(1), pp. 180-189, 2010.

[9] Fomina, M. & Gadd, G. M., *Biosorption: Current Perspectives on Concept, Definition and Application*, Bioresource Technology, **160**, pp. 3-14, 2014.

[10] Ghaedi, M., Hajati, S., Karimi, F., Barazesh, B. & Ghezelbash, G., *Equilibrium, Kinetic and Isotherm of Some Metal Ion Biosorption*, Journal of Industrial and Engineering Chemistry, **19**(3), pp. 987-992, 2013.

[11] Rybak, A., Messyasz, B. & Łęska, B., *Freshwater Ulva (Chlorophyta) as a Bioaccumulator of Selected Heavy Metals (Cd, Ni And Pb) and Alkaline Earth Metals (Ca and Mg)*, Chemosphere, **89**(9), pp. 1066-1076, 2012.

[12] Şeker, A., Shahwan, T., Eroğlu, A. E., Yılmaz, S., Demirel, Z. & Dalay, M. C., *Equilibrium, Thermodynamic and Kinetic Studies for the Biosorption of Aqueous Lead(II), Cadmium(II) and Nickel(II) Ions on Spirulina Platensis*, Journal of Hazardous Materials, **154**(1), pp. 973-980, 2008.

[13] Monteiro, C. M., Castro, P.M.L. & Malcata, F. X., *Cadmium Removal by Two Strains of Desmodesmus Pleimorphus Cells*., Water Air Soil Pollution, **208**, pp. 17-27, 2010.

[14] Gupta, V. K. & Rastogi, A., *Equilibrium and Kinetic Modelling of Cadmium(II) Biosorption by Nonliving Algal Biomass Oedogonium sp. from Aqueous Phase*," Journal of Hazardous Materials, **153**(1), pp. 759-766, 2008.

[15] Awalina, Sulawesty, F., Oktariani, E., Chrismadha, T., Satya, I., Naidida, E. & Setiadi, T., *Freshwater Phytoplankton as Potential Heavy Metal Biosorbent and its Natural Aquatic Physico-Chemical Characteristics s: A Study case on Situ Rawa Kalong-Depok*, International Seminar on Chemical Engineering in Conjunction with Seminar Teknik Kimia Soehadi Reksowardojo (STKSR), 2014.

[16] Awalina, Nurulfadilah, A., Harimawan, A. & Setiadi, T. *Carbon Dioxide Bio-sequestration Potential and Growth Kinetics of Aphanothece sp in A Photo-bioreactor*, in The 22nd Regional Symposium on Chemical Engineering: RSCE, 2015.

[17] Devi, K. U., Swapna, G. & Suneetha, S., *19 - Microalgae in Bioremediation: Sequestration of Greenhouse Gases, Clearout of Fugitive Nutrient Minerals, and Subtraction of Toxic Elements from Waters*, in Microbial Biodegradation and Bioremediation, S. Das, Ed., ed Oxford: Elsevier, pp. 435-456, 2014.

[18] Aksu, Z. & Açikel, Ü., *Modelling of a Single-staged Bioseparation Process for Simultaneous Removal of Iron(III) and Chromium(VI) by using Chlorella vulgaris*, Biochemical Engineering Journal, **4**(3), pp. 229-238, 2000.

[19] Cochrane, E. L., Lu, S., Gibb, S. W. & Villaescusa, I., *A Comparison of Low-cost Biosorbents and Commercial Sorbents for the Removal of Copper from Aqueous Media*, Journal of Hazardous Materials, **137**(1), pp. 198-206, 2006.

[20] Hossain, M.A., Ngo, H., Guo, W. & Nguyen, T., *Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption*, Journal of Water Sustainability, **2**(1), pp. 87-104, 2012.

[21] Sarı, A. & Tuzen, M., *Biosorption of Total Chromium from Aqueous Solution by Red Algae (Ceramium virgatum): Equilibrium, Kinetic and Thermodynamic Studies*, Journal of Hazardous Materials, **160**(2), pp. 349-355, 2008.

[22] Gupta, V. K. & Rastogi, A., *Biosorption of Lead from Aqueous Solutions by Green Algae Spirogyra Species: Kinetics and Equilibrium Studies*, Journal of Hazardous Materials, **152**(1), pp. 407-414, 2008.

[23] Kumar, D. & Gaur, J. P., *Metal Biosorption by Two Cyanobacterial Mats in relation to Ph, Biomass Concentration, Pretreatment and Reuse*, Bioresource Technology, **102**(3), pp. 2529-25352011.

[24] Uluozlu, O. D., Sari, A., Tuzen, M. & Soylak, M., *Biosorption of Pb(II) and Cr(III) from Aqueous Solution by Lichen (Parmelina tiliaceae) Biomass*, Bioresource Technology, **99**(8), pp. 2972-2980, 2008.

[25] Sarı, A. & Tuzen, M., *Kinetic and Equilibrium Studies of Biosorption of Pb(II) and Cd(II) from Aqueous Solution by Macrofungus (Amanita rubescens) Biomass*, Journal of Hazardous Materials, **164**(2-3), pp. 1004-1011, 2009.

[26] Rathinam, A., Maharshi, B., Janardhanan, S. K., Jonnalagadda, R. R. & Nair, B.U., *Biosorption of Cadmium Metal Ion from Simulated Wastewaters using Hypnea Valentiae Biomass: A Kinetic and Thermodynamic Study*, Bioresource Technology, **101**(5), pp. 1466-1470, 2010.

[27] Sari A., & Tuzen, M., *Biosorption of Pb(II) and Cd(II) from Aqueous Solution using Green Alga (Ulva Lactuta) Biomass*, Journal of Hazardous Materials, **152**(1), pp. 302-308, 2008.

[28] Katırcıoğlu, H., Aslım, B., Rehber Türker, A., Atıcı, T. & Beyatlı, Y., *Removal of Cadmium(II) Ion from Aqueous System by Dry Biomass, Immobilized Live and Heat-Inactivated Oscillatoria Sp. H1 Isolated From Freshwater (Mogan Lake)*, Bioresource Technology, **99**(10), pp. 4185-4191, 2008.

[29] Abdel-Aty, A. M., Ammar, N. S., Abdel Ghafar, H. H. & Ali, R. K., *Biosorption of Cadmium and Lead from Aqueous Solution by Fresh Water Alga Anabaena Sphaerica Biomass*, Journal of Advanced Research, **4**(4), pp. 367-374, 2013.

[30] Anastopoulos, I. & Kyzas, G. Z., *Progress in Batch Biosorption of Heavy Metals onto Algae*, Journal of Molecular Liquids, **209**, pp. 77-86, 2015.

[31] Tuzen, M. & Sarı, A., *Biosorption of Selenium from Aqueous Solution by Green Algae (Cladophora hutchinsiae) Biomass: Equilibrium,*

Thermodynamic and Kinetic Studies, Chemical Engineering Journal, **158**(2), pp. 200-206, 2010.

[32] Apiratikul, R. & Pavasant, P., *Batch and Column Studies of Biosorption of Heavy Metals by Caulerpa lentillifera*, Bioresource Technology, **99**(8), pp. 2766-2777, 2008.

[33] Rangsayatorn, N., Upatham, E. S., Kruatrachue, M., Pokethitiyook, P. & Lanza, G.R., *Phytoremediation Potential of Spirulina (Arthrospira) platensis: Biosorption and Toxicity Studies of Cadmium*, Environmental Pollution, **119**(1), pp. 45-53, 2002.

[34] Aksu, Z. *Equilibrium and Kinetic Modelling of Cadmium(II) Biosorption by C. vulgaris in a Batch System: Effect of Temperature*, Separation and Purification Technology, **21**(3), pp. 285-294, 2001.

[35] Freitas, O. M. M., Martins, R. J. E., Delerue-Matos, C. M. & Boaventura, R. A. R., *Removal of Cd (II), Zn (II) and Pb (II) from Aqueous Solutions by Brown Marine Macro Algae: Kinetic Modelling*, Journal of Hazardous Materials, **153**(1-2), pp. 493-501, 2008.