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Column Study on the Removal of Metals from Industrial Effluents using the Biomass *Sargassum* sp

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Abstract – Heavy metals are ubiquitous environmental contaminants in industrialized societies. The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment. Traditional methods have been used to remove heavy metals from effluent include chemical precipitation, chemical oxidation/reduction, ion exchange, electrochemical treatment, evaporation and filtration. Many of these methods are ineffective; resulting in low levels of metal ion removal and can also be economically inefficient. Biomass of brown marine macro algae is a renewable biological resource, which is available in large quantities and can form a good base for the development of biosorbent material. The work considered the parameters of the effluents and the experimental column model for the metal adsorption. Among the experimental model Thomas model fitted the column biosorption data well.

Keywords - Heavy metals, Effluents, Brown algae, Biosorption, Column.

I. INTRODUCTION

Water is the most valuable natural resource existing on this planet. Without this invaluable compound, life on the earth will not be possible. Pollution of water resources is a common occurrence. Pollution caused by industrial waste waters have become a common problem in many countries. Heavy metals are of serious concern because they are not biodegradable and thus, persistent. The removal of toxic heavy metals from waste waters have become the subject of considerable interest due to moral strict legislations introduced to control water pollution (Stratton, 1987). Heavy metal ions present in waste waters are released by various industries such as mining, electroplating, electronic equipment, battery-manufacturing processes, etc. (Aderhold et al., 1996). The excessive exposure of these toxic metals leads to severe damage of lungs, kidneys, skin dermatitis, cancer, etc. (Denkhaus and Salnikow, 2002). Biosorption is an emerging and attractive technology which involves the sorption of dissolved substances by the biomaterials. It is a potential technique used for the removal of toxic heavy metals from the solutions and the recovery of precious metals (Matheickal and Yu, 1999). The major advantages of biosorption over conventional-treatment methods include low cost, high efficiency of metal removal from the dilute solutions, minimization of chemical and/or biological sludge, no additional nutrient requirement,

regeneration of biosorbents and the possibility of metal recovery. Dry seaweed biomass is used as an adsorbent mainly because of its low cost and high metal-binding capacity (Volesky, 1994). Metal-ion uptake by biomass is believed to occur through interactions with the cell walls. This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding agents, include ionic interactions and complex formation between metal cations and ligands on the surface of the seaweeds. Seaweeds offer advantages for biosorption because their macroscopic structures offer a convenient basis for the production of biosorbent particles suitable for sorption process applications (Figueira et al., 2000; Vieira and Volesky, 2000). Hence the research work concentrates on the physico-chemical characteristics of the effluent and optimizing the column on metal adsorption using the biomass *Sargassum* sp.

II. MATERIALS AND METHODS

Biomass preparation

The biomass used in the present study was the brown seaweed *Sargassum* sp., collected from the rocky seashores near Uvari, Tirunelveli District, Tamilnadu, India. After harvesting from sea, the samples were washed in distilled water to remove particulate materials and salts from the surface. They were then dried in an

oven at 60°C for 24hrs and then used as biosorbent for further studies (Da Costa and De Franca, 1996).

Effluent

The effluent used was obtained from Electroplating Metal Finishers, SIPCOT Industrial Estate, Chennai, Tamilnadu. The pH of the waste water was determined on the spot using potable pH meter. The physico – chemical characteristics of the effluent were determined using standard analytical methods (APHA, 19th edn. 1995). The concentrations of heavy metals were detected using AAS.

Column experiment

Fixed bed biosorption experiments were conducted in a glass column and a known quantity of biomass was packed in the column to yield the desired bed height of the sorbent. A peristaltic pump was used to pump the metal solution through the column in the upward direction. To optimize the sorption studies it was carried out in a glass column of 8.3, 8.5 and 12.5 cm of column height with the diameter of 1.2, 1.8 and 3.2 cm respectively. The bed height of the column is 6.7, 7.0 and 9.0 cm and the flow rate was adjusted to 5, 10 and 15ml/min and the effluent concentration was varied between 50, 75 and 100 mg/l. Experiments were conducted to study the effect of bed height, flow rate and the effluent concentration. The aliquot of the effluent at the outlet of the column was collected at regular time intervals. Column effluent samples were analyzed by atomic absorption spectroscopy and the optimized parameters were shown in Table.2.

III. MODELING AND ANALYSIS OF COLUMN DATA

Thomas model

The Thomas model has been used in studies of metal sorption by column experiment. The Thomas model is presented in the Eq.1

$$\frac{C}{C_0} = \frac{1}{1 + \exp(k_t/F(q_0M - C_0V))} \quad (1)$$

C is the effluent metal concentration (mg/l), C₀ the initial metal concentration (mg/l), k_t the Thomas rate constant (ml/min mg), q₀ the maximum metal adsorbed in biomass (mg/g), M is the weight of biomass, V is the throughput volume (l) and F is the volumetric flow rate (ml/min).

Adams - Bohart model

Bohart and Adams established the fundamental equations that describe the relationship between C/C₀ and time in an open system for the adsorption of metal. The relationship between concentration and time in the bed for low concentration and time in the bed for low concentration regions of the breakthrough curve is given by Eq.2

$$\ln \frac{C}{C_0} = kC_0t - kN_0 \frac{z}{u} \quad (2)$$

C₀ and C are the inlet and outlet of metal concentrations (mgL⁻¹), z is the bed depth in cm, u the linear flow rate (cm/min), k is the adsorption rate constant (L/mg.min) and N₀ is the saturation concentration (mg/L).

Wolborska model

It is used for the description of sorption dynamics in the low concentration range of the breakthrough curve and is expressed in the Eq.3.

$$\ln \frac{C}{C_0} = \frac{\beta C_0}{N_0} t - \frac{\beta z}{u} \quad (3)$$

Where β is the kinetic coefficient of external mass transfer (min⁻¹). Expression of the Wolborska solution is equivalent to the Adams – Bohart relation.

Yoon-Nelson model

Yoon and Nelson developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The linearized Yoon-Nelson model for a single component system is expressed Eq.4.

$$\ln \frac{C_t}{C_0 - C_t} = k_{YN} t - \tau k_{YN} \quad (4)$$

Where k_{YN} (1/min) is the rate velocity constant, τ (min) is the time required for 50% adsorbate breakthrough. From a linear plot of ln [C_t/(C₀-C_t)] against sampling time (t), values of k_{YN} and τ were determined from the intercept and slope of the plot.

IV. RESULT AND DISCUSSION

Physico-chemical parameters of the effluent

The electroplating waste water sample is analyzed promptly for determining the physico-chemical characteristics using standard analytical methods (APHA, 1995). The concentrations of heavy metals have been detected using AAS and the parameters of metals before and after adsorption are shown in Table 1.

Column Studies

The prediction of breakthrough curve is required for the successful design of a column-sorption process. The maximum adsorption capacity of an adsorbent is also needed for the design. Various mathematical models can be used to describe the fixed-bed adsorption. Among these, the Thomas model has been widely used by several investigators and the model gives non-zero concentration at time $t = 0$. Comparison of experimentally determined model predicted breakthrough curves are shown in Table 2. Table 3 summarize the model parameters obtained at different bed heights, flow rates and initial metal concentrations. As the bed height is increased, the values of Q_0 increased and the values of k_{Th} decreased. The bed capacity Q_0 decreased and Thomas constant k_{Th} increased with increasing flow rate. In contrast, Q_0 increased and k_{Th} decreased with increasing initial metal ion concentration. In most cases, a negligible difference between the experimental and the predicted values of the bed capacity has been observed.

V. CONCLUSION

Biosorption of heavy metals is one of the promising technologies involved in the removal of heavy metals from waste waters. *Sargassum* sp. was selected for studying biosorption due to its originality and to assess the possibility of utilizing a waste biomass for heavy metal removal. Among the experimental models, Thomas model fitted the column biosorption data well. The selected biomass behaves as an ion exchanger and hence, the process is very rapid and the results obtained

are very promising for further large-scale biosorption studies.

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Table 1. Physico – Chemical Characteristics of the Effluent Before & After Adsorption

S. No	Parameter	Effluent Before Biosorption	Effluent After Biosorption	Method
1	pH	3.000	5.700	-
2	Color	Pale yellow	Colorless	-
3	Turbidity(NTU)	0.002	0.001	-
4	BOD(mg/l)	18.000	15.700	Closed Reflux Titrimetric Method (5210.D)
5	COD(mg/l)	227.00	177.00	Closed Reflux Titrimetric Method

				(5220.D)
6	Copper(mg/l)	0.419	0.112	AAS(Perkin Elmer 3110)
7	Nickel(mg/l)	2.370	0.980	AAS(Perkin Elmer 3110)
8	Chromium(mg/l)	0.500	BDL*	AAS(Perkin Elmer 3110)
9	Zinc(mg/l)	2.680	0.147	AAS(Perkin Elmer 3110)
10	Mercury(mg/l)	0.440	BDL*	AAS(Perkin Elmer 3110)
11	Cadmium(mg/l)	1.202	0.030	AAS(Perkin Elmer 3110)
12	Iron(mg/l)	2.320	0.421	AAS(Perkin Elmer 3110)

Table 2. Parameters of Column at Different Bed Heights, Flow Rates and Effluent Concentrations onto *Sargassum* sp.

Parameters					Adams-Bohart Model			Wolborska Model			Yoon-Nelson Model			Thomas Model		
Column Height (cm)	Bed Height (cm)	Flow Rate (ml/min)	Inlet Conc. (mg/L)	Dia of Column (cm)	N ₀ (mg/L)	K (×10 ⁻⁴)	R ²	β (min ⁻¹)	N ₀ (mg/L)	R ²	T _{YN} (min)	k _{YN} (min ⁻¹)	R ²	K _{th} (ml/min.mg)	q ₀	R ²
8.3	6.5	5	100	1.2	2562.587	0.00022	0.946	4.984814	20770.06	0.946	308.875	0.024	0.956	0.07413	3.7231	0.956
8.5	7.0	5	100	1.8	1515.801	0.00033	0.911	1.528892	4633.005	0.911	129.4259	0.054	0.930	0.06961	11.492	0.963
12.5	9.0	5	100	3.2	2126.543	0.00018	0.960	1.933999	10744.440	0.961	348.050	0.020	0.963	0.06701	14.850	0.930
12.5	9.0	5	100	3.2	1851.768	0.00022	0.980	0.506132	115.030	0.980	309	0.024	0.934	0.07416	12.944	0.966
12.5	9.0	10	100	3.2	3222.222	0.00023	0.909	0.933654	466.8269	0.976	280.160	0.025	0.925	0.07604	11.345	0.925
12.5	9.0	15	100	3.2	3585.859	0.00033	0.911	1.463894	645.8355	0.936	219.9333	0.030	0.911	0.07809	8.7645	0.954
12.5	9.0	5	100	3.2	1266.296	0.00030	0.978	0.475945	2644.140	0.909	251.500	0.026	0.976	0.06567	14.399	0.9888
12.5	9.0	5	75	3.2	649.5567	0.00063	0.973	3.128082	9775.257	0.857	146.4815	0.054	0.986	0.0669	14.138	0.9799
12.5	9.0	5	50	3.2	480.0154	0.00072	0.738	1.528892	2316.503	0.911	113.1667	0.054	0.803	0.06759	12.546	0.9657

Table 3. Optimized Column at Different Bed Heights, Flow Rates and Metal Ion Concentrations (% Yield)

Column Height(cm)	Bed Height(cm)	Flow Rate(ml/min)	Inlet Conc.(mg/L)	Dia of Column(cm)	%Yield
8.3	6.5	5	100	1.2	44.44
8.5	7.0	5	100	1.8	50.00
12.5	9.0	5	100	3.2	62.50
12.5	9.0	5	100	3.2	75.00
12.5	9.0	10	100	3.2	54.45
12.5	9.0	15	100	3.2	40.00
12.5	9.0	5	100	3.2	85.74
12.5	9.0	5	75	3.2	75.00
12.5	9.0	5	50	3.2	42.85