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Antimonite Removal Using Marine Algal Species

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ABSTRACT: Three seaweed species (*Turbinaria conoides*, *Sargassum* sp., and *Ulva* sp.) were examined to assess their ability to sequester antimonite [Sb(III)] ions from aqueous solution. Among these species, both *T. conoides* and *Sargassum* sp. showed higher Sb(III) biosorption potential than *Ulva* sp. The pH-edge experimental results revealed the involvement of negatively charged groups in the biosorption of Sb(III). Biosorption isotherms obtained at pH 6 indicated that *T. conoides* provided higher uptake of Sb(III) (18.1 mg/g) than *Sargassum* sp. (14.9 mg/g) according to the Langmuir model. Kinetic studies indicated that the rates of Sb(III) removal by both brown seaweeds were high, with 95% of the process completed within 45 min. A pseudo-first-order model was found to describe the kinetic data satisfactorily with a high correlation coefficient and low percentage errors. Desorption experiments with 0.1 M HCl showed that it is possible to regenerate *T. conoides* for its continued use as a biosorbent for up to three sorption—desorption cycles without significant loss in sorption capacity.

1. INTRODUCTION

Antimony (Sb) is a naturally occurring element that is found widely in the environment as a result of natural processes, as well as human activities.[1] The main anthropogenic sources from which Sb is released to the environment include flue gas emissions from waste incinerators, smelters, and coal-fired power plants and boilers.[2] World production for Sb is considerably higher, with an estimated Sb mine output of 165000 t in 2008.[3] Sb has a wide range of uses including the manufacture of semiconductors, diodes, flame retardants, lead hardeners, batteries, small arms, tracer bullets, and pigments.[1] Thus, large quantities of antimony compounds are expected to be present in industrial waste and often enter the environment if the treatment of Sb-bearing wastewaters is inadequate.

Sb is not an essential element in plants or animals.[4] Sb and its compounds are considered as pollutants of priority interest by several environmental agencies,[1] with the U.S. Environmental Protection Agency setting a drinking-water standard of 6 μg/L.[5] Its bioavailability and toxicological effects depend on its chemical forms and oxidation state.[6] Sb can exist in a variety of oxidation states ($-$III, 0, III, and V), but it is mainly found in only two oxidation states (III and V) in environmental, biological, and geochemical samples.[7] From thermodynamic equilibrium considerations, it is believed that Sb predominantly exists as Sb(V) in oxic systems and mainly as Sb(III) under anoxic conditions.[8] Trivalent antimonite [Sb(III)] is 10 times more toxic than pentavalent antimonite [Sb(V)].[9]

Owing to its high toxicity, it is very important to remove Sb from waste solutions before it enters into the environment. A few treatment methods have been attempted in the past for the removal of Sb, including adsorption,[10,11] membrane technology,[12] ion exchange,[13] and coagulation—flocculation—sedimentation.[8] In recent years, there has been an increasing interest in utilizing biosorption-based treatment technology for heavy-metal-bearing solutions. Different biosorbents in the genre of bacteria,[14] fungus,[15] algae,[16] and other waste materials[17,18] have performed well in the sequestration of different heavy metal ions from

aqueous solutions. In particular, seaweeds have been identified as effective biosorbents.[16,19] Seaweeds, a renewable natural biomass, proliferate ubiquitously and abundantly in the littoral zones of world oceans.[19] In many beaches, seaweeds are considered a waste biomass, and there has been an intensive search for their efficient utilization. Thus, seaweeds can serve as a cheap and renewable biosorbent for metal remediation. Seaweeds are usually found in three basic colors (divisions): brown (Phaeophyta), red (Rhodophyta), and green (Chlorophyta). Among these types, brown seaweeds have proved to be efficient in metal biosorption[16] because of their polysaccharide content. The cell walls of brown seaweed have a fibrillar compartment formed mainly of cellulose microfibrils embedded in an amorphous matrix of acid polysaccharides linked to each other by proteins.[20,21] The acid polysaccharides are mainly composed of alginic acids and sulfated fucans. The alginic acids are linear carboxylated copolymers constituted by different proportions of 1,4-linked β-D-mannuronic acid (M-block) and α-L-guluronic acid (G-block).[22] The M- and G-block sequences display significantly different structures, and their proportions in the alginate determine the physical properties and reactivity of the polysaccharide.[23] Acidic polysaccharides found in the cell wall of brown algae have been associated with the metal biosorption capacity of these organisms.

The use of biosorption technology for the removal of arsenic (As) has been widely studied by a number of research groups.[24] However, the removal of Sb using biotechnology has received little attention despite the similarities between As and Sb. Biosorbents employed for Sb removal include lichen,[25] *Saccharomyces cerevisiae*,[26] and *Ascophyllum nodosum*.[27] More attempts are required to understand the interactions of different biomaterials with antimony species. In this context, the sequestration

of Sb(III) by two brown marine algae (*Sargassum* sp. and *Turbinaria conoides*) and a green alga (*Ulva* sp.) was investigated under a variety of experimental conditions. The key factors that affect the biosorption process were subsequently studied and optimized to maximize the removal of Sb(III).

2. MATERIALS AND METHODS

2.1. Preparation of Biomass and Antimony Solutions. The brown seaweed, *Sargassum* sp., was collected from beaches of Labrador Park, Singapore. The green seaweed, *Ulva* sp., was collected from the shores of Sentosa Island, Singapore. The other brown seaweed, *Turbinaria conoides*, was collected from the beaches in Mandapam region, Tamilnadu (India). All seaweeds were initially sun-dried in the sampling sites immediately after collection. In the laboratory, all seaweeds were washed extensively with deionized (DI) water to remove sand and other impurities. After being oven-dried overnight, the seaweed samples were grounded in a blender and subsequently sieved to obtain an average particle size of 0.75 mm for usage in experiments. A stock solution of Sb(III) was prepared by dissolving solid potassium antimony(III) tartrate trihydrate in DI water to a concentration of 100 mg/L.

2.2. Sorption and Desorption. Several 250 mL Erlenmeyer flasks containing antimony solutions (100 mL) spiked with marine algal biomass were used to conduct batch experiments. For pH-edge studies, 100 mg/L of Sb(III) solution at different pH values (2−7) was brought into contact with three marine algal species of 0.2 g each in separate Erlenmeyer flasks kept in a incubated rotary shaker (23 ± 2 °C) that were agitated at 160 rpm for 3 h. The solution pH was initially adjusted and maintained using 0.1 M HCl or NaOH. After agitation, the suspension was filtered, and the filtrate was analyzed for Sb concentration. Similar experimental protocols were followed for isotherm studies, except that the concentration of Sb was varied from 10 to 100 mg/L. For kinetic studies, at specific time intervals (on the order of 5−10 min), samples were withdrawn from the Erlenmeyer flasks and analyzed for Sb concentration. Sb concentrations in the dissolved phase were measured by inductively coupled plasma−atomic emission spectrometry (ICP-AES, PerkinElmer Optima 3000 DV). The samples were filtered using a 0.45-μm PTFE membrane filter and subsequently diluted to less than 10 mg/L prior to analysis by ICP-AES.

For desorption experiments, the seaweed biomass that had previously been exposed to 100 mg/L of Sb solutions at pH 6 was separated from the solution by filtration. The Sb-loaded seaweed biomass was then brought into contact with 50 mL of 0.1 M HCl for 1 h on a rotary shaker at 160 rpm. The remaining procedure was the same as that employed in the biosorption experiments.

All experiments were done in duplicate, and the reported data are the mean values of two independent measurements. Isotherm and kinetic model parameters were evaluated by nonlinear regression using SigmaPlot (version 4.0, SPSS, Chicago, IL).

3. RESULTS AND DISCUSSION

3.1. Effect of pH and the Role of Functional Groups in Sb(III) Binding. Solution pH usually plays an important role in the interaction of solutes with a sorbent. Specifically, it affects the solution chemistry of the solute, as well as the functional groups present in the sorbent. To examine the effect of solution pH on the interaction between Sb(III) and the marine algal biomass, a
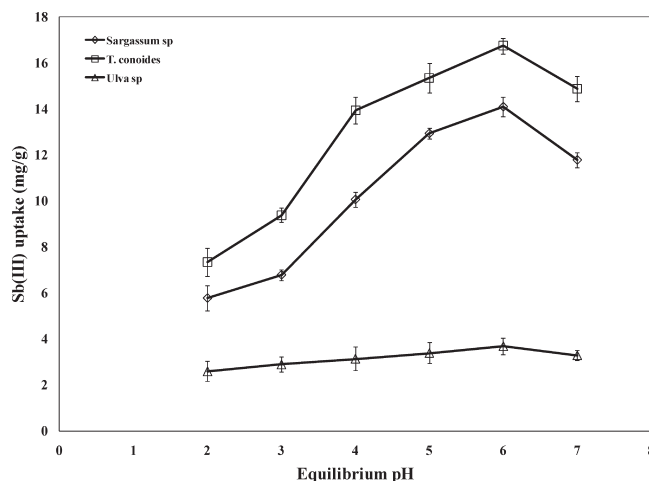
Figure 1. Effect of equilibrium pH on Sb(III) biosorption by three seaweeds.

set of experiments was conducted over a pH range of 2−7. The results obtained from these experiments are shown in Figure 1. These experiments were conducted with an initial concentration of Sb(III) of 100 mg/L and a biosorbent dose of 2 g/L at a temperature of 23 ± 2 °C. As can be seen from Figure 1, both brown algae showed much better performance than the green alga in the sequestration of Sb(III) from the aqueous solution. *T. conoides* exhibited the highest Sb(III) biosorption. Also, under the examined pH conditions, the biosorption potential of all three marine algae increased with increasing pH and reached a maximum at pH 6. A further increase in pH resulted in a decline in the Sb(III) uptake.

In the aqueous solution, Sb(III) exists as $[SbO]^+$ and $[Sb(OH)_2]^+$ species at pH < 3, whereas $HSbO_2$ and $Sb(OH)_3$ species predominate in the pH range of 3−10, and $[SbO_2]^-$ species predominate at pH > 10.[11] At low pH values, excess H^+ ions compete with cationic antimony ions for binding onto the biomass surface, leading to a low uptake of Sb(III) by the algal biomass. As the pH increases, the biomass surface becomes more negatively charged and, thus, favors the Sb uptake. Carboxyl groups are prevalent in seaweeds and are responsible for the biosorption of different metal ions.[16] In particular, brown seaweeds contain more carboxyl groups because of their alginate content.[16] Hence, relatively higher biosorption performance was observed for the brown seaweeds than for the green seaweed. The decrease in the biosorption performance at pH > 6 can be attributed to the pK_a values of the negative functional groups of the marine algae. For instance, the pK_a value of carboxyl groups in seaweed usually lies between 3.6 and 4.5.[28,29] Efforts were also made to identify the role of carboxyl groups in the Sb(III) binding. For this purpose, all three seaweeds were decarboxylated by treatment with methanol. This treatment leads to esterification of the carboxylic acids present in the biomass through the reaction

$$biomass-COOH + CH_3OH \xrightarrow{H^+} biomass-COOCH_3 + H_2O$$

$$(1)$$
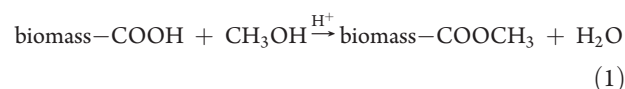
After decarboxylation, the biosorption potentials of all three seaweeds were affected. In particular, the Sb(III) biosorption capacity of *T. conoides* was severely affected, with an 82.3%
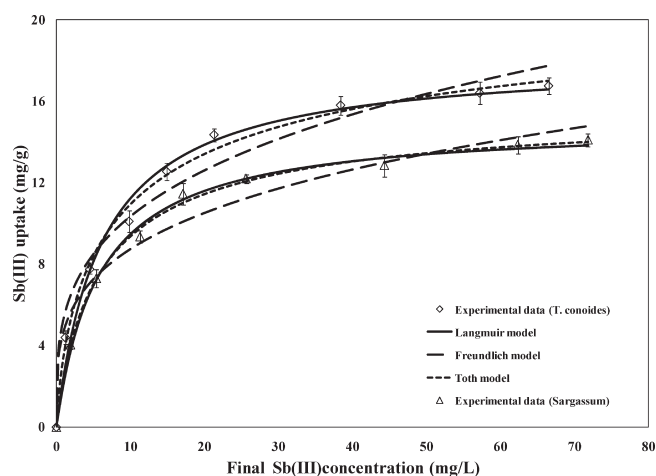
9865

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Figure 2. Sb(III) biosorption isotherms at pH 6.

reduction compared to its original uptake capacity. On the other hand, the uptake capacities of *Sargassum* and *Ulva* biomasses decreased by 72.1% and 45.3%, respectively. This trend clearly shows the involvement of other negatively charged functional groups such as sulfonate $(-OSO_3)$ and phosphonate $(-OPO_3^{2-})$ in seaweed biomass during the uptake of Sb(III). However, no attempts were made to identify the role of each of these groups on Sb(III) biosorption. In general, the negatively charged functional groups were mainly responsible for Sb(III) biosorption.

3.2. Isotherm Studies. The potential application of the biosorbent material is judged by how much sorbate it can attract and retain in an immobilized form.[30] To evaluate the uptake of Sb(III) quantitatively, it is often useful to examine the biosorption isotherm curve, which is a plot of the sorption uptake (Q) and final equilibrium concentration of residual sorbate remaining in the solution (C_f). For isotherm studies, only brown seaweeds were considered because of their high biosorption potential toward Sb(III). Biosorption isotherms were evaluated by varying the Sb(III) concentration in the range of 10−100 mg/L at a fixed pH value of 6.0 (Figure 2). Favorable isotherms with a steep slope were obtained for both seaweeds. In general, the steep increase in the isotherm generally indicates the degree of affinity of the sorbate toward the sorbent. In all cases, the uptake of Sb(III) increased with increasing Sb(III) concentration and reached saturation at higher equilibrium concentrations. Comparing the algal species, *T. conoides* exhibited the highest Sb(III) uptake of 16.8 mg/g at pH 6.

Modeling of the Sb(III) isotherm data was attempted using the Langmuir,[31] Freundlich,[32] and Toth[33] models, which can be represented as follows:

Langmuir model

$$q = \frac{q_{max}b_L C_e}{1 + b_L C_e} \qquad (2)$$

Freundlich model

$$q = K_F (C_e)^{1/n} \qquad (3)$$

Toth model

$$q = \frac{q_m b_T C_e}{[1 + (b_T C_e)^{1/n_T}]^{n_T}} \qquad (4)$$

Table 1. Isotherm Model Constants for Sb(III) Biosorption at pH 6

constant	*T. conoides*	*Sargassum* sp.
Langmuir Model		
q_{max} (mg/g)	18.1	14.9
b_L (L/mg)	0.16	0.17
R^2	0.98	0.99
error (%)	3.20	0.74
Freundlich Model		
K_F (mg/g) (L/mg)$^{1/n}$	5.37	4.74
n	3.51	3.75
R^2	0.97	0.96
error (%)	4.95	3.27
Toth Model		
q_{max} (mg/g)	22.6	15.9
b_T (L/mg)	0.34	0.22
n_T	1.79	1.24
R^2	0.99	0.99
error (%)	0.48	0.65

where q_{max} is the maximum metal uptake (mg/g), b_L is the Langmuir equilibrium constant (L/mg), b_T is the Toth model constant, and n_T is the Toth model exponent. The selection of these models to represent the present system was made for two reasons: (a) the model constants are easy to interpret and (b) the Sb(III) isotherms were L-shaped.[34] The Langmuir adsorption isotherm has traditionally been used to quantify and make comparative evaluations of the performance of different biosorbents. It also serves to estimate the maximum metal uptake values, which cannot be done experimentally. The constant b_L represents the affinity between a sorbent and a sorbate. The model constants of the Langmuir model confirmed that *T. conoides* performed better toward Sb(III) biosorption than *Sargassum* sp. (Table 1).

The relationship between the Sb(III) uptake capacity of the algae and the residual Sb(III) concentration can also be described using the Freundlich equation. The Freundlich isotherm was originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. For the present system, the Freundlich isotherm did not provide satisfactory fits to the data compared to the Langmuir equation. According to the Freundlich equation, the isotherm does not reach a plateau as C_e increases. Thus, the model can be reasonably applied only in the low to intermediate concentration ranges. From Table 1, it is obvious that *T. conoides* exhibited higher K_F and n values than *Sargassum* sp. High values of K_F and n indicate that the binding capacity reached a higher value and the affinity between the biomass and metal ions was also higher. The experimental values of n were greater than unity for both algae, indicating favorable biosorption.

To improve the fitting to the biosorption isotherm data, a three-parameter isotherm model, namely, the Toth model, was also used. The Toth isotherm, derived from potential theory, has proven to be useful in describing the sorption in heterogeneous systems, such as phenolic compounds absorbing onto carbon. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, namely, that most sites have sorption energies less than the mean value.[35] As expected, the
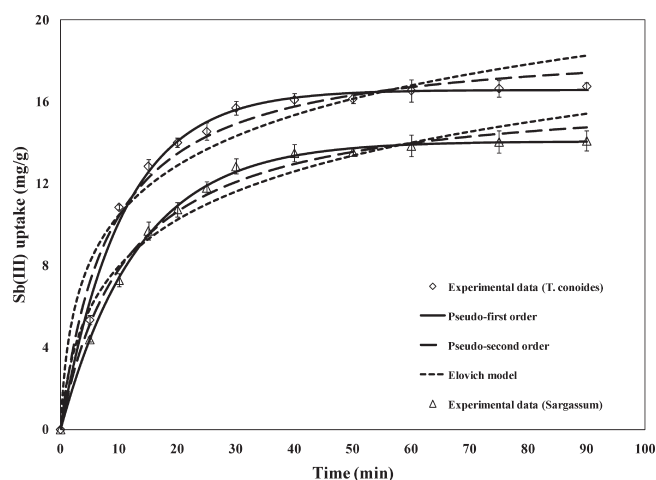
Figure 3. Sb(III) biosorption kinetics at pH 6.

Toth model described the isotherm data satisfactorily with high R^2 and low percentage error vales (Table 1). The successful application of the Toth model to the present data supports the fact that the surfaces of the biosorbents were heterogeneous and contained different functional groups.

3.3. Kinetics. The kinetics of sorption that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics defining the efficiency of sorption. Therefore, kinetic experiments were conducted to understand the biosorption behavior of the three algal biomasses toward Sb(III) (Figure 3). It was observed that the rate of Sb(III) biosorption by all three algal biomass was high during the initial stages of the reaction and then decreased to a relatively low level, leading to equilibrium. This can be attributed to the availability of a large number of vacant binding sites for sorption during the initial stage; after a lapse of time, the occupation of the remaining vacant sites would be difficult because of the repulsive forces between the solute molecules on the solid and bulk phases. On comparing the rates of biosorption by the two algae, no significant difference was observed (Figure 3). However, the extents of Sb(III) biosorption by the two algae were clearly different.

The kinetic behavior of Sb(III) biosorption has been examined using several models. Kinetic models provide information on the biosorption kinetic rates and insights into mechanisms involved in the biosorption process such as mass transfer and chemical reactions. Three kinetic models were employed in this work:

Elovich model

$$q_t = \frac{1}{b}\ln(1 + abt) \tag{5}$$

Pseudo-first-order model

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{6}$$

Pseudo-second-order model

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{7}$$

where a is the initial adsorption rate $[mg/(g \cdot min)]$, b is the desorption constant (g/mg), q_t is the amount of metal sorbed at

Table 2. Kinetic Model Constants for Sb(III) Biosorption at pH 6

constant	T. conoides	Sargassum sp.
Experimental Results		
q (mg/g)	16.8	14.1
Elovich Model		
$a\ [mg/(g\cdot min)]$	6.18	3.02
b (g/mg)	0.27	0.28
R^2	0.93	0.95
error (%)	2.84	2.19
Pseudo-First-Order Model		
q_e (mg/g)	16.6	14.1
k_1 (min^{-1})	0.095	0.075
R^2	0.99	0.99
error (%)	0.94	0.08
Pseudo-Second-Order Model		
q_e (mg/g)	19.0	16.5
$k_2\ [g/(mg\cdot min)]$	0.006	0.005
R^2	0.97	0.98
error (%)	1.99	1.31

time t (mg/g), q_e is the amount of metal sorbed at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), and k_2 is the pseudo-second-order rate constant $[g/(mg \cdot min)]$.

Initially, the Elovich equation was used to describe the Sb(III) kinetics data. This equation is useful in describing adsorption on highly heterogeneous surfaces, when the interactions are predominantly chemical in nature. The analysis of the modeling results (Table 2) revealed that Sb(III) biosorption onto *T. conoides* recorded high a value, which represents the initial rate of adsorption. On considering the data prediction, the Elovich model was unable to predict the data accurately, as relatively low correlation coefficients and high percentage error values were obtained for both algal species. To improve the accuracy of prediction, the pseudo-first-order equation was used to analyze the kinetics data. The results (Table 2) revealed that the pseudo-first-order equation was able to describe the kinetics, well with high correlation coefficients and low percentage error values. Also, the model was able to predict the experimental equilibrium uptake values accurately. In the case of pseudo-second-order kinetics, the model overpredicted the kinetics data in both systems. Even with very high correlation coefficients and low percentage errors, the model results did not agree well with the experimental uptake values (Table 2). A comparison of the kinetic data as predicted by the Elovich, pseudo-first-order, and pseudo-second-order models with the experimental values is presented in Figure 3.

3.4. Desorption and Disposal of Biosorbent. To assess the potential application of the biosorption process, biomass reuse and recovery of the biosorbed solute are the two important attributes to consider in terms of treatment cost considerations.[14] Examination of Figure 1 reveals that Sb(III) can be easily desorbed under strongly acidic conditions, and thus, desorption experiments were attempted using 0.1 M HCl. The results were positive, and 0.1 M HCl exhibited greater than 99.2% desorption of Sb(III) from the *T. conoides* and *Sargassum* biomasses. This high performance further confirms the involvement of negatively charged functional groups in the

biosorption process, as H$^+$ ions could easily exchange with bound Sb(III) ions under strongly acidic conditions. Considering biomass weight loss at the end of a sorption—desorption cycle, *Sargassum* biomass lost 19% compared to only 3.5% lost by *T. conoides*. Because *T. conoides* is known for its rigidity, the use of a highly acidic desorbent medium apparently had no influence on the physical structure of the biomass.

The biomass after desorption was subsequently reused to study its potential to biosorb Sb(III). The biosorption process was repeated for three sorption—desorption cycles. Because a significant biomass weight loss was observed with *Sargassum* biomass, only *T. conoides* biomass was reused in regeneration experiments. Interestingly, the *T. conoides* biomass retained its original biosorption capacity in all three cycles examined, with no significant deviation. In the first, second, and third cycles, *T. conoides* exhibited Sb(III) biosorption capacities of 16.4, 16.1, and 15.6 mg/g, respectively, aided by consistently high elution efficiencies of over 99% by 0.1 M HCl.

After using the seaweeds through several cycles of biosorption to remove metal ions, their ultimate disposal should be addressed. Several options are available, including disposal in existing landfills, incineration, or further utilization in other applications. Disposal in landfills and incineration are relatively costly and not suitable in many counties because of environmental regulations. If Sb(III) is completely stripped from the biomass, seaweeds can also be reused in other practical applications such as compost for soils[36] or biogas production.[37]

4. CONCLUSIONS

The present study examined three seaweed species for the removal of Sb(III) from aqueous solutions. The important findings drawn from this study are summarized as follows:

- Brown seaweeds (*T. conoides* and *Sargassum* sp.), because of the presence of alginate, performed better in Sb(III) biosorption compared to a green seaweed (*Ulva* sp.).
- Isotherm experiments revealed that *T. conoides* can bind Sb(III) with a maximum capacity of 18.1 mg/g, according to the Langmuir model. However, examining the isotherm with different models revealed that the Toth model described the experimental data with high correlation coefficients and low percentage errors, as it can account for heterogeneous biosorption processes, as are usually encountered with seaweeds.
- The rate of biosorption was found to be high, with equilibrium being attained within 45 min. Among several models, the pseudo-first-order model predicted the equilibrium uptake value well, with a high correlation coefficient and low percentage error values.
- Desorption and subsequent reuse of biomass was possible with only the *T. conoides* biomass. With the aid of regeneration with 0.1 M HCl, *T. conoides* was reused for three sorption—desorption cycles without significant loss in sorption capacity.
- With the advantages of being inexpensive, being abundant, and having good mechanical strength, the natural biomaterial *T. conoides* has potential for the treatment of Sb(III)-bearing wastewaters.

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