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Study of Green Seaweed Biochar for Lead Adsorption from Aqueous Solution

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ABSTRACT

The current work used a batch study to investigate the efficiency of *Ulva lactuca* carbon for lead adsorption from aqueous solution. For the optimization study, the effects of several parameters such as pH, Adsorbent dosage, effective contact time, and initial concentration on lead removal were also considered. pH 3 was observed to be the most beneficial. The Langmuir isotherm, which represents mono-layer adsorption, yielded a maximum lead absorption of 3.49 mg/g. SEM was used to examine surface adsorption behavior, and FTIR was used to detect probable functional groups involved in the bio-adsorption experiment. This study shows that biochar made from the marine algae *Ulva lactuca* is effective for waste water treatment.

Keywords: Heavy metal, Lead, Adsorption, Bio-removal, Waste water treatment, Biochar.

INTRODUCTION

With growing development, pollution levels are rising, disrupting the ecological balance and posing a health risk if not effectively handled. Acid, alkalis, anions (sulphides, sulphites, and cyanide), detergents, sewage, nutrient, and metal, toxic waste, pesticide, radionuclide, and various organic compounds are released as a pollutant.[1] Safe and sufficient quantity is a basic requirement of humans. The interval between water demand and fresh water availability is rising day by day. There is an urgent need to develop methods that can keep the pollution in check and protect our environment while being economical at the same time.[2]

Heavy metals and other hazardous chemicals, generated from natural or industrial sources, act as serious threats to mankind[3]. Among various heavy metals, lead is a particularly toxic metal even at the lowest exposure. The production and consumption of lead ore, metal compounds, and lead containing products are worldwide phenomena. Lead is widely used in battery manufacturing. Global consumption of lead is increasing day by day. Lead is causing cardiovascular diseases, development abnormalities, neurologic and neurobehavioral disorders. Lead is also considered teratogenic. Lead especially affects the blood, central nervous system, kidneys, reproductive system and immune system. Lead is toxic to flora, fauna and microbes. Despite the dramatic worldwide production, consumption and release of lead compounds in the environment, there is no efficient way for recycling[4].

Conventional treatments like ion exchange, chemical precipitation, membrane filtration, coagulation flocculation are not economical. Removal and recovery of heavy metal from the effluent is necessary for environmental concerns. The introduction of efficient and cost-effective technology for the environment friendly treatment of industrial wastewater can help to achieve a cleaner and more sustainable development[5]. Amongst all effluent treatments activated carbon (AC) is the most widely used adsorbent material for the separation of contaminants from wastewater because of its broad adaptability[6]. The main downside of the utilization of activated carbon is its higher cost of synthesis and regeneration[7]. Because of its lower synthesis cost than activated carbon, biochar is now being potential alternative[8]. This study focused on low cost biochar for lead removal from aqueous solution.

MATERIAL AND METHOD

Algal collection and biomass preparation

Fresh green algae species *Ulva lactuca* was collected from the Okha coast, Dwarka district, Gujarat. To eliminate dirt and other pollutants, it was cleaned with tap water. It was sun-dried for 24 hours. The alga was then placed in a 60°C oven for 2 h to remove any leftover moisture. After drying the algae, it was shredded, crushed and sieved to obtained uniform size particles (0.71 mm) and kept in a muffle furnace at 450°C temperature for 20 min in order to convert it into carbon.

Preparation of standard metal solution

The standard solution of 1000 mg/L Merck Certified Reference Material (CRM) of lead solution was used. All chemicals used were A.R grade.

Batch Adsorption experiment

The batch study of lead biosorption began with an optimal pH study for 60 min on constant agitation time. The sample was filtered using Grade A Whatman filter paper after 60 min and the initial and final concentrations of aqueous solutions were measured using an Air acetylene Thermo Fisher Scientific SA13020291 Atomic Adsorption Spectrophotometer (A.A.S). After achieving the optimal pH, various biosorption characteristics such as effective dose, duration, and optimal concentration were investigated. During each experiment, one parameter is changed while the others remain fixed in order to get the best possible environmental circumstances.

Effect of pH on Biosorption

A series of flasks containing 3 to 7 pH of 100 mL lead solution, 0.5 g adsorbent dosage, 120 RPM, 5 mg/L concentration for 60 min were used to evaluate the optimum pH for biosorption. The pH of the aqueous solutions was adjusted by 0.2 M H_2SO_4 and 0.1M NaOH during an experiment. The pH is significant factor for adsorption because it affects the surface charge of the adsorbent and the degree of ionization in the experiment[10]. It is observed that heavy metal biosorption is generally effective at lower pH because binding site may not activate in basic conditions[9]. In our biosorption analysis, we found pH 3 to be the optimum pH, as shown in Fig. 1. Dursun discovered that pH of the solution affects both metal binding sites on the cell surface and the chemistry of metal in solution as more surfaces are available for treatment.[10] The ideal pH was determined by a flask with a better lead removal rate.

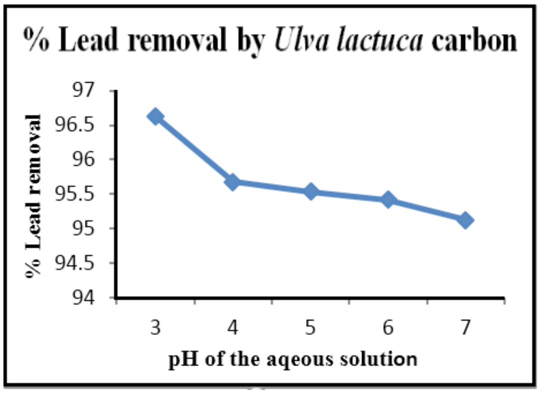


Fig. 1. Effect of pH on biosorption

Effect of Adsorbent dose on bio-adsorption

Various doses of seaweed carbon were taken in conical flaks containing 100 mL lead solution, pH 3 (obtained by pH optimization), 120 RPM speed, and 60 min contact period to determine the effective dose of carbon. The difference in before and after adsorption treatment outcomes is used to estimate the optimal duration. A flask with more adsorption phenomenon is thought to be the ideal adsorbent dose for removing lead. The effect of biomass dose on lead is shown in Fig. 2. Due to the increasing availability of adsorbent, the metal uptake rate rose as the carbon dosage was raised. The curve's initial tendency was upward, which could be attributed to the large number of unoccupied active sites in the adsorbent. This curve shifted gradually by the end, which can be attributed to the saturation of the adsorbent's active sites. Sari Ahmet *et al.,* and Alyuz Bilge *et al.,* achieved a similar graphical trend in their experimental work.[11,12]

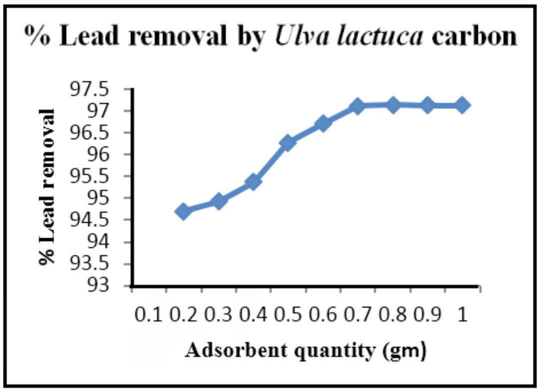


Fig. 2. Effect of adsorbent dose on biosorption

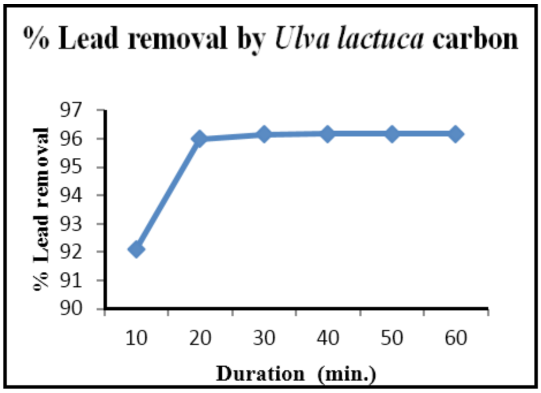


Fig. 3. Effect of Contact time on biosorption

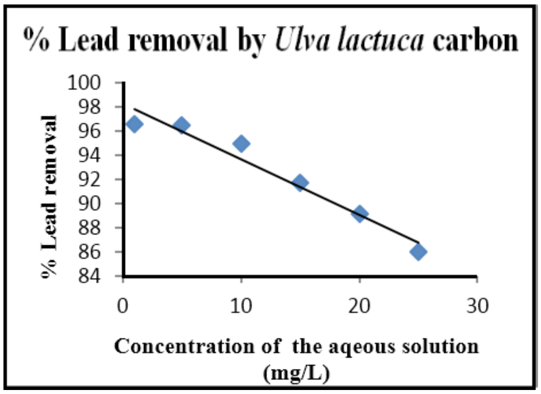


Fig. 4. Effect of Concentration on biosorption

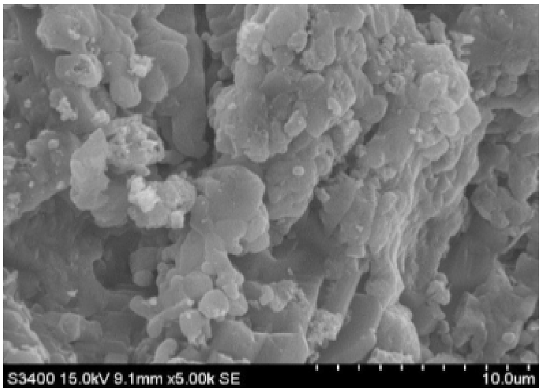


Fig. 5. *Ulva lactuca* carbon untreated

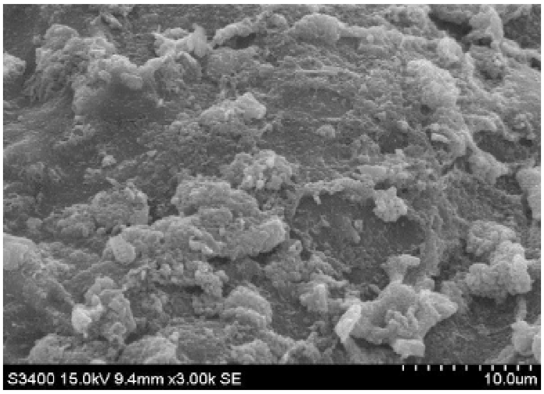


Fig. 6. SEM image of *Ulva lactuca* carbon after lead adsorption

Effect of Contact Time on bio-adsorption

The effect of contact time for biosorption was studied for one hour on 10 min interval basis by keeping other parameters as a constant (pH 3, 0.8 gm adsorbent obtained from optimization study). The data obtained from the biosorption of lead on *Ulva lactuca* carbon showed that the optimum contact time is 30 minute. It was sufficient to achieve equilibrium after that biosorption of lead did not change.

Effect of Concentration on bio-adsorption

The effect of various concentrations of the lead solution was studied within a 1-25 mg/L range. pH 3, adsorbent dose 0.8 g/100 mL taken for 30 min in an orbital shaker at 120 RPM. In the experimental study, the lead uptake gradually decreased with an increase in concentration. This phenomenon occurs due to the saturation of adsorbent sites available in the adsorbent. Maximum adsorption occurs at pH 3 for 5 mg/L concentration.

Scanning Electron Microscope (SEM)

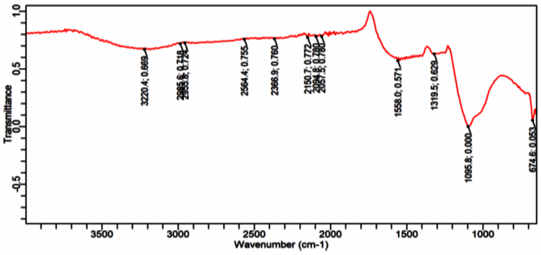
Scanning Electron Microscope (SEM) is used to determine surface phenomena before and after treatment of adsorbent.

The results of the SEM investigation revealed considerable morphological changes in the carbon structure before and after lead adsorption. Before adsorption, the surface of the carbon picture was more porous. After adsorption, the SEM picture revealed a substantial layer of lead deposition and pore wall thickness.

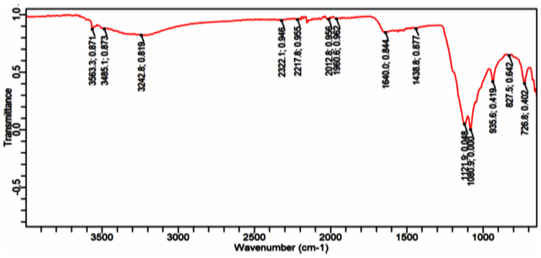
Fourier Transmission Infrared Spectrophotometer

FTIR method is used to detect frequency change in adsorbent before and after treatment with lead. FTIR spectra for treated and untreated samples of carbon were recorded by KBr pellets method operated on FTIR spectrophotometer. For transformation of absorbance into transmittance percentage data processing was performed.

The presence of C-O, O-H, and other functional groups in Ulva lactuca carbon responsible for lead adsorption was demonstrated by FTIR analysis. After lead adsorption, the peaks in wave numbers 935.6, 1640 and 3242.8 disappeared indicating an interaction between *Ulva lactuca* carbon and lead (Graph 1& 2). Due to lead, there was also a vibration shift in the *Ulva lactuca* carbon peak before and after adsorption (726.8 to 674.6, 1080.9 to 1095.8, 1640 to 1558, 3485.1 to 2333.8). (Table 1). Metal chelation was corroborated by these overall alterations in wave number. Due to stretching vibrations, the adsorption peak detected in untreated *Ulva lactuca* carbon 3485.1 and 3563.3 proved that the material is carbon.[13]



Graph. 1. FTIR Graph before lead adsorption



Graph. 2. FTIR Graph after lead adsorption

Table 1: FTIR Peak table

Sr. No	Standard Adsorption frequency	Functional group	Compound	Blank *Ulva lactuca* carbon	Functional group	*Ulva lactuca* treated with lead	Functional group
1	480-410	S-S	Disulphide	726.8, 827.5	C-Cl	674.6	C-Cl
2	600	C-S, C=S	Sulfate	935.6	O-H	-	-
3	1084.1-1038.1, 1015	C-F, Si-O, S=O, C-O	Cellulose carbohydrates Sulfonides &				
		Glucose	1080.9, 1121.9	C-O	1095.8	C-F	
4	1244, 1228	P-O	Phosphine/ Phosphate	-	-	-	-
5	1405, 1400-1200,1415	C-O, O-H, CH_3-N	Cutin	-	-	-	-
6	1560	C=C, C-O	Lignin	-	-	1558.0	N-H bending vibration
7	1653, 1660 -1655	C=O, C-N, N-H	Ester Pectin	1640	C=C alkene	-	-
8	2360	C-O, P+H	Phosphine	-	-	2150.7	CΞ C
9	2960-2850	N-H, CH_3 & CH_2	Aliphatic compound	3242.8	N-H	-	-
10	3300	NH, O-H	Polysaccharide, Aminoacids	3485.1, 3563.3	O-H	2933.8	-C-H strech

Adsorption Isotherm

Adsorption isotherm is the study of the quantity of adsorbed heavy metal. This model is used for development of equations for designing purpose. Adsorption capacity (mg/g) was studied using the below equation.[14]

Adsorption capacity = $(C_o - C_e)*V/m$

Where C_o is the intial concentration of lead standard
C_e is final concentration of lead standard after adsorption
V is the volume of sample taken
M is mass of adsorbent taken

Adsorption of lead by *Ulva lactuca* is studied by below two models.
(1) Langmuir isotherm
(2) Freundlich isotherm

Langmuir isotherm
Langmuir isotherm is below:

$$C_e/q_e = (1/q_o b) + (c_e/q_o) \quad (1)$$

Langmuir isotherm can be obtained by plotting a graph of $1/C_e$ against $1/q_e$. Slope and the intercept can be calculated using this graph. Langmuir constant b is calculated using this method.

Freundlich Isotherm
German physical chemist Herbert Max Finley Freundlich has represented this isotherm in 1909. This model gives an idea for sorption on the heterogeneous surface.

Freundlich Isotherm is expressed by the following equation.

$$\text{Log } q_e = \log K_f + 1/n \log C_e \quad (2)$$

This value is obtained by plotting log C_e versus log q_e. K_f and n in graph obtained by intercept and slope of graph respectively.

Comparison of Langmuir and Freundlich model for adsorption are listed in Table 2

Table 2: Comparison of Langmuir and Freundlich model for adsorption are listed in table 2

Sr. No	Langmuir			Freundlich		
	Q_{max}	b	R_2	N	K_F	R_2
1	3.4965	1.05926	0.999	0.653	1.44	0.962

From the above results, Langmuir isotherm appears more suitable than Freundlich isotherm. It shows mono-layer adsorption rather than multi-layer adsorption. In Freundlich isotherm, n value is less than one representing adsorption to be a chemical process.

Desorption and reusability
Desorption of heavy metal from seaweed carbon by 0.1M HNO_3 was studied for its reusability purpose. After eluting with 0.1M HNO_3, desorbing aqueous solution was measured using Atomic adsorption spectrophotometer. Effeciency of desorption can be measured as below.

$$\text{Desorption recovery} = C_1/C_2*100$$

Where C_2 is the concentration of the adsorbate on the surface of adsorbent and C_1 is the concentration of adsorbates in the solution after desorption process.

Ulva lactuca carbon recovery = 4.0777/4.5800*100

Lead desorption by *Ulva lactuca* carbon achieved 89% recovery.

Table 3: Literature review of Lead removal by seaweed carbon:

Sr. No	Seaweed species	Solution medium	Removal rate	Optimum conditions	Reference
1	*Ulva lactuca* carbon treated with KOH in 3:1 ratio	Aqeous solution	83.34 mg/g	pH 5, Contact time 60 min,, adsorbent dose 0.8 g/L, Concentration 60 mg/L	(15)
2	*Ulva fasciata* species treated with calcium chloride (CCUC), sodium carbonate (SCUC), sodium sulphate treated (SSUC)	Aqeous solution	22.93 mg/g, 24.15 mg/g, 23.47 mg/g	pH 4, contact time 60 min, adsorbent dose 0.15 g/100 mL, Concentration 10 mg/L	(16)
3	Gracilaria changii Activated carbon	Aqeous solution	0.1 mg/g	pH 6, contact time 30 min,	(17)

CONCLUSION

Biosorption of lead using *Ulva lactuca* carbon has been studied in this research. The results of these experiments strongly suggested that *Ulva lactuca* carbon is cost-effective and capable of removing lead from aqueous solutions. Carbon can be reused by removing lead after being treated with 0.1M HNO_3. We can conclude from a comparison of literature review data that seaweed carbon is more efficient when activated than when untreated.

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Conflict of interest

The authors declare that there is no conflict of interest.

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