Equilibrium and kinetic modelling of cadmium (II) biosorption by Dried Biomass *Aphanothece* sp. from aqueous phase

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Abstract. The Biosorption of cadmium (II) ions on dried biomass of *Aphanothece* sp. which previously grown in a photobioreactor system with atmospheric carbon dioxide fed input, was studied in a batch system with respect to initial pH, biomass concentration, contact time, and temperature. The biomass exhibited the highest cadmium (II) uptake capacity at 30ºC, initial pH of 8.0±0.2 in 60 minute and initial cadmium (II) ion concentration of 7.76 mg/L. Maximum biosorption capacities were 16.47 mg/g, 54.95 mg/g and 119.05 mg/g at range of initial cadmium (II) 0.96-3.63 mg/L, 1.99-8.10 mg/L and 6.48-54.38 mg/L, respectively. Uptake kinetics follows the pseudo-second order model while equilibrium is best described by Langmuir isotherm model. Isotherms have been used to determine thermodynamic parameter process (free energy change, enthalpy change and entropy change). FTIR analysis of microalgae biomass revealed the presence of amino acids, carboxyl, hydroxyl, sulfhydryl and carbonyl groups, which are responsible for biosorption of metal ions. During repeated sorption/desorption cycles, the ratio of Cd (II) desorption to biosorption decreased from 81% (at first cycle) to only 27% (at the third cycle). Nevertheless, due to its higher biosorption capability than other adsorbent, *Aphanothece* sp. appears to be a good biosorbent for removing metal Cd (II) ions from aqueous phase.

1. Introduction

The existence of heavy metals in water and waste water has increasing due to the industrial waste water in the water bodies. Cadmium (Cd) is one of big toxic three heavy metals together with mercury (Hg) and lead (Pb) posing the greatest hazard to human health. Once Cd enters into aquatic ecosystem it can be accumulated through the trophic chain and produce toxic effect and *terratogenic* changes in aquatic ecosystem components including of human as top consumer in food chain [1]. Mainly, source of Cd which release into aquatic environment through waste streams come from process of electroplating, smelting, and some manufacturing (plastic, alloy, pigment, battery, mining, refining). In the other hand there are some strict regulation in term of limit of Cd content in wastewater and drinking water, which must be about 0.100 and 0.05 mg/L. To address that requirement, there are some
conventional technology for Cd removal from wastewater, for example chemical precipitation, chemical oxidation or reduction, evaporation, adsorption and ion exchange has been developed. But, those processes seem ineffective or obviously expensive, moreover if concentration of metal in waste water occurs in order 0.1 to 100 mg/L. Therefore, it is necessary to develop more economically feasible technique to remove this metal from waste water [2].

Various biomass have been investigated for Cd uptake including yeast, fungi, bacteria, agricultural waste, macro algae, microalgae and others. Recently, microalgae applications in waste water treatment for removing heavy metals (including of Cd) has been exploited. It has been known that microalgae have outstanding accumulation capacity of heavy metals even at low concentration. Particularly if microalgae originated and isolated from polluted waters. By using their biomass, it will allow to facilitate a development of inexpensive biosorbent for alternative metals removal technology. There are numerous potentials microalgae species with different capability to bind heavy metals ion, which each of capability depends on type of microalgae, type of heavy metals and physic-chemical conditions that may give significant effect on biosorption process. Therefore it is necessary to investigate a more detail regarding to specific microalgae capability to bind heavy metal in its biomass and many factors which affected on its process [2,3].

The aim of present study was to assess Cd biosorption Cd of wild strain freshwater microalgae *Aphanothece* sp. that had been previously isolated from a heavy polluted urban lake namely Situ Rawa Kalong–Depok, and then cultivated, harvested and processed into a biosorbent in laboratory of Bioprocess engineering-Dept. of Chemical engineering-ITB. Assessment involves of Fourrier Transform Infra-Red (FT-IR) spectrum characters; the influence of some operational condition parameter (pH, initial Cd concentration, biosorbent concentration, contact time, and temperature of solution) against biosorption efficiency. Biosorption uptake also has been quantified by means of two sorption models: Langmuir and Freundlich as well as two kinetic models: pseudo first order and pseudo second order. Furthermore, the effect of 1 M HCl as desorbing eluent on biosorption-desorption capacities and comparison due to its biosorption capability with other biosorbent were also considered.

2. Material and methods

2.1. Biosorbent preparation

*Aphanothece* sp was isolated from urban hyper eutrophic lake namely Situ Rawa Kalong-Depok. According to [3], this microalgae is belong to unicellular blue green algae (Cyanobacter), may form colonies with oval-shaped or oblong cells clustered densely and evenly within firm and abundant mucilage, although the mucous sheaths of individual cells are indistinct. The cells have granules but lack vacuoles. Its cells size are 1-4μm broad and 2-8 μm long. Cultivation in laboratory environment was conducted in a photobioreactor system which consisted of three bioreactors with each of them was 3 L in volume, illuminated with ~5700 to 6000 lux of daylight lamps, temperature range was 28-30 ºC and continuously aerated with 3L/minute of compressed air with atmospheric carbon dioxide input for 14 days. Harvesting was conducted by centrifugation in 6000 round per minutes (rpm) for 15 minutes in 25ºC resulting blue green wet pellets, which then dried in oven 60ºC for 7x24 hours. Dried biomass then crushed and sieved into particle size of 354 µm, stored in polyethilen bottle until biosorption experiments. Elemental analysis of % Carbon (C), Hydrogen (H), Nitrogen (N) and Sulfur (S) was conducted by using Labconco CHNS Analyzer. According to the result *Aphanothece* sp mainly involves 42.53%C, 6.43%H, 7.71%N and 0.51%S. Moisture content was 93.16-99.72%. The existence of functional groups which responsible for metal biosorption identification was confirmed by Fourier Transform Infra-Red (FTIR) analysis by using FTIR Prestige 21 Shimadzu (which recorded at 500 to 4500 cm⁻¹ ) prior to biosorption test.
2.2. Preparation and analysis of Cd solution
Cd stock solution (1000 mg/L) for biosorption was prepared in demineralized water with analytical grade salt of CdCl$_2$.2.5H$_2$O. The stock solution was diluted with demineralized water in order to prepare solutions of the desired concentrations. Biosorption studies were performed in 100 mL clear capped bottles. Pre-weighed dried biomass was added to each bottles and constantly agitated at 120 rpm at 30ºC, until the equilibrium was reached. At the end of biosorption, sample was filtered and collected in poly ethylene bottles. Cd content in filtrate was determined by an atomic absorption spectrophotometer model A-7000 (Shimadzu, Japan) at wavelength 226.502 nm. The absorption capacities were obtained by mass balance calculation (equation 1)

$$q_t = (C_0 - C_t) \frac{V}{w}$$  \hspace{1cm} (1)

Where $C_0$ and $C_t$ are the initial and concentration of solution at time t (mg/L), $q_t$ is concentration of Cd on biosorbent (mg/g), $V$ is the volume of Cd solution (L) and $W$ is the mass of the biosorbent used (g).

The efficiency of Cd biosorption was calculated as according to equation (2)

$$Biosorption \% = \left( \frac{C_0 - C_f}{C_0} \right) \times 100$$  \hspace{1cm} (2)

Where $C_0$ and $C_f$ are the initial and final metal concentrations.

All the experiments were performed in a batch set up taking two replicates and average values were reported. Standard deviations were found to be within ±1.3%.

2.3. Biosorption studies
The biosorption of Cd (II) ions on dried microalgae biomass of Aphanothece sp was investigated in batch biosorption- equilibrium experiments. The effect of solution pH, biomass concentration, contact time and temperature on biosorption efficiency and initial Cd concentration on biosorption rate and capacity were studied according to [5,6]. The effect of pH was studied using a pH meter (Ohaus starter 3000, USA) in the range 3.0 to 11.0 and the desired pH of the solution was maintained by adding buffer solutions which respectively pH 3 (buffer KH$_2$Phtalate and 0.1 M HCl); pH 5 (buffer KH$_2$Phtalate and 0.1 M NaOH); pH 7 and pH 8 (buffer KH$_2$PO$_4$ and 0.1 M NaOH); pH 9 (buffer Na$_2$tetaborate and 0.1 M HCl); and pH 11 (buffer Na-bicarbonate and 0.1 M NaOH). To determine the effect of biosorbent concentration, different biosorbent concentration 0.1 to 2.0 g/L were varied and suspended in Cd (II) solution of 7.9 mg/L. The sorption procedure was the same as described earlier.

To obtain biosorption isotherms and kinetics, the biosorbent (0.1 g/L) was suspended in Cd solutions (initial concentration range 0.96 to 53.38 mg/L), carried out in 30ºC. While thermodynamic study performed in 27, 30, 32, 37, 42, 47 and 50 ºC. The time required for reaching equilibrium condition was estimated by drawing samples at regular interval of time until equilibrium was reached.

2.4. Successive biosorption-desorption cycles
In order to determine the reusability of the biosorbent, consecutive biosorption-desorption cycles were repeated three times. HCl 1 M was evaluated for its capacity to desorb Cd (II) from metal loaded biosorbent. The biomass Cd loaded was placed in the HCl 1 M and agitated in shaker with 120 rpm agitation for 60 minutes at 30ºC. After each of biosorption-desorption cycle, the biomass was washed with demineralized water and reconditioned for biosorption in the succeeding cycle.
3. Result and discussion

3.1. FTIR spectrum of dried biomass of Aphanothece sp.

The transmittance spectrum of native or metal unloaded dried biomass of Aphanothece sp. with initial concentration of Cd 7.9 mg/L is shown in Figure 1. As seen on Figure 1, the broad and strong band at 3388.93 cm\(^{-1}\) is attributed to overlapping of -OH and N-H stretching vibration. While the band at 2926.01 cm\(^{-1}\) is assignment to the –CH stretch. The band peaks at 1651.07 and 1450.47 cm\(^{-1}\) recognized to asymmetric and symmetric stretching vibration of C=O groups. The bands 1242.16 and 1074 cm\(^{-1}\) assign to stretching of C-O groups on the biomass surface. Some bands in the fingerprint region attributed to sulfur esters S-OR and disulfide S-S. This FTIR spectra indicate the presence of ionizable functional groups (such like carboxyl, amino, amide and hydroxyl) which capable to interact with protons or ions. Those obtained data also suggested the presence of functional groups on the microalga cell surfaces and also on the biosorption mechanism which is dependent on functional groups especially carboxyl, hydroxyl, amines and amides.

![Figure 1. Fourier Transformed Infra-Red spectra of natural dried Aphanothece sp biomass.](image)

3.2. Biosorption of Cd (II) ion

3.2.1. Influence of biosorbent concentration

The effect of biosorbent concentration on Cd (II) ions was examined using different biomass concentration in the range 0.1-2.0 g/L as presented on Figure 3. Results show that the biosorption efficiency is highly dependent on the decrease in biosorbent concentration. The biosorption efficiency of Cd ion in this study was attained at about biomass concentration 0.1 g/L and it sharply declined over higher biosorbent concentrations. This pattern could be explained as a consequence of partial aggregation of biomass at higher concentration, which results in a decrease in effective surface area for the biosorption. Similar trend also reported by [7] for the adsorption of Cd by dried biomass of red
seaweed *Hypnea valentinae*. Therefore, the optimum biomass concentration was selected as 0.1 g/L for further experiments.

**Figure 2.** Effect of biosorbent concentration on the biosorption of Cd (II) ions on dried algal biomass *Aphanothece sp* from aqueous solutions: temperature 30ºC, initial Cd (II) concentration 7.9 mg/L, pH 8 (average values of two tests, error < 1.5%)

3.2.2. **Effect of contact time**

One of important parameter which affecting biosorption process is contact time. Figure 2 shows the effect of contact time on Cd biosorption on dried biomass of *Aphanothece sp* from aqueous solutions (at six different initial Cd concentration). The plot indicates that the remaining Cd ion becomes unchanged after 60 minutes. This represents the equilibrium time at which an equilibrium Cd ion is presumed to have been attained. These obtained data were further used to evaluate the kinetics of the biosorption process.

**Figure 3.** Effect of contact time on the biosorption of Cd (II) ions on dried algal biomass *Aphanothece sp* from aqueous solutions: temperature 30ºC, biomass concentration 0.1 g/L (average values of two tests, error < 1.5%)

3.2.3. **Effect of pH**

Based on earlier biosorption studies, metal biosorption is strongly affected by pH of solution. So, Cd (II) biosorption in this study is also a function of pH solution. As seen on Figure 4, biosorption efficiency were highest in pH 8 and steeply declined at pH 9. The pH value in solution influences both
of cell surface metal binding sites and metal chemistry in water. At low pH, cell wall ligands were closely associated with hydronium ions (H$_3$O$^+$) and restricted the approach of metal cations as a result of the repulsive force. As the pH increased, more ligands such as carboxyl, imidazole, phosphate, hydroxyl and amino groups would be exposed and carried negative charges with subsequent attraction of metallic ions which have positive charge and then biosorption proceeded on to biosorbent surface [8]. The decrease of metal binding for pH upper than 8.0 is due to the complexation of Cd (II) by hydroxyl (OH$^-$) group which would prevent biosorption. Increasing of biosorption efficiency seem occurred at pH 11, but it is due to formation of more precipitation not biosorption. Since the highest biosorption efficiency which was not accompanied by precipitation occurred at pH 8, therefore all of the next biosorption experiments were conducted at pH 8. Further, modelling development was based on the experiment results which performed at pH 8.

![Graph](image.png)

**Figure 4.** Effect of pH on the reduction of Cd (II) ions by dried algal biomass of *Aphanothece sp* from aqueous solutions: temperature 30ºC, initial Cd (II) concentration 1.3 mg/L (average values of two tests, error < 1.1%)

3.2.4. Effect of temperature

Figure 5 show the effect of temperature solution on Cd (II) biosorption by dried algal biomass *Aphanothece sp*. The highest biosorption efficiency attained at 30ºC while the lowest efficiency found at 47ºC. This result indicated biosorption of Cd (II) ions on dried algal biomass *Aphanothece sp* from aqueous solutions was proceed in exothermic nature. Temperature rising then lead to declining of biosorption efficiency (from 95.32% at 30ºC to 79.46% at 47ºC). This finding occurred may be caused by either the damage of active binding sites in the biomass [9] or the tendency to desorb metal ions from the interface of biomass to the solution as the increasing of temperature implemented in the process [10].
Figure 5. Effect of temperature on the reduction of Cd (II) ions by dried algal biomass *Aphanothece sp* from aqueous solutions: pH 8, initial Cd (II) concentration 7.9 mg/L and biomass concentration 0.1 g/L, contact time 60 minute (average values of two tests, error < 1.5%)

3.3. Isotherms modelling

Langmuir and Freundlich isotherms were used to quantitatively describe metal biosorption by the tested microalgae biomass. The Langmuir model is expressed by the linearized equation

\[
\frac{C_e}{q_e} = \frac{C_m}{q_m} + \frac{1}{K_L q_m}
\]

where \(q_e\) is the equilibrium metal ion concentration on the biosorbent (mg/g), \(C_e\) is the equilibrium metal ion concentration in the solution (mg/L), \(q_m\) is the monolayer biosorption capacity on biosorbent (mg/g), and \(K_L\) is the Langmuir biosorption constant (L/mg) relating to free energy of biosorption. The plots of \(\frac{C_e}{q_e}\) versus \(C_e\) were drawn as shown in Figure 6 for three different initial concentration of Cd to calculate these constants whereas Table 1 present calculation results from the linearized equation form of the isotherms at all initial concentration over the whole concentration range studied and the extremely high correlation coefficients. These values of the correlation coefficients strongly support the fact that cadmium–dried biomass biosorption data closely follow the Langmuir model of sorption.

Figure 6. Langmuir isotherm equation fitting in linear form of Cd (II) on dried *Aphanothece sp*. 
The linearized Freundlich model is represented by the equation:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  

(4)

where \( K_F \) and \( n \) are constant related to the sorption capacity and intensity. The plots of \( \ln q_e \) versus \( \ln C_e \) (figure not shown) were drawn to calculate the values of \( K_F \) and \( 1/n \) which are given in Table 1. It was found that the plots exhibit deviation from linearity and the correlations coefficients indicate, the data are not well correlated to Freundlich correlation coefficients compared to Langmuir correlation coefficients. This result also reported by [9] which applied dried biomass of marine microalgae \textit{Ulva lactuca} to remove Cd (II) from aqueous solution.

Table 1. Langmuir and Freundlich isotherm constants for the biosorption of Cd on dried \textit{Aphanothece} sp biomass at different initial concentration of Cd in solution at pH 8, biomass concentration 0.1 g/L and temperature 30ºC with standard deviation ± 1.2 %

| Range of Initial Cd conc. (mg/L) | Langmuir constants \( q \text{max (mg/g)} \), \( K_L \text{ (L/mg)} \), \( R^2 \) | Freundlich constants \( K_F \text{ (mg/g(L/g)) } \), \( ^{1/n} \), \( n \), \( R^2 \) |
|---------------------------------|---------------------------------------------|-----------------------------------------------|
| 0.96-3.63                      | 16.47, 5.23, 0.998                        | 17.07, 2.190, 0.949                           |
| 1.99-8.10                      | 54.95, 1.06, 0.993                        | 27.030, 1.520, 0.759                          |
| 6.48-53.38                     | 119.05, 3.00, 0.997                       | 101.93, 1.760, 0.683                          |

3.4. Thermodynamic study

The free energy change (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)), and entropy change (\( \Delta S^0 \)) for this study were calculated using following equations:

\[
\Delta G^0 = -RT \ln K_d
\]  

(5)

Where \( R \) is universal gas constant (8.314 J/mol K), \( T \) is temperature (K) and \( K_d \) is \( \frac{q_e}{C_e} \) represent the distribution coefficient (Rathinam et al., 2010). By considering the following equation, the \( \Delta H^0 \) and \( \Delta S^0 \) of biosorption were estimated from the slope and intercept of the plot \( \ln K_d \) versus \( 1/T \) yields.

\[
\ln K_d = \left( \frac{\Delta S^0}{R} \right) - \left( \frac{\Delta H^0}{RT} \right)
\]  

(6)

Table 2 show the calculation results from those calculations. As shown in Table 2, it can be said that biosorption of Cd (II) ions by dried biomass of \textit{Aphanothece} sp performed in exothermic reaction since \( \Delta H^0 \) was negative due to decrease in adsorption on successive increase in temperature. Meanwhile, \( \Delta G^0 \) was negative which dictated a spontaneous process. The negative value of \( \Delta S^0 \), reveals the decreased randomness at the solid-solution interface during the binding of Cd ions on the active site of the biosorbent. These results is confirmed with [11] which reported that biosorption of selenium by dried biomass of green algae \textit{Maugeotia genuflexa} was also proceeded in spontaneous and exothermic reactions followed by decreasing of randomness at the solid-solution interface during the fixation of selenium ions on the active sites of the biosorbent.
Table 2. Thermodynamics parameters for the biosorption of Cd on dried Aphanothece sp. biomass at different temperature with standard deviation ± 1.0 %

| Temperature (K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol K) |
|-----------------|-------------|-------------|---------------|
| 303             | -12.80      | -72.87      | -0.20         |
| 310             | -11.08      |             |               |
| 315             | -10.21      |             |               |
| 320             | -9.15       |             |               |
| 323             | -8.89       |             |               |

3.5. Kinetic modelling

Conclusion on controlling mechanism of biosorption process commonly obtained from kinetic model fitting on experimental data. The high diversity of surface groups on algal cell wall such as carboxyl, phosphate, hydroxyl, amino, imidazole etc. suggested that there are many types of biosorbent-metal ions interactions. Two important kinetic models used in this study, namely the pseudo first order (equation 7) and pseudo second order (equation 8). Those linearized equations are written as follow:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left( \frac{1}{q_e} \right) t \]

Where \( q_t \) and \( q_e \) (mg/g) are the amounts of the metal ions adsorbed at t time and equilibrium, t is time (minute), \( k_1 \) is rate constant for pseudo first order (calculated from plotting \( \ln(q_e - q_t) \) against \( t \) ) and \( k_2 \) is rate constant for pseudo second order (determined from plotting \( \frac{t}{q_t} \) versus \( t \)). Those plotting results are presented on Table 3. It can be concluded from the \( R^2 \) and the similarity of \( q_e \) experiment to \( q_e \) calculated values, that the biosorption of Cd (II) ions on dried biomass of Aphanothece sp well followed the pseudo second order kinetic model. This pseudo second order kinetic model described kinetic behavior of biosorption process with chemical sorption being the controlling step [12].
Table 3. Biosorption rate constants $q_e$ estimated and coefficient of correlation associated to the Lagergren Pseudo-first and second order for dried Aphanothece sp biomass at different initial Cd concentrations

| Initial conc (mg/L) | $q_{e,exp}$(mg/g) | Pseudo First Order rate constants | Pseudo Second Order rate constants |
|---------------------|-------------------|----------------------------------|-----------------------------------|
|                     |                   | $k_1$ (min$^{-1}$) | $q_{e,cal}$(mg/g) | $R^2$ | $k_2$ (g/mg.min) | $q_{e,cal}$(mg/g) | $R^2$ |
| 2.0                 | 9.96              | 2.29E-02           | 9.45               | 0.969 | 5.40E-02         | 8.67              | 0.996 |
| 3.6                 | 23.46             | 1.29E-02           | 23.57              | 0.949 | 1.91E-02         | 19.01             | 0.997 |
| 5.4                 | 53.75             | 2.91E-01           | 42.84              | 0.962 | 4.95E-03         | 52.63             | 0.992 |
| 6.5                 | 43.90             | 1.25E-02           | 42.84              | 0.952 | 6.84E-02         | 36.63             | 0.998 |
| 9.8                 | 95.43             | 1.50E-02           | 88.2               | 0.863 | 5.38E-03         | 96.15             | 0.993 |
| 19.5                | 104.50            | 5.90E-02           | 129.32             | 0.945 | 6.36E-03         | 107.53            | 0.996 |
| 53.4                | 388.90            | 4.30E-02           | 320.86             | 0.937 | 7.18E-04         | 400.00            | 0.997 |

3.6. Comparison with other adsorbent
Table 4 compared maximum biosorption capacities obtained in this study with some other values reported by other researchers. The biosorption capacity for cadmium by using dried biomass of Aphanothece sp was higher in magnitude compared to other reported microalgae biomass as well as other types of biosorbent. As presented on Table 4, biosorption capacity of microalgae (Chlorella vulgaris, Spirulina platensis, Oedogonium sp and Chlamydomonas reinhardtii) were comparable with biosorption capacity of Aphanothece sp. Furthermore, biosorption capacity of Aphanothece sp compared to macroalge (Gelidium sp), peat and pine bark, is higher up to nine magnitudes. Meanwhile if compared to hazelnut shells (example of agricultural waste biomass), it was 19 times greater. According to [13] functional groups characters on surface of cell wall determines the extent of biosorbent affinity for metal ions bonding. Microalgae are more abundant with anionic functional groups than other type of biomass which presented in Table 4. Anionic functional groups such as carboxyl, phosphate, pyruvate, amide, extracellular polysaccharide, lipoproteins, etc are have great capability to bind metal ions by electrostatic forces and coordination bound (involving amino, carboxylic, sulfhydryl, phosphate, thiol and sulfate groups). Biosorption by dried biomass is better than precipitation since its ability to adjust of pH changes during sorption process. It also more advantageous than ion exchange and reverse osmosis in terms of its sensitivity to presence of suspended solids, organics, and other heavy metals. These finding demonstrate the eminence of dried biomass Aphanothece sp as biosorbent for removing Cd (II) ions from aqueous phase.

Table 4. Biosorption capacities for Cd (II) using different low cost biosorbtent (at room temperature)

| Biosorbent         | Biosorption capacity (mg/g) | pH  | References |
|--------------------|------------------------------|-----|------------|
| Aphanothece sp     | 119.05                       | 8.00| This study |
| Peat               | 22.5                         | 5.00| [14]       |
| Pine bark          | 28                           | 7.50| [15]       |
| Hazelnut shells    | 5.42                         | 6.00| [16]       |
| Chlorella vulgaris | 85.3                         | 4.00| [17]       |
| Gelidium sp        | 18                           | 5.30| [18]       |
| Spirullina platensis | 98.04                      | 6.00| [19]       |
| Chlamydomonas reinhardtii | 42.60       | 6.00| [8]        |
| Oedogonium sp.     | 88.20                        | 5.00| [20]       |
3.7. Biosorption-desorption cycle

Biosorption-desorption experiments are useful in elucidation of the mechanism of sorption reaction and also to assess the regeneration capacity of the biosorbent for reuse in more economic manner. In this study, 1 M HCl desorbing solution was tested for Cd (II) desorption from the metal loaded biomass of dried Aphanothece sp (Table 5). The amount of desorption provides insight into the nature of biosorbent-Cd ions bonding and also on the ion exchange property of the biosorbent. Reusability of Aphanothece sp for Cd (II) removal from aqueous phase was three successive cycles of biosorption-desorption which carried out in batch system. Cadmium solution test was 7.2 mg/L was selected, since when concentration of metal below 100 mg/L, conventional technology to remove metal from aqueous phase will be inefficient. As seen, in three successive runs, the uptake capacity of biosorption was relatively unchanged. But in case of desorption, there was observed decreasing trend up to only 27% in third cycle from 81 % in first cycle. This result also confirmed [8] which reported declining trend in last desorption process around of 22% by using Chlamydomonas reinhardtii and acid desorbing eluent when removing Hg (II) ions from aqueous solution. Apparently, it caused by acids deteriorating effect on biomass and may dissolving certain polysaccharides which contain metal binding sites. It suggest HCl 1 M is too concentrated being used as desorbing eluent in this study.

| Cycle 1 | Cycle 2 | Cycle 3 |
|---------|---------|---------|
| Biosorption (B) | 59.93 | 63.51 | 58.23 |
| Desorption (D) | 48.71 | 44.77 | 15.62 |
| Ratio (D/B) | 0.81 | 0.70 | 0.27 |

Table 5. Successive cycle of biosorption and desorption of Cd (II) by dried Aphanothece sp biomass in batch system. Desorption by HCl 1 M, contact time 60 minutes. Data presented as means of two replicates with standard deviations 1.5 to 2.0 %.

4. Conclusion

The batch biosorption system in this study provides significant information regarding biosorption of cadmium on dried biomass of cyanobacteria Aphanothece sp. in terms of optimum pH and biomass concentration for maximum removal of Cd (II) ions from aqueous solution. This study indicated that dried biomass of Aphanothece sp. is an effective biosorbent for Cd (II) removal. The maximum Cd (II) biosorption capacity has been found to be 119. 05 mg/g of dry weight biomass at biosorbent concentration 0.1 g/L in 60 minute of contact time with initial Cd concentration 6.48-53.38 mg/L and optimum pH of 8.0. The Langmuir adsorption model and Pseudo second order kinetic models were fitted well to experimental data, it means that these adsorption and kinetics model are the best suited mathematical models for describing biosorption process of Cd (II) by dried biomass of Aphanothece sp from aqueous phase. HCl 1M as desorbing eluent is not affected biosorption capacity during 3 cycles of biosorption-desorption but it reduced uptake capacity of desorption process up to only 27% of capacity at third biosorption-desorption cycle. With the advantage of high metal biosorption capacity, the dried biomass of Aphanothece sp. has potential to be used as an efficient and economic biosorbent material for removing cadmium ions in aqueous phase.

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