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Equilibrium and Kinetic Study on Biosorption Of Chromium Using Tamarindus Indica as a Biosorbent

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Abstract

The contamination of aquatic and ecosystem is taking place because of toxic metals releasing from chemical process industries without prior treatment of effluent. There could be a great need of research on withdrawal of poisonous metal ions from effluents releasing from various industries. The heavy metal chromium is one among them. Batch biosorption procedure was adapted to find the potential of the agricultural waste biomaterial Tamarind tree bark (*Tamarindus Indica*) for biosorption of chromium. The process parameters such as agitation time, biomass quantity, metal ion concentration and pH were estimated on removal of Chromium by tamarindus indica biosorbent. The process parameters evaluated are agitation time-40minutes, biomass dose-1.6gm, metal ion concentration-10mg/l and pH-6. The equilibrium data has been analysed with Freundlich and Langmuir models. The given data was correlated well to Langmuir model than Freundlich. The adsorption kinetics were also calculated and R^2 value was found to be 0.993. The kinetic data was best followed to pseudo second order kinetics. The chromium removal percentage was determined 87.23% using tamarindus indica. The results revealed the agricultural waste material of tamarind tree bark is suitable for biosorption of chromium from waste water.

Keywords: Chromium; biosorption; tamarind tree bark; equilibrium models; kinetics

Introduction

Pollution of toxic metals is a burning environmental problem to address nowadays. This problem is due to urbanization. The industrial development may also cause environmental damage from effluents containing toxic metals. The heavy metals releasing from various chemical process industries such as refinery, dyeing and textile are lead, mercury, chromium, zinc and copper. From these toxic metals chromium is one of more toxic metal affecting human and ecosystem. When concentration of chromium exceeds the allowable limit leads to cancer (1).

The traditional methods available for removal of toxic metals are precipitation, ultrafiltration, Phyto remediation, and electro dialysis and reverse osmosis. These processes have the drawbacks of partial separation, high cost and sludge formation. Also these techniques are not suitable for removal of metals present at low concentration in effluent (2). In order to address the above issues a new technique such as biosorption came into picture. Biosorption is a less expensive, easy, no side effects and eco-friendly process for removal of heavy toxic metals even at low concentration of metals (3).

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Many studies have been done on removal of chromium using various adsorbents of living and non- living microorganisms. Hassan rezaei reported the removal of chromium is 72% using spirulina. Mishra investigated on waste plant material of prtulaca oleracea for Cr removal and obtained 79% removal. Abdulsalam has done the research on tannery wastes of oil-free Moringa oleifera cake and sweet potatoes peels for removal of chromium and reported the results of 59 and 74% of removal efficiency (4).

The present research work was done on tamarind tree bark, which was an agricultural waste as a biosorbent for removal of chromium toxic metal. The dead cells are easily available, low cost, no nutrient supply and have the good binding efficient character than living cells. In this investigation the process parameters such as agitation time, dosage, metal ion concentration and pH were analysed (5).

Materials & Method

Preparation of biosorbent

The tamarind tree bark (*Tamarindus Indica*) was collected from Rudravaram village in Andhra Pradesh. The bark was washed with deionized water many times for removal of dirt. The cleaned bark was dried in hot air oven at 70°C for a period of 48 hrs. After drying tamarind bark was crushed by using roll crusher. The powdered biomaterial was sieved for getting required uniform size particles. The prepared biomaterial stored in a dark place for future use (6).

Stock solution

1.214 gm of potassium dichromate was dissolved in a 500ml distilled water for preparation of chromium stock solution in a conical flask. This stock solution was diluted for preparation of various concentration of required quantity as per the experiment. The solution pH was adjusted with HCl or NaoH. The chemicals which were used in this work are analytical grade and Merck company.

Experimental procedure

The one parameter biosorption model has been followed for evaluation of process parameters such as agitation time, biosorbent dose, concentration of metal ion and solution pH. The stock solution of 50ml was taken in a beaker. Biosorbent of 1 gm is added to this solution. Then the sample was kept in shaker for a period of 50 minutes at room temperature for effective agitation by maintaining 150rpm. After agitation time sample was withdrawn from the shaker and filtered by using filter paper. The filtrate was analysed with spectrophotometer to find the concentration of metal ion biosorbed by the biosorbent. The percentage removal of chromium was calculated with the following equation (7).

Percentage removal of chromium= Ci–Co / Cix 100

Here, C_o, final concentration of sample, C_i initial concentration of the sample. The same procedure has been followed to find the optimum process conditions such as biomass dosage (0.1 -1.5gm), metal ion concentration (10-100 mg/l) and pH (1-11) on adsorption onto the tamarind tree bark (8).

Sorption isotherms and kinetic study

The absorption potential of tamarind tree bark was evaluated by adsorption isotherms. The surface properties were known by calculating constants. In this work Freundlich and Langmuir isotherms were analysed to find the equilibrium relationship between sorbate and sorbent. Freundlich model is based on heterogeneous adsorption onto the biosorbent (9). Langmuir model was based on homogeneous adsorption onto the surface of the biosorbent with same energy distribution. The degree of sorption was analysed by kinetic study. The Pseudo first order and second order kinetics were tested to evaluate the rate of biosorption.For this 50ml of sample having 10mg/l concentration was taken in a flask and to this 1gm of biosorbent having size of 82.5 micron was added. Then sample was stirred for a period of optimum time. After this, final concentration of chromium was analysed by using spectrophotometer (10).

Thermodynamic study

The thermodynamic parameters were estimated to know the nature of the biosorption. In biosorption changes may occur and can be explained by the three thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG). These parameters could be evaluated by carrying out the adsorption experiments at different temperatures.

The thermodynamic parameters such as $\Delta G°$ (kJ/mol), $\Delta H°$ (kJ/mol) and $\Delta S°$ (J/mol.K) were calculated using below equations:

$$\Delta G° = -RT \ln Ke$$

$$\ln Ke = \Delta S°/ R - \Delta H°/ RT$$

$$\Delta G° = \Delta H° - T\Delta S°$$

Results and Discussion

Agitation time

50 ml of sample was taken in a beaker and agitated at a speed of 150 rpm to find the optimum time by keeping dosage, concentration and pH parameters at constant. The chromium percentage removal was analysed by taking agitation time range from 1 to 60 minutes. It was observed from figure that chromium removal rate was increased continuously from 72.6% to 87.1% till time reaches to 40 minutes. After 40minutes, chromium removal percentage was no change even increases in time and gone to the saturation at 60 minutes. This was considered as an optimum time to get maximum percentage removal of chromium (Figure.1). The results stated that the chromium was sorbed faster rate at initial time, because of more active sites available for biosorption of chromium metal ions onto the tamarind tree bark biosorbent at initial stage. So, the optimum agitation time was considered as 40 minutes (11). The above results were well followed with the other researchers such as 50 minutes required for soya bean powder (12) and for cork powder 60 minutes was required to reach equilibrium.

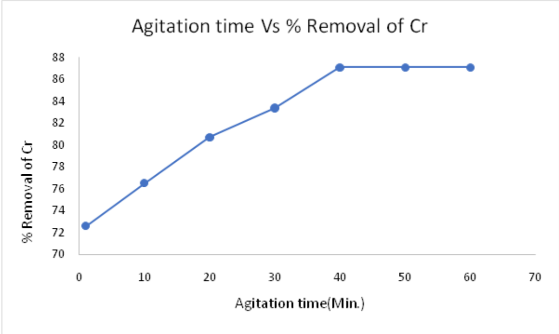

Figure .1 Percentage removal of chromium with agitation time

Initial chromium metal ion concentration

50 ml of sample was taken in a beaker to estimate the effect of chromium metal ion on biosorption of chromium. It was noticed from figure.2 that as chromium metal ion concentration increases from 10-60mg/l, the percentage removal of chromium was declined from 86.4 to 65.1%. This was due to adsorptive active sites available at lower concentration were high for chromium sorption. As concentration increases the available active sites for biosorption of metal ions become less (13). So, the removal rate was more at low concentration compare to a highest concentration (14). The optimum chromium metal ion concentration was considered as 10 mg/l.

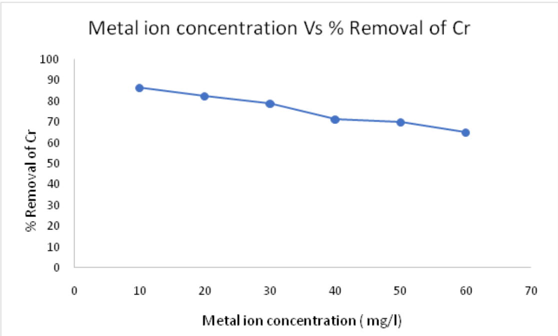

Figure .2 Percentage removal of chromium with metal ion concentration

Dosage

50 ml sample of was taken in a beaker by keeping agitation time, concentration and pH at constant level to analyse the effect of biosorbent dose on removal of chromium. The dosage ranges of 0.2-2.0gm were considered. The changes in percentage removal of chromium with increasing biosorbent dosage were shown in figure.3. It was stated that chromium removal percentage was increased from 66.8% to 87.4 % with increased tamarind tree bark biosorbent from 0.2 gm dose to 1.6 gm. The removal percentage of chromium could be raised because of more amount of active sites/surface area available for binding of chromium ions at higher biomass (15). The number of active sites and transfer of metal ions were depended on the amount of biosorbent (16). So, the optimum biomass dose was considered to be 1.6gm.

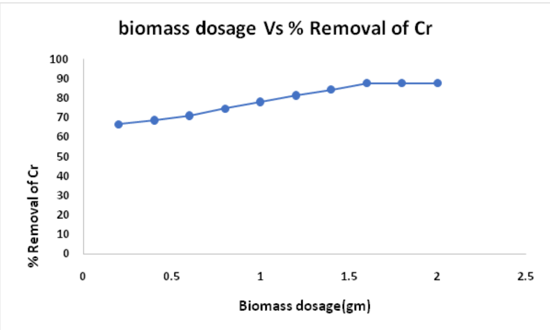

Figure .3 Percentage removal of chromium with biomass dosage

pH

The solution pH was significantly influenced the Chromium removal rate due to hydrogen ions. It effects on functional groups present on to the surface of sorbent and solution chemistry. From figure.4, it was observed that initial pH values of 1-4, the chromium percentage was low due to protons have to compete with binding sites present on sorbent surface. As pH increases from 5-6, the chromium removal percentage was increased and gone to 87% at a pH of 6 as a result of less number of protons on the surface and decrease in repulsion. The more positive charge on adsorbent surface at lower pH values, which restricted the metal ions due to repulsion (17). After the pH of 6 the removal rate was decreased because of precipitation of metal ions and formation of complexes (18). So, the pH was considered to be 6.

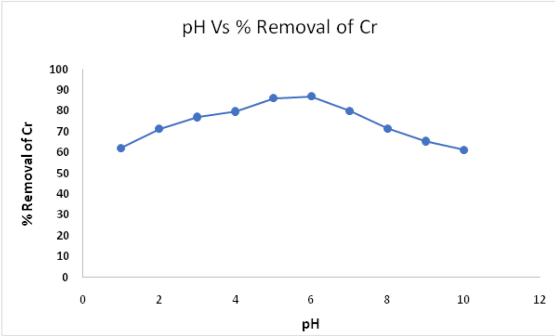

Figure .4 Percentage removal of chromium with pH

Adsorption isotherms

Adsorption isotherms explain the distribution of chromium metal ions between sorbate and sorbent. The degree of sorption also well explained by Freundlich and Langmuir isotherm models.

Freundlich isotherm is $q_e = k_f * C_e^n$

Metal uptake – qe, Ce – concentration after adsorption, figure.5, n=0.6611, R^2=0.957,it was concluded that Freundlich model does not

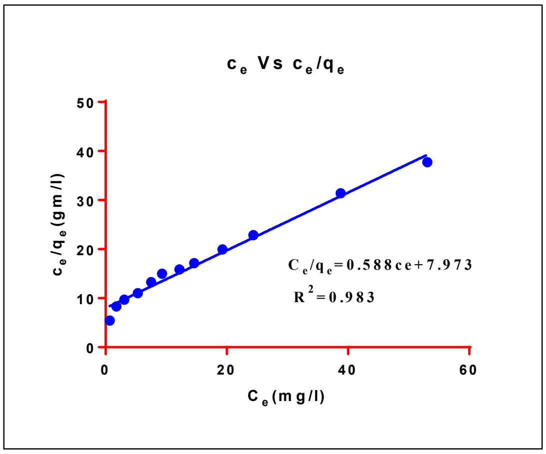

Figure .5 Langmuir isotherm

suitable for the given experimental data.The same can be obsereved with other study such removal of chromium using red alga (19).

Langmuir model was expressed by the formula: $C_E / qe = C_E / Q_m + 1 / (b^*Q_m)$

From figure.6, $R^2 = 0.983$ and $1/n<1$. Langmuir model was well corellated to given data. So,the equilibrium data best followed to langmuir model (20).

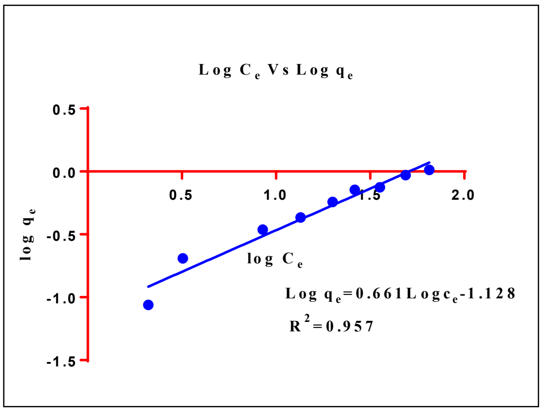

Figure.6 Freundlich isotherm

Kinetics

The kinetics were most important to evaluate the biosorbent performance and know uptake rate. Inorder to interprete the kinetic data, two rate expressions such as pseudo first order and second order rate equations were analysed (21).

The rate equation for first order was gives as follows

$Log(qe-q_t) = Log\ qe - (k_f / 2.303) \times t$

Here qe = Chromium sorbed at equilibrium; q_t= Chromium sorbed at any time t; k_f (min^{-1}) = rate constant. A plot of $Log(q_e-q_t)$ vs t gives k_f and $LogQ_e$ slope and intercept respectively.The kinetic parameters for biosorption of chromium evaluated are k_f-0.0457 , qe -0.638 and R^2-0.974 shown in figure.7.

The rate equation for second order was given by

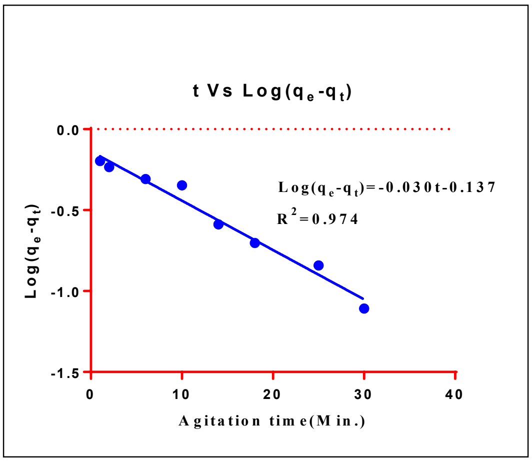

Figure.7 First order kinetics

$(t/q_t) = (1/k_f q_t^2) + (1/q_e)\ t$

Here q_t - the quantity of Chromium biosorbed at any time t , k_s - rate constant.The constants calculated are k_f-0.752,q_e-0.611 and R^2-0.993 shown in figure.8. From the above results, it was cleared that the data were best correlated to second order kinetics. The biopolymer of lignin also followed the same (22).

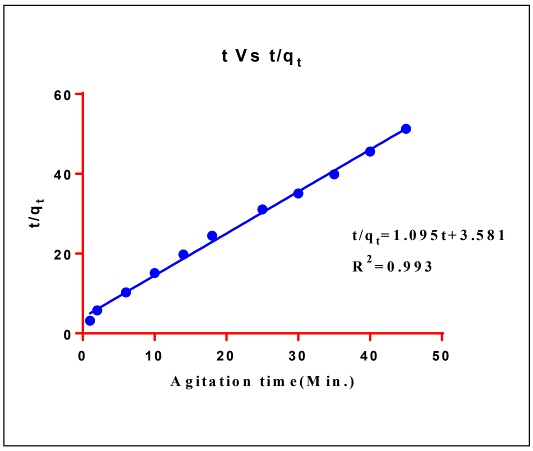

Figure.8 Second order kinetics

Thermodynamic study

Form table.1 results revealed that biosorption process is an endothermic process

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Table 1: Thermodynamics study

S.No	Initial chromium concentration, C_0, mg/l	Final chromium concentration, $C_{e,}$ mg/l	Temperature, T, ^{0}K	1/T, K^{-1}x10^{-3}	q_e=(C_0-C_e)/m, mg/gm	Log (q_e/C_e)
1	20	7.02	293	3.412969	0.389439	-1.2559
2	20	5.6	303	3.30033	0.432043	-1.11266
3	20	4.2	313	3.194888	0.474047	-0.94743
4	20	3.1	323	3.095975	0.507051	-0.78631
5	20	1.8	333	3.003003	0.546055	-0.51804

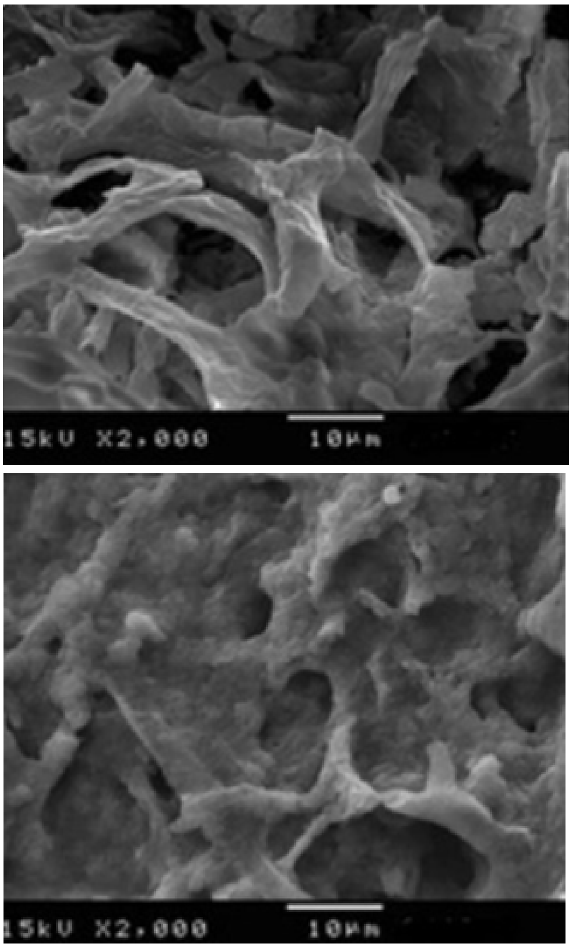

Figure.9 SEM structure of Tamarind tree bark a) befor b)after biosorption

due to positive value of enthalpy and the physical sorption plays a role in biosorption of chromium. The value of entropy above zero confirms the irreversibility of the biosorption process. The negative value of Gibbs free energy shows the reaction was spontaneous.

Scanning electron microscopic analysis

The SEM of tamarind tree bark is shown in figue.9. It was observed that before and after adsorption of chromium metal ion the biosorbent surface is different. Before sorption the uneven surface of the tamarind tree bark promotes the metal ion sorption by having number of active sites on the surface. After the biosorption surface of the biosorbent became uniform, because of present of metal ions onto the surface of the tamaring tree bark. The morphology of tamarind tree bark finally indicated that it is more suitable for biosorption of metal ions (24).

Conclusion

The investigation was done to find the potential of tamarind tree bark for biosorption of chromium from waste water. The experimental findings revealed the optimum agitation time was 40 minutes for chromium removal, optimum dosage is 1.6gm, initial metal ion concentration was 10mg/l and pH was 6. The data well correlated to Langmuir model. The biosorption process followed the pseudo second order kinetics. In conclusion, the cheapest, eco-friendly and agricultural tamarind tree bark was favourable for removal of heavy metal chromium and percentage removal was 87.23%.

Conflict of Interest

No Conflict of Interest

Acknowledgement

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