

Characterization of the Adsorption of the Lead (II) by the Nonliving Biomass *Spirogyra neglecta* (Hasall) Kützing

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Abstract: Problem statement: Conventional techniques for removing dissolved heavy metals are only practical and cost-effective when applied to high strength wastes with heavy metal ion concentrations greater than 100 ppm. The possibility of using a nonliving algal biomass to solve this problem was carried in this study. Lead (II) was used in this study because it had been reported to cause several disorders in human. **Approach:** The nonliving algal biomass was obtained from a filamentous green alga *Spirogyra neglecta*. The effects of initial concentration and contact time, pH and temperature on the biosorption of lead (II) by the nonliving algal biomass were studied. The equilibrium isotherms and kinetics were obtained from batch adsorption experiments. The surface characteristics of the nonliving algal biomass were examined using scanning electron microscope and Fourier Transformed Infrared. The maximum adsorption capacity of the nonliving algal biomass was also determined. **Results:** Maximum adsorption capacity of lead (II) was affected by its initial concentration. Adsorption capacity of lead (II) increased with the pH and temperature of lead (II) solution. Langmuir isothermic model fitted the equilibrium data better than the Freundlich isothermic model. The adsorption kinetics followed the pseudo-second-order kinetic model. The nonliving algal biomass exhibited acaves-like, uneven surface texture along with lot of irregular surface. FTIR analysis of the alga biomass revealed the presence of carbonyl, amine and carboxyl group which were responsible for adsorption of lead (II). The maximum adsorption capacity (q_{max}) of lead (II) by the nonliving biomass of *Spirogyra neglecta* was 132 mg g^{-1} . **Conclusion:** The maximum adsorption capacity for lead (II) by the nonliving biomass of *Spirogyra neglecta* was higher than reported for other biosorbents. Therefore, it had a great potential for removing lead (II) from polluted water. Its use will also need to consider the various factors that affect biosorption process.

Key word: Adsorption, kinetics, *Spirogyra neglecta*, Langmuir model, second order model

INTRODUCTION

The presence of heavy metals in water systems has become a problem due to their harmful effects on human health even at low concentration in the environment. Lead (II) is among the most toxic heavy metal ion affecting the environment^[1]. The current EPA and WHO drinking water standard for lead (II) is 0.05 mg L^{-1} and $10 \mu\text{g L}^{-1}$, respectively. Lead (II) accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney diseases, nervous disorders and sickness even death^[2]. It is therefore, essential to remove lead (II) from wastewater before disposal. Conventional techniques for removing dissolved heavy metals such as chemical precipitation, carbon adsorption, ion exchange, evaporation and membrane processes^[3], are

only practical and cost-effective when applied to high strength wastes with heavy metal ion concentrations greater than $100 \text{ ppm}^{[4]}$. Low strength heavy metal containing wastewaters generally cannot be treated successfully with such methods.

Adsorbent materials (biosorbents) derived from suitable biomass, on the other hand, has been shown to remove and recover of heavy metal ions from wastewater streams even at low concentrations. The phenomena of adsorption has been described in a wide range of living biomass like fungi^[5], bacteria^[6,7], yeast^[8], moss^[9], aquatic plants^[10] and algae^[11,12]. Algae is one of the most promising biosorbents^[13]. Different algal species often had different sorption characteristics. The sorption characteristics have shown to be influenced by pH, metal ion concentration, temperature, other metal ions^[3].

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This study describes the adsorption of lead (II) by a nonliving biomass of a freshwater green alga identified as *Spirogyra neglecta* (Hasall) Kützing. Morphology of the nonliving algal biomass and its functional groups were also investigated.

MATERIALS AND METHODS

Chemical: All the reagents were of AR grade either from Germany or Starform-Malaysia. Stock solution of lead (II) was prepared using lead (II) nitrate (Plumbum II Nitrat, brand SYSTERM) in distilled water. Lead (II) solutions of different concentrations were obtained by diluting the stock solution. Standard solution of lead (II) (250 mg L^{-1}) for atomic adsorption spectrophotometer was obtained from Germany. Standard acid and base solutions (0.1N HCl and 0.1N NaOH) were used for pH adjustments.

Equipments:

- AAS atomic adsorption spectrophotometer Model AA-6200 (Shimadzu, Japan) at a wavelength of 283.3 nm
- pH meter (Eutch Instrument, Japan)
- FT-IR spectrometer Fourier transform infrared
- SEM scanning electron microscopy (JEOL 6400, Japan)

Preparation of biosorbent: Fresh sample of algal biomass of *Spirogyra neglecta*, was collected from a pond in Rimba Bukit Kiara in Kuala Lumpur, Malaysia. The sample was washed with distilled water five times to remove dirt (sand and epiphytes) The sample was subsequently kept on a filter paper to then dried in an oven at 45°C for 72 h. The dried sample was then ground to powder using Igate stone pestle and mortar. The dried sample powder was then sieved to select the particles $300\text{-}425 \mu\text{m}$ using a standard testing sieve (Omron, UK). The powder of the wanted size (biosorbent), was then stored in plastic container at room temperature room and to used as the biosorbent and for subsequent analysis.

Effects of initial concentration and contact time: The adsorption of lead (II) ions on the dried biomass *Spirogyra neglecta* was investigated in batch adsorption equilibrium experiments. The experiment was performed by mixing 0.05 g of dried algae in 50 mL of the synthetic metal solutions. The pH of solution was kept without any pH treatment. The mixtures were mixed slowly with a rotary shaker at a rate of 150 rpm for 60 min at temperature room. The solid biomass was

separated from the liquid phase with membrane filter $0.45 \mu\text{m}$, The concentration of lead (II) remaining in residual solution after a time lapse from the beginning of the experiment was determined by taking the residual solution absorbance on by atomic absorption spectrophotometer (AAS) Model AA-6200 (Shimadzu, Japan) at a wavelength of 283.3 nm. (All measurements were carried out in an air/acetylene flame). The above was conducted on five different initial concentration of lead (II) i.e., 50, 100, 150, 200 and 250 mg L^{-1} .

Effect of pH: The effect of solution pH on the lead (II) removal was examined by varying the initial pH of the solution from pH 3 to pH 6. The pH was adjusted using 0.1N HCl and 0.1N sodium hydroxide (NaOH), magnetic stirrer was used to agitate the solution continuously and measurement using pH meter (EUTCH instrument, Japan). The Pb initial concentration was fixed at 150 mg L^{-1} with 0.05 g of the biosorbent agitation 1 h, rotation speed 150 rpm under temperature room.

Effect of temperature: The effect of temperature on the adsorption of lead (II) by the biosorbent was studied by setting the temperature of the shaking incubator. This study was carried out at three different temperatures ($40, 50$ and 60°C) effect of temperature on the adsorption. The same initial concentration of lead (II) and pH was use in this study.

Determination of the adsorption capacity: The metal uptake can be calculated from:

$$q = \frac{V(C_e - C_t)}{W} \quad (1)$$

Where:

- q = The metal uptake (mg metal g^{-1} biomass)
- C_e = The initial metal concentrations in the solution (mg metal L^{-1} fluid)
- C_t = The metal concentrations in the solution (mg metal L^{-1} fluid) at time t
- V = The volume of solution
- W = the dry weight (g) of the added biosorbent

Biosorption isothermic and kinetic models:

Attempt was carried out to describe biosorption isothermics and kinetics of lead (II) by the nonliving biomass of *Spirogyra neglecta*. Langmuir and Freundlich isothermic models, Pseudo-first-order-kinetic and Pseudo-Second-order-kinetic models were used. Data used was obtained from section Effects of initial concentration and contact time.

Langmuir isothermic model can be written in non-linear form as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \quad (2)$$

Where:

q_{\max} = The monolayer adsorption capacity of the adsorbent (mg g^{-1}) is the (maximum amount adsorbed)

K_L = The Langmuir adsorption constant (L mg^{-1})

C_e = The equilibrium metal ion concentration in the solution (mg L^{-1})

q_e = The equilibrium metal ion concentration on the adsorbent (mg g^{-1})

The solid phase equilibrium metal concentration which is the amount of metal adsorbed on the biomass surface in a batch system is calculated using the following mass balance equation:

$$q = \frac{V(C_e + C_t)}{W} \quad (3)$$

Where:

q = The metal uptake (mg metal g^{-1} biomass)

C_e = Initial metal concentrations in the solution (mg metal L^{-1} fluid)

C_t = Final metal concentrations in the solution (mg metal L^{-1} fluid)

V = The volume of solution

W = The dry weight (g) of the added biosorbent

The Freundlich isothermic model is written as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Where:

K_f = A constant relating the adsorption capacity (Freundlich constants)

$1/n$ = An empirical parameter relating the adsorption intensity, (which varies with the heterogeneity of the material)

To describe the kinetics of the biosorption of lead (II) by the nonliving algal biomass, two models used: Pseudo-first-order-kinetic and Pseudo-Second-order-kinetic models. The pseudo first-order model is presented by the following equation^[25]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

Where:

q_e and q_t (mg g^{-1}) = The amounts of lead (II) adsorbed on the algal biomass at equilibrium and time in mg g^{-1}

K_1 = Constant of pseudo first-order adsorption

The pseudo second-order model is presented by the following equation^[26]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \quad (6)$$

Morphology of biosorbent: Scanning electron microscope examination of the biosorbent was done under SEM (JEOL 6400, Japan) to study the surface texture and morphology of the biosorbent. Sample of the biosorbent was prepared based on technique and procedure of Gabriel^[14].

Functional groups of biosorbent: Detection of functional groups in the biosorbent was done using the Fourier Transformed Infrared (FTIR). A sample of the biosorbent was mixed with KBr disc. The mixture was analyzed using FTIR in the range $370.0\text{-}4000.0 \text{ cm}^{-1}$.

RESULTS

Effects of initial concentration and contact time: The adsorption of lead (II) increased with time and at certain point in time, it reached a constant value beyond which no more lead (II) was further removed from solution (Fig. 1). Maximum adsorption took place within the first 60 min. The amount of lead (II) adsorbed at the equilibrium time was the maximum adsorption uptake by the adsorbent.

Effect of pH: The results of the adsorption lead (II) ions by the biosorbent are shown in Fig. 2. It shows that the process is a function of pH. In this study, adsorption of lead (II) by the biosorbent increased until at pH 6.0.

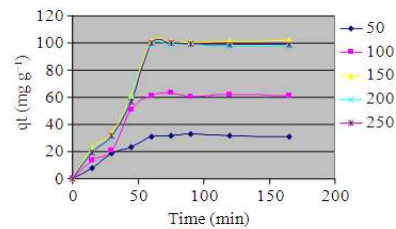


Fig. 1: Effect of initial concentration and contact time on adsorption of lead (II) by nonliving biomass *Spirogyra neglecta*

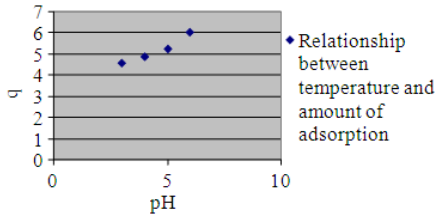


Fig. 2: Effect of pH on adsorption of lead (II) by nonliving biomass *Spirogyra neglecta*

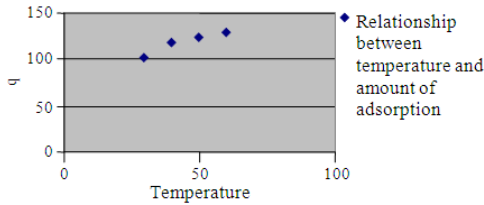


Fig. 3: Effect of temperature on adsorption of lead (II) by nonliving biomass *Spirogyra neglecta*

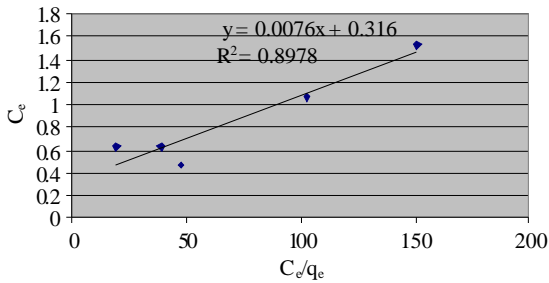


Fig. 4: Langmuir adsorption isotherm of lead (II) by the nonliving biomass of *Spirogyra neglecta*

Effect of temperature: Lead (II) adsorption uptake was found to increase with the increase in temperature (Fig. 3).

Determination of the adsorption capacity: The maximum adsorption capacity (q_{max}) of lead (II) by the nonliving algal biomass was 132 mg g^{-1} .

Biosorption isothermics and kinetics Figure 4 shows the plots of C_e versus C_e/q_e were drawn to calculate the values of K_L which are shown in Table 1.

The equilibrium relationship between metal adsorption and residual metal is typically hyperbolic^[24].

Figure 5 shows the plots of $1/q_e$ versus $1/C_e$ were drawn to calculate the values of K_F and $1/n$ which are shown in Table 1

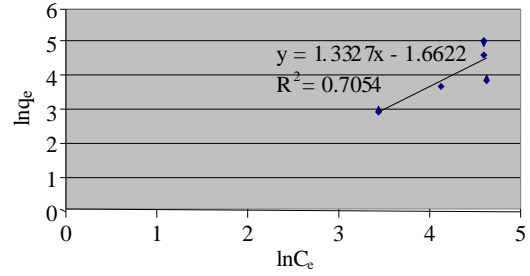


Fig. 5: Freundlich adsorption isotherm of lead (II) by the nonliving biomass of *Spirogyra neglecta*

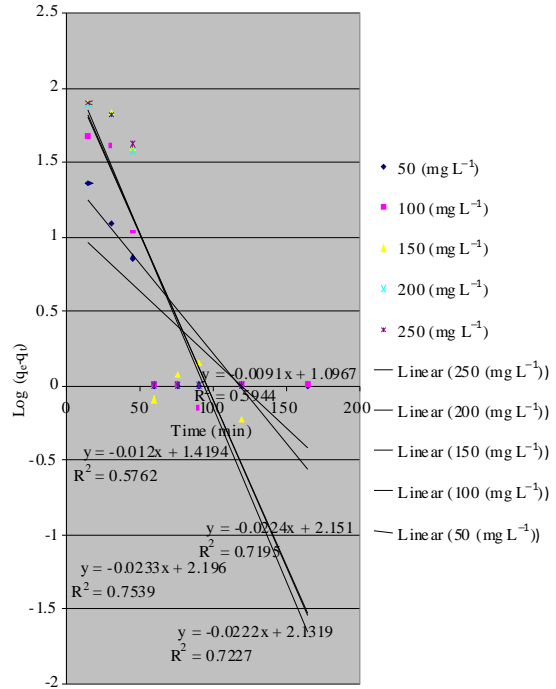


Fig. 6: Pseudo-first-order kinetic adsorption of lead (II) by the nonliving biomass of *Spirogyra neglecta*

Table 1: Langmuir and Freundlich constants

Parameter	Temperature	
Langmuir	Temperature	
q_{max} (mg g^{-1})	132.0000	30 ± 1
k_L (L mg^{-1})	0.0230	30 ± 1
R_L^2	0.8978	30 ± 1
Freundlich	Temperature	
k_f (L mg^{-1})	0.1897	30 ± 1
n	0.7500	30 ± 1
R_f^2	0.7054	30 ± 1

The plot $\ln(q_e - q_t)$ versus t as shown in Fig. 6 gives the slope of K_1 and intercept of $\ln q_e$. The values of K_1 and correlation, R_1 obtained from the Fig. 6 for adsorption of lead (II) on the biomass algal at 30°C are shown in Table 2.

Table 2: First order kinetic model

Con mg L ⁻¹	First order kinetic model			
	q _e (mg g ⁻¹) exp	q _{ei} (mg g ⁻¹)	K ₁	R ₁
50 mg L ⁻¹	30.8	12.49	0.021	0.5944
100 mg L ⁻¹	61.4	26.26	0.028	0.5762
150 mg L ⁻¹	102.1	157.03	0.054	0.7539
200 mg L ⁻¹	97.2	135.49	0.051	0.7227
250 mg L ⁻¹	98.8	141.58	0.052	0.7195

Table 3: Second order kinetic model

Con. mg L ⁻¹	Second -order kinetic model		
	q _{e2}	K ₂	R ₂
50 mg L ⁻¹	40.650	1406.040	0.9108
100 mg L ⁻¹	95.230	2834.220	0.7535
150 mg L ⁻¹	166.660	12815.640	0.7648
200 mg L ⁻¹	166.660	14134.980	0.6867
250 mg L ⁻¹	175.430	16052.590	0.6875

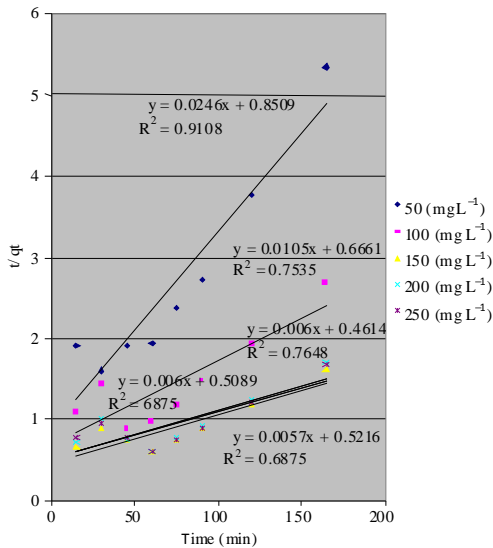
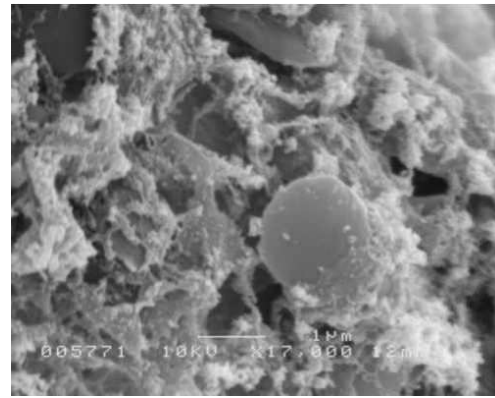


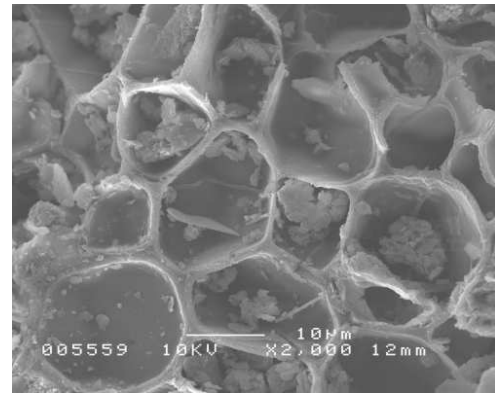
Fig. 7: Pseudo-second-order kinetic adsorption of lead (II) by the nonliving biomass of *Spirogyra neglecta*

Figure 7 showed the plots of t/q_t versus t at various initial concentrations. K_2 is the second order adsorption rate constants. The values of parameters K_2 , q_e and correlation coefficients were shown in Table 3. The correlation coefficients obtained were greater from R_1 .

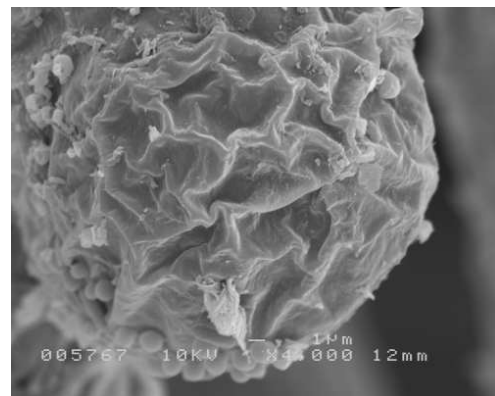
Morphology of nonliving biomass of *Spirogyra neglecta*: Fig. 8a-d. It was evident from the micrographs that the biosorbent sample after-before adsorption. The algae exhibits acaves-like, uneven surface texture along with lot of irregular surface.



(a)



(b)



(c)

Fig. 8a-c: SEM image the biomass particles, with and without adsorbed metal

The Fourier Transform Infrared Spectrometer (FTIR) analysis: The result is shown in Fig. 9. It displayed a number of absorption peaks, indicating the complex nature of the biomass examined. The broad absorption peak around 2923 cm^{-1} is indicative of the existence of bonded carboxyl group (C-H).

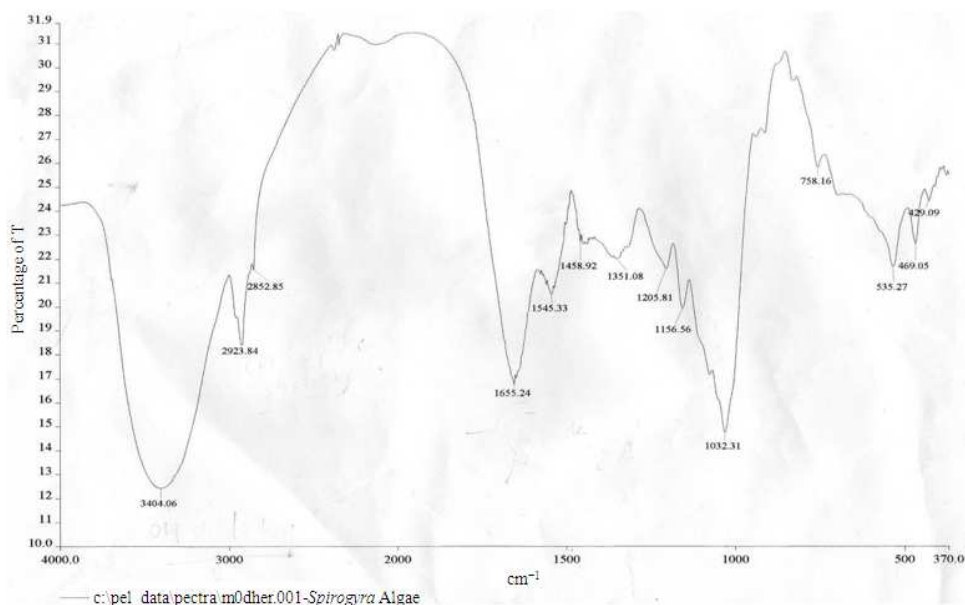


Fig. 9: Peaks for nonliving biomass of *Spirogyra neglecta* obtained from FTIR analysis

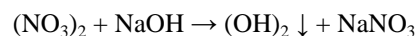
The peak observed at 1655 cm^{-1} can be assigned to the (C = O) carbonyl group. The peak observed at 3404.06 cm^{-1} can be assigned to the (N-H) amine group. The peak observed at 1032 cm^{-1} can be assigned to the (C-O) carbonyl group.

DISCUSSION

Effects of initial concentration and contact time: The results revealed that the lead adsorption was fast at initial stage of the contact period and then became slower near the equilibrium. This phenomenon was due to the fact that a large number of vacant surface site were available for adsorption during the initial stage. Near the equilibrium the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phase.

Effect of pH: These results suggest that the adsorption of metals on the biomass surface is controlled by ionic attraction. At low pH values, the inactivated cell surface becomes more positively charged, to reduce the attraction between metal ions and functional groups at the cell wall. In contrast, when the pH increases, the cell surface is more negatively charged and the process of retention is favored^[16,17]. Until a maximum adsorption is reached around pH 6. At pH higher than 6, precipitation of insoluble metal hydroxides takes place

restricting the true adsorption studies according to formula:



lead (II) adsorption is maximized at pH6.0, a value which agrees with the results obtained by^[18] on their study of lead (II) by *Pseudomonas putida*. Seki *et al.*^[21] studied the function of pH on adsorption of lead (II) by *Rhodobacter sphaeroides* and reported that the maximum pH is around 6.0. The pH of metal solution has been shown to play an important role in the adsorption process^[19].

Effect of temperature: The adsorption reaction for the endothermic processes could be due to the increase in temperature increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution^[20] also noted similar observations and they suggested that the increase in adsorption uptake with increase in temperature might be due to the possibility and in the total pore volume of the adsorbent, an increase of number of active sites for the adsorption as well as an increase in the mobility of the adsorbate molecules. Meena *et al.*^[21] reported that the increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the adsorbent or due to the decrease in

the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreased. Temperature could influence the desorption and consequently the reversibility of the adsorption equilibrium also^[22]. Increase in temperature will be followed by a decrease in adsorption capacity. This is because the rise in temperature damage active binding sites in the biomass^[23].

Langmuir and Freundlich adsorption isotherms:

The correlation coefficients were extremely high, as shown in Table 1. These values of the correlation coefficients strongly support the fact that the lead–algal biomass adsorption data closely follow the Langmuir model compared to the Freundlich correlation coefficients. The high degree of correlation for the linearized Langmuir relationship suggests a single surface reaction with constant activation energy is the predominant sorption step and possibly the predominant rate-controlling step.

Pseudo-first-order and Pseudo-Second-order kinetic model:

The values of R1 relatively small for the pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of lead (II) by algal biomass. These results imply that the adsorption system adheres to the pseudo second-order kinetics which further suggests that chemisorption is the rate-controlling step^[36]. Therefore, the pseudo-second-order rate kinetic model best described the experimental data.

Characterization of the biosorbent:

Scanning electron microscope: These caves in biomass evidence the increase surface adsorption of lead.

The Fourier Transform Infrared Spectrometer (FTIR) analysis:

The results indicated that the biomass has a variety of functional groups, such as carboxyl and amine and these groups are involved in almost all potential binding mechanisms. Depending on the pH value of the aqueous solution, these functional groups participate in metal ion bindings^[15].

Comparison with other adsorbents: The monolayer adsorption capacity (q_{max}) obtained in this study is compared with those obtained for other organisms. This is summarized in Table 4. The q_{max} value obtained in this study is higher than the q_{max} value of other organisms.

Table 4: Uptake capacities for lead (II) of various adsorbents at room temperature

Adsorbent	q_{max} (mg g ⁻¹)	Literature
<i>Chlamydomonas reinhardtii</i>	96.30	[29]
<i>Gelidium algae</i>	64.00	[30]
<i>Zoogloea ramigera</i>	82.80	[31]
<i>Pseudomonas aerogenosa</i>	23.00	[7]
<i>Cyclotella cryptic</i> (diatom)	26.28	[32]
<i>Bacillus</i> sp.	92.27	[33]
<i>Arthrobacter</i> sp.	130.00	[13]
<i>Phanerochaete chrysosporium</i>	134.00	[28]
<i>Rhizopus arrhizus</i>	76.40	[34]
<i>Arthrobacter</i> sp.	130.00	[14]
<i>Rhizopus arrhizus</i>	76.40	[34]
<i>Spirogyra neglecta</i>	132.00	This study

CONCLUSION

This study shows that nonliving biomass of *Spirogyra neglecta* has the potential to remove heavy metals in polluted water. The adsorption for lead (II) was quick, as maximum removal took place 1 h of contact time. The maximum adsorption capacity for lead (II) is higher than reported for other biosorbents of lead (II) by the nonliving biomass of *Spirogyra neglecta* are characterized by the initial concentration of lead (II), temperature and pH of the solution, Adsorption isothermal models and functional group. These are useful in predicting the behavior of the biosorbent under the different conditions so that it can be used effectively to remove heavy metals such as lead. Using nonliving biomass of *Spirogyra neglecta* has an advantage because the alga is one of most ubiquitous species of *Spirogyra* in Malaysia. However, the ability of the nonliving biomass of the alga to adsorb other metals will also need to be studied.

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