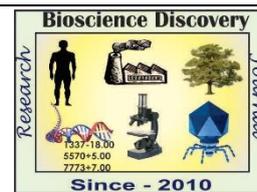


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Research Article



In- vitro adsorption of Pb on low cost and Eco-friendly Biosorbent *Sargassum*

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Abstract

Biosorption is an effective technique for removal of heavy metals from waste water. In this study, the experiments prior conducted in batch using brown algae *Sargassum* as adsorbent to optimize several parameters (pH, contact time, biosorbent dosage, temperature) were conducted for continuous column experiment. FTIR of *Sargassum* was performed to identify its functional groups. The equilibrium sorption data were fitted into Langmuir and Freundlich isotherm. Of the two isotherms R² value of Langmuir model was high 0.984 and it showed to be a perfect fit for isotherm model. The surface chemistry study by SEM and EDX also proved *Sargassum* as a potential adsorbent for heavy metal removal.

INTRODUCTION

Contamination of waste water and soil with heavy metal ions is a complex problem, so from environmental point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation in food chain (Stafiej *et al.*, 2008). Moreover, metals in vary site in their elemental state are not subjected to further biodegradative process (Kanchana *et al.*, 2014).

Lead being one of the “big 3 toxic” heavy metal is of profound concern, as it is implemented in a significant number of industries (Selantia *et al.*, 2004). Lead damages different body organs and has a teratogenic effect causing still birth in women and affecting fetus (Volesky *et al.*, 1994). Several conventional methods have been employed to remove heavy metal ions from wastewater. (Dursun, 2006). Because of several drawbacks like expensive chemicals, low efficiency on small concentrations, disposal problems make these conventional techniques unsuitable to use (Satapathy *et al.*, 2006). Hence an eco-friendly, economically feasible and

effect technique biosorption is needed which could easily solve the heavy metal discharge problem (Selvam *et al.*, 2013). The major advantages of biosorption include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and / or biological sludge, no additional nutrient required, and regeneration of bio sorbent and possibility of metal recovery (Kratochvil *et al.*, 1998). Marine algae, an abundant renewable natural biomass, harvested and cultivated in many parts of the world is an effective biosorbent material for biosorption of heavy metal. It has been used as a dead and non-living material for heavy metal removal (Ofer *et al.*, 2003). There are divergent mechanisms explaining metal uptake by marine algae. The use of brown algae *Sargassum* was taken as a biosorbent as the functional group present on the cell wall of brown algae play a key role in adsorption of heavy metal (Usha *et al.*, 2015)

The objective of present work was to evaluate the potential of brown algae *Sargassum* for heavy metal removal.

Column application for algal materials was studied for maximum capacity per gram. Evaluation of equilibrium sorption data using notable adsorption isotherms such as Langmuir and Freundlich isotherms were applied. FTIR analysis of *Sargassum* was detected before and after adsorption. SEM and EDX were also carried out for surface chemistry of algal sample.

MATERIALS AND METHOD

Metal ion solution:

Stock solution of lead nitrate was prepared (100mg/l) using $Pb(NO_3)_2$ in distilled water. The working solution was prepared by diluting stock solution to appropriate volumes.

Preparation of algal powder:

The marine algae *Sargassum sp.* was collected from veraval coast (20.9° N, 70.36° E), Junagadh during (December, winter season). The alga was washed with tap water and distilled water. The alga was sundried and then it was oven dried at 60°C for 24-48 hours. Then the dried algal material was grounded. The powdered material was used as adsorbent after sieving as a column packed biomass.

Adsorption experiment:

Previously optimized batch experiment (pH: 5.0, temperature 25° C, biomass dosage: 1 gm, contact time: 60 min) was further conducted for continuous column experiment to obtain maximum binding capacity of heavy metal per gram of algal sample. The algal sample were also regenerated using 0.1M EDTA for desorption experiment.

Continuous flow column system:

The adsorption experiment was carried out in column made up of glass. The column was equipped with a stopper for controlling column flow rate. To enable a uniform inlet flow of solution into the column glass beads of 1.5mm diameter were packed

to attain a height of 2 cm. A known quantity of biomass of *Sargassum sp.* was placed in column to yield desired sorbent bed height of 10 cm, maintaining constant flow rate of 1.5ml/ min. Lead solution of different concentrations (10, 20, 30, 40, and 50) ppm with pH: 5.0 were fed upward inside the column to get desired flow rate. Lead solutions at the exit of the column were collected at different time interval and were analyzed.

Instrumentation:

Heavy metal content in all the filtrates was quantified using atomic absorption spectroscopy (AAS). The amount of metal sorbed at equilibrium q_e (mg/gm), which represents heavy metal uptake was calculated from difference in metal concentration in aqueous phase before and after adsorption according to following equation:

$$q_e = \frac{C_i - C_e}{W} * V$$

Where, V is the volume of metal solution (L), C_i and C_e are initial and equilibrium concentration of metal solution (mg/L) respectively and W is the mass of dried algae (gm) packed in column.

Percentage of removal of heavy metal by *Sargassum* was estimated by:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} * 100$$

RESULTS AND DISCUSSION:

FTIR spectral analysis:

Figure 1 and 2 shows FTIR spectra (4000-2000 cm^{-1}) curves for dried *Sargassum*. Peaks like (3174,98 ;1639,98 ;1154,96 ;1089,95 ;830,98) shifted to 3372,84 ; 1637,89 ; 1418,95; 1228,94 ; 1053,90 ;849,97;791,98) after loading the algae with lead. This was probably due to attachment of heavier metal atom to an active functional group. The peaks observed confirm presence of carboxylic acids, amines, hydroxyl ions and carbonyl groups among others on algal surface.

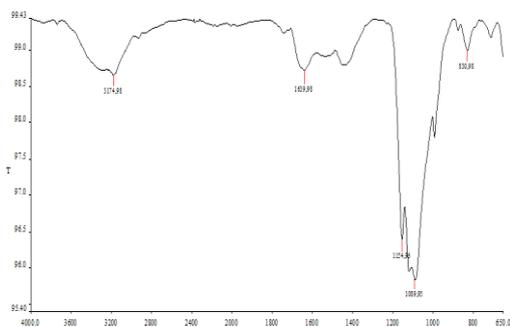


Fig: 1 Biomass before adsorption

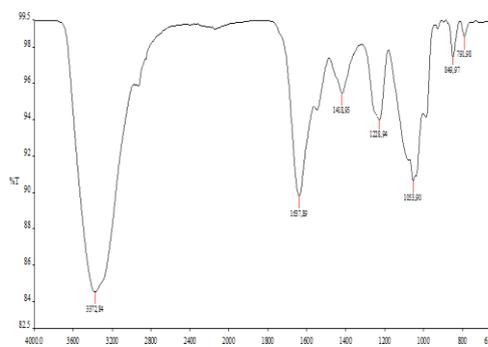


Fig: 2 Biomass after adsorption

Adsorption Isotherms:

Several models of adsorption isotherm have been used. In this context two different isotherm models (Langmuir and Freundlich) were used in order to determine the biosorption of lead. The Langmuir model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. (Vermeulan *et al.*,1966). Based on these assumptions, Langmuir represented the following equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

Langmuir adsorption parameters were determined by transforming the above equation into linear form.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where: C_e = the equilibrium concentration of adsorbate (mg/L-1), q_e is the amount of metal adsorbed per gram of adsorbent at equilibrium (mg/g), Q_0 is maximum monolayer coverage capacity (mg/g), K_L is Langmuir isotherm constant (l/mg).

Freundlich model can be applied to a multilayer adsorption on a heterogenous surface along with interaction between adsorbed molecules. These data fit the empirical equation proposed by freundlich:

$$Q_e = K_f C_e^{1/n}$$

Where K_f is Freundlich Isotherm constant (mg/g), n is adsorption intensity; C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the amount of metal adsorbed per gram of the adsorbate at equilibrium (mg/g) . The linearized form of freundlich equation is:

$$\log Q_e = \log k_{f+1/n} \log C_e$$

Table: 1 Langmuir and Freundlich Isotherm constants for adsorption of Pb unto *Sargassum* biomass

Metal ion	Langmuir isotherm				Freundlich isotherm			
	Q_0 (mg/g)	K_L (L/mg)	R_L	R^2	$1/n$	n	K_f	R^2
Pb ²⁺	20.04	0.164	0.136	0.984	0.328	3.048	15.5	0.922

The results of modelling curve for both isotherms are shown in figure 3 and 4. Constants and correlation coefficient are presented in table: 1.

It can be seen that adjustment of Langmuir equation leads to the best experimental data with R^2 0.984. However, with Freundlich model R^2 of 0.922 is obtained.

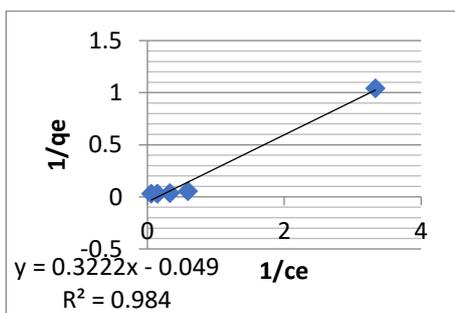


Fig: 3 Langmiur adsorption Isotherm

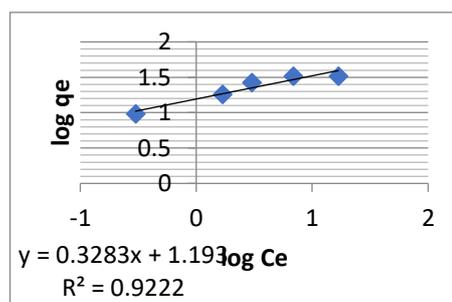


Fig: 4 Freundlich adsorption Isotherm

Characterization of biosorbent:

Scanning electron microscope (SEM) / EDX:

SEM offers topographical and elemental information of solids with virtually large depth of

field. In present study surface morphology of control and biosorbed algae were observed using SEM.

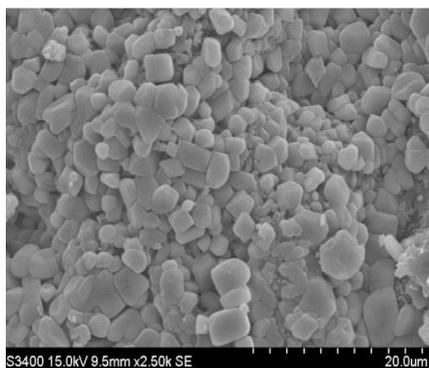


Fig: 5 Normal alage

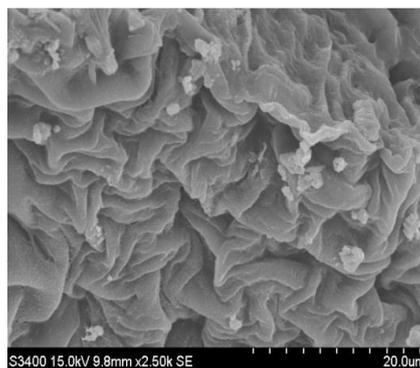


Fig: 6 Algae after adsorption

It is clear that lead has been sorbed on active sites of biosorbent. The figure: 6 confirms the effective adsorption of lead by observing difference in surface morphology of biosorbent before and after biosorption

Samples of biomass before and after metal adsorption were observed using the SEM/EDX technique with the aim of identifying

microstructures and determining chemical composition. An EDX spectrum of algal biomass before and after adsorption is shown in figure 7 and 8.

Presence of Pb shown in figure 8 after adsorption suggests bonding of metal cations on algal surface by interaction with negatively charged functional groups.

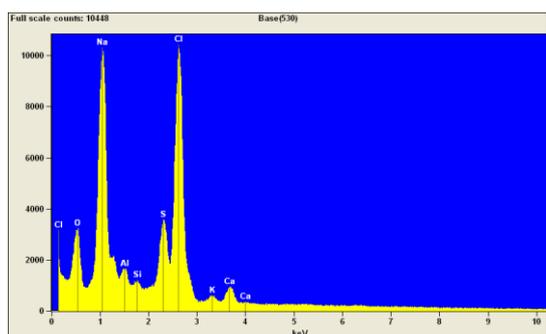


Fig: 7 Before lead adsorption

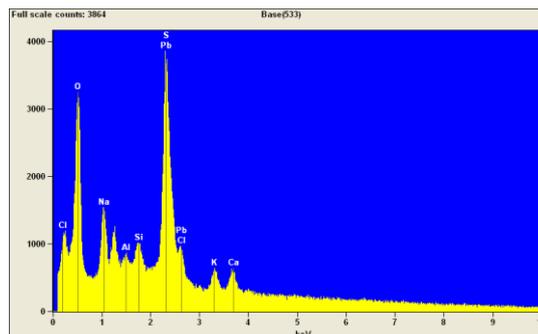


Fig: 8 After lead adsorption

DISCUSSION:

(Olal *et al.*, 2016) expresses that algae is a good adsorbent for biosorption and is effective for heavy metal removal. Moreover the FTIR spectra shows active functional group responsible for lead attachment. Davis *et al.*, 2003 also suggests the same results. Bishnoi *et al.*, 2007 postulates presence of lead on *Sargassum* surface after biosorption as analysed by SEM/EDX. Similar results were observed in above experiment. Even the isotherm results proved *Sargassum* effective for adsorption and Langmuir isotherm showed perfect fit for sorption in above studies.

Dried biomass of *Sargassum* has been identified as an effective biosorbent to remove lead ions from aqueous solution. Laboratory trials do

show potential of *Sargassum* for commercialization, since it is technically feasible, eco-friendly with good metal binding capacity. The equilibrium data of adsorption are in good agreement with the models of isotherm. The adsorbent can be regenerated using 0.1 M EDTA as a desorbate and biomass can be reused without any loss of metal binding capacity. This adsorbent can be a good choice for adsorption of not only Pb but also other heavy metal ions in waste water. The surface chemistry studies SEM/EDX also proved *Sargassum* as an effective biosorbent.

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