

# Removal of Cu(II) and Pb(II) by *Pithophora oedogonia*: Sorption, desorption and repeated use of the biomass

Alpana Singh, Dhananjay Kumar, J.P. Gaur\*

Laboratory of Algal Biology, Department of Botany, Banaras Hindu University, Varanasi 221005, India

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## Abstract

Maximum sorption of Cu(II) and Pb(II) by dried filamentous green alga *Pithophora oedogonia* occurred at pH 4.5 and 5.0, respectively. Chemical pretreatment could not appreciably enhance the metal sorption ability of the biomass. HCl and EDTA desorbed 92–96% of the sorbed metal from the metal-loaded biomass. Sorption and desorption of both the test metals were very rapid attaining an equilibrium within 15 min. The time course data of both the processes fitted well to the pseudo-first and the pseudo-second-order Lagergren kinetic models with  $r^2 \geq 0.979$ . The isotherm equilibrium of Cu(II) and Pb(II) followed the Redlich-Peterson and Sips model very well with  $r^2 \geq 0.991$ . The sorption of Cu(II) and Pb(II) at varying biomass doses could be well defined by linear and hyperbolic decrease, respectively. The regenerated biomass of *Pithophora* has better reusability for Pb(II) than for Cu(II). A good mechanical strength of *Pithophora* biomass was apparent as only 10–15% loss of biomass occurred at the end of the fifth cycle.

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**Keywords:** *Pithophora*; Copper(II); Lead(II); Sorption isotherm; Sorption–desorption cycle

## 1. Introduction

All heavy metals, including those required in small amount for the physiological machinery of living organisms, are extremely toxic at high concentrations [1]. Therefore, heavy metal burden of industrial wastewaters need to be substantially reduced before discharging them into water bodies. Dissatisfaction with conventional methods of metal removal from wastewater has led to a surge in efforts aimed at finding out suitable alternatives. In this regard, a variety of non-biological and biological materials have been screened for their metal sorbing ability with the ultimate objective of employing them for the treatment of metalliferous wastewaters.

Non-biological materials that have been tested for their metal sorbing ability include activated carbon [2], commercial resins [3,4], bagasse fly ash [5–7], red mud [8], metal hydroxides [9], clay [10], soil [11], etc. Diverse kinds of biomass have also been tested for their ability to sorb and remove metal ions. Some of the major advantages of using biomass for metal removal include

low cost, proficient and rapid sorption of metal ions even from low metal concentrations, regeneration of biomass and possible recovery of metal ions after sorption [12]. Considering the aforesaid advantages, metal sorbing potential of biomass derived from organisms belonging to such diverse groups as bacteria, fungi, algae, higher plants, etc., have been assessed [1,12,13]. In so far as algae are concerned, most of the earlier studies on metal sorption have remained confined to seaweeds [14]. Filamentous algae may be a good alternative for removing metal ions from aqueous system due to ease in their harvesting after metal sorption, good mechanical strength and easy availability. Unfortunately, literature on the use of filamentous algae in metal sorption is scant [15–19] and the subject indeed needs emphasis.

Metal sorption ability of a biomass can be profitably exploited only with adequate knowledge of conditions favoring biosorption, and the possibility of reuse of biomass after the process. However, optimal conditions for sorption and biomass regeneration vary depending on the type of biomass and metal ion [1]. Hence, these conditions must be adequately defined before using a biomass for the metal sorption process. Similarly, a chemical agent capable of efficiently desorbing metal ions from the metal-loaded biomass without inhibiting its subsequent metal sorption ability, need to be searched for the regeneration of biomass.

\* Corresponding author. Tel.: +91 542 2307147x342.

E-mail address: [gaurjp@yahoo.co.in](mailto:gaurjp@yahoo.co.in) (J.P. Gaur).

While the literature on metal biosorption is plentiful, only a few reports deal with regeneration and repeated use of biomass.

Taking the above points into consideration and in the light of our earlier finding that *Pithophora oedogonia* has a remarkable ability to sorb Cu(II) and Pb(II) from aqueous solution [18], the present study was planned to study the effect of pH and to develop a pretreatment strategy for optimizing the sorption of Cu(II) and Pb(II) by this organism. A functional relationship was developed for defining the sorption and removal of metal ions as a function of biomass concentration. The present study also compares the kinetic behavior of metal sorption and desorption, which may give a clue to the probable mechanisms of these processes.

## 2. Theoretical background

### 2.1. Lagergren kinetic equations for metal sorption and desorption

The pseudo-first-order Lagergren rate equation is applicable when the rate of sorption is proportional to the number of the vacant sites on the biosorbent [20,21]. The pseudo-first-order rate equation for the sorption process can be written as following [21]:

$$q_{1S} = q_E(1 - \exp^{-k_{1S}t}) \quad (1)$$

where  $q_E$  and  $q_{1S}$  are metal sorbed ( $\text{mg g}^{-1}$ ) on the biosorbent at equilibrium and at any time  $t$ , respectively. The parameter  $k_{1S}$  is the first-order rate constant ( $\text{min}^{-1}$ ), which may be defined as the rate of sorption when the availability of the vacant sites is unity.

The pseudo-second-order Lagergren kinetics is used when the rate of sorption is proportional to the square of the number of unoccupied sites [20,21]. The pseudo-second-order rate equation can be written as follows [21]:

$$q_{2S} = \frac{q_E^2 \cdot k_{2S} \cdot t}{1 + k_{2S} \cdot q_E \cdot t} \quad (2)$$

where  $k_{2S}$  is the rate constant of sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $q_E$  the amount of metal sorbed at equilibrium, and  $q_{2S}$  is the amount of metal sorbed at time  $t$  ( $\text{mg g}^{-1}$ ).

Similar to sorption, the pseudo-first-order and pseudo-second-order Lagergren rate expressions for desorption process can be written as follows:

$$q_{1D} = q_E(1 - \exp^{-k_{1D}t}) \quad (3)$$

$$q_{2D} = \frac{q_E^2 \cdot k_{2D} \cdot t}{1 + k_{2D} \cdot q_E \cdot t} \quad (4)$$

where  $q_E$  is the total amount of loaded metal ( $\text{mg g}^{-1}$ ),  $q_E$  may also be the total amount of the desorbed metal at equilibrium for 100% desorption efficiency. The parameters  $q_{1D}$  and  $q_{2D}$  are the amount of metal desorbed at any time  $t$  ( $\text{mg g}^{-1}$ ) as per pseudo-first and pseudo-second-order rate equation, respectively, and  $k_{1D}$  ( $\text{min}^{-1}$ ) and  $k_{2D}$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are, respectively the first-order and the second-order desorption rate constants.

### 2.2. Isotherm models

Freundlich, Langmuir, Redlich-Peterson and Sips models are the commonly used adsorption isotherm models for defining the sorption of metal ions. The Redlich-Peterson and Sips models were used in the present study for defining the equilibrium of sorption of Cu(II) and Pb(II) by the *Pithophora* biomass. The goodness-of-fit of the Freundlich and Langmuir model is not discussed here in detail as it has already been done in our earlier study on the same test alga [18].

### 2.3. Redlich-Peterson model

The Redlich-Peterson model is a three parameter extended form of the Langmuir model. This is just a mathematical function that may define the data reasonably well, however, its two parameters, namely,  $a_{RP}$  ( $\text{l g}^{-1}$ ) and  $b_{RP}$  ( $\text{l mg}^{-1}$ ) <sup>$n_{RP}$</sup> , do not convey any physico-chemical meaning [21]. The parameter  $n_{RP}$  is a dimensionless parameter that reflects heterogeneity of the binding surface. If the value of  $n_{RP}$  is set to unity, the isotherm assumes a Langmuir form, and thus we can say that the Redlich-Peterson isotherm is a variant of the Langmuir isotherm. Nevertheless, if the concentration of sorbate is low and  $n_{RP} = 1$ , it changes into a linear form that is well known as Henry's law [22]. The mathematical expression of the above said model is as follows [21]:

$$q = \frac{a_{RP} \cdot C_{eq}}{1 + b_{RP} \cdot C_{eq}^{n_{RP}}} \quad (5)$$

### 2.4. Sips model

The Sips model, some times also called as the Langmuir-Freundlich (LF) model, is a combination of Langmuir and Freundlich models. The mathematical expression of the Sips model can be given by Eq. (6):

$$q = \frac{q_S(b_S \cdot C_{eq})^{n_S}}{[1 + (b_S \cdot C_{eq})^{n_S}]} \quad (6)$$

where  $q_S$  ( $\text{mg g}^{-1}$ ) is Sips  $q_{\text{max}}$  and  $b_S$  ( $\text{l mg}^{-1}$ ) is analogous to the Langmuir affinity constant. The parameter  $n_S$  is a measure of heterogeneity of the binding surface. If the value of  $n_S$  approaches unity at high concentration of the sorbate, Eq. (6) is reduced to a Langmuir form. However, at low sorbate concentration and  $n_S < 1$ , it is reduced to a Freundlich form. Similar to the Redlich-Peterson model, if concentration of sorbate is low and the value of  $n_S$  approaches unity, the Sips model is also shortened to a linear form [22,23].

## 3. Materials and methods

### 3.1. The test alga

The oven-dried biomass of *P. oedogonia* was used as the biosorbent. The biomass was collected from a nearby pond, and washed several times with Milli-Q water. The biomass was dried in a hot air oven at 80 °C, and ground with mortar and pestle

and sieved to get the dried particles of the size about 0.5 mm. The moisture content of the dried biomass, its ash content and equilibrium pH (at 25 °C) were 8.2, 2.9 and 5.3%, respectively. The cell wall of the test alga is known to contain chitin [24], which enriches this biosorbent in metal binding sites.

### 3.2. Metal sorption and desorption

To assess the effect of pH on Cu(II) and Pb(II) sorption, batch experiments were conducted in 100 ml Erlenmeyer flasks, each containing 10 mg of the biomass in 10 ml of metal solution [10 or 100 mg l<sup>-1</sup> of Cu(II) or Pb(II)]. Metal solutions were prepared using their analytical grade salts CuCl<sub>2</sub>·2H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub>. The pH of the solution was adjusted within the range 3.0–7.0, using 0.1 M NaOH or HCl. The flasks were kept on a shaker at 80 rpm and 25 °C for 30 min. Thereafter, the biomass was separated using membrane filter of 0.45 μm pore size and the metal content in the filtrate was determined by a flame atomic absorption spectrophotometer (Perkin Elmer, model 2380).

Eight different pretreatments, namely, HCl (0.1 mM), HNO<sub>3</sub> (0.1 mM), NaOH (0.1 mM), ammonium acetate (0.1 mM), 5% (v/v) HCHO, 90% (v/v) methanol, 90% (v/v) acetone, and hot water (60 °C) were selected for the present study. The pretreatment was performed keeping 10 mg of biomass in 10 ml of treating agent on a shaker at 80 rpm for 30 min at 25 ± 2 °C. For hot water treatment, the dried biomass was kept in water bath for 15 min at 60 °C. After various pretreatments, the algal cells were separated and washed 4–5 times with Milli-Q water. The washed biomass was again dried in an oven and tested for metal sorption capacity. The biomass was incubated for 30 min in a solution containing 100 mg l<sup>-1</sup> Cu(II) or Pb(II) at pH 4.5 and 5.0, respectively. After incubation in metal solution, the biomass was separated and the filtrate was analyzed for metal content.

A 0.1 M concentration of different chemical agents (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, and EDTA), and Milli-Q water were tested for desorption of the test metals from the metal-loaded biomass. The biomass was loaded with the test metals by exposing 10 mg dried biomass to 10 ml of metal solution [100 mg l<sup>-1</sup> of Cu(II) or Pb(II)] for 30 min on a rotary shaker. Metal desorption was studied by shaking 10 mg of metal-loaded biomass in 10 ml of different desorbing agents for 30 min. Thereafter, the biomass was separated by filtration and the filtrate analyzed for metal content.

For kinetic study, pre-weighted biomass (500 mg) of *Pithophora* was suspended in 500 ml of 100 mg l<sup>-1</sup> Cu(II) or Pb(II) solution. Likewise, the kinetics of metal desorption was studied by taking 200 mg biomass, previously loaded with Cu(II) [20.54 mg g<sup>-1</sup> dry weight] or Pb(II) [51.56 mg g<sup>-1</sup> dry weight] in 200 ml of 0.1 M HCl. The filtrate was collected at various time intervals for both sorption and desorption experiments and analyzed for metal content.

Experiments were conducted to determine the sorption of Cu(II) and Pb(II) at different biomass concentrations (0.1–2.0 g l<sup>-1</sup>) taking two concentrations (10, 100 mg l<sup>-1</sup>) of the test metals in the solution. The data thus obtained were fitted in mathematical equations for determining the functional relation between metal sorption and biomass concentrations.

In order to evaluate the feasibility of using the biomass during successive sorption–desorption cycles, a 50 ml metal solution [100 mg l<sup>-1</sup> Cu(II) or Pb(II)] having 50 mg dried biomass of the test alga was incubated for 30 min on a shaker. Thereafter, the metal-loaded biomass was harvested and suspended in 0.1 M HCl to recover the metal from the biomass. After gentle agitation for 30 min, the biomass suspension was filtered and the metal content in the filtrate was measured. The regenerated biomass was washed in Milli-Q water to remove excess of acid till the pH of the washings reached neutrality and thereafter, resuspended in the metal containing solution for the next sorption run. In all, five successive cycles of metal sorption–desorption were run.

### 3.3. Modeling of metal sorption and removal

In a previous study [18], we have used Langmuir and Freundlich equations to model metal sorption by *Pithophora*. The Langmuir model fitted better to the data than the Freundlich model. In the present study, the fitness of the other two widely used models, namely, Redlich–Peterson and Sips, was also assessed. A mathematical relationship between metal removal and metal concentration in the solution was also established by finding out the equations that best fitted to the data on metal removal from different metal concentrations in the solution.

## 4. Results and discussion

### 4.1. Effect of pH on metal sorption

Sorption of metal ions was strongly affected by the initial pH of the metal solution. Maximum sorption of Cu(II) and Pb(II) from both the tested concentrations of the test metals occurred at pH 4.5 and 5.0, respectively (Fig. 1). Sorption of Cu(II) and Pb(II) increased with a rise in pH from 3 to 4.5 or 5, respectively. It is well known that the functional groups of biomass, such as, carboxylic group, are protonated at low pH and thus unavailable for binding the metal ions. As pH increases, the con-

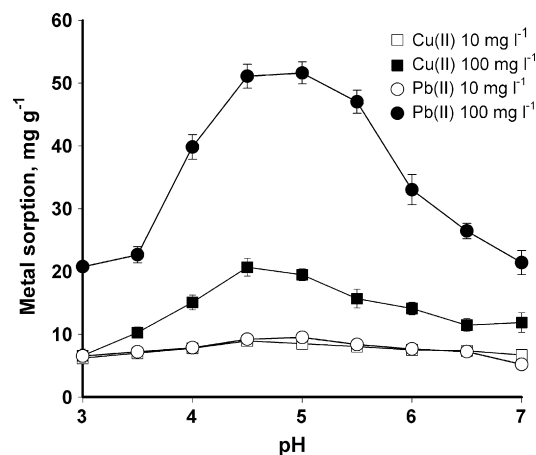


Fig. 1. Effect of pH on metal sorption by *Pithophora* from solution containing 10 and 100 mg l<sup>-1</sup> of Cu(II) or Pb(II). The biomass concentration and the contact time were 1 g l<sup>-1</sup> and 30 min, respectively. Vertical bars show mean ± S.D. of three replicates.

Table 1  
Effects of various pretreatments (30 min) on metal sorption ability of *Pithophora*

Treating agent	% Change in metal sorption ability	
	Cu(II)	Pb(II)
Hot water (60 °C) for 15 min	-18.2 ± 0.7	-24.5 ± 1.2
Ammonium acetate (0.1 mM)	-13.7 ± 1.0	-16.0 ± 1.8
Methanol (90%)	-10.8 ± 1.1	-12.3 ± 1.8
Acetone (90%)	-11.5 ± 1.1	-21.2 ± 2.0
Formaldehyde (5%)	-01.7 ± 1.0	-01.1 ± 0.2
Hydrochloric acid (0.1 mM)	+08.9 ± 1.2	+10.2 ± 0.2
Nitric acid (0.1 mM)	+05.2 ± 1.0	+05.5 ± 0.3
Sodium hydroxide (0.1 mM)	+07.4 ± 1.1	+02.6 ± 0.1

N.B.: '+' and '-', respectively, denote increase and decrease relative to the control (untreated biomass). Data denote mean ± S.D. of three replicates.

centration of protons in the solution decreases, and hence these functional groups efficiently release their protons in the solution and become available for the binding of positively charged metal ions. The other possible explanation for enhanced metal sorption with increase in pH is lowering of concentration of protons in the solution that are known to compete with metal ions for the binding sites. The present findings are in consonance with other workers who have similarly reported an increase in metal sorption with a rise in pH from 3 to 5 [1]. The effect of pH on Cu(II) and Pb(II) sorption by the test alga was more pronounced at 100 mg l<sup>-1</sup> than at 10 mg l<sup>-1</sup> concentration of these metal ions. The greater availability of metal ions in the former instance obviously enhanced the chances of their collision with the binding sites thereby enhancing their sorption.

#### 4.2. Effect of biomass pretreatment on metal sorption

Results show about 2–10% increase in sorption of the test metals following, NaOH, HNO<sub>3</sub> and HCl pretreatment of *Pithophora* biomass (see Table 1). Alkali pretreatment probably provided more anionic metal binding sites to the biosorbent by eluting H<sup>+</sup> ions from the functional sites. Similarly, acid pretreatment seems to have washed out the cationic species, which were bound to the negatively charged metal binding sites and thus enhanced the sorption of the metal ions [19]. The above observation shows a good agreement with our earlier findings on another filamentous alga *Spirogyra neglecta* [19]. The metal sorption ability of *Pithophora* decreased following its pretreatment with hot water, methanol, acetone and formaldehyde. It seems that hot water deteriorated the metal binding sites of the biomass, and similarly organic solvents dissolved away certain water insoluble substances, such as, lipids, which were apparently important in metal binding [19]. Ammonium acetate pretreatment reduced metal sorption ability of *Pithophora*, however, it has been found to increase Cd(II) sorption on *Ulva lactuca* by 40% [25].

#### 4.3. Screening of desorbing agents

Eight different chemical agents were tested for desorbing the test metals from the metal-loaded biomass of *Pithophora* (see Table 2). Maximum desorption of Cu(II) [>92%] and Pb(II) [>96%] occurred with EDTA and HCl followed in decreas-

Table 2  
Desorption of Cu(II) or Pb(II) from the metal-loaded biomass of *Pithophora* by various chemical agents (0.1 M)

Desorbing agent	% Desorption	
	Cu(II)	Pb(II)
EDTA	92.3 ± 2.5 <sup>a</sup>	96.2 ± 2.1 <sup>a</sup>
HCl	91.2 ± 2.6	96.1 ± 2.7
HNO <sub>3</sub>	89.5 ± 2.4	92.3 ± 2.2
H <sub>2</sub> SO <sub>4</sub>	85.1 ± 2.7	85.1 ± 2.6
NaOH	27.6 ± 1.9	44.3 ± 1.7
CaCl <sub>2</sub>	15.2 ± 1.6	19.7 ± 2.0
Na <sub>2</sub> CO <sub>3</sub>	22.8 ± 1.5	13.4 ± 1.1
Milli-Q water	10.7 ± 0.9	07.8 ± 0.5

<sup>a</sup> Mean ± S.D. of three replicates.

ing order by HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>, CaCl<sub>2</sub>·2H<sub>2</sub>O and Milli-Q water. Superiority of mineral acids and EDTA in desorbing metal ions from the metal-loaded biomass was also reported by earlier workers [1]. However, EDTA cannot be used for metal desorption in a commercial process as it is costlier than HCl, and moreover its disposal may cause serious environment problems.

#### 4.4. Kinetics of metal sorption and desorption

Time course of Cu(II) and Pb(II) sorption by *Pithophora* was studied and the data have been shown in Fig. 2. Sorption of Cu(II) and Pb(II) by the test organism was very rapid attaining the equilibrium within 15 min. Fig. 2 also depicts the data of desorption of Cu(II) and Pb(II) from the metal-loaded biomass of *Pithophora* using HCl as the desorbing agent. Desorption of Cu(II) and Pb(II) also occurred rapidly, generating a pattern that closely matched that for metal sorption. The rapid sorption and desorption of metals by *Pithophora* biomass can be considered as desirable characteristics of this particular biosorbent for commercial application [19].

The time course data of sorption and desorption of Cu(II) and Pb(II) were fitted to the pseudo-first and pseudo-second-order Lagergren kinetic models (Fig. 2), and the estimated parameters are shown in Table 3. The data fit very well to both the models ( $r^2 \geq 0.979$ ). Vilar et al. [21] also showed that the sorption of Cd(II) by *Gelidium* and algal waste could be very well defined by both the models. Such a behavior may be due to the fact that the selected concentrations of both the reactant species (i.e., biomass and metal concentration, or HCl in the case of desorption) are not in the rate governing range, and initial excess of any of the reactants may give a mixed response. Furthermore, it is also likely that the order of sorption as well as desorption is in fraction so that it remains between the first- and the second-order. It is fairly well known that metal desorption mainly involves the process of ion exchange, in which protons or other ions of the desorbing agent replace metal ions from the binding sites [1,26]. Since the general pattern of sorption and desorption matched very well and kinetic parameters of both the processes have almost similar values (see Table 3), it appears reasonable to conclude that ion exchange is the principal mechanism of metal sorption by the test alga.

Table 3

Kinetic parameters of the pseudo-first-order and the second-order rate models for the sorption and desorption of Cu(II) and Pb(II) by *Pithophora*

Metal	Pseudo-first-order Lagergren model			Pseudo-second-order Lagergren model		
	$q_E$ (mg g <sup>-1</sup> )	$k_{1S}$ (min <sup>-1</sup> )	$r^2$	$q_E$ (mg g <sup>-1</sup> )	$k_{2S}$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$r^2$
Sorption						
Cu(II)	20.27	0.31	0.998	21.05	0.04	0.998
Pb(II)	51.13	0.29	0.998	53.03	0.01	0.986
Metal	Pseudo-first-order Lagergren model			Pseudo-second-order Lagergren model		
	$q_E$ (mg g <sup>-1</sup> )	$k_{1D}$ (min <sup>-1</sup> )	$r^2$	$q_E$ (mg g <sup>-1</sup> )	$k_{2D}$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$r^2$
Desorption						
Cu(II)	18.91	0.18	0.997	20.88	0.01	0.979
Pb(II)	49.93	0.23	0.999	53.80	0.01	0.989

#### 4.5. Modeling of metal sorption and removal

The two parameters pertaining Freundlich and Langmuir isotherms have already been discussed in our earlier study [18]. Here, we have taken three-parameter extended isotherms, namely, the Redlich-Peterson and Sips model, for defining Cu(II) and Pb(II) sorption data (see Table 4). The  $r^2$  value clearly shows that Sips ( $r^2 = 0.999$ ) and Redlich-Peterson ( $r^2 = 0.997$ )

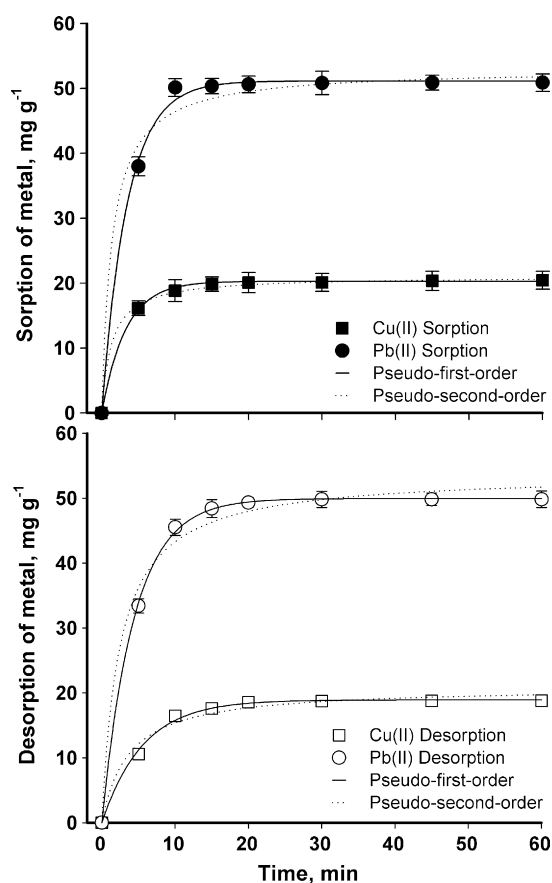


Fig. 2. Kinetics of sorption or desorption of Cu(II) and Pb(II) by *Pithophora*. The solution used for metal sorption contained 100 mg l<sup>-1</sup> of Cu(II) [pH 4.5] or Pb(II) [pH 5.0] and biomass concentration 1 g l<sup>-1</sup>. Desorption of Cu or Pb from the metal-loaded biomass was carried out using 0.1 M HCl at 25 °C. Sorption and desorption data were fitted to the pseudo-first and pseudo-second-order Lagergren kinetic models by the non-linear regression method.

models best define Cu(II) sorption, followed in decreasing order by Langmuir ( $r^2 = 0.991$ ) and Freundlich ( $r^2 = 0.920$ ) models. Likewise, Redlich-Peterson ( $r^2 = 0.998$ ) and Sips ( $r^2 = 0.991$ ) models best defined sorption of Pb(II) on *Pithophora* biomass, followed in decreasing order by Langmuir ( $r^2 = 0.961$ ) and Freundlich ( $r^2 = 0.910$ ) models. Vilar et al. [21] and El-Naas et al. [27] also observed the superiority of the Redlich-Peterson and Sips model over other models for defining the sorption data. However, the Langmuir model provides more information than the Redlich-Peterson model as its parameter  $q_{max}$  reveals the maximum sorption capacity of the biomass and the constant  $b$  reflects the affinity of the sorbate molecules for the biomass surface. The Redlich-Peterson model seems just a mathematical function and its parameters  $a_{RP}$  and  $b_{RP}$  have no physico-chemical meaning [21]. The Sips model fitted better to the present data than the Langmuir model because the predicted value of the Sips sorption maximum ( $q_S$ ) was closer to the experimental maximum for both the test metals, whereas the Langmuir model showed a higher value of  $q_{max}$  for Pb(II) [18]. The exponential parameters of the Redlich-Peterson ( $n_{RP}$ ) and Sips model ( $n_S$ ) do convey physico-chemical meanings to some extent and both reflect the heterogeneity of the binding surface with their values ranging between 0 and 1 [22,23]. The value of the above said parameters generally remains below unity, but they were  $>1$  for both the test metals in the present case. The value of  $n_{RP}$  and  $n_S > 1$  is not commonly observed, but has also been reported by some other workers [27–29]. It seems that types and distribution of the binding sites on biomass surface are extremely complex in nature, and hence a natural sorbent, like *Pithophora*, will not completely follow any ideal assumption of sorption theory.

Mathematical expressions were developed for the removal of Cu(II) and Pb(II) by *Pithophora* from various external concentrations of these metals. The non-linear regression method was used, and the constants of the best-fitted equations are given in Table 4. The removal Cu(II) and Pb(II) followed hyperbolic and exponential decay equations, respectively, with their increasing concentration in the solution. The derived equations successfully predict percent removal of the test metals by *Pithophora* from solutions containing their various concentrations. Such equations seem to have tremendous potential for application in metal removal processes.

Table 4  
Parameters of various models tested for defining the sorption and removal of Cu(II) and Pb(II) by *Pithophora* biomass

	Model	Metal	Parameters
Sorption	Redlich-Peterson model (see Eq. (5))	Cu(II)	$a_{RP} = 1.27 (1 \text{ g}^{-1}), b_{RP} = 0.03 (1 \text{ mg}^{-1})^{n_{RP}}, n_{RP} = 1.11, r^2 = 0.997$
		Pb(II)	$a_{RP} = 0.91 (1 \text{ g}^{-1}), b_{RP} = 0.0002 (1 \text{ mg}^{-1})^{n_{RP}}, n_{RP} = 1.76, r^2 = 0.998$
	Sips model (see Eq. (6))	Cu(II)	$q_S = 21.36 (\text{mg g}^{-1}), b_S = 0.03 (1 \text{ mg}^{-1}), n_S = 1.36, r^2 = 0.999$
		Pb(II)	$q_S = 57.16 (\text{mg g}^{-1}), b_S = 0.003 (1 \text{ mg}^{-1}), n_S = 1.65, r^2 = 0.991$
Removal	Hyperbolic decay ( $\% R = a \cdot b / (b + C_{eq})$ )	Cu(II)	$a = 118, b = 23.38, r^2 = 0.999$
	Exponential decay ( $\% R = a \cdot \exp^{-b \cdot C_{eq}}$ )	Pb(II)	$a = 99.09, b = 0.007, r^2 = 0.998$

#### 4.6. Metal sorption as a function of biomass concentration

Biomass provides binding sites for the sorption of metal ions, and hence its availability strongly affects the sorption of metal ions from the solution (Fig. 3). Effects of biomass availability on metal sorption were assessed at 10 and 100 mg l<sup>-1</sup> concentrations of both the test metals. The sorption of both the test metals decreased with increase in concentration of biomass in the solution due obviously to decrease in availability of metal ions per unit biomass concentration [1]. However, Cu(II) and Pb(II) showed different patterns of decrease in sorption. The sorption of Cu(II) followed a linear pattern, but that of Pb(II) showed a hyperbolic decay (see Table 5). As discussed earlier, different patterns obtained may be due to variable tendency of metal ions to bind onto the biosorbent. Unlike sorption, removal of Cu(II) and Pb(II) showed an increase with increase in biomass concentration following the exponential and hyperbolic rise, respectively (see Table 5). An increase in removal can be simply explained by the fact that at higher concentration of biomass, a greater number of sites become available for binding the metal ions [1]. The derived functional relations between sorption (and removal) and biomass concentration can be directly used, without performing any experiment, for quantifying sorption (and removal) for the concentrations of metal and biomass that lie

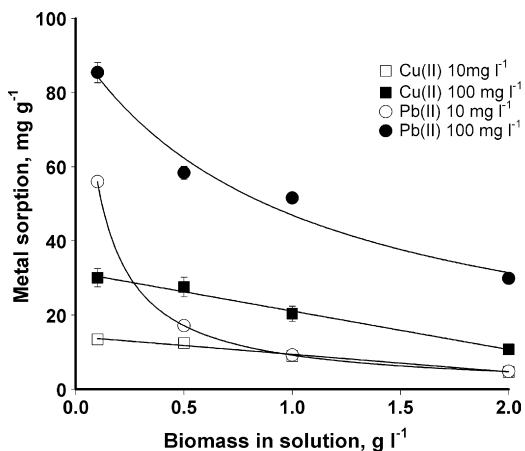


Fig. 3. Effect of biomass concentration on sorption of Cu(II) and Pb(II). Experiment was conducted at 10 and 100 mg l<sup>-1</sup> concentrations of the test metals and at 25 °C. The contact time was 30 min and the initial pH of the metal solution was adjusted to 4.5 and 5.0 for Cu(II) and Pb(II), respectively. Data were fitted to mathematical expressions using non-linear regression method, and the best fits have been only shown in the figure.

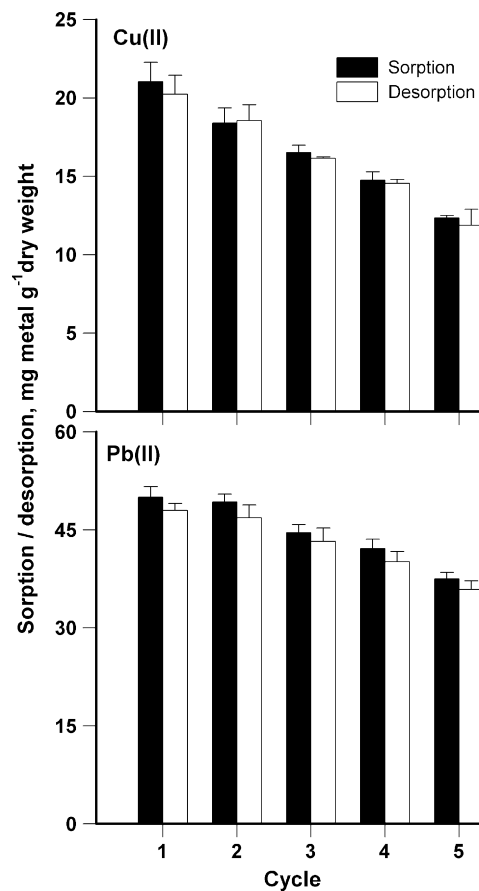


Fig. 4. Successive cycles of Cu(II) and Pb(II) sorption and desorption by *Pithophora*. Metal loading of the biomass was performed in a solution containing 100 mg l<sup>-1</sup> of Cu(II) or Pb(II) at 25 °C for 30 min and the biomass concentration 1 g l<sup>-1</sup>. To regenerate the biomass for the next cycle, 0.1 M HCl was used as the desorbing agent using 1 g l<sup>-1</sup> of metal-loaded biomass.

within the range used in the present study. However, one problem with this type of derivation is that it is an intrinsic property of the system and might change if we change the experimental conditions.

#### 4.7. Successive cycles of metal sorption and desorption

Five successive cycles of sorption and desorption of both the test metals were carried out in the batch system to assess the reusability of *Pithophora* biomass for metal sorption (Fig. 4).

Table 5  
Functional relationships of metal sorption and removal with biomass concentration in the batch system

Criteria	Metal	(mg l <sup>-1</sup> )	Functional form	Type equation	Derived equation	r <sup>2</sup>
Sorption	Cu(II)	10	Linear decay	$f = y_0 + a \cdot x$	$q^a = 14.14 - 4.74[B]^b$	0.992
		100	Linear decay	$f = y_0 + a \cdot x$	$q = 31.48 - 10.39[B]$	0.995
	Pb(II)	10	Hyperbolic decay	$f = a \cdot b / (b + x)$	$q = 9.90 / (0.077 + [B])$	1.00
		100	Hyperbolic decay	$f = a \cdot b / (b + x)$	$q = 95.22 / (1.03 + [B])$	0.971
Removal	Cu(II)	10	Exponential rise	$f = a(1 - \exp^{-b \cdot x})$	% R = 98.12(1 - exp <sup>-2.05[B]</sup> )	0.989
		100	Exponential rise	$f = a(1 - \exp^{-b \cdot x})$	% R = 22.55(1 - exp <sup>-1.94[B]</sup> )	0.989
	Pb(II)	10	Hyperbolic rise	$f = a \cdot x / (b + x)$	% R = 99.65[B] / (0.079 + [B])	1.00
		100	Hyperbolic rise	$f = a \cdot x / (b + x)$	% R = 88.76[B] / (0.883 + [B])	0.980

<sup>a</sup> Metal sorption in mg g<sup>-1</sup> dry weight.

<sup>b</sup> Biomass concentration in g l<sup>-1</sup>.

Since HCl pretreatment was found to enhance the metal sorption ability of the biomass by 10%, an increase in metal sorption was also anticipated during successive cycles of sorption and desorption. However, no increase was evident, and sorption of both the test metals actually decreased after each successive cycle (Fig. 4). After five sorption–desorption cycles, the sorption of Cu(II) and Pb(II) by the biomass decreased by 41 and 25%, respectively. The use of higher concentration (100 mM) of HCl for metal desorption, compared to a mere 0.1 mM used for biomass pretreatment, seems to have deteriorated the biomass thereby diminishing its metal sorption ability after each cycle of sorption and desorption. The test biomass is superior to *Sargassum bacculari* that showed nearly 52% decrease in Cu(II) sorption ability at the end of the first sorption–desorption cycle [30], but slightly inferior to *S. neglecta* that displayed, respectively 11 and 27% short-fall of Cu(II) and Pb(II) sorption at the end of the fifth cycle [19]. It deserves mention that the decrease in Pb(II) sorption ability of *Pithophora* at the end of the fifth cycle is far less than that for Cu(II). Hence, *Pithophora* biomass has better reusability during successive cycles of sorption and desorption for Pb(II) than for Cu(II). The decrease in metal sorption ability of *Pithophora* during successive cycles is also lesser than that obtained for Cd(II) (45%) and Co(II) (70%) sorption by *Phormidium valderianum* after five sorption runs [31]. The biomass of *Pithophora* has a good mechanical strength as only 10–15% loss of biomass was recorded at the end of the fifth cycle. The loss of biomass is lesser than that recorded by Ahuja et al. [32] and Nakajima and Sakaguchi [33] who, respectively showed nearly 31 and 50% loss of biomass after five sorption–desorption cycles.

#### 4.8. Comparison of metal binding capacity of *Pithophora* with other adsorbents

The monolayer sorption capacity (Langmuir  $q_{\max}$ ) of *Pithophora* for Cu(II) and Pb(II) were compared with that of the other sorbents (see Table 6). Cu(II) and Pb(II) sorption capacity of *Pithophora* is higher than that of many filamentous algae and activated carbon, comparable with unicellular green algae, but lower than that of *S. neglecta*, *Spirogyra* sp., *Cladophora fascicularis*, seaweeds and commercial resins. But low cost, easy availability, ease in harvesting due to filamentous nature, and

Table 6  
Cu(II) and Pb(II) sorption capacity (Langmuir  $q_{\max}$ ) of some common adsorbents

Adsorbent	$q_{\max}$ (mg g <sup>-1</sup> )		pH	Reference
	Cu(II)	Pb(II)		
Activated carbon				
Granular AC	5.08	16.58	5.0	[2]
Powdered AC	4.45	26.94	5.0	[2]
Commercial resins				
Duolite GT-73	61.64	–	4.8	[3]
Amberlite IRC-718	127.10	290.08	4.8	[3]
Amberlite 200	88.97	352.24	4.8	[3]
Unicellular algae				
<i>Chlorella miniata</i>	23.26	–	6.0	[34]
<i>Chlorella vulgaris</i>	18.75	–	6.0	[34]
<i>Chlorella vulgaris</i>	–	97.37	4.0	[35]
Seaweeds				
<i>Ascophyllum nodosum</i>	29.29	–	–	[36]
<i>Chondrus crispus</i>	–	194.97	3.5	[37]
<i>Fucus vesiculosus</i>	–	228.95	3.5	[37]
<i>Padina gymnosperma</i>	–	65.07	3.5	[37]
<i>Gracilaria corticata</i>	–	53.99	4.5	[38]
<i>Ulva lactuca</i>	–	126.39	4.5	[38]
Filamentous algae				
<i>Cladophora glomerata</i>	–	73.56	4.5	[38]
<i>Cladophora calliciaema</i>	14.08	40.50	5.0	[18]
<i>Cladophora fascicularis</i>	–	198.5	5.0	[39]
<i>Hydrodictyon reticulatum</i>	8.72	24.00	5.0	[18]
<i>Spirogyra neglecta</i>	40.83	90.19	5.0	[18]
<i>Spirogyra</i> sp.	133.32	–	5.0	[17]
<i>Aulosira fertilissima</i>	21.77	31.12	5.0	[18]
<i>Pithophora oedogonia</i>	23.08	71.13	5.0	[18], This study

good mechanical strength make *Pithophora* an attractive metal biosorbent.

## 5. Conclusions

*Pithophora* biomass has a great potential to sorb Cu(II) and Pb(II) at pH 4.5 and 5.0, respectively. No pretreatment substantially enhanced the metal sorption ability of the biomass, except for a slight increase following HCl pretreatment. Both the pseudo-first and the pseudo-second-order Lagergren kinetic models fitted well to the time course data of sorption and

desorption of both the test metals without any perceptible difference in their  $r^2$  value. The obtained kinetic parameters may be useful in designing a large-scale metal removal process. The Redlich-Peterson and Sips models showed a good agreement with the isotherm data. The removal of Cu(II) and Pb(II) followed exponential and hyperbolic decay equation, respectively, with their increasing concentration in the solution. Similarly, the removal of Cu(II) and Pb(II) at increasing biomass doses could be well defined by exponential and hyperbolic rise, respectively. Although HCl efficiently desorbed the test metals from the metal-loaded biomass, it caused 25–41% reduction of metal sorption, which includes the reduction due to 10–15% loss of biomass, at the end of the fifth cycle. This limitation necessitates the search for a better metal desorbing agent for commercial exploitation of *Pithophora* biomass. Nevertheless, the ability of *Pithophora* to rapidly and efficiently sorb and desorb metal ions, together with good mechanical strength, make it a good candidate for metal removal from wastewater.

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