EQUILIBRIUM AND KINETIC STUDY FOR BIOSORPTION OF LEAD USING PACKED COLUMN BY MARINE GREEN ALGAE ULVA LACTUACA

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ABSTRACT

Water pollution is an ongoing global problem which requires evaluation regularly. In that phenomenon the water pollution causing metals plays a key role. The removal of metals like lead, nickel etc are required to maintain healthy environment. In the present work, the removal of Lead is performed by marine green algae ulva lactuaca which is a natural and eco-friendly process. After the removal, kinetics and thermodynamic parameters like ΔG,ΔH, ΔS are performed to determine the efficiency for the removal of lead. Various isotherms like Langmuir, Freundlich and Temkin are performed and the yield value of 7.057 mg/g is found to be best in Langmuir with a rate of 0.9941.

Keywords: biosorption, heavy metals, marine green algae ulva lactuaca, Isothermal models, Thermodynamics.

INTRODUCTION

Water pollution is the leading worldwide cause of deaths and diseases. Harmful impacts of arsenic, mercury and lead were known since old times, but methodological considers of harmfulness level of overwhelming metals show up from 1868. Heavy metal contamination affects large areas worldwide. . The no biodegradable nature of Lead is the prime reason for its prolonged persistence in the environment. The Removal of lead plays a key role in maintaining hygienic environment. The natural biosorption technique is considered to be the best because of it easy availability and its high effective efficiency then other methods used in removal of heavy metals from industrial effluent, [4] biosorption was identified as the best in consideration of various advantages including its economical and easy availability.

EXPERIMENTAL PROCEDURE

Collection of Biosorbent:

Marine green algae ulva lactuaca is collected from Visakhapatnam beach.

Preparation of Biosorbent:

The Marine green algae ulva lactuaca is then collected, washed, dried, recultivated. The ulva lactuaca is then kept for growth in a standard culture medium for 24 hrs in an incubation at 24± 2 °C. The algae biomass is then agitated at 1000 rpm for 15 min. The biomass washed 5 times. Then, they are grinded and sieved at 200µm size and dried completely. The biomass resulted at an exponential growth rate is obtained. The obtained sample is used for biosorption of lead.

Collection of Sample:

Wastewater was collected from beach area nearby industries around Visakhapatnam.[7]

PROCEDURE

50 cm height and 5 cm inner diameter dimensioned pyrex made glass column is taken and fitted tightly with stopcock at opening of the column [8]. The column is then packed by the sodium alginate beads entrapped with marine green algae ulva lactuaca is adjusted tightly

without voids. Then the packed bed arranged is pressed gently to maintain its consistency as shown in Fig. 1.The Weight of the marine green algae ulva lactuaca packed in the column are recorded.[9]

Fig.1 Column packed with Marine green algae ulva lactuaca

The wastewater containing lead is made to flow through the marine green algae ulva lactuaca bed column using a peristaltic pump at rate flow 2mL/min.[10] The biosorption process of marine algae ulva lactuaca is carried away and the finally treated wastewater sample is then collected from the bottom of the column with respect to connected outlet as shown in above figure. The resulted concentration of lead after treated through the fixed bed column filled with ulva lactuca was studied. The post- treated sample solutions are collected for every 30 min interval using Atomic adsorption spectroscopy. This process is continued until the concentration of inlet and outlet consistency is found to be same. [11]

RESULTS AND DISSCUSION

Biosorption of lead is carried out using packed column by marine green algae ulva lactuaca..

Adsorption Isotherms:

1.1. **Langmuir Isotherm**

The Langmuir sorption isotherm has been used in biosorption processes for various pollutants removal. Langmuir theory is based on the assumption that the biosorption takes place at specific homogeneous sites within the biosorbent .[12]

The Langmuir equation is given as:

$(C_e/q_e)=1/(q_{max}.b)+(C_e/q_{max})$ (1)

Where,

Ce = concentration of the lead at equilibrium(ppm)

qe = amount of lead adsorbed at equilibrium,(mg/g)

qmax = maximum biosorption capacity, (mg/g)

b= Langmuir constant (L/mg)

Fig. 2 shows the plot of the Langmuir equation (1), (Ce / qe) vs. (Ce), which indicates a straight line with slope and intercept as 1/qmax and1/bqmax respectively. From the plot of Langmuir equation, the maximum biosorption capacity (qmax) is found to be 7.057 mg/g and Langmuir constant (b) is found to be 0.114 L/mg.

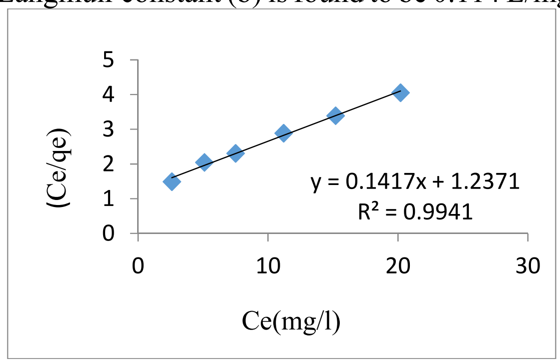

Fig.2 Langmuir Isotherm for biosorption of lead

1.2. **Freundlich Isotherm**

Freundlich isotherm indicates that, the concentration of solute in the solution at equilibrium (C_{eq}) is raised to the power of m, the amount of solute biosorbed being q_{eq}, then C_{eq}/q_e is a constant at a given temperature, which is expressed by the following equation:

$\log q_e = \log K_F + (1/n) * \log C_{eq}$ (2)

Fig. 3 shows the plot of log q_{eq} vs log C_{eq}. From the plot, the biosorption / distribution coefficient (K_F) is found to be 1.0167 and the value of (n) is 1.834

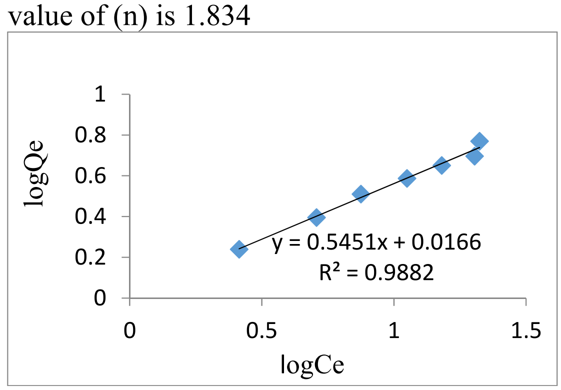

Fig.3 Freundlich isotherm for biosorption of lead

1.3. Temkin Isotherm: This model involves that the presence of indirect biosorbate / biosorbent interactions and suggests that interactions of the heat biosorbed by all molecules in the layer would decrease linearly. Temkin isotherm is given as:

$$q_e = B \ln C_e + B \ln k_T \quad (3)$$

Here $B = RT/b_T$

Where, b_T and K_T are Temkin isotherm constants.

Fig. 4 shows a plot of q_{eq} vs $\ln C_{eq}$, which is a straight line with slope of RT/b_T and intercept of $B\ln K_T$.

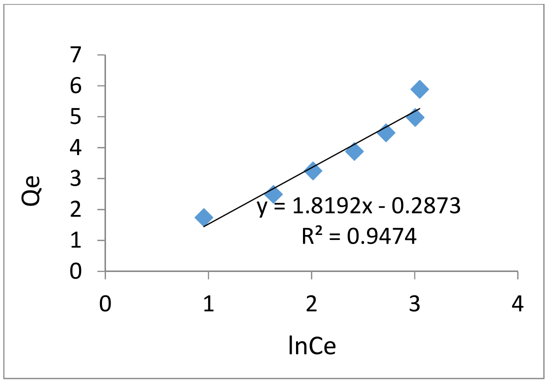

Fig.4 Temkin Isotherm for bio sorption of lead

From the plot, Temkin constants are found to be b_T =1476.15 J/mol and K_T = 0.8539 L/mg with R^2value =0.9474

The isotherm constants obtained from the above three isotherms are compared and listed in Table-1. The best fit equilibrium model is determined based on the linear regression coefficient (R^2). From the table, it is observed that the biosorption data are well represented in both Langmuir and Freundlich isotherms by marine algae ulva lactuaca for lead biosorption with higher R^2 of 0.9941 and 0.9882 respectively, followed by Temkin isotherm with R^2 value of 0.9474.

Langmuir model	Freundlich model	Temkin model
q_{max} = 7.057 mg/g b = 0.114 L/mg R^2 = 0.9941	1/n = 0.5451 K_F = 1.0167 R^2 = 0.9882	b_T = 1476.15 J/mol K_T = 0.8539 L/mg R^2 = 0.9474

Table-1: Isotherm constants

2.0. KINETIC STUDIES:

The kinetics of the biosorption data was observed using two different kinetic models as pseudo-first order and pseudo-second order. These models correlate solute uptake, which is important in predicting the reactor volume [13].

2.1. Pseudo-First Order Model

The possibility of biosorption data following Lagergren pseudo-first order kinetics is given by

$$dq/dt = k_1 (q_{eq} - q)$$

$$\ln(q_{eq} - q_t) = -k_1 t + \ln q_e \quad (4)$$

Where,

q is the amount of biosorbate at time t (mg/g),

q_{eq} is the biosorption capacity at equilibrium (mg/g),

K_1 is the rate constant of the pseudo-first-order model (min^{-1}).

Values of rate constant (K_1) and q_{eq} for biosorption of lead are determined from the plot of ln (q_{eq}-q_t) vs. time (t), shown in Fig 5. The intercept of the plot is equal to ln q_e. The correlation coefficient for pseudo first order is 0.949.

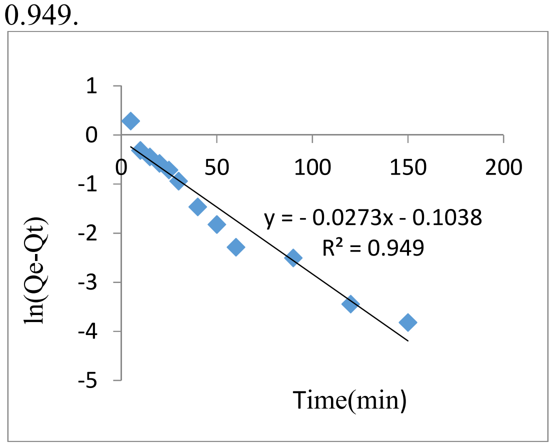

Fig.5 First Order kinetics for biosorption of lead

2.2. Pseudo-Second Order Model

A pseudo-second order model proposed by Ho and McKay which is used to explains the sorption kinetics. This model is based on the assumption that the biosorption follows second order chemisorptions. The pseudo-second order model can be expressed as

$$dq/dt = K_2 (C_{eq} - q)^2 \quad (5)$$

Separating the variables in Eq. (5) gives

$$(dq)/((C_{eq}-q)^2) = K_2 dt \qquad (6)$$

Integrating Eq. (6) for the boundary conditions q=0 to q=q at t=0 to t=t, Eq. (6) simplifies to

$$(t/q_t) = (t/q_e) + 1/(k_2.q_e^2) \qquad (7)$$

Where t is the contact time (min), q_{eq} is the amount of lead adsorbed at equilibrium (mg/g) and q is the amount of lead biosorbed at any time, t (mg/g). The correlation coefficients were found to be 0.999 for initial concentrations 10 ppm to 50 ppm. If second order kinetics is applicable, the plot Fig.6, t/q_t versus time (t) of equation (7) should given a linear relationship from which the constants q_{eq} and K_2 can be determined

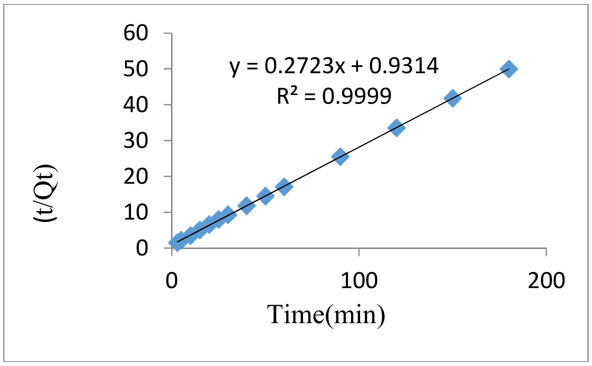

Fig:6: Second Order kinetics for biosorption of lead

3.0 Effect of Thermodynamic parameters:

The change in variation during biosorption can be explained by three main thermodynamic parameters. These include entropy change (ΔS), enthalpy change (ΔH) and Gibb's free energy (ΔG). The negative value of ΔH indicates that the process is exothermic and the positive value of ΔH indicates that the process is endothermic. The thermodynamic parameters for the biosorption process were computed from the plot of ln (C_S/C_{eq}) vs. 1/T, shown in Fig. 7, here ($K_C = C_S/C_e$).

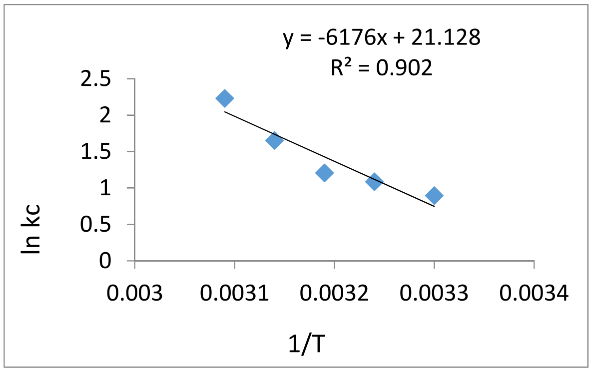

Fig.7 Effect of temperature for biosorption of lead

The free energy change for lead ions on to marine algae ulva lactuaca were determined using the equilibrium constant obtained from surface concentrations at each initial concentration. From plot, slope (ΔH/R) =6176 J/mol and Thermodynamic parameters values are listed in the Table -2.

S. NO.	Temperature (K)	lnK	ΔH (kJ/mol)	ΔG= (-RT lnKC) kJ/mol)	ΔS =(ΔH-ΔG)/(T) (kJ/mol.k)
1	323	2.23	51.34	-5.991	0.1775
2	318	1.65		-4.374	0.1752
3	313	1.20		-3.144	0.1740
4	308	1.08		-2.779	0.1757
5	303	0.89		-2.255	0.1769

Table.2. Thermodynamic parameters values for biosorption of lead

CONCLUSION

In the present scenario, the toxic metals like lead present in industrial wastewater is a main key for the water pollution. Lead is considered to be the main reason in causing health hazards. Because of lead toxicity, it is best to remove its concentration from the wastewater with decreases the effect of health disorders. In present work, the removal of lead is carried away using an eco- friendly process like marine green algae like ulva lactuaca. The removal of lead is observed and its kinetics isotherms are performed. Various isotherms like Langmuir, Freundlich and temkin are conducted and the results are concluded as the best fit in Langmuir and yield of 7.057 mg/g. and the thermodynamic parameters are performed and resulted as R^2= 0.9941. The isotherms are observed and concluded that biosorption of lead by marine green algae ulva lactuaca is considered to be best in pseudo second order kinetics method at a high removal rate. Free energy and entropy are found to be negative and positive respectively means spontaneous and disorderness at solid-liquid interface is high.

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