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Equilibrium studies on biosorption of chromium on *Psidium guajava* leaves powder

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ABSTRACT

Biosorption process has been proposed as an efficient, potential, cost effective way of removing toxic metals from industrial effluents at low concentrations. In the present study a new biosorbent material, agro waste Psidium guajava leaves powder was used as an adsorbent. Studies on the removal of Chromium from aqueous solutions using Psidium guajava leaves powder were undertaken. The effect of metal concentration, pH of aqueous metal solution, temperature and weight of biomass were studied. The results indicate that the amount of Chromium adsorbed increased with increase in metal concentration, weight of biomass and pH of the aqueous phase. Finally an experimental equation was developed to estimate the equilibrium distribution of Chromium between Guava leaf biomass and aqueous metal solution incorporating various parameters studied.

Keywords: Biosorption, Chromium removal, Psidium guajava, plots.

INTRODUCTION

Now a day's environmental pollution control plays a major role in the society. Rapid industrialization has generating large quantities of liquid effluents from heavy metals such as Chromium, Cobalt, Nickel, Mercury, Uranium, Selenium, Zinc, Arsenic, Gold, Silver, Copper and Manganese, ect. Heavy metals are toxic and non-biodegradable pollutants released into the environment by industrial, mining and agricultural activities [1]. The conventional treatments used to remove heavy metals from waste waters are precipitation, coagulation, reduction and membrane processes, ion-exchange and adsorption. However, the application of such processes is often restricted because of technical and or economic constraints. For example, the precipitation processes cannot guarantee the metal concentration limits required by regulatory standards and produce wastes difficult to treat; on the other hand, ion-exchange and adsorption processes are very effective but require expensive adsorbent materials and difficult plant management [2].

In this general setting, the search for a new economical and effective heavy metal adsorbent focuses on biomaterials such as bacterial and algal biomasses [3]. The advantages of biosorption lie in both the good performance and metal removal, often comparable with their commercial competitors (ion-exchangers) and cost effectiveness; making use of algae and raw materials of fermentation and agricultural processes[4].Different forms of non-living plant materials such as rice husk [5], sawdust [6] and cone biomass [7] have been widely investigated as potential biosorbents.

Agriculture, forestry and fisheries have been generating large quantities of various biomass wastes and some of them contain various natural materials with interesting functional groups, such as carboxyl, hydroxyl, amidocyanogen and so on. Psidium guajava leaves powder is one of the valuable biomass wastes.

In this study, the use of Guava Leaf powder as biosorbent for Chromium bisorption from artificial waste waters and was aimed at optimization of removal of the Chromium.

EXPERIMENTAL SECTION

Preparation of biosorbent of guava leaf powder (GLP)

Mature guava leaves used in the present study was collected from Andhra University College of Engineering, Visakhapatnam. The collected material was thoroughly washed with distilled water three to four times to remove dust and other impurities. Then sun dried the washed leaves. Dried leaves were then grinded, screened. Dried guava leaf powder was keeping in plastic containers stored in humidifier for further use [8]. This fine powder was used as an adsorbent. The physical and chemical characteristics of the guava leaf powder (GLP) were determined, and results showed below.

Physical and chemical properties of GLP used in the experiments

Moisture content (%)	4.77
Volatile matter (%)	69.91
♦Ash (%)	19.56
Fixed carbon (%)	5.76
Average particle size	75-300 μm

Preparation of Chromium Stock Solution:

The stock solution of 1000mg/L of chromium was prepared by dissolving 5.685g of 99.5 % K₂Cr₂O₇ (analytical grade) in 1 L of distilled water. 90mg/L of chromium solution was prepared by taking 90mL of 1,000mg/L synthetic solution in a 1,000mL volumetric flask and adding distilled water up to the mark. Similarly, chromium solutions of varying concentrations were prepared. Solutions of 0.1N H₂SO₄ or 0.1N NaOH were added for pH adjustment.

Biosorption Studies:

Batch studies were conducted in 250ml Erlenmeyer flasks to elucidate the best operating conditions, which enhance Chromium adsorption. The flasks containing solution and guava leaf powder were shaken on an orbital shaking machine for the required amount of time. The pH of solution ranging from 1 to 12 was adjusted to the required value using 0.1N H₂SO₄ and 0.1N NaOH. The initial concentrations of Chromium ions were varied from 23.4 to 280 mg/l (23.4, 47.8, 73.2, 94.1, 123.4, 147.6, 172.9, 185, 247.2 and 280 mg/l). Different amounts of biomass ranging from 10 to 50 g (10, 20, 30, 40 and 50 g/L.) were contacted with 100ml Chromium solution. The adsorption capacity C_s was estimated. Samples were collected at regular intervals of time to estimate the time required for attainment of equilibrium and all the experimental runs were conducted for a period more than that of equilibrium time. The percentage removal of Chromium is calculated as (Co-Ct) x 100/Co. The amount of Chromium adsorbed per unit mass of the biosorbent, qt in mg/g is computed by using the expression: qt = (Co-Ct)/m. From these data, the equilibrium agitation time, optimum biosorbent size and dosage are identified. The experiments are repeated at these optimum values by varying the initial concentrations of Chromium in the aqueous solution, volume of the aqueous solution, pH of the aqueous solution and temperature. From the experimental data we calculate the thermodynamics and kinetics. The experimental conditions investigated are shown in table.1

S. No.	Parameter	Values Investigated
1	Agitation time, t, min	1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120,180, 240 and 300
2	Biosorbent size, dp, µm	45, 75 and 150
3	Biosorbent dosage, w, g/L	10, 20, 30, 40 and 50.
4	Initial concentration of Chromium, Co, mg/L	23.4, 47.8, 73.2, 94.1, 123.4, 147.6, 172.9, 185, 247.2 and 280
5	pH of the aqueous solution	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12
6	Temperature, K	283, 293, 303, 313, 323 and 333

Table.1: Experimental conditions investigated

RESULTS AND DISCUSSION

Equilibrium distribution studies using biomass, guava leaf powder, as adsorbent for removal of Chromium were undertaken. It is essential to know the time required for reading the condition of equilibrium. Experiments were conducted to estimate the time required to reach the equilibrium by taking an initial charge of 100ml aqueous metal solution and known weight of biomass and thoroughly shaking the mixture using orbital shaking machine. The results show that the metal concentration in aqueous solution decrease with increase in time and reaches plateau

after a period less than 1 hr indicating the attainment of equilibrium. Hence, all the samples were shaken for more than 1hr 30 min in order to ensure that the equilibrium has attained.

Effect of agitation time:

Biosorption equilibrium was defined, as the time required for heavy metal concentration to reach a constant value during Biosorption. The equilibrium agitation time was determined by plotting the % removal of Chromium against agitation time in fig.1. For various 'w' values in the interaction time intervals of 1 min to 300 min. For 45 μ m size of 50 g/L biosorbent, 84.3 %(1.5054mg/g) of Chromium was adsorbed in the first 5 min. The % biosorption was increased hurriedly up to 60 min reaching 92.7 % (3.99 mg/g). From 60 to 180 min. the biosorption was marginally and gradually increased from 92.7 % to 93.8 %. Beyond 180 min, the % biosorption was constant indicating the attainment of equilibrium conditions. The maximum biosorption of 93.8 % (1.681 mg/g) was attained for 180 min of agitation time with 50 g/L of 45 μ m size biosorbent mixed in 50 mL of aqueous solution (C0 = 90 mg/L). The rate of biosorption was fast in the initial stages because adequate surface area of the biosorbent was available for the biosorbent due to Vander Waal's forces of attraction and results in decreased of available surface area. The biosorbent, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted. 180min equilibrium agitation time was reported earlier with treated sawdust [3].

Effect of biosorbent Size and Dosage:

The biosorption data were presented in Fig. 2 with percentage removal of chromium as a function of biosorbent size. The biosorption of chromium increased from 84.6% (1.5228/g) to 93.4% (1.681/g) as the biosorbent size decreased from 150 to 45 µm with 50 g/L dosage, at 303K for Co=90 mg/L. With a decrease in biosorbent size, surface area of the biosorbent increases and the number of active sites on the biosorbent are better exposed to the adsorbate. The percentage removal of chromium is drawn against biosorbent dosage for 45 µm biosorbent size in Fig. 3. The removal of chromium increases from 84.2% (7.578mg/g) to 93.4% (1.68mg/g), with an increase in dosage from 10 to 60 g/L. Such behavior is obvious because with an increase in dosage, the number of active sites available for chromium removal would be more. The change in percentage removal of chromium is marginal [from 91.8 (2.066mg/g) to 93.4% (1.4mg/g)] when 'w' is increased from 40 to 60 g/L. So, all other experiments are conducted at 50 g/L dosage. Barala et al. [13] reported an optimum adsorbent dosage of 40 g/L with 88.67% (3.04mg/g) removal of chromium from 100mg/L chromium aqueous solution with the adsorbent calcined bauxite.

Effect of pH of the aqueous solution:

pH controls biosorption by influencing the surface charge of the biosorbent, the degree of ionization and the species of adsorbate. In the present investigation, Chromium biosorption data were obtained in the pH range of 1 to 12 of the aqueous solution (C0 = 90 mg/L) using 40 g/L of 45 μ m size biosorbent. The effect of pH of aqueous solution on % removal of Chromium was drawn in fig.4. The % removal of metal was increased from 57.76 % (1.299mg/g) to 95.64 % (2.152 mg/g) as pH was increased from 1to 7 and decreased beyond pH value of 8. % biosorption was marginally increased from 85.96% (1.934 mg/g) to 95.64% (2.152 mg/g) as pH increases for 2 to 7. Low pH depresses biosorption of Chromium, due to competition with H⁺ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Cr ions replace H⁺ ions bound to the biosorbent (or forming part of the surface functional groups such as OH, SO4, etc [21].A maximum chromium removal of 86.6% (10mg/g) was reported at pH=3 onto treated sawdust [3] as pH was varied from 2 to 10.

Effect of initial concentration of Chromium in the aqueous solution:

The effect of initial concentration of chromium in the aqueous solution on the percentage removal of chromium is shown in Fig. 5. The removal of chromium decreased from 99.1% to 45.5% with an increase in C_0 from 22.5mg/L to 180mg/L at 303 K, while the uptake capacity increased from 0.45 to 1.64mg/g. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the biosorbent (since the amount of biosorbent is kept constant). These plots also confirm that the % removal decreases with an increase in temperature. The metal uptake capacities obtained for various adsorbents are shown in Table 2. The removal of chromium decreased from 61% to 30.4% using waste pomace of olive oil factory in the range of initial concentration from 50 to 200mg/L, whereas the uptake capacity increased from 6.1 to 12.15mg/g [18]. Tunali et al. [14] conducted experiments for adsorption of chromium on neurospora crassa in the C_0 range of 25 to 250mg/L and reported 1 to 9.15mg/g increase in the uptake capacity.

Isotherms for biosorption of Chromium:

An isotherm is the equilibrium relationship between the concentration of metal in the fluid phase and the concentration on the adsorbent at a given temperature. Freundlich isotherm (Freundlich, 1907) is $q_e = Kf Ce^n$ or log

 $q_e = \log Kf + n \log C_e$. Freundlich isotherm was drawn between log Ce and log qe shown in Fig. 6. The following equation was obtained at $d_p = 45 \mu m$ varying the initial concentration of Chromium: $\log q_e = 0.431 \log Ce - 0.22 R=0.98$ The slopes (n) of the above equation 0.43 satisfying the condition of 0 < n < 1 for favourable biosorption. Freudlich isotherm describes the biosorption with rice husk (Kishore and Xiaoguang, 2008) and lignite [17] (Dinesh and Subhash chander, 2006). Langmuir isotherm [19] (Langmuir, 1918) is the most widely used two- parameter equation. The relationship of a hyperbolic type form: (Ce/qe) = 1/bqm + Ce/qm. Fig.7 is drawn between (Ce/qe) and Ce for dp = 45 μ m varying the initial concentration of Chromium. The slope (1/qm) and the intercept (1/bqm) are calculated from the graph. The equation obtained from the graph was: (Ce/qe) = 0.21 Ce + 0.58, with R = 0.99. The slope (1/qm) is 0.21 and the intercept (1/bqm) 0.58. The separation factor (RL) value of 0.168 < 1 indicates favorable biosorption. The correlation coefficient obtained for Langmuir isotherm was higher than that obtained for Freundlich isotherm [19] (Martin and Cheung, 2006) suggested that Langmuir isotherm for biosorption with sargassum biomass (qm = 0.629 mg/g and b = 0.567). Biosorption with pseudomonas aerations (Rosa María and Perez Silva, 2009) were explained by Langmuir isotherm.

$$q_e = \frac{AC_e}{1 + BC_e^{g}}$$
$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln B$$

Redlich and Peterson [20] proposed a three parameter isotherm to incorporate features of both Langmuir and Freundlich equations. It can be described as follows:

where A (L/g) and B (L/ mg) were the Redlich-Peterson isotherm constants and 'g' was the Redlich – Peterson isotherm exponent that lies between 0 and 1. The linear form of the equation is, Although a linear analysis is not possible for a three parameter isotherm, the three isotherm constants (A, B and g) can be evaluated from the pseudo linear plot using trial and error optimization method. Fig.8 shows the Redlich – Peterson plot drawn between ln [A(Ce/qe)-1] and ln Ce. For the present experimental data the equation obtained from the plots drawn in fig. for A = 1L/mg (assumed), V = 50 mL, T = 303 K and dp = 45 μ m is ln [(Ce/qe)-1) = 0.819ln Ce + 0.4317. Redlich-Peterson isotherm constants A (L/mg), B (L/mg) and Redlich-Peterson isotherm exponent (g) for w = 40 g/L, C₀ = 94 mg/L and dp = 45 μ m are 1L/mg, 1.5398 L/mg and 0.819 respectively. Tempkin isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface and it is based on the following equation qe = RT ln(ATCe)/bT The linear form of Tempkin isotherm can be expressed as qe = (RT/ bT) ln(AT) + (RT/bT) ln(Ce)

where $AT = \exp [b(0) \times b(1) / RT]$, b(1) = RT/bT is the slope, $b(0) = (RT/bT) \ln (AT)$ was the intercept and b = RT/b(1) The present data were analysed according to the linear form of Tempkin isotherm and the linear plot is shown in fig.9. The equation obtained for Chromium biosorption was: $qe = 0.82 \ln Ce + 0.1$ with a correlation coefficient 0.81. The isotherm constants obtained for various isotherm models were shown in Table-3. The best fit model is determined based on the linear regression correlation coefficient (R). From the table, it was found that biosorption data were well represented by Langmuir isotherm with higher correlation coefficient of 0.99, followed by Freundlich, Redlich-Peterson and Tempkin isotherms with correlation coefficients of 0.98, 0.977 and 0.81 respectively.

Kinetics of biosorption:

The data regarding biosorption kinetics is necessary for the design of industrial columns. The order of adsorbate – biosorbent interactions has been described traditionally by the pseudo first order model of Lagergren (1898) or by pseudo second order kinetics in certain cases. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows pseudo first order rate of equation of Lagergren: (dqt/dt) = Kad (qe–qt). Plot of log (qe–qt) versus't' gives a straight line for first order kinetics. In case of pseudo second order kinetics, (dqt/dt) = K (qe–qt)2 is applicable. This equation can be written as (t/qt) = (1/Kqe2) + (t/qe). If the pseudo-second order kinetics is applicable, the plot of (t/qt) versus t gives a linear relationship that allows computation of qe and K. Lagergren plot of log (qe–qt) versus agitation time (t) for the present investigation was drawn in Fig.10 and the resulting equations are: log (qe – qt) = - 0.01 t - 0.07, R= 0.99 for dp= 45 µm, log(qe–qt) = - 0.02 t -0.7, R= 0.96 for dp= 75 µm log (qe–qt) = - 0.01 t - 0.411, R= 0.91 for dp= 150 µm The pseudo-second-order model was applied to assess the suitability of the rate equation for the present data. The plots (t/qt) versus (t) for the present data are shown in Fig. 11 for dp= 45 µm. The plots for dp = 75 and 150 µm are not shown. The second order rate equations obtained are compiled in Table 4. The results show that the correlation coefficients for second order rate equations (0.999) are higher than those for the first order rate equations. Hence, the pseudo second order rate equation is more

suitable to explain the biosorption. The second order rate constant (K) values are varied from 1.289 to 0.108 g/(mg-min).

Thermodynamics:

Biosorption was usually exothermic and the amount adsorbed at a given concentration decreases as the temperature increases, in accordance with Le-Chateliers principle. The thermodynamic criterion for biosorption was well explained by evaluation of the three important thermodynamic parameters. They are change in enthalpy (Δ H), Gibbs free energy change (Δ G) and entropy change (Δ S). Net enthalpy change (Δ H) is related to Δ G and Δ S as Δ G= Δ H - T(Δ S). The Van't Hoff's equation is log(qe/Ce) = - (Δ H/2.303R)(1/T) + (Δ S/2.303R)Where (qe /Ce) is called the biosorption affinity. Δ H and Δ S values are calculated from slope = - Δ H/(2.303R) and intercept = Δ S/(2.303R) Experiments were conducted to understand the biosorption behavior of Chromium with respect to temperature for w = 40 g/L and dp = 45 µm and the data are shown in Figure 12 with log (qe/Ce) as a function of (1/T). The equation obtained was log (qe/Ce) = -1.191(1/T) + 4.387 for V = 50mL Thermodynamic parameters calculated for biosorption of Chromium on Psidium guajava powder are shown in Table 5.

Table-2: Various Bisorbents and metal uptake capacities

Author (Ref. No)	Biosorbent	Result			
Hang yang [26]	Hydride surfactant templated	⁹ / ⁰ / ⁰ / ⁰ / ⁰ / ⁰ / ¹			
	mesoporous	// Kenioval 66.2, 2 - order knettes (K =627.65 g/minoE/min), Eongmun isotherm			
Dinesh [31]	Lignite	$q_t = 25.84 \text{ mg/g}$, Longmuir isotherm, exothermic nature			
Anthoula[27]	Clinoptilolite	$q_t = 7.69 mg/g$			
Zakaria [25]	Cyanobacterium	Freundlich isotherm ($K_f=63$, $1/n = 1.7$), $q_t = 906 \mu g/mg$			
Ahmad bin[28]	Granular activated carbon	$q_t = 2.54 \text{ mg/g}$, Longmuir isotherm (n=3.69)			
Tsui [24]	Brown seaweed	qt= 1.45 mg/g			
Durali Mendil[29]	penicillium italicum	% removal = 95, q _t = 11.4mg/g			
Chojnacka[30]	Ricciafluitans	$q_t = 5.76$ mg/g, first order kinetics, Longmuir, exothermic nature			
Veglio[32]	Free cells of Arthrobacter species	$q_t = 406 \text{mg/g}$, Longmuir,			

Table-3: Isotherm constants

Freundlich isotherm	Langmuir isotherm	Redlich-Peterson isotherm	Tempkin isotherm
$K_{\rm f} = 0.602, L/g$	$q_m = 4.762, mg/g$	A = 1, L/g	A _T = 1.085, L/mg
n = 0.43, g/L	b = 0.2658, L/mg	g = 0.819	$b_{\rm T} = 3072.12$
R = 0.98	R = 0.99	R = 0.977	R 0.81

Table-4: Second order kinetics

For $d_p = 45 \ \mu m$					
W, g/L	Equation	K, (g/mg-min)	R		
10	$(t/q_t) = 0.57 t + 0.347$	0.936	0.99		
20	$(t/q_t) = 0.46 t + 0.369$	0.637	0.99		
30	$(t/q_t) = 0.351 t + 0.332$	0.368	0.99		
40	$(t/q_t) = 0.25 t + 0.186$	0.336	0.99		
50	$(t/q_t) = 0.13 t + 0.09$	0.188	0.99		

Table-5: Thermodynamic parameters for biosorption of manganese for various C₀ values

C No	C ₀ , mg/L -ΔS kJ/(mol	AS IrI/(mol V)	-ΔH kJ/mol	ΔG, kJ/mol at different temperatures, K				
5. NO.		- $\Delta S KJ/(1101-K)$		283	293	303	313	323
1	23.4	0.1990	60.102	-3.785	-1.795	0.195	2.185	4.175
2	47.8	0.1840	53.726	-4.767	-3.037	-1.307	0.423	2.153
3	73.2	0.1790	50.316	-1.64	0.08	1.80	3.52	5.24
4	94	0.1670	45.374	1.687	3.357	5.027	6.697	8.367
5	123.4	0.1660	43.792	3.186	4.846	6.506	8.166	9.826
6	147.6	0.1610	41.311	4.818	6.448	8.078	9.708	11.338
7	172.9	0.1590	39.595	5.968	7.578	9.188	10.798	12.408
8	185.0	0.1567	39.358	5.639	7.229	8.819	10.409	11.99
9	247.2	0.1562	37.694	6.652	8.219	9.786	11.308	12.920
10	280.1	0.1490	37.582	6.623	8.185	9.747	11.308	12.87



Fig.1 Effect of agitation time on % removal of Chromium



Fig.2 % Removal of Chromium as a function of biosorbent size



Fig. 3 % removal of Chromium as a function of biosorption



Fig.4 Effect of pH of aqueous solution on % removal of Chromium



Initial concentration of Chromium in aqueous solution Co, mg/L

Fig.5 Effect of initial concentration of Chromium on % removal of Chromium





Fig.8 Redlich- Peterson isotherm for biosorption of Chromium w.r.t. concentration





Fig. 10 First order kinetics for biosorption of Chromium



Fig. 11 Second order kinetics for biosorption of Chromium



CONCLUSION

Investigations were carried out to find out the equilibrium, kinetics and Thermodynamic parameters for biosorption of manganese from an aqueous solution using Psidium guajava leaf powder. The analysis of the experimental data result in the following conclusions. The equilibrium agitation time for Chromium biosorption was 180 minutes. The percentage removal of Chromium from an aqueous solution increases with a decrease in the particle size of the biosorbent. The percentage removal of Chromium was increased significantly with increase in biosorbent dosage.

Increase in the volume of the aqueous solution results in gradual decrease in the percentage removal of Chromium. With an increase in the initial concentration of Chromium in the aqueous solution, the percentage removal of Chromium from the aqueous solution was decreased. Percentage removal of Chromium from the aqueous solution increases significantly with increase in pH from 1 to 7. Thereafter percentage removal decreases for further increase in pH. In the range of variables studied, percentage removal was increased from 60.62% (1.3639mg/g) to 99.7% (2.243mg/g). The kinetic studies show that the biosorption of Chromium was better described by pseudo second order kinetics. The thermodynamic data show that percentage biosorption decreases with increase in temperature. The investigation also reveals that: The exothermic nature of biosorption as ΔH was negative, the reversibility of biosorption initially as ΔS was negative and biosorption tending towards irreversibility as ΔS was increasing. The spontaneity of the biosorption as ΔG was negative, and increase in ΔG value with an increase in temperature indicates that the biosorption of Chromium was less favorable.

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