Research Journal of Pharmaceutical, Biological and Chemical Sciences

Biosorption of Chromium (VI) from an aqueous solution onto *citrus limonium peel*

Sumalatha B[1*#], Prasanna Kumar Y[2] and King P[3]

[1] Department of Chemical Engineering, Vignan University, Vadlamudi,A.P, India
[2] Visakha Institute of Engineering & Technology, Visakhapatnam, A.P, India
[3] Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam, A.P, India

ABSTRACT

The effective removal of Cr (VI) from an aqueous solution in a batch system using of low-cost biosorbent *Citrus limonium peel* was studied. The effect of process parameters including solution pH, biosorbent dosage, initial Cr (VI) concentration, contact time, biosorbent size and temperature was studied. The optimum solution pH for Cr (VI) biosorption by biosorbent was 6 with the optimal removal of 91.82 %. The biosorbent dosage 0.1 g was enough for optimal removal. The equilibrium was achieved at 75 min of contact time. The equilibrium data were well described by Langmuir, Freundlich, Dubinin- Redushkevich and Temkin biosorption isotherms. Sorption equilibrium exhibited better fit to Freundlich isotherm (R^2 = 0.994) than Langmuir isotherm (R^2 = 0.984), Dubinin-Redushkevich isotherm (R^2 = 0.979) and Temkin isotherm (R^2 = 0.968). Furthermore, to determine the biosorption mechanism, a detailed analysis has been conducted by testing kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation, Intra-particle diffusion and Boyd equation. Results clearly indicate that the pseudo second-order kinetic model was found to be correlate the experimental data strongest than other kinetic models.

Keywords: Biosorption,Chromium(VI),Citrus limonium peel, isotherm models, kinetic models.

Corresponding author
Email id:

1. INTRODUCTION

Removal of substantial metals from modern wastewater is of essential significance since they are not just creating sullying of water bodies and are additionally harmful to numerous living things. Modern procedures produce wastewater containing substantial metal contaminants. Since the greater part of substantial metals are non degradable into nontoxic final results, their fixations must be lessened to satisfactory levels before releasing them into condition. Various regular treatment innovations have been considered for treatment of wastewater with organic substances. Among them, adsorption is found to be the best technique. Commercial activated carbon is viewed as the best material for controlling the organic load [1].

Hexavalent chromium is very toxicant to flora and fauna. According to WHO drinking water guideline concentration for total chromium in drinking water is 50µg/l [2]. The metal species Cr is considered as profoundly dangerous, it could go about as a carcinogen, mutagen, and teratogen in the organic system. It has too been noticed that drawn out introduction to the metal species could bring about skin sensitivities and cancer in human beings [3].

The primary target of this work was to evaluate the biosorption capacity of *citrus limonium peel*, for the effective removal of Cr (VI) from an aqueous solution by varying solution pH, contact time, biosorbent dosage, initial Cr (VI) concentration, biosorbent size and temperature. Equilibrium isotherms (Langmuir, Freundlich, Dubinin- Redushkevich (D-R) and Temkin) for biosorption of Cr (VI) onto *citrus limonium peel* were described. Kinetic models (pseudo- first-order, pseudo-second-order, Elovich, Intra particle diffusion and Boyd model) were utilized to understand the probable biosorption mechanism.

2. EXPERIMENTAL

2.1 Preparation of biosorbent

Citrus limonum peel was collected from juice shops and washed with de-ionised water several times to remove impurities. Then completely dried in sunlight for about 3-4 weeks. It was crushed into small pieces and was powdered using domestic mixer. The test powder was graded using BSS sieve set to get the required average size for using as biosorbent. In the present study the powdered materials in the range of 75-212 µm average particle size were then directly used as biosorbent without any pre-treatment. This biosorbent powder was stored in moisture free glass bottles.

2.2 Preparation of synthetic sample

A stock solution of 1000 mg/l of Cr(VI) was acquired by dissolving potassium dichromate (Merck Company) in distilled water. The test solutions of various concentration 20,40,60,80,100 mg/l were prepared from the stock solution. The solution pH was balanced utilizing 0.1M HNO_3 and 0.1M NaOH toward the start of the trial and not controlled subsequently. The conical flasks (250 ml) were shaken at 180 rpm in a temperature controlled rotatory shaker.

2.3 Batch Experimental Procedure

The batch method was employed at room temperature to examine the biosorption of Cr (VI) by biosorbent. This method was used to determine the biosorption capacity, stability of biosorbent and optimum sorption conditions. The parameters were studied by adding biosorbent with solution of Cr (VI) in 250 ml reagent bottle. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, the content was separated from the biosorbent by filtration, using Whatmann filter paper and amount of Cr (VI) in the supernatant/filtrate solutions was analysed by using AAS. The Cr (VI) concentrations biosorbed on the biosorbent were calculated from the difference between initial Cr (VI) content (C_i) and Cr (VI) content after biosorption (C_e). The following equation was used to compute the percentage biosorption of Cr (VI) by the biosorbent.

$$\% \text{ Biosorption} = \frac{C_i - C_e}{C_i} X100 \qquad (1)$$

where C_i and C_e are the initial concentration and equilibrium concentration of the Cr(VI) in mg/l. Biosorptive quantity was calculated by the following equation:

$$q = (C_0 - C_e)\frac{v}{w} \qquad (2)$$

where q = amount of metal biosorbed (mg/g), v = volume of solution (ml), w = mass of biosorbent(g), C_o = initial concentration of the solution (mg/l) and C_e = equilibrium concentration of the solution (mg/l).

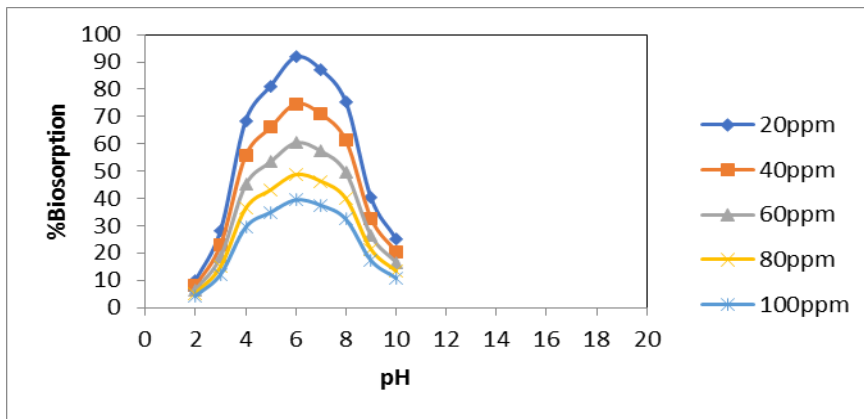## 3. RESULTS AND DISCUSSION

3.1. Effect of pH of the solutio

Fig1: Effect of pH on Cr(VI) removal by *citrus limonium peel* for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The biosorption limit of the biosorbent and speciation of metals in the solution was pH dependent. The influence of pH was more on the solubility of metal ions and the concentration of the counter ions on the functional groups of the biosorbent cell walls. Fig.1 shows the effect of pH on the biosorption of chromium ions in aqueous solution. Maximum biosorption capacities was obtained at 6. At low pH value of 2, the biosorption capacity for the metal ions was observed to be moderate, due to the competition between hydrogen ions and chromium metal ions at the sorption sites. As the pH value increased, the availability of negatively charged cell surfaces will be more, allowing greater metal uptake [3]. If the pH value is > 6, the formation of insoluble chromium hydroxide precipates suppresses the contact of metal with the biosorbent.
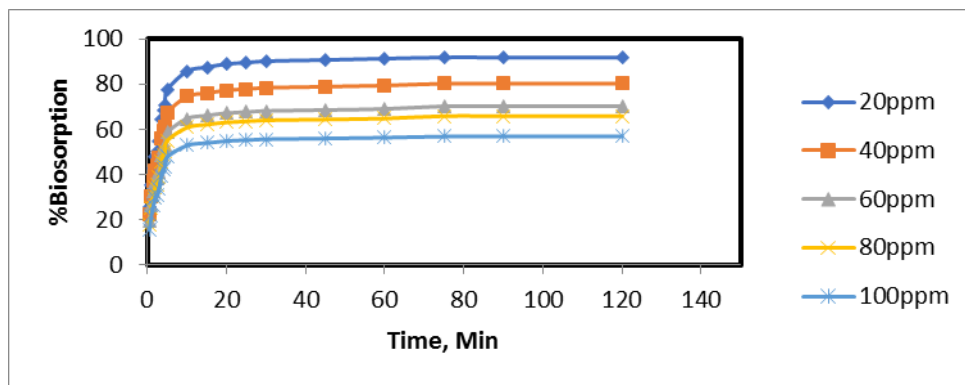
3.2. Effect of contact time

Fig2: Effect of contact time on Cr(VI) removal by citrus limonium peel for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

Fig.2 demonstrate the clarified biosorption time of chromium by *citrus limonium peel* from solutions containing 20-100 mg/l of chromium ion independently. As found in the figure, the biosorption equilibrium was established at 75 min for chromium metal. This recommended that the biosorption process was very quick. Such fast biosorption process has been correlated with the attributes of the biomass, and its physico-chemical interactions with the metal ion. The impact of contact time on percentage biosorption of chromium onto *citrus limonium peel* was studied over an agitation time of 0.5-120 min, using 0.1 g of *citrus limonium peel*, 30 ml of 20 mg/l of metal concentration at pH 6, temperature 303^0 K and 180 RPM shaking speed. The results depicted in Fig.2 indicate that the percentage biosorption increases from 25.58 to 91.81% for chromium upto contact time of 75 min with 20 mg/l of concentration [4]. It was also observed that as the concentration increased from 20ppm to 100ppm,there is a decreased trend observed in %biosorption from 91.81% to 56.87%   due to the biosorbent can not accommodate much more biosorbate available in the solution.
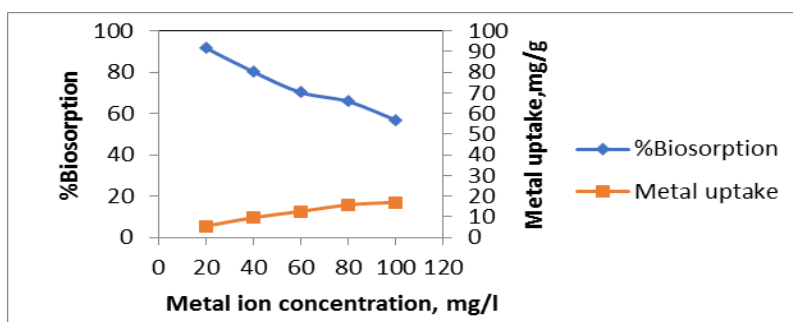
3.3 Effect of Metal ion concentration

Fig3: Effect of metal ion concentration on biosorption capacity of Cr(VI)by citrus limonium peel of 0.1g/ 30ml of biosorbent concentration.

The initial concentration of metal ion in the solution plays a key role as a driving force to defeat the mass transfer resistance between the aqueous and solid phases. From the data it was observed that the chromium metal uptake increased and percentage biosorption of the metals decreased with an increase in the initial metal ion concentration. This increase (5.5 to 17.06 mg/g) was the result of increase in the driving force i.e. concentration gradient. However, the percentage biosorption of chromium onto *citrus limonium peel* was decreased from 91.8 to 56.8%. Despite the fact that an increase in metal uptake was observed, the decrease in percentage biosorption might be ascribed to absence of adequate surface area to accommodate much more metal available in the solution. The percentage biosorption at higher concentration levels demonstrates a decreasing trend, whereas the equilibrium uptake of chromium shows an inverse trend. At lower concentrations the greater part of the chromium ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher initial chromium ion concentrations. At higher concentrations, the lower biosorption yield was due to the saturation of biosorption sites. Subsequently, the purification yield can be expanded by diluting the wastewaters containing high metal ion concentrations [5].

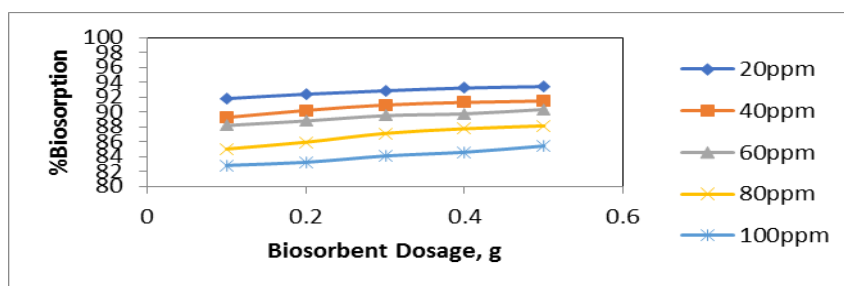### 3.4 Effect of biosorbent dosage
3.5

Fig4: Effect of biosorbent dosage on Cr(VI) removal by citrus limonium peel for 20, 40, 60, 80, 100mg/l metal and 0.1 to 0.5g/30ml of biosorbent concentration.

The sorption capacity of Cr (VI) onto *citrus limonium peel* by varying biosorbent dosage from 0.1g to 0.5g is shown in Fig.4. From the results it was found that the biosorption of Cr (VI) increased with an increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dosage was because of increase of ion exchange site ability, surface areas and the number of available biosorption sites. It was observed that as the biosorbent concentration increased % biosorption decreased [6].
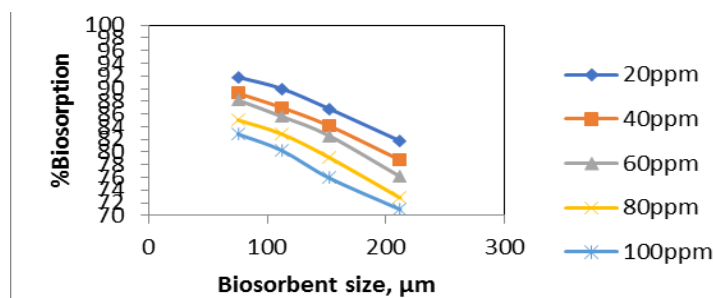
3.5 Effect of biosorbent size

Fig5: Effect of biosorbent size on Cr(VI) removal by citrus limonium peel for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The particle size can affect the sorption properties of the sorbent. Experiments were performed using different particle sizes of the biosorbent (75-212μm) at 303^0K, and initial concentration of 20 mg/l. For the most part, the smaller the biosorbent particles, the greater the amount of metal ions could be biosorbed. Nearly higher biosorption with smaller biosorbate particles may be due to the fact that smaller particles give a larger external surface area. Additionally, for a large particle size a portion of the inside pores of the *citrus limonium peel* could be unapproachable by the Cr(VI) ions. Access to all pores is encouraged through small size particles. As a result the amount of Cr(VI) biosorbed onto *citrus limonium peel* decreased with an increase in the particle size of the biosorbent.
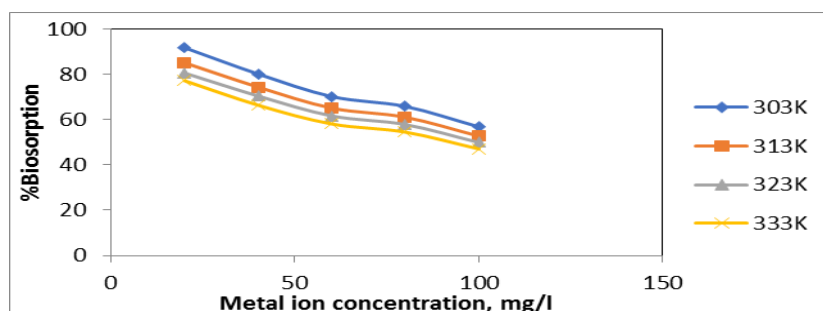
3.6 Effect of temperature

Fig6: Effect of temperature on Cr(VI) removal by citrus limonium peel for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The rate of biosorption is a function of initial metal ion concentration as well as its temperature. The percent biosorption of chromium onto *citrus limonium peel* is shown in Fig.6 as a function of the initial metal ion concentration at 303, 313, 323 and 333 K. The percentage biosorption of chromium ions onto citrus limonium peel was decreased from 91.81 to 77.23% as the temperature increased from 303 to 333 K at 20 mg/l. The percentage biosorption at higher temperature levels shows a decreasing trend because at lower temperatures, all chromium ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher temperatures. This happens because of more interaction of the ions in solution due to convection. At higher temperatures, lower biosorption yield is due to the mobilization of ions in solution because of highly energized ions. As a result, the purification yield can be increased by reducing the temperature. The decrease of the percentage biosorption at increased temperature indicated that the biosorption of chromium ions onto citrus limonium peel is exothermic in nature.

4. Equilibrium studies

Freundlich, Langmuir, D-R and Temkin isotherms were used to describe the equilibrium between biosorbed ions on the biomass cell (q_e, q) and ions in the solution (C_e, q).
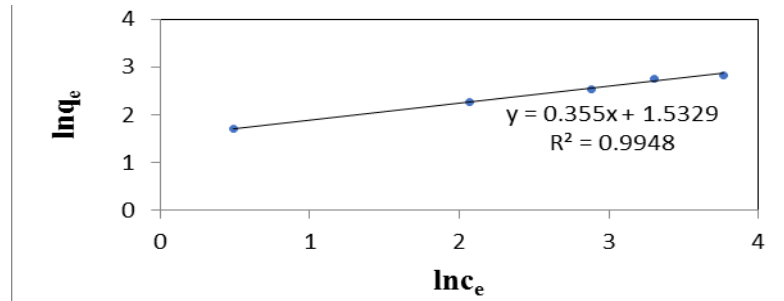
4.1 Freundlich isotherm

Fig7: Freundlich biosorption isotherm at 0.1g/30ml of biosorbent concentration.

The empirical Freundlich equation is used for modeling the sorption on heterogeneous surface. The Freundlich equation[3] is represented as

$$q_e = K_f C_e^{1/n} \qquad (3)$$

K_f and 1/n are experimental constants, K_f is an indication of the biosorption capacity of the biosorbent; n indicates the effect of concentration on the biosorption capacity and represents the biosorption intensity.

The equation can be linearized in the following logarithmic form

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (4)$$

These values of n and K_f can be acquired from the slopes and the intercepts of the linear plots individually. The logarithmic plot of sorbed and equilibrium concentration gives a straight line with a coefficient of determination is 0.994 indicating that sorption data fitted well with the Freundlich model (Fig.7). The value of 1/n for chromium is 0.355 g/l and K_f value is 4.627 mg/g and tabulated in Table 1.

The magnitude of K_f and 1/n shows easy separation of chromium ion from an aqueous solution with high biosorptive capacity of citrus limonium, especially at 303K and pH 6.
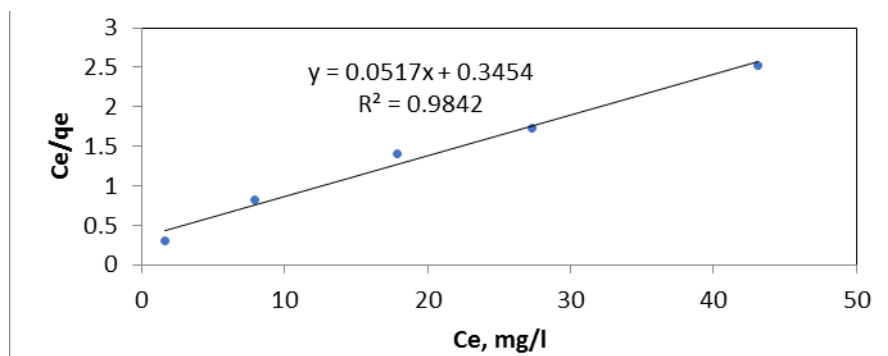
4.2 Langmuir isotherm

Fig8: Langmuir biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Langmuir isotherm equation is represented as [3]

$$q_e = \frac{q_{max} C_e K_l}{1 + C_e K_l} \qquad (5)$$

After rearrangement

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{C_e}{q_{max}} \qquad (6)$$

These values q_{max} and K_l (where K_l is the biosorption equilibrium constant) can be acquired from the slopes and the intercept of the linear plot. In Fig.8 C_e/q_e is plotted against C_e yielding a straight line with R^2 (0.984). The value of q_{max} (19.6 mg/g) was calculated from the slope of the linear plot, whereas the value of K_l (0.1478 l/mg) was derived from the intercept.

4.3 Dubinin– Radushkevich isotherm
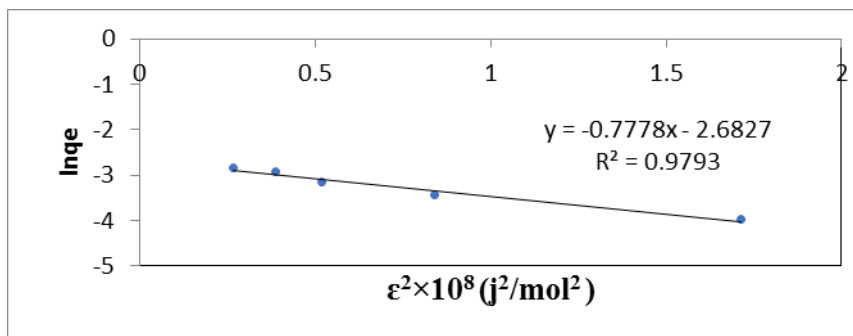

y = -0.7778x - 2.6827
R^2 = 0.9793

Fig9: D-R biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Linearized D-R equation is [4]

$$\ln q_e = \ln q_m - \beta \, \varepsilon^2 \qquad (7)$$

where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential, which is calculated from the following relation;

$$\varepsilon = RT \, \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

Equilibrium data for the biosorption is plotted as ln q_e vs ε^2, as shown in Fig9. The two constants β and q_m were calculated from the slope (β) and intercept (ln q_m) of the line, respectively. The values of biosorption energy E was obtained by the following relationship.

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (9)$$

The mean free energy gives information about biosorption mechanism, whether it is physical or chemical biosorption. If E value lies between 8 KJ/mol and 16 KJ/mol, the biosorption process take place chemically and E < 8 KJ/mol, the biosorption process of the physical in nature. In the present work, E value (8.021 KJ/mol) is greater than 8 KJ/mol, hence the biosorption of Cr (VI) onto citrus limonium is of chemical in nature .
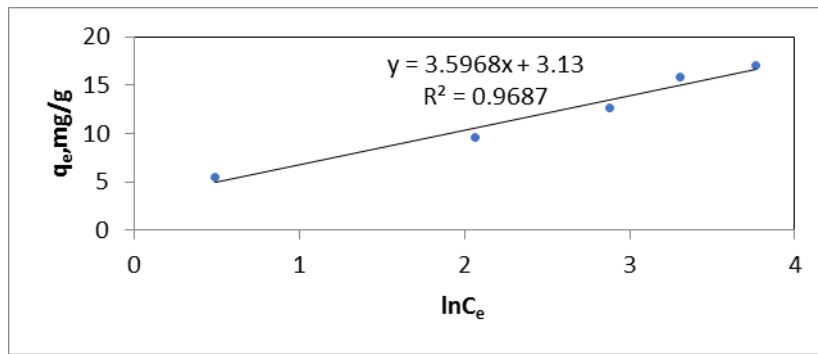
4.4 Temkin isotherm

Fig10: Temkin biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Linearized Temkin isotherm is given by the equation[7]

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad\qquad (10)$$

where b_T is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (l/g). Equilibrium data for the biosorption is plotted as q_e vs ln C_e, as shown in Fig.10. The two constants b_T and A_T were calculated from the slope (RT/b_T) and intercept (RT/$b_T$lnA_T) of the plot respectively. The values of A_T, b_T and regression coefficient (R^2) shown in table1.

All the four equilibrium models were fitted to the equilibrium data. Table-1 represents the calculated isotherm constants. Based on the linear regression correlation coefficient R^2 the best fit equilibrium model was determined. From the table it was evident that the sorption data were very well represented by Freundlich isotherm for chromium with an higher correlation coefficient of 0.994, followed by Langmuir, D–R and Temkin, with a correlation coefficient of 0.984, 0.979, and 0.968 respectively.

Table1: Constant values of Langmuir, Freundlich, D-R, Temkin isotherm constants

Isotherm	Isotherm constants and coefficients	
Langmuir	$q_{\max}(mg/g)$	19.6
	$k_l(l/mg)$	0.147
	R^2	0.984
Freundlich	$K_f(mg/g)$	4.627
	1/n(g/l)	0.355
	R^2	0.994
Dubinin – Radushkevich	β	0.777x10^{-8}
	E(KJ/mol)	8.021
	$q_{\max}(mg/g)$	6.84x10^{-2}
	R^2	0.979
Temkin	$A_T(L/mg)$	2.387
	b_T (J/mg)	700.54
	R^2	0.968

5. Kinetic studies
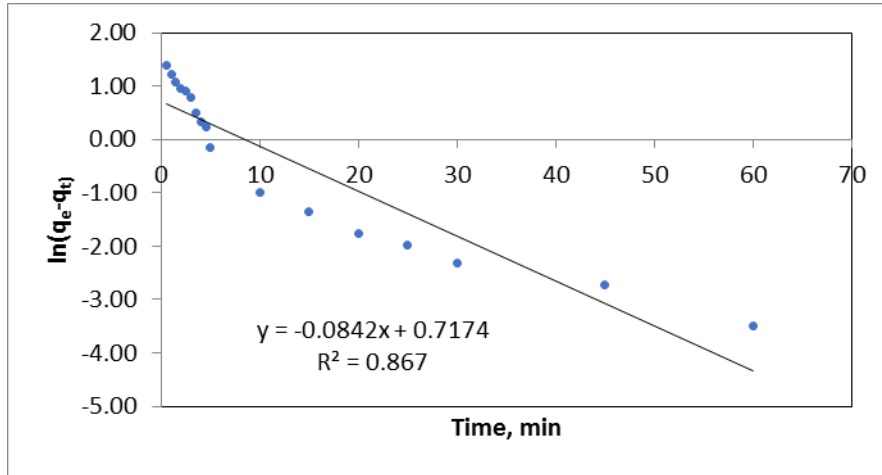
5.1 The Pseudo First-Order Equation

Fig11: pseudo first order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The kinetics equation proposed by Lagergren has been used to describe the biosorption of biosorbate from an aqueous solution. The pseudo first-order model is described by the following Equation

$$\frac{dq}{dt} = k_1 (q_e - q_t) \qquad (11)$$

where q_e is the amount of metal ion adsorbed on biosorbent at equilibrium (mg/g), q_t is the amount of metal ion adsorbed on biosorbent at time 't' (mg/g) and k_l is Lagergren constant (min^{-1}). Integrating the above equation and transforming to log scale

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (12)$$

Linear plot of $\ln(q_e - q_t)$ against time indicates whether this kinetic model is applicable or not for biosorption process. The results of kinetic parameters are shown in table2.

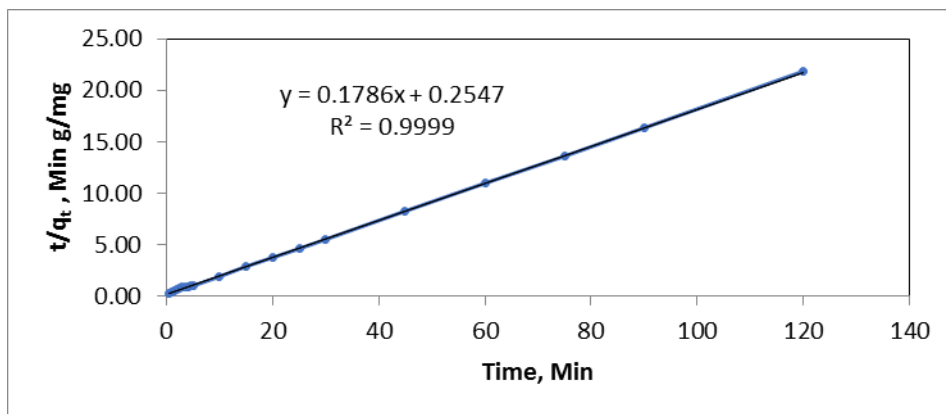### 5.2 The Pseudo Second-Order Equation

Fig12: pseudo second order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The pseudo second-order kinetic model is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e} t \qquad (13)$$

Where q_e = amount of adsorbed metal ion on biosorbent at equilibrium (mg/g), q_t = amount of adsorbed metal ion (mg/g) on biosorbent at time 't', k_2 = second order rate constant (g/mg min). A linear plot of t/q vs t indicates whether this model of biosorption is applicable for this case or not.

The values of constants of kinetic models obtained from the plots for biosorption of Cr(VI) onto citrus limonium peel at 303^0K are shown in Table 2. The data showed good agreement with the pseudo second-order kinetic model (R^2 = 0.999). However, the value of the determination coefficient (R^2) indicates the applicability of the pseudo second-order model for describing the experimental results to a higher degree of accuracy. In addition, Fig.12 and Table 2, show that the q values (q_e,cal) determined from the pseudo second-order model were closer to the experimental q values (q_e, exp) than those determined from the pseudo first-order model.

Table.2: Biosorption rate constants, qe estimated and coefficient of correlation associated to the pseudo-first and second-order biosorption for the citrus limonium peel biomass

Metal	$q_{e\ Exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		K_1(min^{-1})	q_e cal(mg/g)	R^2	K_2	q_e cal(mg/g)	R^2
Chromium	5.51	0.084	2.048	0.867	0.124	5.617	0.999

### 5.3 Intra-particle diffusion model
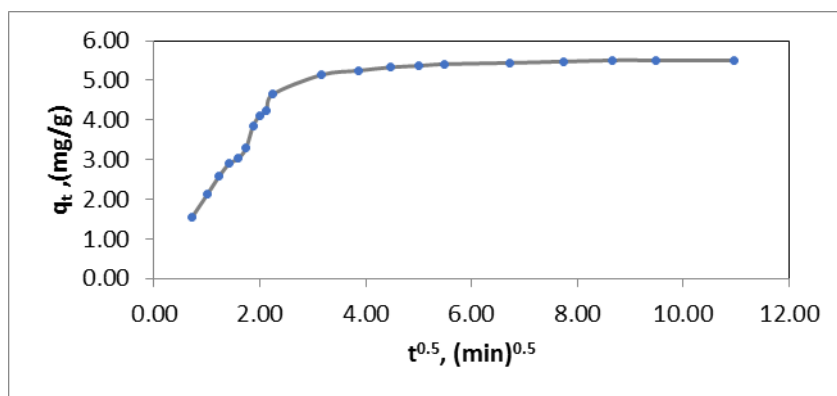
Fig13: Intra particle diffusion model for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The intra-particle diffusion model is used to investigate the diffusion controlled biosorption system. The probability of the intra-particle diffusion was explored by using the following equation

$$q_t = k_{id}t^{0.5} + C \qquad (14)$$

where q_t (mg g^{-1}) is the biosorption capacity at any time t (min), k_{id} is the intra particle diffusion rate constant (mg g^{-1} min$^{1/2}$), C is the value of intercept which gives an idea about the boundary layer thickness, i.e., the larger intercept; the greater is the boundary effect. The plot of q_t vs. the square root of time obtained for the biosorption of Cr(VI) onto *citrus limonium peel* is shown in Fig.13. The intra particle rate constant k_{id} is 0.327(mg g^{-1} min$^{1/2}$) and intercept C is 2.98. The plot is not linear over the whole time range, indicating that more than one step is involved in the biosorption of metal ions. If the intra-particle diffusion is the only rate-controlling step then the plot should pass through the origin, else the boundary layer diffusion affects the biosorption to some degree. The linear curve is deviated from the origin or near saturation because of the differences in the mass transfer rate in the initial and final stages of biosorption. The plot is not passing through origin indicating that the intra particle diffusion is not the only rate determining factor.

5.4 Elovich model:
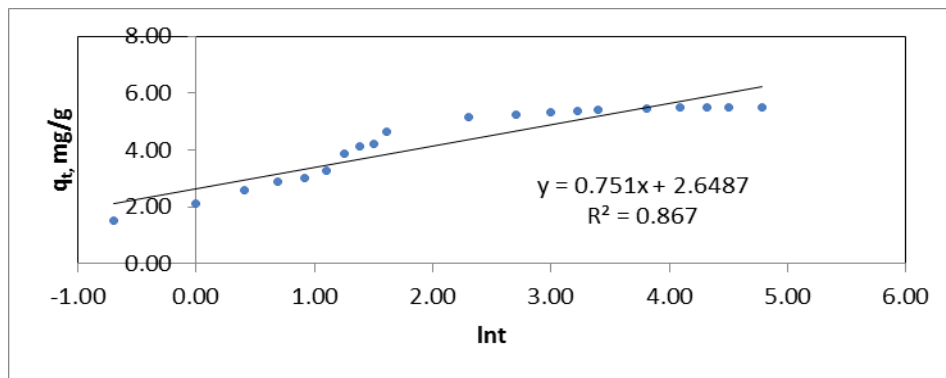
Fig14: Elovich model for 20 mg/l of metal and 0.1g/30 ml of biomass concentration.

The Elovich equation has been applied satisfactorily to some chemisorption processes. The Elovich equation can be written in the following form

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \frac{1}{b}\ln t \qquad (15)$$

where a (mg g^{-1} min^{-1}) is the initial sorption rate and b (g mg^{-1}) is the desorption constant related to the extent of surface coverage and activation energy for chemisorption. The parameters (1/b) and (1/b) ln(ab) can be obtained from the slope and intercept of the linear plot of q_t vs. ln$_t$ (Fig.14). The plot is linear with good correlation coefficient (R^2) of 0.867. This suggests that the sorption process follows the pseudo-second-order kinetic model based on the assumption that the rate determining step may be chemisorption, involving valence forces through sharing or exchange of electrons between biosorbent and biosorbate.

5.5 Boyd model:
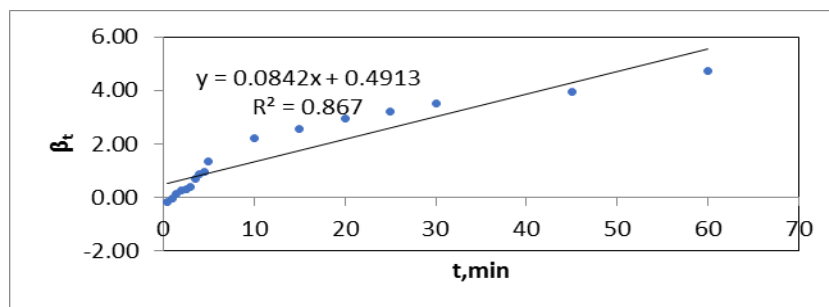
Fig15: Boyd model for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

Boyd model is applied to check whether sorption proceeds via film diffusion or intraparticle diffusion mechanism. The model can be expressed in the following form

$$F = \left(1 - \frac{6}{\pi^2}\right)\exp\left(-\beta_t\right) \qquad (16)$$

where F= q_t/q_e; q_e is the amount of metal ions biosorbed at equilibrium (mg g^{-1}), q_t represents the amount of ions biosorbed at any time t (min) and B$_t$ is a mathematical function of F. Eq. (16) can be rearranged by taking the natural logarithm to obtain the equation

$$\beta_t = -0.4977 - \ln(1 - F) \qquad (17)$$

The plot of B$_t$ vs. t is shown in Fig.15, which is linear with the correlation coefficient (R^2) is 0.867. The outcomes recommend that the biosorption procedure is controlled by film diffusion.

CONCLUSION

The batch experiments were conducted with the biomass of *citrus limonium peel* and it exhibited the potential of Cr(VI) removal from an aqueous solution. Optimum pH, contact time, initial metal ion concentration, dosage, temperature and size for biosorption in this study were 5,75 min, 20mg/l, 0.1g, 303^{0}K and 75μm respectively. With an increase in the initial metal ion concentration percentage of biosorption decreased and metal ion uptake capacity increased. It was observed that percentage of biosorption increased and metal ion uptake capacity decreased by increase in the amount of biomass. The biosorption process followed the Freundlich isotherm model. Kinetic studies on the biosorption of Cr(VI) onto *citrus limonium peel* revealed that experimental data were fitted with the pseudo second-order kinetic model and that film diffusion initially controls the sorption process. Based on the experimental data it was notified that *citrus limonium peel* is an appropriate biosorbent for the removal of chromium from an aqueous solution.

REFERENCES

[1]   Madhukar J, phadtare, prof.S.T.Patil,(2015), Removal of heavy metal from industrial waste water, International Journal of Advanced Engineering Research and Studies, IV/III/04-08.
[2]   WHO, Guidelines for drinking-water quality, recommendations, 4th ed., World Health Organization: Geneva, 2011.
[3]   Hassan Rezaei, (2016) Biosorption of chromium by using Spirulina sp., Arabian Journal of Chemistry 9, 846–853.
[4]   Anukthi C. Poojari, Sandip D. Maind and Satish A. Bhalerao,(2015), Effective removal of Cr (VI) from aqueous solutions using rind of Orange (Citrus sinensis), (L.) Osbeck, *Int.J.Curr.Microbiol.App.Sci* 4(4): 653-671.
[5]   Nour T. Abdel-Ghani and Ghadir A. El-Chaghaby, biosorption for metal ions removal from aqueous solutions: a review ofrecent studies, International Journal of Latest Research in Science and Technology, Volume 3, Issue 1: Page No.24-42 ,January-February 2014.
[6]   Gupta, V. K., Shilpi Agaerwal, and Tawfik A. Saleh. "Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes." Water research 45.6 (2011): 2207-2212.
[7]   Albadarin, Ahmad B., et al. "Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent." Chemical Engineering Journal, 179 (2012): 193-202.
[8]   [8]. N.Gamze Turan,Osman nuri ergan(2009), Removal of cu(II) from leachate using natural zeolite as a landfill linear material, Journal of hazardous materials, 167,696-700.
[9]   Hu, Bingjie, and Hanjin Luo. "Adsorption of hexavalent chromium onto montmorillonite modified with hydroxyaluminum and cetyltrimethylammonium bromide." Applied Surface Science 257.3 (2010): 769-775.
[10]   Wang, Qihui, et al. "Adsorption of chromium (III), mercury (II) and lead (II) ions onto 4-aminoantipyrine immobilized bentonite." Journal of hazardous materials 186.2 (2011): 1076-1081.
[11]   Cronje, K. J., et al. "Optimization of chromium (VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride." Desalination 275.1 (2011): 276-284.
[12]   Anandkumar, J., and B. Mandal. "Adsorption of chromium (VI) and Rhodamine B by surface modified tannery waste: Kinetic, mechanistic and thermodynamic studies." Journal of hazardous materials 186.2 (2011): 1088-1096.
[13]   Juan Manuel, Vargas-Morales, et al. "Hexavalent Chromium Removal by Citrus limonium Shell." Open Journal of Inorganic Non-metallic Materials 2012 (2012).
[14]   Choudhary, Sudesh, Varsha Goyal, and Seema Singh. "Removal of copper (II) and chromium (VI) from aqueous solution using sorghum roots (S. bicolor): a kinetic and thermodynamic study." Clean Technologies and Environmental Policy 17.4 (2015): 1039-1051.
[15]   B.Sumalatha, K.Kiran kumar, A.Venkatanarayana,D.John babu,T.C.Venkateswarlu(2014), Biosorption of Fluoride from Aqueous Solution on Citrus limonium, *Research J. Pharm. and Tech*. 7(5), 554-560.
[16]   D. John Babu, B. Sumalatha, T.C. Venkateswarulu,K. Maria Das and Vidya P. Kodali, Kinetic, Equilibrium and Thermodynamic Studies of Biosorption of Chromium (VI) from Aqueous Solutions using Azolla filiculoidus, journal of pure and applied microbiology, August 2014. Vol. 8(4), p. 3107-3116.