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Studies on biosorption of Cadmium on *Psidium guajava leaves* powder using statistical experimental design

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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 bisorbent material Psidium guajava leaves powder was used as an biosorbent. Studies on the removal of cadmium from aqueous solutions using Psidium guajava leaves powder. The experiments were designed by Box-Behnken design method (3-1 fractional factorial design). The effect of metal concentration, pH of aqueous metal solution and weight of biomass was studied. The results indicate that the amount of Cadmium biosorbed increased with increase in metal concentration, weight of biomass and pH of the aqueous phase. Finally an empirical equation was developed to estimate the equilibrium distribution of Cadmium between Psidium guajava biomass and aqueous metal solution incorporating various parameters studied. The % biosorption decreases with an increase in temperature. The equilibrium data are well fitted by Langmuir (R=0.99), Freundlich (R=0.98), Reddlich-Peterson (R=0.94) and Tempkin (R=0.84) isotherm models in that order. The data are well represented by second order kinetics with a rate constant value of 0.089 *g/(mg-min).The maximum uptake capacity is* 4.28 *mg/g at pH = 4, in 50 mL of the aqueous solution for 20 g/L of 38µm diameter biosorbent*

Keywords: Biosorption, Cadmium removal, Psidium guajava, statistical design, Kinetics and thermodynamics.

INTRODUCTION

Rapid industrialization has generating large quantities of liquid effluents from heavy metals such as cadmium, cobult, lead, chromium, Nickel, mercury, uranium, selenium, zinc, arsenic, gold, silver, copper and Manganese, ect. Heavy metals are toxic and bio-degradable pollutants released in to the environment by mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives, paper and pulp industries, leather tanning, organochemicals, petrochemicals fertilizers, etc. and agricultural activities(*Byrne Brower J. et.al,1997*). The conventional treatments methods are used to remove heavy metals from waste water are chemical precipitation, lime coagulation, ion exchange; reverse osmosis, Adsorption and solvent extraction (Rich and Cherry, 1987).ion exchange and adsorption process are very effective but more expansive and difficult to maintenance of the plant (Beccari M.et.al, 1986).

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to Biosorption, based on metal binding capacities of various biological materials such as bacterial and algal biomasses (Volesky, et.al, 1986) (Volesky, et.al, 1995).the advantages of Biosorption is an efficient, potential and cost effective way of removing toxic and heavy metals from industrial effluents with comparing the other alternative methods. Different types of bisorbent materials such as non-living plant materials like corn husk, rice husk (Khalid.N.et.al, 1988), saw dust (Holan.Z.R.et.al, 1995) and cone biomass (Ucun H, et.al, 2003) have been investigated as potential bisorbent by different investigators.

Recent Biosorption experiments have focused attention on waste materials, which are by-products or the waste materials from large-scale industrial operations such as olive mill solid residues (Pagnanelli, et al 2002), activated sludge from sewage treatment plants (Hammaini et.aI, 2003), biosolids (Norton et al 2003), aquatic macrophytes (Keskinkan et aI. 2003), dewatered waste activated sludge (Norton et aI. 2003) from a sewage treatment plant for the Biosorption of zinc from aqueous solutions. The adsorption characteristics of copper zinc and lead on submerged aquatic plant Myriophyllum spicatum studied by Keskinkan et al. (2003). In the present investigation has been carried out on the potential of the biomass has been assessed for the removal of cadmium by using guava leaf powder as a bisorbent material. The effects of various parameters have been studied and the results are presented in this paper.

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. 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 Cadmium stock solution

2.3049 g of 99% $3\ CdSO_4\ 8H_2O$ was dissolved in 1 L of distilled water to prepare 1000 ppm of Cadmium stock solution. Synthetic samples of different concentrations of Cadmium were prepared from this stock solution by appropriate dilutions. 100 ppm Cadmium salt stock solution was prepared by diluting 100 mL of 1000 ppm Cadmium stock solution with distilled water in 1000 mL volumetric flask up to the mark. Similarly solutions with different metal concentrations such as 25, 50, 75, 100, 125, 150, 200, 250 and 300 ppm were prepared.

$$\text{Cadmium equivalent to 1g} = \frac{\text{Molecular wt. of 3 } CdSO_4\ 8H_2O \text{ X } 100}{\text{Atomic wt. of Cd X Purity}}$$

Studies on equilibrium, kinetics and thermodynamics of Biosorption

The initial concentration of Cadmium in the aqueous solution is analyzed in an Atomic Absorption Spectroscopy (AAS, Perkin Almer, model-200, 288.8 nm wave length) and found to be 90 mg/L. 50 mL of aqueous solution is taken in a 250 ml conical flask and 0.05 g (1 g/L) of 38 μm size biomass is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature (303 K) for 1 min. Similarly 15 more samples are prepared in conical flasks adding 1 g/L of 38 μm size biomass and exposed to varying agitation times. These samples are filtered separately with 40 no. Whatman filter papers and the filtrates are analyzed in AAS to obtain final concentrations of Cadmium. The same experimental procedure is repeated with other Biosorbent sizes (63 and 125 μm) for various agitation times and for other dosages (2, 5, 10, 20 and 30 g/L). The percentage removal of Cadmium is calculated as $(C_o\text{-}C_t)$x $100/C_{o.}$ The amount of Cadmium adsorbed per unit mass of the biosorbent, q_t in mg/g is computed by using the expression: $q_t = (C_o\text{-}C_t)/m$. 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 Cadmium 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

Table.1: Experimental conditions investigated

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, d_p, μm	38, 63 and 125
3	Biosorbent dosage, w, g/L	1, 2,5,10, 20 and 30
4	Initial concentration of Cd, C_o, mg/L	23.4, 47.8, 73.2, 90,123.4, 147.6, 172.9, 1 185.0, 239.2 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

Statistical Design of Experiments

Factorial design is employed to reduce the total number of experiments in order to achieve optimization of the system (Montgomery, 2001; Box, 1978; Brasil *et al*, 2005). Factorial design allows the simultaneous study of the effects that several factors may have on an optimization of a particular process. The factorial design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. One of the simplest types of factorial designs used in experimental work is one having two levels (2^k) (Montgomery, 2001; Box, 1978). In a full factorial experiment, responses are measured at all combinations of the experimental factor levels. The combination of factor levels represents the conditions at which responses will be measured.

In the investigation of Cadmium removal using *Psidium guajava leaves* from aqueous solution could depend on initial concentration of metal ion, pH of the aqueous solution and weight of the biomass. Others variables such as speed of shaker 160 rpm, volume of the aqueous solution 50ml and temperature 30°C, optimum agitation time 60min were kept constant The effect of the variables and their interactions were measured by performing a set of 10 experiments containing two central points, in order to evaluate the standard deviation of each factor and to detect if there is any inflection point[16-17] forming the 2^3 full factorial designs given in Table.2. The factor levels were coded as -1(low), 0 (central) and 1 (high) (Montgomery, 2001; Box, 1978). Each factor presents four high values, four low values and two medium values. For analysis of data Statistica version 6.0 was employed.

Table.2: Factorial Design Containing Two Central Point

Run	Conc.	pH	B. Volume	C_S
1	-1.00000	-1.00000	-1.00000	362.0000
2	-1.00000	0.00000	1.00000	136.6000
3	-1.00000	1.00000	0.00000	259.0000
4	0.00000	-1.00000	1.00000	197.3300
5	0.00000	0.00000	0.00000	449.0000
6	0.00000	1.00000	-1.00000	928.0000
7	1.00000	-1.00000	0.00000	290.0000
8	1.00000	0.00000	-1.00000	820.0000
9	1.00000	1.00000	1.00000	433.3300
10	0.00000	0.00000	0.00000	432.0000

Factors	Levels		
	-1	0	1
C_O (mg/l)	50	100	150
pH	2	4	6
Biomass Volume(ml)	5	10	15

RESULTS AND DISCUSSION

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 cadmium against agitation time in fig.1. For various ‘w’ values in the interaction time intervals of 1 min to 300 min. For 38 μm size of 20 g/L biosorbent, 79.3 %(3.57 mg/g) of cadmium was adsorbed in the first 5 min. The % biosorption was increased hurriedly up to 60 min reaching 88.7 % (3.99 mg/g). From 60 to 180 min. the biosorption was marginally and gradually increased from 88.7 % to 89.1%. Beyond 180 min, the % biosorption was constant indicating the attainment of equilibrium conditions. The maximum biosorption of 88.7% (3.99 mg/g) was attained for 60 min of agitation time with 20 g/L of 38 μm size biosorbent mixed in 50 mL of aqueous solution (C_0 = 90 mg/L). The rate of biosorption was fast in the initial stages because adequate surface area of the biosorbent was available for the biosorption of cadmium. As time increases, more amount of cadmium gets adsorbed onto the surface of the biosorbent due to Vander Waal’s forces of attraction and results in decreased of available surface area. The bisorbent, normally, forms a thin one molecule thick layer over the surface.

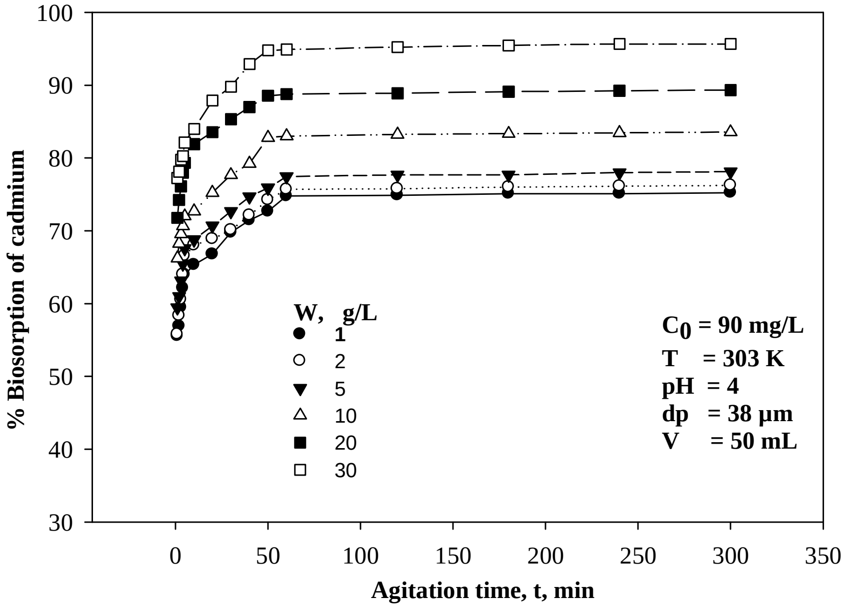


Fig1. Effect of Agitation time on % biosorption of Cadmium

Effect of biosorbent dosage and size

The percentage removal of cadmium was drawn against biosorbent dosage for 38 µm size biosorbent in fig.2. The biosorption of cadmium was increased from 74.78% (67.4 mg/g) to 94.89 % (2.85 mg/g) with an increase in biosorbent dosage from 1 to 30 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for cadmium removal would be more. The change in percentage removal of cadmium was marginal from 88.8 % (3.99 mg/g) to 94.89% (2.85 mg/g) when 'w' was increased from 20 to 30 g/L. Hence all other experiments were conducted at 20 g/L dosage.

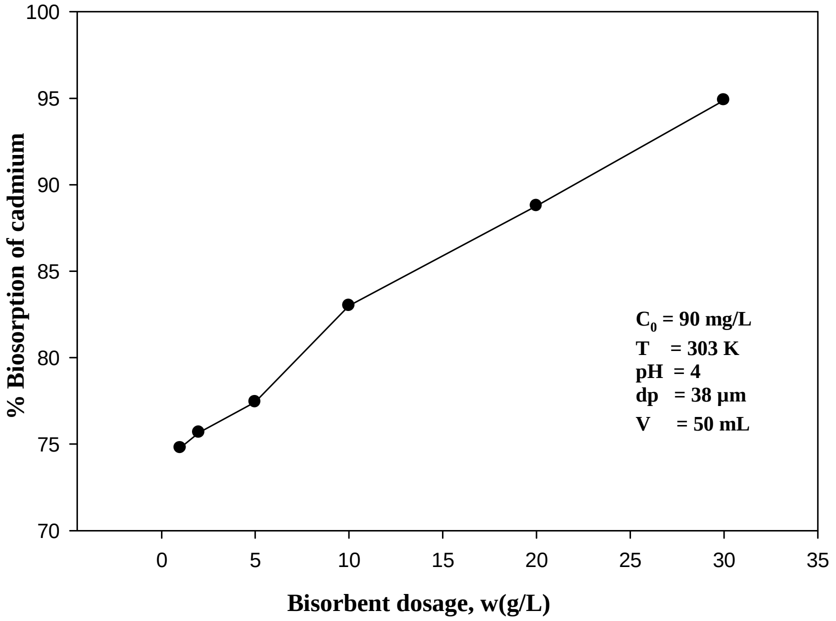


Fig.2 % Biosorption of cadmium as function of biosorbent dosage

The variations in % removal of cadmium from the aqueous solution with biosorbent size (38 µm, 63 µm and 125 µm) were obtained at different dosages at the equilibrium agitation time of 60 min shown in Fig.3 with % removal of cadmium as a function of biosorbent size. The percentage removal of cadmium was increased from 69.78% (3.14 mg/g) to 88.78% (3.99 mg/g) as the biosorbent size decreases from 125 to 38 µm for w = 20 g/L. With an increase in biosorbent sizes, surface area of the biosorbent increases, there by the number of active sites available on the biosorbent are better exposed to the adsorbate.

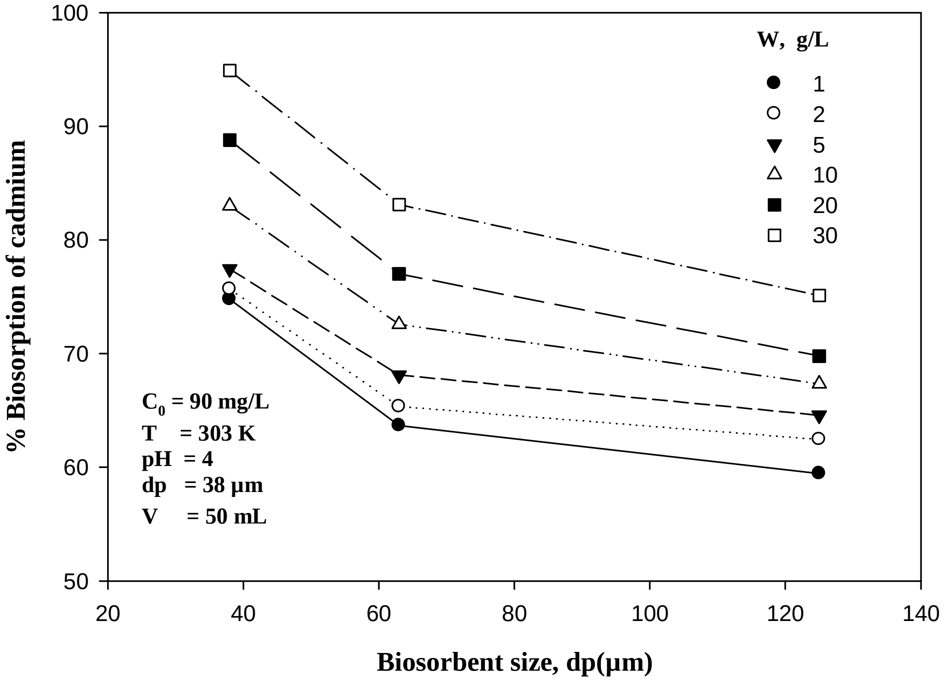


Fig.3 % Biosorption of Cadmium as function of Bisorbent size

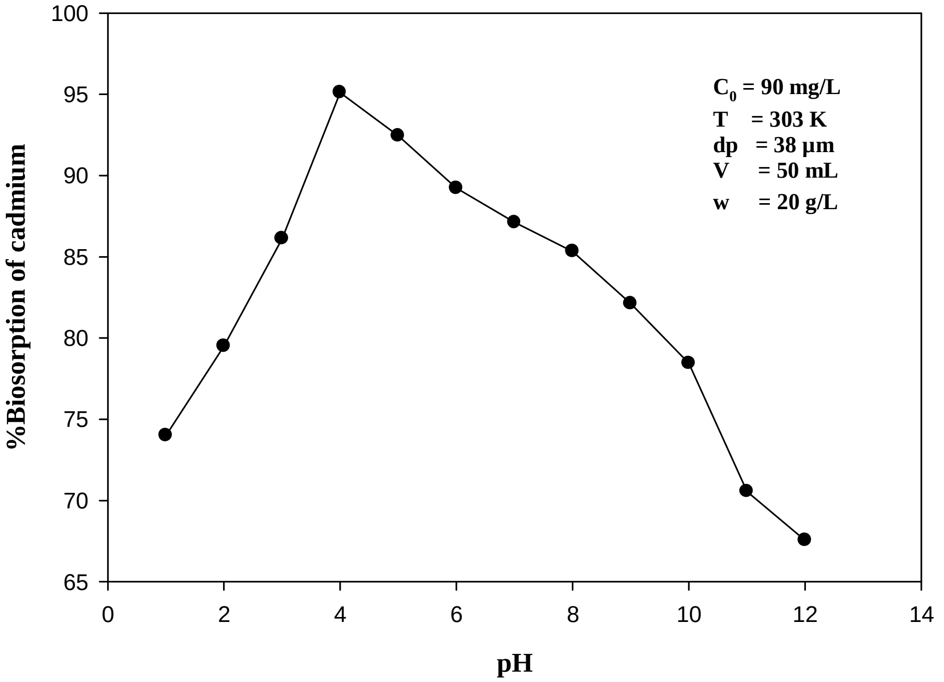


Fig.4 Effect of pH on %biosorption of cadmium

Effect of pH of the aqueous solution

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of adsorbate. In the present investigation, cadmium biosorption data were obtained in the pH range of 1 to 12 of the aqueous solution (C_0 = 90 mg/L). The effect of pH of aqueous solution on % removal of cadmium was drawn in fig.4. The % removal of metal was increased from 74.0 % (3.33 mg/g) to 95.11 % (4.28 mg/g) as pH was increased from 1to 4 and decreased beyond pH value of 5. % biosorption was marginally increased from 79.5% (3.58 mg/g) to 95.1% (4.28 mg/g) an pH increases for 2 to 4. Low pH depresses biosorption of cadmium, due to competition with H+ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Cd ions replace H+ ions bound to the biosorbent (or forming part of the surface functional groups such as OH, SO_4, etc).

Effect of initial concentration of cadmium in the aqueous solution

The effect of initial concentration of cadmium in the aqueous solution on the percentage removal of cadmium was shown in fig.5. The percentage removal of cadmium was decreased from 99.7% (1.167mg/g) to 43.1 %(11.85mg/g) with an increase in C_0 from 23.4 mg/L to 280 mg/L in the temperature range of 283 to 333 K while the uptake capacity was increased from 1.17 to 11.85mg/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. These plots also confirm that the % removal decreases with an increase in temperature.

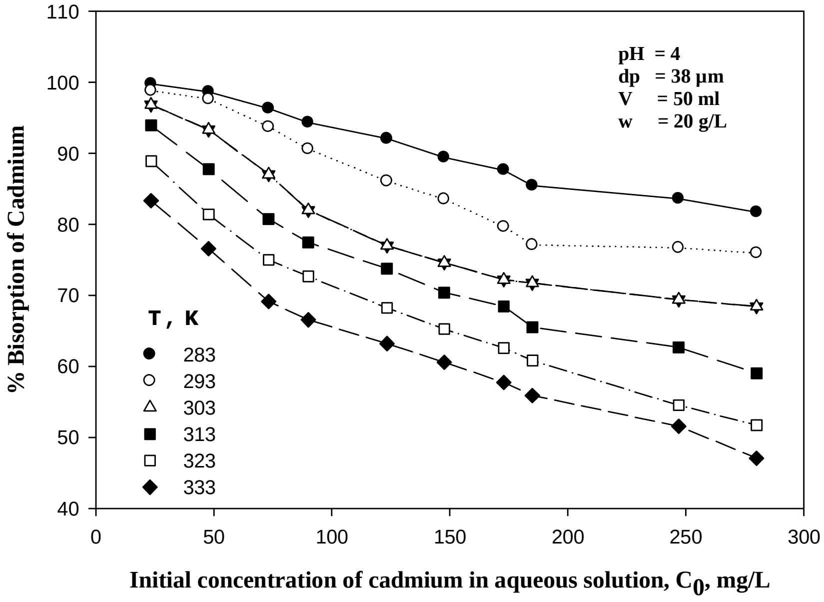


Fig. 5 Effect of initial concentration of cadmium on %bisorption of Cd

Isotherms for bio-sorption of cadmium

Freundlich isotherm is the equilibrium relationship between the concentration of the metal in the fluid phase and its concentration in the biosorbent at a given temperature. Freundlich (19*06*) presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges.

(Freundlich, 1907) Freundlich isotherm was shown between log Ce and log qe in Fig. 6. The following equation was obtained log qe = 0.098 log Ce + 0.424 with R^2=0.98.The slopes (n) of the above equation 0.098 satisfying the condition of 0 < n < 1 for favorable biosorption.

Langmuir isotherm (Langmuir, 1918) is the most widely used two- parameter equation with the relationship of a hyperbolic type form: (Ce/qe) = 1/bqm + Ce/qm. Fig.7 drawn between (Ce/qe) and Ce The slope (1/qm) and the intercept (1/bqm) are calculated from the graph. The equation obtained from the graph was: Ce/qe = 0.64 + 0.15 Ce with R^2 = 0.99. The separation factor (RL) value of 0.234 < 1 indicates favorable biosorption. *Panda et al(2006)* reported that cadmium biosorption data could better fit with Langmuir isotherm model and reported maximum biosorption capacity of 35 mg/g of husk of Lathyrus sativus (HLS) at pH = 5. *Gaikwad (2004)* examined Langmuir, Freundlich isotherms for adsorption of Cd (II) in activated char coal derived from coconut shell and the values of Freundlich and Langmuir constants are 7.274 and 0.037 at 40^0C. Redlich and Peterson (Ayhan Demirbas., *et.al,2005*) proposed a three parameter isotherm to incorporate features of both Langmuir and Freundlich equations. It can be described as follows:

$$q_e = \frac{\mathrm{AC_e}}{1+\mathrm{BC_e}^{g}}$$

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,

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

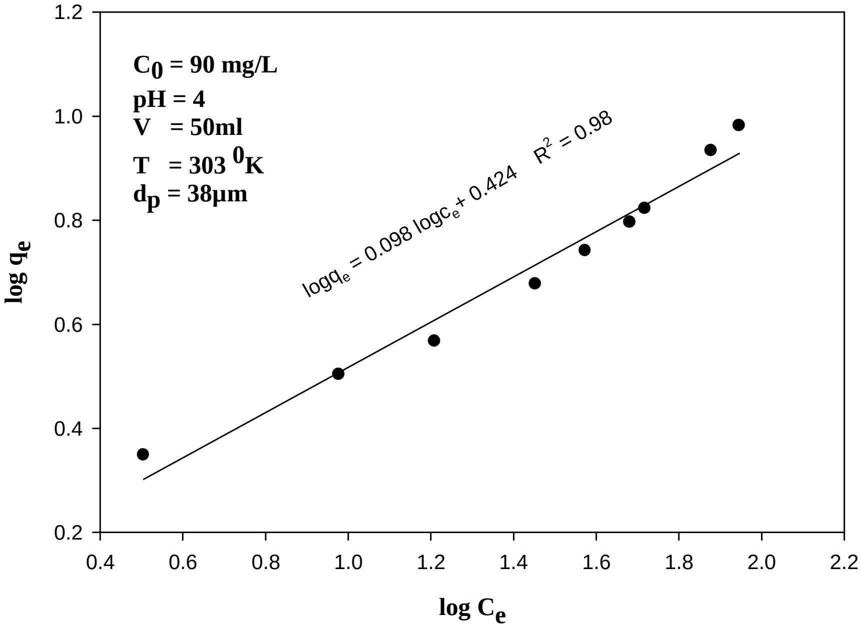


Fig.6 Frendlich isotherm for biosorption of Cadmium

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. The Redlich – Peterson plot drawn between ln [A (Ce/qe)-1] and ln Ce. From the fig.8

ln [(Ce/qe)-1]= 0.853lnCe-1.44 with R^2 = 0.977.

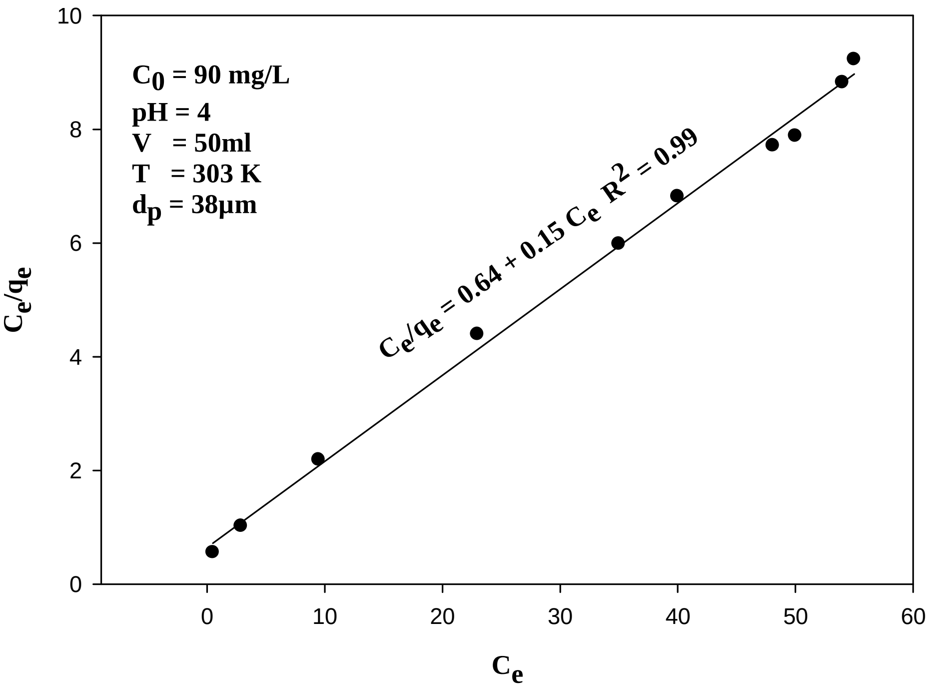


Fig. 7 Langmuir isotherm for biosorption of cadmium

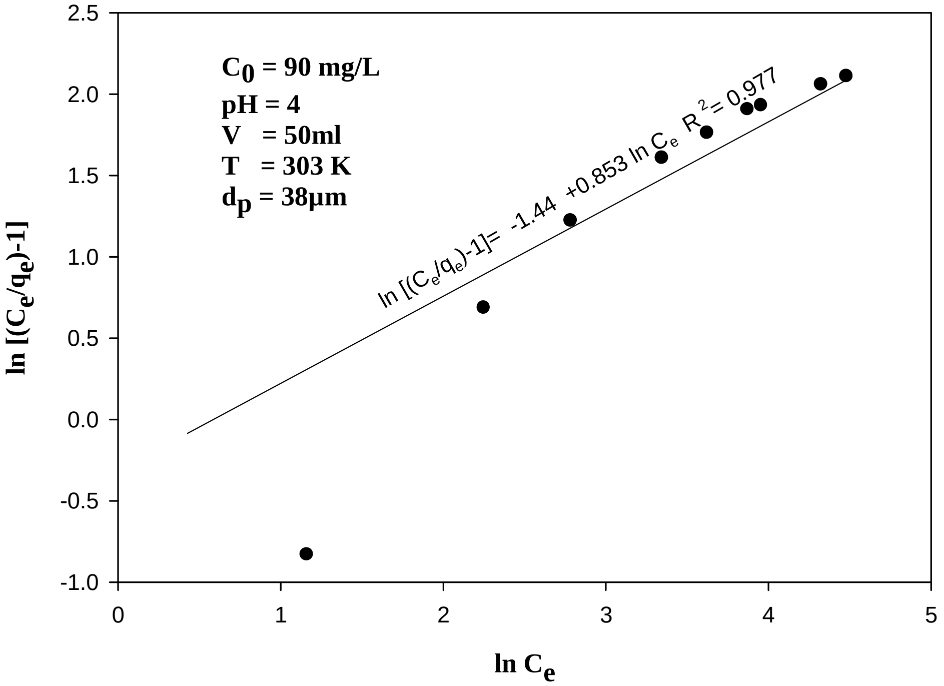


Fig. 8 Redlich - peterson isotherm for biosorption of Cadmium

Redlich- Peterson isotherm constants A (L/mg), B (L/mg) and Redlich- Peterson isotherm exponent (g) 303 K and dp = 38 µm were 1L/mg, -1.44 L/mg and 0.85 respectively. Tempkin isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface and it was 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) x 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 analyzed according to the linear form of Tempkin isotherm and the linear plot was shown in fig.9. The equation obtained for cadmium biosorption was: qe = 0.378 lnCe +1.617 with R^2 = 0.84 a correlation coefficient 0.84. The isotherm constants obtained for various isotherm models were shown in *Table-3*. The best fit model was determined based on the linear regression correlation coefficient (R^2). 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, 0.977and 0.84 respectively.

Table.3: Isotherm constants

Freundlich isotherm	**Langmuir isotherm**	**Redlich-Peterson isotherm**	**Tempkin isotherm**
K_f = 0.098, L/g	q_m = 6.67, mg/g	A = 1, L/g	A_T= 2.085, L/mg
n = 0.423, g/L	b = 0.234, L/mg	g = 0.853	b_T = 6668.3
R^2 = 0.98	R^2 = 0.99	R^2 = 0.94	R^2 = 0.84

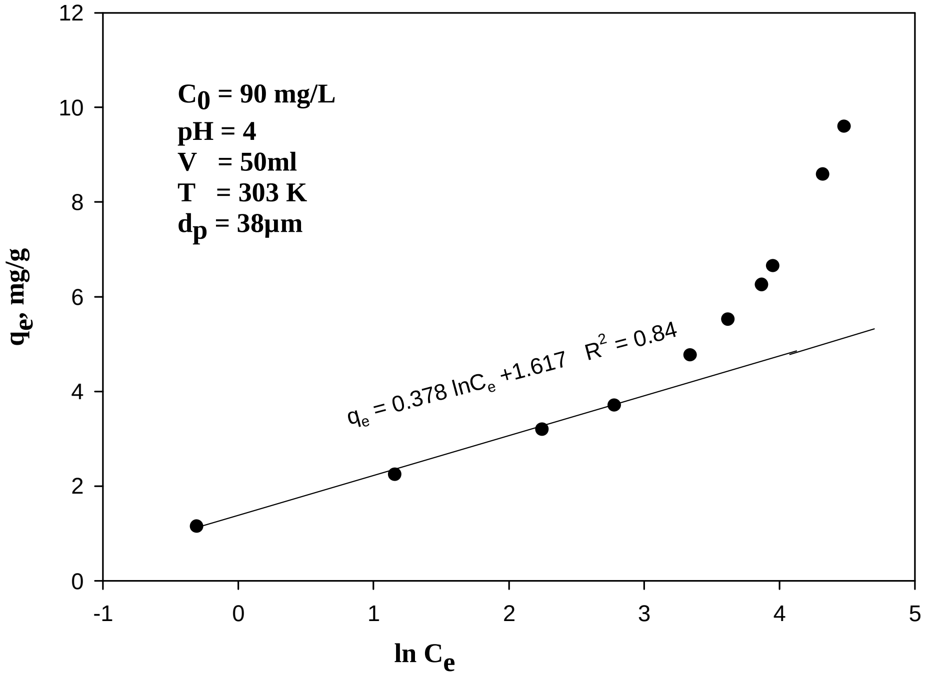


Fig. 9 Tempkin isotherm for biosorption of Cadmium

Table.4: Second order kinetics

For d_p = 38 μm

W, g/L	Equation	K, (g/mg-min)	R^2
1	$(t/q_t) = 0.44\ t + 0.746$	0.2595	0.99
2	$(t/q_t) = 0.3\ t + 0.55$	0.1636	0.99
5	$(t/q_t) = 0.16\ t + 0.396$	0.0646	0.99
10	$(t/q_t) = 0.08\ t + 0.19$	0.0336	0.99
20	$(t/q_t) = 0.03\ t + 0.75$	0.001	0.99
30	$(t/q_t) = 0.018t + 0.048$	0.0067	0.99

Kinetics of Biosorption

Biosorption kinetics the data 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) = K_{ad} (q_e–q_t). Plot of log (q_e–q_t) versus't' gives a straight line for first order kinetics. In case of pseudo second order kinetics, (dqt/dt) = K (q_e–q_t)2 is applicable. This equation can be written as (t/q_t) = (1/Kqe2) + (t/q_e). 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 (q_e -q_t) versus agitation time (t) for the present investigation was drawn in Fig.10 and the resulting equations are:log (q_e – q_t) = 0.017 t - 0.07, R^2= 0.96 for dp= 38 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 were shown in Fig. 11 for dp= 38 μm. The second order rate equations obtained were compiled in *Table 4*. The results show that the correlation coefficients for second order rate equations (0.999) were 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 were varied from 0.259 to 0.0067g/(mg-min).

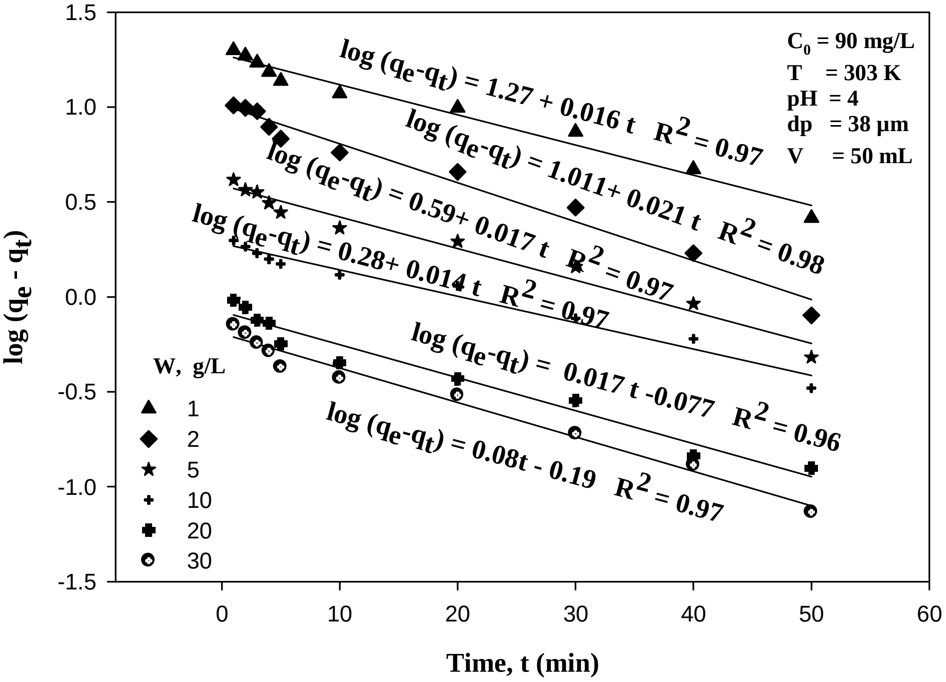


Fig.10 First order kinetics for biosorption of cadmium

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 (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS). Net enthalpy change (ΔH) is related to ΔG and ΔS as ΔG= ΔH - T(ΔS). The Van't Hoff's equation is log(qe/Ce) = - (ΔH/2.303R)(1/T) + (ΔS/

2.303R)Where (q_e /C_e) is called the biosorption affinity. ΔH and ΔS values are calculated from slope = -ΔH/(2.303R) and intercept = ΔS/(2.303R) Experiments were conducted to understand the biosorption behavior of cadmium with respect to temperature and the data were shown in Fig 12 with log (q_e/C_e) as a function of (1/T).

Table.5: Thermodynamic parameters for Biosorption of manganese

S. No.	C_0, mg/L	-ΔS kJ/(mol-K)	-ΔH kJ/mol	ΔG, kJ/mol at different temperatures, K					
				283	**293**	**303**	**313**	**323**	**333**
1	23.4	0.26	80.37	-6.79	-4.19	-1.59	1.01	2.51	3.8
2	47.8	0.18	54.61	-3.099	-1.27	-0.07	1.21	3.53	5.33
3	73.2	0.141	40.32	-0.417	0.7	2.1	1.73	3.61	6.21
4	90.0	0.138	39.48	-0.43	0.95	-0.09	3.5	4.9	6.3
5	123.4	0.119	32.15	1.527	2.72	3.605	4.78	5.96	7.14
6	127.6	0.102	26.47	2.396	3.416	4.436	5.46	6.27	7.141
7	172.9	0.087	21.83	2.97	3.79	4.59	5.401	6.47	7.43
8	185	0.081	19.65	3.36	4.23	5.19	5.83	6.63	7.496
9	239.2	0.08	19.12	3.43	4.38	5.03	6.02	6.84	7.656
10	280	0.082	19.52	3.686	4.506	5.32	6.15	6.97	7.79

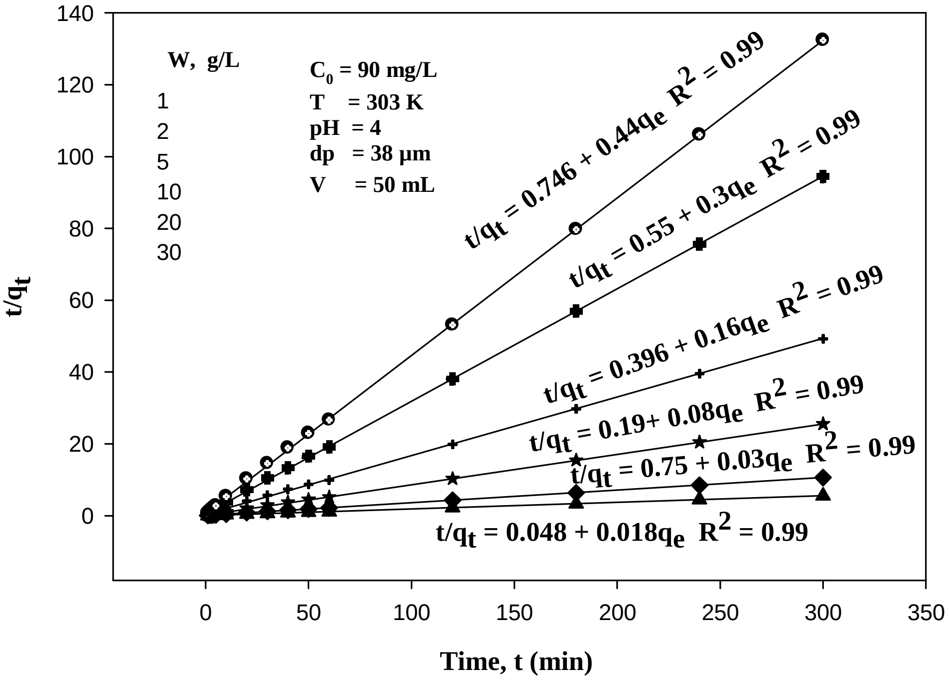


Fig.11 Second order kinetics for biosorption of cadmium

The equation obtained was log (q_e/C_e) = -2062(1/T) - 7.23 for C_0 = 90mg/L Thermodynamic parameters calculated for biosorption of Cd on to Psidium guajava leaves powder were shown in *Table 5*.

Effect of Statistical Experimental design

The Biosorption of cadmium metal ions in batch Biosorption depends on various factors such as agitation time, pH, biosobent size, dosage, concentration of the metal solution and biomass (biosorbent) quantity. The optimization of all these variables using univariate procedure is very tedious because any variable is optimized by varying just one factor each time fixing the others. The value achieved by this procedure is fixed and other factors will be varying by the time.

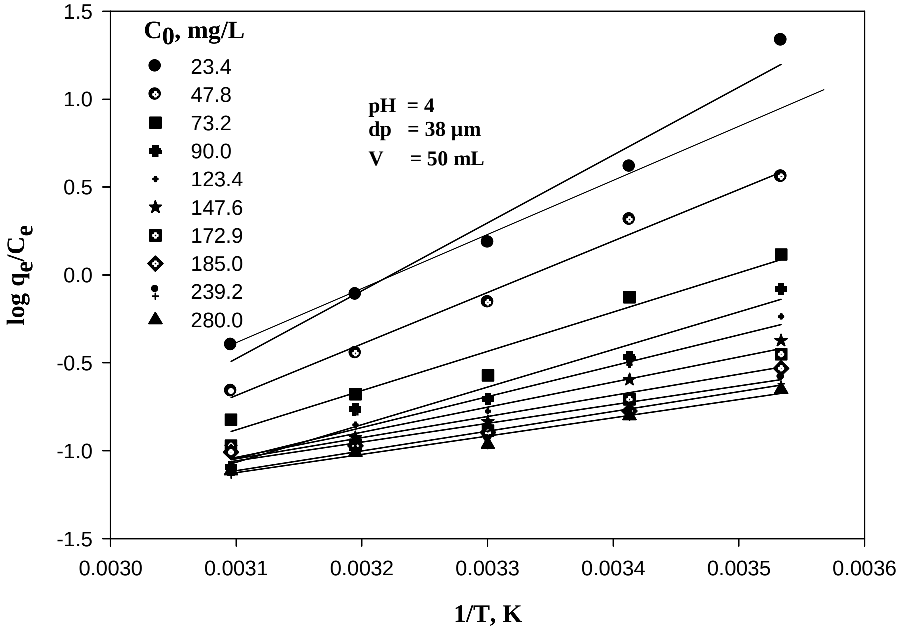


Fig.12 Effect of temparature on biosorption of cadmium w.r.t initial concentration (Von't hoff plot for biosorption of Cadmium)

Table.6: Regr. Coefficients; Var.:CS; R-sqr=.99612; Adj:.98837 (Spreadsheet1)
3 3-level factors, 1 Blocks, 10 Runs; MS Residual=768.0264 DV: CS

Factor	Regressn coeff.	Std.Err.	t(3)	p	-95.%	+95.%
Mean/Interc.	436.892	18.33062	24.9796	0.000141	399.556	516.228
(1)Conc. (L)	129.955	11.31390	11.5747	0.001385	94.949	166.961
Conc. (Q)	-136.254	18.33062	-7.5461	0.004825	-196.661	-79.988
(2)pH (L)	118. .500	11.31390	11.3577	0.001464	92.494	164.506
pH (Q)	-51.959	18.33062	-2.9437	0.060331	-112.296	4.377
(3)B. Volume(L)	-213.790	11.31390	-19.7801	0.000282	-259.796	-187.784
B. Volume(Q)	126.841	18.33062	8.1743	0.003830	91.504	208.177

The disadvantage of this univariate procedure is that the best condition could not attained because the interactions among the all the factors disregarded and also it is not known in the set of other fixed variables was fixed at other levels the results will leads to the same optimization. In order to overcome this disadvantages statistical design of experiments can be carried to achieve the best optimization of any possible system obviously not all the factors could be studied because it would lead to the need of performing so many experiments that would invalidate the advantage of using statistical design of experiments.

In this work the factors screened were initial metal concentration, pH and volume of biosorbent. The experiments given in Table 2 were carried out and solid metal loading was estimated. The software package Statistica version 6.0 was employed in order to obtain the effect of these variables. The regression analysis was performed to fit the response function to the experimental data. The result of the analysis was given in Table 2. The significance of each coefficient was determined by t-test and p-values which are listed in the table. The larger the magnitude of t-value and smaller the p-value, more significant in the corresponding coefficient (Adinarayana *et al*, 2003).

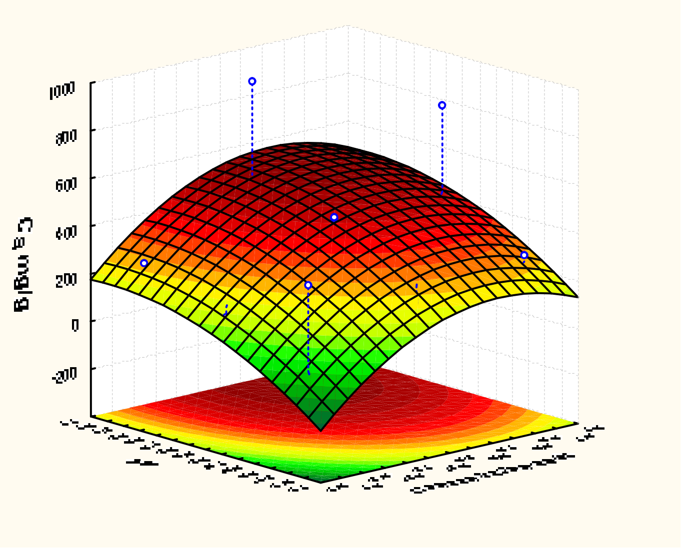


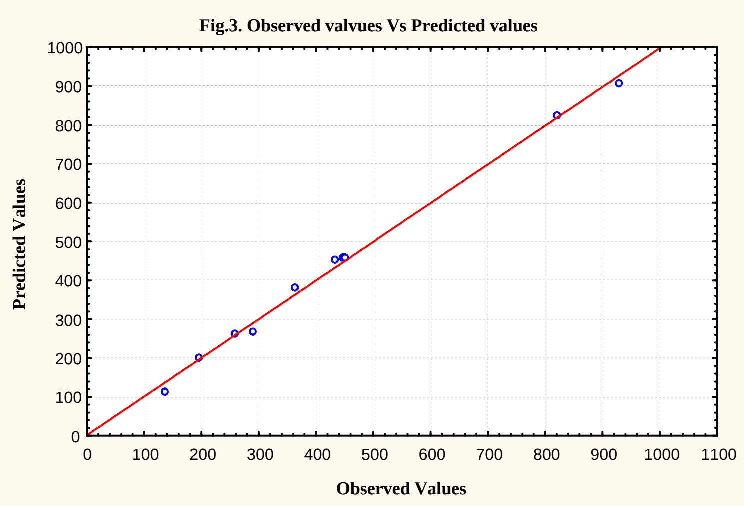
Fig.13. Response surface plot for the effect of pH and metal concentration

The response surface to estimate the uptake efficiency of Cd over independent variables pH, initial metal Concentration is depicted in figure 13. The points giving the maximum uptake of Cd were found to be at a pH of 6. Increase in pH resulted in an increase in Cd uptake. The poor sorption of Cd in the low pH range could have been due to competition with the H^+ ions for metal binding sites on the biomass cells, while the increase in pH favors metal sorption mainly because of negatively charged groups (Sar *et al*, 1999).

Based on the above analysis the cadmium uptake is given by the following equation

$$C_S = 436.892 + 129.355C_O + 118.500pH - 213.790B - 136.254\, C_O^2 - 126.841\, B^2$$

The related data table was shown in *Table.6.* The above equation fits data well with an R^2 deviation of 0.99. The below figure shows the variation of predicted value with that of the observed value and it clearly shows that the fitness of the proposed equation is very good.



CONCLUSION

Investigations were carried out to find out the equilibrium, kinetics and Thermodynamic parameters for biosorption of cadmium from an aqueous solution using Psidiumguajava leaf powder Percentage removal of cadmium from the aqueous solution was increased significantly with increase in pH from 1 to 4.Thereafter percentage removal was decreased for further increase in pH. In the range of variables studied, percentage removal was increased from 74.0 % (3.33 mg/g) to 95.11 % (4.28 mg/g). The kinetic studies showed that the biosorption of cadmium was better described by pseudo second order kinetics. The percentage biosorption decreases with increase in temperature. The investigation also revealed 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 cadmium was less favorable.

From the use of an experimental design we conclude that allowed the rapid screening of a large experimental domain for optimization of the cadmium biosorption of biomass *Psidium guajava leaves*. The fit of the model was checked by the determination coefficient (R^2). In this case, the value of the determination coefficient (R^2= 0.99).

Nomenclature

***b**, Langmuir equilibrium constant, L/mg; **Co**, Initial concentration of Cd in aqueous solution, mg/L; **Ct**, Concentration of Cd aqueous solution after 't ' min, mg/L; **Ce,** Equilibrium biosorption concentration of Cd, mg/L; **dp**, biosorbent size, μm; Δ**G** Change in Gibbs free energy, KJ/mol; Δ**H**, Change in enthalpy, J/mol; **K**, Second order rate constant, g/(mg min); **Kf,** Freundlich coefficient for Cd in aqueous solution, L/g; **Kad,** First order rate constant,* min^{--1}*; **m,** Amount of biosorbent taken per 1L of aqueous solution, g/L; **n,**Freundlich constant for Cd in aqueous solution; **qe**, Mass of solute adsorbed per mass of biosorbent at equilibrium, =* $(C_o–C_e)/m$*, mg/g; **qt**, Mass of solute adsorbed per mass of biosorbent at '**t** ' min, =* $(C_o–C_t)/m$*, mg/g;* q_t*, Langmuir monolayer capacity, mg/g; **RL** Separation factor for Cd in aqueous solution,* $1/(1+bC_e)$*;* R^2*, Correlation coefficient; Δ**S**, Change in entropy, J/(mol K); **t**, Agitation time, min; **T**, Absolute temperature, K; **V**, Volume of aqueous solution, **w**, Biosorbent dosage, g or g/L, B=biomass of guava leaf powder.*

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