International Journal of Botany Studies
www.botanyjournals.com
ISSN: 2455-541X
Received: 15-12-2021, Accepted: 30-12-2021, Published: 15-01-2022
Volume 7, Issue 1, 2022, Page No. 291-295

Optimization study of lead biosorption using *Sargassum johnstonii* biomass

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Abstract
Biosorption of lead from an aqueous solution onto *Sargassum johnstonii* macro algae dry powder was evaluated using various operating parameters like pH, adsorbent quantity, particle size, duration and lead concentration in our study. Isotherms and kinetic studies were conducted to determined adsorption phenomena. These studies indicate that seaweed biomass act as convincible alternative for the treatment of heavy metal contaminated effluent.

Keywords: bio-adsorption, wastewater treatment, seaweed biomass, isotherm study, Lead optimization

Introduction

Heavy metal-contaminated wastewater is rapidly being released into the atmosphere, either directly or indirectly, especially in economically developing nations [1]. Heavy metals commonly found in wastewater are poisonous, non-biodegradable, and have a lengthy half-life [2]. Due to heavy metal toxicity in the discharging environment, its presence in contaminated water has increased public interest [3]. The removal of heavy metals from effluent has become a source of worry, particularly in a region where water recycling is the norm. The recovery of these heavy metals from wastewater has become a major environmental controversy in recent years [4]. Heavy metals such as lead, copper, mercury, chromium, and nickel are frequently released into water resources as a waste by industries, causing harm to ecosystems and human health [6,7].They are not biodegradable and bearing tendency to accumulate in living tissues, especially in humans beings, producing a variety of illnesses and physiological abnormalities, including harm to the central nervous system [5, 8]. Lead is the most common and one of the most dangerous heavy metal contaminants, reaching water sources from a variety of industrial operations including mining, oil refining, metal plating and finishing, and battery manufacture [7, 9]. Some non-dangerous disorders, such as anemia, diarrhea, and headaches, can be noticed at low concentrations of lead ions in the blood, but at greater concentrations (>10 g/L), the liver, kidney, neurological, and reproductive systems can be adversely impacted [10, 11]. Various methods are available for separation of heavy metals from effluent like Chemical precipitation [12], ion exchange [13, 14], reverse osmosis [15], membrane filtration, and adsorption [14, 15]. These methods have some drawbacks, including insufficient metal removal, the formation of excess hazardous sludge that necessitates a particular disposal approach, high starting and operating costs, and a high energy requirement [16]. When compared to existing treatments, the adsorption of heavy metal was shown to be one of the most effective solutions for effluent treatment. Agricultural waste, industrial byproducts, biomass, biological and organic materials, polymeric materials, and zeolites can all be used as adsorbents [17]. Adsorption tests were carried out to see if seaweed biomass might be used as an alternate method for removing lead ions from synthetic effluent. The effect of operational parameters like pH of the solution, seaweed biomass dosages, seaweed size and contact timing on adsorption was examined.

Material and Method

Biomass preparation

Sargassum johnstonii macro algae were collected from Okha Coast, Gujarat, India. Biomass prepared via following step wise procedure like washing, drying, heating, grinding and sieving. Dirt particles on seaweed surface and other contaminations were removed using tap water & distilled water after that seaweed samples were sundried to evaporate moisture for 24 hours. Then biomass was heated in to oven for drying at 60°C temperature for 2 hour. Dry seaweed was grounded using mortal and pestal and sieved for getting uniform particle size using standard sieve (0.71mm, 0.85mm, 1mm). This biomass samples were stored in Ziplock bag for adsorption study.

Batch sorption study

Batch sorption study has been carried out to evaluate the capability of seaweed powder to remove lead ion from aqueous solution. Synthetic effluent contain lead was used in this study. Lead working solutions were prepared from 1000mg/L Merck certified standard. For optimization study, a weighed amount of seaweed biomass was added to different conical flasks containing lead aqueous solutions. The suspensions were shaken for a predetermined amount of time at 120 RPM at room temperature using orbital shaker.
The effect of various operating parameter like pH, seaweed dose, seaweed particle size, lead concentration and contact time on adsorption were studied using this method.

Effective pH optimization

pH optimization is a significant parameter to determine during batch study because metal adsorption is highly affected by the solution pH and it basically impacted on electric charge of adsorbent surface. To study the effect of pH (3, 4, 5, 6, and 7) for lead removal, 5 gm dry seaweed powder, 120 RPM speed, and 5 mg/L lead solution were taken for 24 hours in conical flask. For maintain pH of suspension 0.1N H_2SO_4 and 0.1N NaOH were used during experiments. Experiments results indicated lead ion removal efficiency decreased with higher pH value.

Effective Adsorbent dose optimization

Effective adsorbent dose is another significant parameter for designing adsorption study at large scale because of economic reason. Adsorption phenomena depended on adsorbent surface area and number of active adsorption site. As the dose increases, active available site increase. To determine optimum dose of adsorbent various doses of seaweed powder was (1, 1.5, 2, 2.5 and 5 gm) taken for 100 ml of lead aqueous solution. In this research, it was examined that lead adsorption rate is increased with adsorbent dose up to certain extent after that adsorption phenomena became stable due to limited availability of lead ions in to aqueous solution.

Effective particle size optimization:

Three different particle sizes of *Sargassum johnstonii* seaweed 0.71mm, 0.85mm and 1mm were taken in this experiment. Adsorbent with higher particle size (1 mm) was less effective than adsorbent having lower particle size. These phenomena proved that there is immediate relationship between particle size and surface area. Smaller particles have higher surface area and higher adsorption capacity.

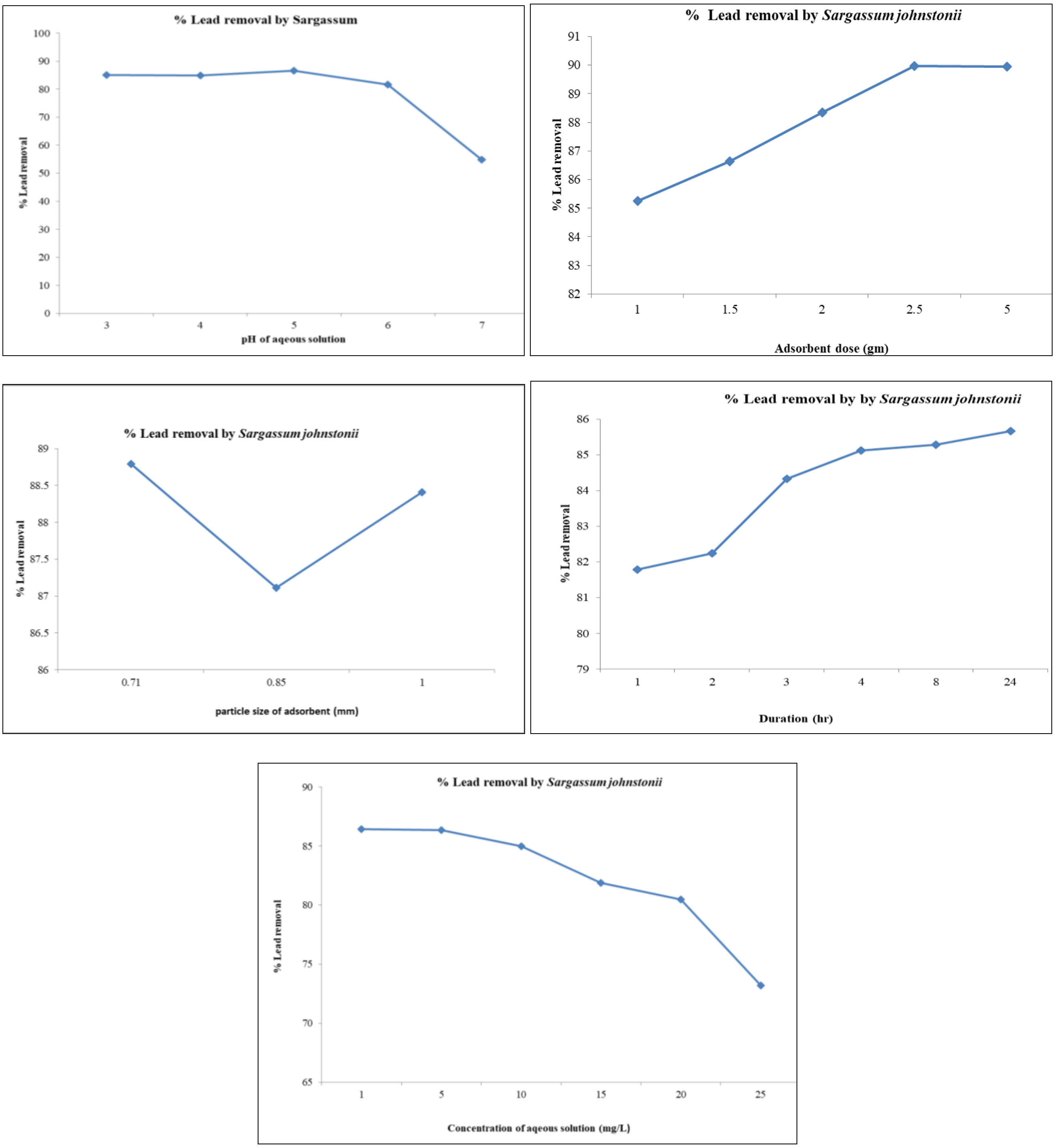

Fig 1: Effect of various parameters on biosorption of lead

Effective Concentration optimization

Initial concentration is important parameter to determine because of higher lead concentration, adsorbent surface become saturated and impacted on availability of binding sites on the adsorbent. To determine impact of initial metal ion concentration on lead adsorption, concentration of 1-25 mg/L lead solutions were taken in separate conical flasks having pH 5, 2.5 gm/100 ml adsorbent dosage for 24 hour duration at 120 R PM. During experiments, strong relationship was observed between adsorbent concentration and lead removal rate. Adsorption gradually decreased as the concentration increased.

Effective Time optimization:

Equilibrium time study for lead adsorption was carried out by agitating conical flask containing 100 ml lead solution for 24 hours and some quantity of aqueous solution has been taken out on interval basis and other parameters during study kept as a constant (pH 5, 0.71 mm, and 2.5 gm adsorbent obtained from pH optimization study) for study % lead removal at specific time. Graphical study of lead adsorption on *Sargassum johnstonii* biomass proved that 24 hours is the best contact period. It was enough to achieve equilibrium, and the biosorption of lead did not change as a result.

Bioadsorption Isotherm

Adsorption isotherm is used to study of mechanism procedure between adsorbent surface and lead ion and they are model using this isotherm. Isotherm modeling gives specific constant which revel surface property of adsorbent and adsorbent affinity toward pollutant. Adsorption capacity (mg/g) was studied using the below equation. The correlation coefficient values were used to determine the applicability of the isotherms.

$$\text{Adsorption capacity} = (C_1-C_2)*V/m$$

Where

C_1 is the initial concentration of lead standard

C_2 is the final concentration of lead standard after adsorption

V is the sample volume

M is mass of adsorbent taken

Lead adsorption by *Sargassum johnstonii* biomass is studied by below two models [19].

1. Langmuir Model
2. Freundlich Model

The correlation coefficient values were used to determine the applicability of the isotherms.

Langmuir Model

Langmuir isotherm is expressed by below equation:

$$C_e / q_e = (1 / q_o b) + (ce / q_o)$$

The plot of residual concentration of lead remaining in the solution $1/C_e$ against equilibrium lead ion loading $1/q_e$ plotted in this study. Value of Q_{max} and Langmuir constant b obtained using slope and the intercept. This model positive outcome assumes the production of a single layer of adsorbate molecules on the surface.

Freundlich Model

This model describes vacant sites with distant energies and heterogeneous surface adsorption.

Freundlich model is represented by equation below.

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

In this model graph of log Ce versus log qe was plotted. Kf and n in graph obtained by intercept and slope of graph respectively. In this study R^2=0 irreversible, $0<R^2<1$ favorable and $R^2>1$ is denoted as unfavorable process.

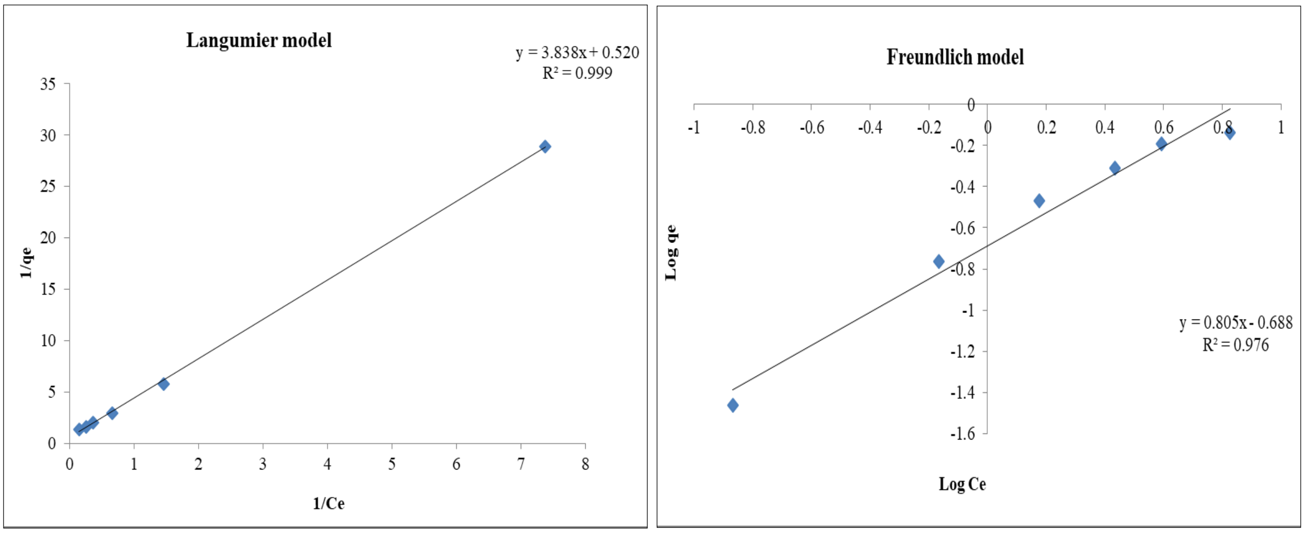

Fig 2: Langmuir and Freundlich modeling

Table 1: Langmuir and Freundlich constant

Sr. No	Langmuir model				Freundlich model			
	Q_{max}	b	R_L	R^2	n	1/n	K_F	R^2
1	1.92	0.5	0.28	0.999	1.24	0.805	0.20	0.976

The Kinetic study

The Kinetics study is conducted to determine the factors that influence adsorption rate and chemical reaction speed. The adsorption mechanism is determined by the physical and chemical properties of the adsorbent, as well as the mass transfer process.

The results of the tests were utilized to investigate the kinetics of metal ion adsorption. Using pseudo first-order and pseudo second-order kinetics, the rate kinetics of lead adsorption onto seaweed biomass was investigated [20].

Pseudo first order

The Pseudo first order is used to perform to determine reactions. First-order kinetic is expressed as

$$\text{Log } (q_e-q_t) = \log q_e - k_1{*}t/2.303$$

Where, qt and qe are the adsorbate amounts (mg/g) at time t (min) and at equilibrium. The constant k_1 and q_e can be acquired from the slope and graph of the graph of log (q_e-q_t) vs. time. The values of k_1 at different sorbate concentrations are represented in Table 2. The R^2 values in Table 2 indicate that the pseudo first-order model is not suitable to describe the adsorption behaviour. The pseudo-second-order kinetic study for adsorption kinetics is expressed as:

$$t/q_t = 1/k_2q_e^2 + 1{*}t/q_e$$

Where, k_2 (g/mg hr) is the second-order rate constant determined from the plot of t/q_t vs. t. The pseudo-second-order equation was based on the solid phase's adsorption capacity (Ho and McKay1998).

The plot indicates that the possibility of chemisorption playing a significant role in the rate-determining phase cannot be discounted. The plot's extremely high linearity proved this fact.

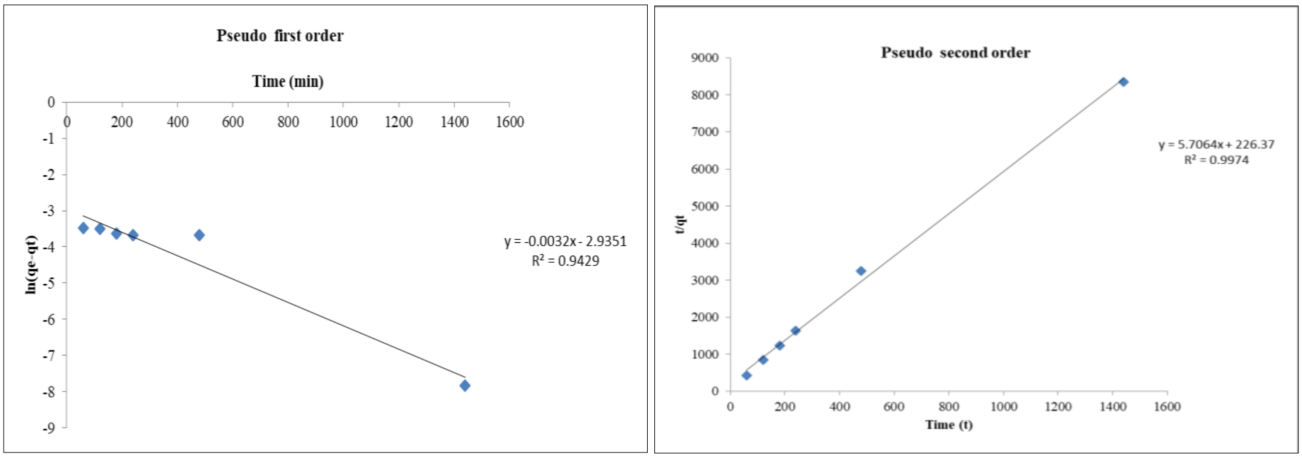

Fig 3: Kinetic Modeling

Table 2: Pseudo first order & Pseudo second order constants

Sr. No	Pseudo first order			Pseudo second order		
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2(g/mg.min)	R^2
1	0.053	-0.00013	0.942	0.175	0.00077	0.997

Conclusion

The adsorption capability of seaweed biomass for the removal of lead from an aqueous solution was proven in this work.

The equilibrium period for lead elimination was determined to be 24 hours. For lead adsorption, the optimal dose of biomass was determined to be 2.5g/L, with removal efficiencies of 86%. Lead was removed to their maximal levels at pH 5. Lead adsorption on seaweed biomass followed a pseudo second-order kinetic model. Even though adsorption is advantageous for the Freundlich isotherm, the Langmuir model fits the experimental data better than the Freundlich model.

Acknowledgement

We would like to thank Vitthalbhai Patel & Rajratna P.T.Patel Science College and Sardar Patel University, Vallbh Vidhyanagar, Anand, Gujarat, India for their support.

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