# Biosorption of chromium by agricultural waste, *Anacardium occidentale* testa powder: characterization, kinetic, isothermic and thermodynamic studies

**Swarnalatha. G[1*], Chandrakala Gunturu[1] and Sureddy V Naidu[2]**

[*] Department of Chemistry, Mahathi College of Pharmacy, Madanapalli-Andhra Pradesh- 517319, India.
[1,2]Centre for Biotechnology, Department of Chemical Engineering, Andhra University, Visakhapatnam530003 India
[1*]Professor, [1] Research Scientist, [2] Professor
[1]swarnapchem@gmail.com ,[2] nicechandoo@gmail.com,[3] profnaidu90@gmail.com

***Abstract***: The study on low-cost biosorbent such as *Anacardium occidentale* testa powder was used to remove chromium from aqueous solutions. Based on $R^2$ values, the Langmuir ($R^2$ = 0.9927) model fitted the equilibrium biosorption data best, confirming monolayer adsorption of chromium on to the biosorbent surface. The biosorption of chromium was best described by pseudo-second order ($R^2$ =0.9902) kinetics since at all concentrations, the $R^2$ values were higher than the corresponding pseudo-first order ($R^2$=0.9278) values.Based on thermodynamic parameters the biosorption of chromium by *Anacardium occidentale* testa powder was found to be spontaneous, endothermic and feasible under optimized conditions.

***Index Terms***: Biosorption, *Anacardium occidentale* testa powder, Chromium, Kinetics and SEM

## I. Introduction

Industries like fuel production units, atomic energy stations, electroplating and fertilizer industry, leather and electrical appliance manufactory, and iron enterprises generate enormous wastes containing large amount of toxic heavy metals discarded into the environment resulting in ecological imbalance [1]. Numerous disorders and diseases are caused by the deposition of heavy metals like lead, mercury, cadmium and chromium at the top of the toxicity list [2]

Chromium exists in several oxidation states, but the most stable and common forms are Cr (0), the trivalent Cr (III), and the hexavalent Cr (VI) species. Cr (VI) in the forms of chromate ($CrO_4^{2-}$), dichromate ($Cr_2O_7^{2-}$), and $CrO_3$ are considered the most toxic forms of chromium, as it presents high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in the environment.

The main source of Cr (VI) ions are produced from industries like plating, alloying, tanning, water corrosion, textile, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber industries[3]. Cr-VI ions are more toxic than Cr-III ions, Cr (VI) ions are powerful epithelial irritant and also considered as a human carcinogen. Cr (VI) ions are toxic to many plants [4] aquatic animals [5] and microorganisms [6]. It also been reported that human kidney and liver are damaged due to high chromium dosage[7] and in low doses it causes skin irritation and ulceration[8]. Many studies identified that 10 ppm Cr (VI) ions as the threshold at which not more than 10% of exposed individuals developed skin sensitization. Chronic health effects are observed in human population when exposed to approximately 20,000 μg Cr-VI/L in drinking water contaminated by a ferrochrome plant caused mouth sores, diarrhea, stomach pain, indigestion, vomiting, and higher levels of white blood cells than the reference population. Environmental Protection Agency has concluded that the only chromium (VI) should be classified as a human carcinogen. Exposure to chromium (VI) ions resulted in complications during pregnancy and child birth. In aquatic ecosystems chromium causes hardness, rise in temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations [9,10]. In animals $Cr^{+6}$ produced cancers, reproductive harm, behavioral changes, reduced growth and survival using experimental doses through food, water or injections. Metallic Cr and $Cr^{+3}$ are non-toxic [11].When plants are exposed to excess chromium, toxic effects are reduced growth, decreased chlorophyll production causing yellow leaves, narrow leaves, small root systems, decreased or complete inhibition of seed germination, delayed growth, decreased seed yield, wilting and death [12, 13].EPA has a drinking water standard of 0.1 milligrams per liter (mg/l) or 100 parts per billion (ppb) for total chromium.

Among many conventional techniques[14], adsorption is very attractive owing to its easy operation and high efficiency to treat water contaminated with low concentrations of heavy metals, i.e.,<100mg/L.Continuous attempts were developed to produce low-cost adsorbents derived from industrial, agricultural and aquatic wastes e.g., cucumber peel [15],rapeseed biomass [16],cotton stalk and peanut hull [17],olive tree pruning waste [18],pine tree cone [19],Sea shell[20], forest by-products and waste[21,22] algae[23],fungi[24] agricultural waste[25].Activated carbon[26]. Agricultural biomass wastes are promising raw materials since they are increasingly generated.

*Anacardium occidentale* testa powder can be used as a potential source of biosorbent. It belongs to the family *Anacardiaceae*, native to Northeast Brazil, India, Southeast Asia and Africa. The Cashew nut is an high value product from this tree but the testa is one of the by-products obtained from processing of cashew nuts, and it is not been considered as animal feed. The cashew nut testa is a reddish-brown skin that covers the cashew kernel. The skin is reported to be rich in hydrolysable tannins and polyphenols [27]. Polyphenols, extracted from plants, are characterized by the abundant phenolic hydroxyls that are capable of chelating with transition-metal ions, especially for those metal species with *d*-orbits[

Because of the strong chelating ability of phenolic hydroxyls towards transition metals, the polyphenol-based cashew nut testa powder showed to be potential and efficient sorbent for the removal of chromium from aqueous solutions.

## II.Materials and methods

### Preparation of *Anacardium occidentale* testa powder

*Anacardium occidentale* testa was collected from Vetapalem, Prakasam, Andhra Pradesh. The testa were cleanly washed with water and then with distilled water, dried in sun until it became colorless and crispy. They were grinded to powder, separated into desired sizes using BSS sieves and stored in air tight plastic bags.

### Scanning electron Microscope (SEM) studies

The pretreated biosorbent samples were examined in Scanning Electron Microscope and electron probe micro analyzer. The samples were coated with ultra thin film of gold by an ion sputter JFC-1100 and exposed under SEM.The working height was 15 mm with a voltage ranging from 10 to 15 kV.The compositional image analyses of untreated and treated samples as shown in the Figures 1&2 were taken using equipment at 15 kV and 40-100 nA beam current.

### Biosorption studies

The initial concentrations of chromium in the aqueous solutions were analyzed in an Atomic absorption spectrophotometer (Perkin Elmer A Analyst 200 model) and found to be 20 mg/L, wave length is 357.87 nm, and sensitivity check is 4.0 mg/L. The procedures adopted for the biosorption of chromium is optimized by using following parameters.

### Effect of agitation time

50 mL of aqueous solution (initial concentration of chromium was 20 gm/L) was taken in each 250 mL conical flasks and 10 g/L of 53 μm size biosorbent was added and exposed to varying agitation times (3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 min). These samples were shaken on an orbital shaker at 180 rpm at 30$^{\circ}$C for 1 min. These samples were filtered separately with Whatman filter paper and the filtrates were analyzed in AAS to obtain final concentrations of chromium and the equilibrium agitation time was calculated and the data is shown in Figure 3.

### Effect of biosorbent size

10 g/L of biosorbent of different sizes (53, 75, 105, 125 and 152 μm) were added to 250 mL conical flasks containing each 50 mL of aqueous solution and the contents were agitated in an orbital shaker. The optimum

biosorbent size was determined from the data as shown in Figure 4.

## Effect of pH on the aqueous solution

To study the influence of pH on chromium biosorption, 50 mL of aqueous solution was taken in 250 mL conical flasks. The pH values of the solutions were adjusted to 2, 3, 4, 5, 6, 7 and 8 in separate flasks by adding required amounts of 0.1 N $H_2SO_4$ or 0.1N NaOH. 10 g/L of 53 µm size biosorbent was added separately to these flasks. The samples were shaken on an orbital shaker at $30^oC$ for equilibrium agitation time and the results are depicted as shown in the Figure 5.

## Effect of initial concentration on the chromium in aqueous solution

50 mL of aqueous solution was taken in a 250 mL conical flask using different concentrations (20, 50, 80, 120 and 150 mg/L) and 10 g/L of 53 µm size biosorbent was added. The sample was kept in continuous contact for equilibrium agitation time by shaking on an orbital shaker at $30^0C$ and the results were depicted as shown in the Figure 6.

## Effect biosorbent dosage

The experiments were repeated for the dosages ranging from (0.25, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5 and 3.0g) of 53 µm size biosorbent for equilibrium agitation time. From these data, optimum biosorbent dosage was identified and the results were depicted as shown in the Figure7.

## Effect of temperature

50 mL of aqueous solution containing 20 mg/L of chromium was taken in 250ml of conical flasks. 10 g/L of 53 µm size adsorbent was added in each of these flasks and were shaken in an orbital shaker for equilibrium agitation time for five different temperatures (283, 293, 303, 313 and 323K) and the results were depicted as shown in the Figure 8.

## Kinetic and thermodynamics studies

In order to determine the order of the biosorption rate, 50 mL of aqueous solution containing 20 mg/L of chromium was taken in each of twelve conical flasks. 10 g/L of 53 µm size biosorbent was added in each flask. The conical flasks were shaken on an orbital shaker for different time intervals at $30^0C$. They were settled, filtered and the filtrates were analyzed to find the final concentrations of chromium. The effect of temperature (283-323K) on biosorption rate and evaluation of the enthalpy of adsorption (ΔH), entropy of adsorption (ΔS) and Gibbs free energy (ΔG) were determined.

## III.Results and discussion

The potential of dry *Anacardium occidentale* testa powder as a biosorbent for the biosorption of chromium metal present in an aqueous solution is determined. The effects of various parameters on biosorption of chromium are studied. The measured data consists of initial and final concentration of chromium in the aqueous solution, agitation time, biosorbent dosage, biosorbent size, pH of the aqueous solution and temperature of the aqueous solution. The experimental data are obtained by conducting batch experiments.

**SEM analysis for untreated and chromium treated *Anacardium occidentale* testa powder**

The analysis of untreated *Anacardium occidentale* testa powder as shown in Figure1 indicates that the powder is devoid of chromium. The Figure 2 shows the analysis of *Anacardium occidentale* testa powder loaded with chromium. The SEM analysis shows variation in the surface structure compared to unloaded one. Irregular spikes are accumulated on the surface and porous structure is also noticed indicating biosorption of chromium by *Anacardium occidentale* testa powder.
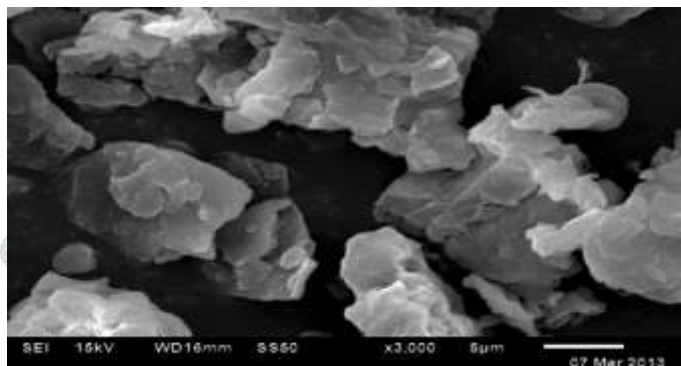


**Fig.1** Electron micrographs of untreated *Anacardium occidentale* testa powder
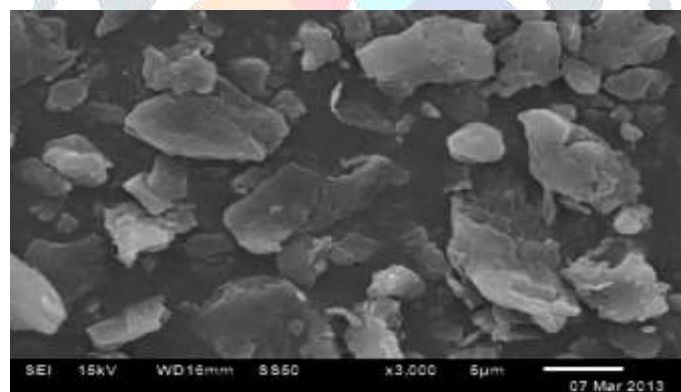


**Fig.2** Electron micrographs of chromium treated *Anacardium occidentale* testa powder

**Effect of agitation time**

Duration of equilibrium biosorption is defined as the time required for heavy metal concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the % biosorption of chromium against agitation time as shown in Figure 3, for the interaction time intervals between 1 to 180 min. For 53 μm size of 10 g/L biosorbent dosage, 41.46 % (2.058 mg/g) of chromium is biosorbed in the first 5 min. The % biosorption is increased briskly up to 40 min reaching 59.16 % (2.958 mg/g). Beyond 50 min, the % biosorption is constant indicating the attainment of equilibrium conditions [28, 29].
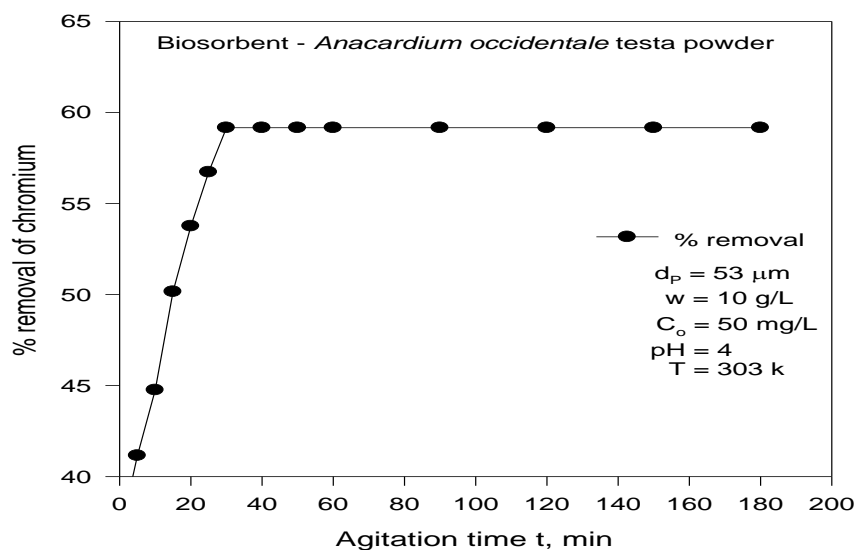
**Fig.3** Effect of agitation time on % biosorption of chromium

The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of chromium. As time increases, more amount of chromium gets biosorbed onto the surface of the biosorbent due to Vanderwaal's forces of attraction and resulted in decrease of available surface area. The biosorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the biosorbent capacity is exhausted. The maximum percentage of biosorption is attained at 40 minutes. The percentage biosorption of chromium becomes constant after 40 min. Therefore, all other experiments are conducted at this agitation time.

**Effect of biosorbent size**

The variations in % biosorption of chromium from the aqueous solution with biosorbent size are obtained.The results are drawn in Figure 4 with percentage biosorption of chromium as a function of biosorbent size. The percentage biosorption is increased from 42.72 (2.136 mg/g) to 59.08 (2.954 mg/g) as the biosorbent size decreases from 150 to 53 μm.  This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the numbers of active sites on the biosorbent are better exposed to the biosorbate.
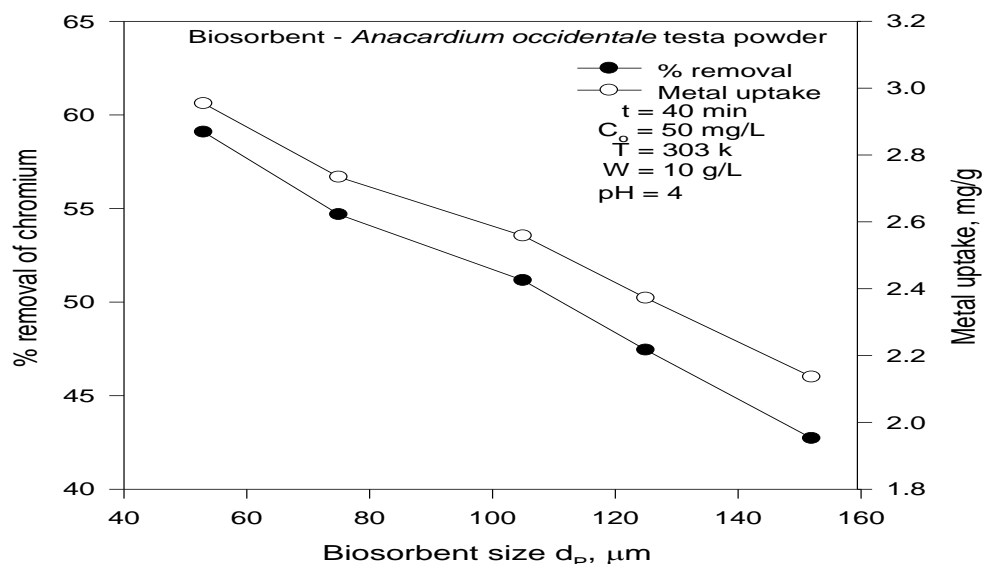
**Fig.4** Effect of biosorbent size on % biosorption of chromium

## Effect of pH

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of biosorbate. In the present investigation, chromium biosorption data are obtained in the pH range of 2 to 8 of the aqueous solution ($C_0$= 50 mg/L) using 10 g/L of 53 μm size biosorbent and is shown in Figure 5. The % biosorption of chromium is increased from 50.64 % (2.532 mg/g) to 65.36 % (3.268 mg/g) as pH is increased from 2 to 5 and decreased beyond the pH value of 5 % biosorption is decreased from pH 6 to 8 reaching 63.52 % (3.176 mg/g) from 52.72 % (2.636 mg/g). Low pH decreases biosorption due to competition with $H^+$ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Chromium ions replace $H^+$ ions bound to the biosorbent [30, 31]
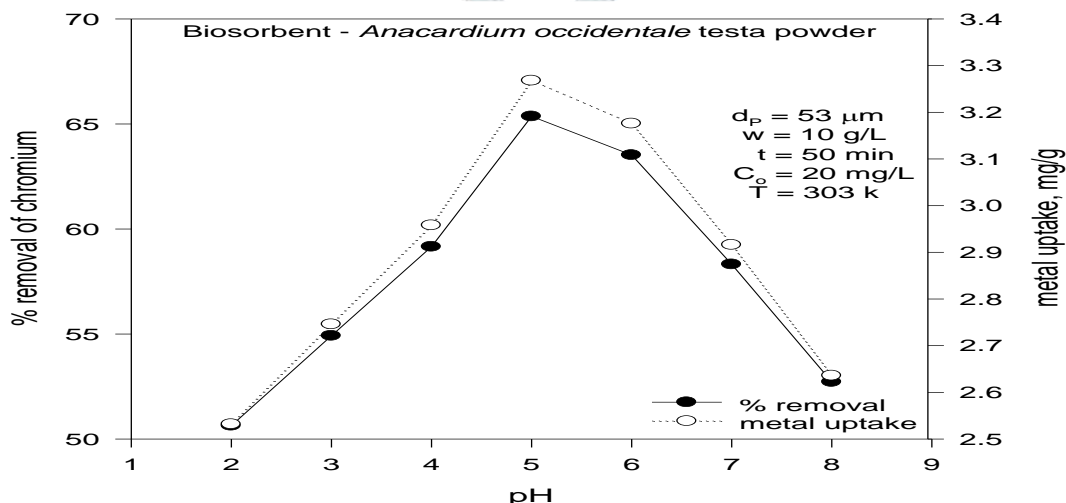


**Fig.5** Effect of pH on % biosorption of chromium

**Effect of initial concentration for the biosorption of chromium**

The effect of initial concentration of chromium in the aqueous solution on the percentage biosorption of chromium is shown in Figure 6. The percentage biosorption of chromium is decreased from 65.60 % (0.8375 mg/g) to 43.99 % (2.0492 mg/g) with an increase in $C_0$ from 20 mg/L to 200 mg/L [32]. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent.
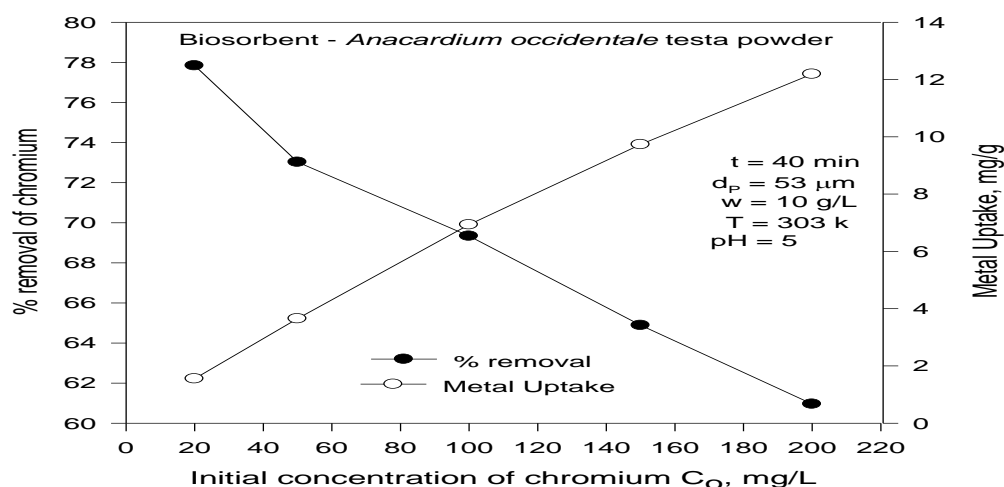


**Fig.6** Effect of initial concentration for the biosorption of chromium

**Effect of biosorbent dosage**

The percentage biosorption of chromium is drawn against biosorbent dosage for 53 μm size biosorbent in Figure7. The biosorption of chromium increased from 62.30 % (2.4920 mg/g) to 75.90 % (0.6072 mg/g) with an increase in biosorbent dosage from 5 to 25 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for chromium biosorption would be more. The change in percentage biosorption of chromium is marginal from 75.90 % (0.6072 mg/g) to 78.40 % (0.3136 mg/g) when 'w' is increased from 25 to 50 g/L. Hence all other experiments are conducted at 25 g/L dosage [33, 34].
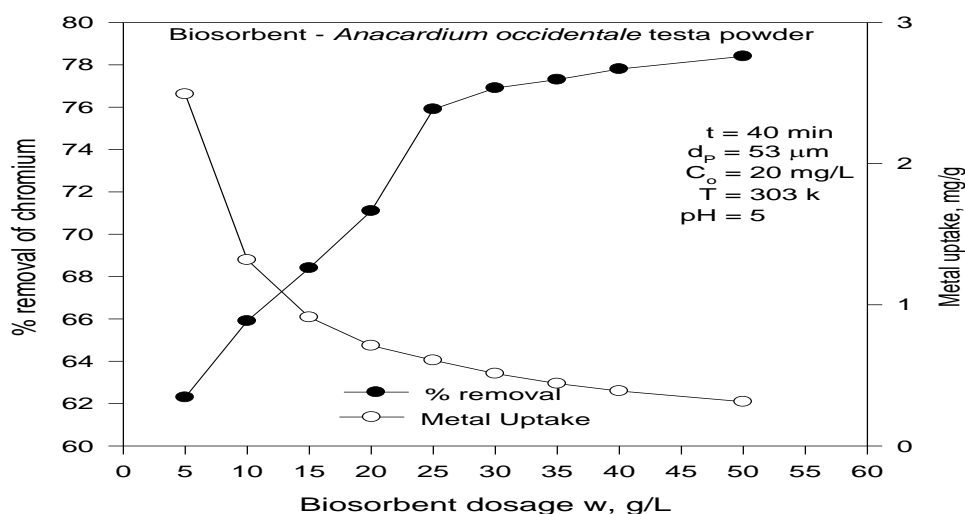
**Fig.7** Effect of biosorbent dosage on % biosorption of chromium

## Effect of Temperature

The effect of temperature on the equilibrium metal uptake was significant. The effect of changes in the temperature on the chromium uptake is shown in Figure 8.
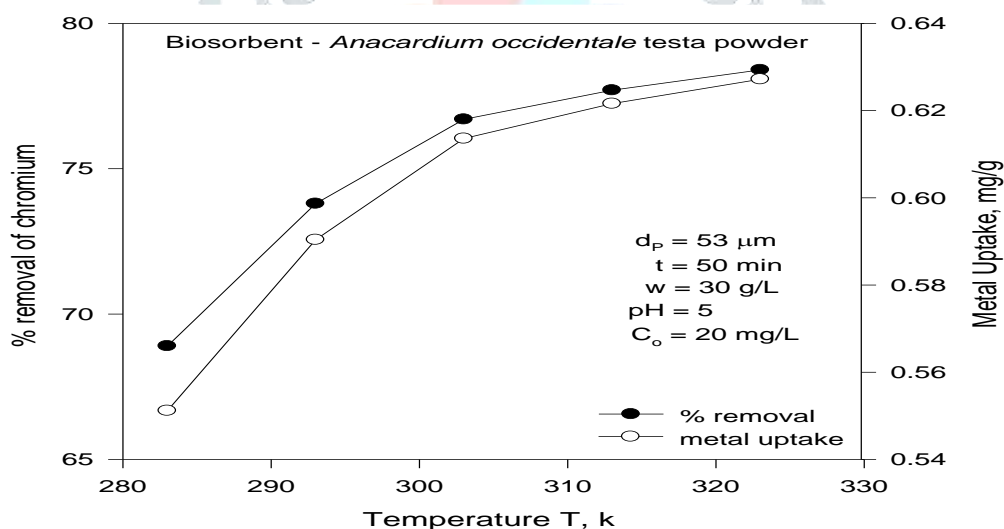


**Fig.8** Effect of temperature for the biosorption of chromium

When temperature was lower than 303 K, Chromium uptake increased with increasing temperature, but when temperature was over 303 K, the results were on the contrary. This response suggested a different interaction between the ligands on the cell wall and the metal. Below 303 K, chemical biosorption mechanisms played a dominant role in the whole biosorption process; biosorption was expected to increase by increase in the temperature [33, 34], while at higher temperature, the % biosorption increased is very minute and marginal.

**Isotherms for biosorption of chromium using *Anacardium occidentale* Testa Powder**

**Langmuir isotherm**

Langmuir isotherm [35] is drawn for the present data and shown in Figure 9. The equation obtained 'n' $C_e/q_e$ = 0.06843 $C_e$ + 5.05471 with a good linearity (correlation coefficient, $R^2 \sim 0.9927$) indicating strong binding of chromium ions to the surface of *Anacardium occidentale* testa powder.
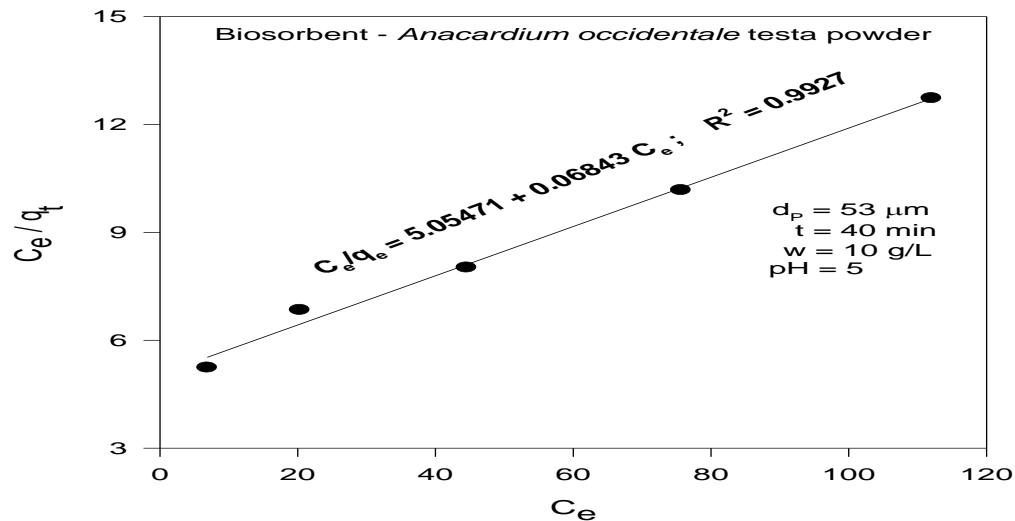


**Fig.9** Langmuir isotherm for biosorption of chromium

**Freundlich isotherm**

Freundlich isotherm [36] is drawn between ln $q_e$ and ln $C_e$ and is shown in Figure 10 and the resulted equation is ln $q_e$ = 0.69709 ln $C_e$ − 1.02833; the resulting equation has a correlation coefficient of 0.9920. The 'n' value in the above equations satisfies the condition of $0 < n < 1$ indicating favorable biosorption.
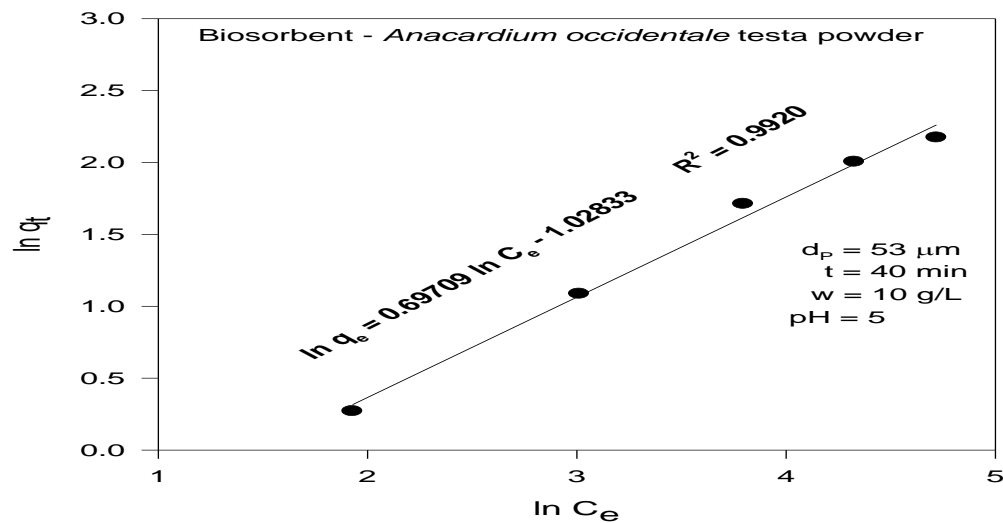
**Fig.10** Freundlich isotherm for biosorption of chromium

## Temkin isotherm

The present data are analyzed according to the linear form of Temkin isotherm [37] and the linear plot is shown in Figure11.The equation obtained for chromium biosorption is $q_e = 2.73474 \ln C_e - 4.5133$ with a correlation coefficient 0.9697.The best fit model is determined based on the linear regression correlation coefficient (R). From the Figures 9, 10 and11 it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9927, followed by Freundlich and Temkin isotherms with correlation coefficients of 0.9920 and 0.9697 respectively as shown in Table.1.
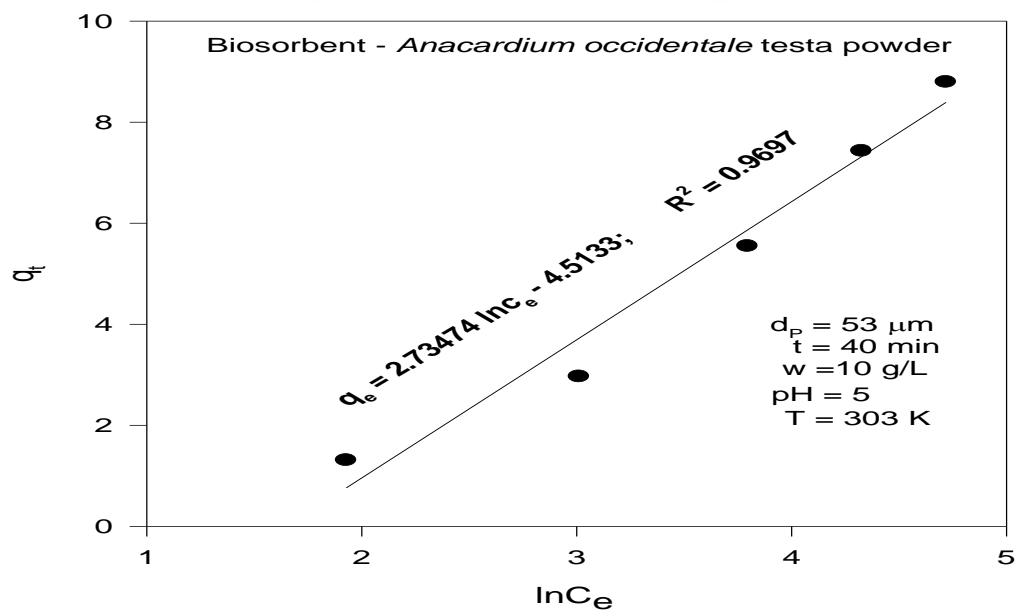


**Fig.11**Temkin isotherm for biosorption of chromium

**Table1**

**Isotherms constants**

| Langmuir | Freundlich | Temkin |
|---|---|---|
| $q_m = 14.613$ | $k_f = 0.3576$ | $A_T = 0.2287$ |
| $b = 0.0135$ | $n = 0.69709$ | $b_T = 3613.79$ |
| $R^2 = 0.9927$ | $R^2 = 0.9920$ | $R^2 = 0.9697$ |

**Kinetics of biosorption**

In the present study, the kinetics are investigated with 50 mL of aqueous solution ($C_0 = 20$ mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagergren [38] plots of log ($q_e$-$q_t$) versus agitation time (t) for biosorption of chromium the biosorbent size (53 μm) of *Anacardium occidentale* testa powder in the interaction time intervals of 1 to 180 min, first order kinetics and second order kinetics are drawn in Figures12,13
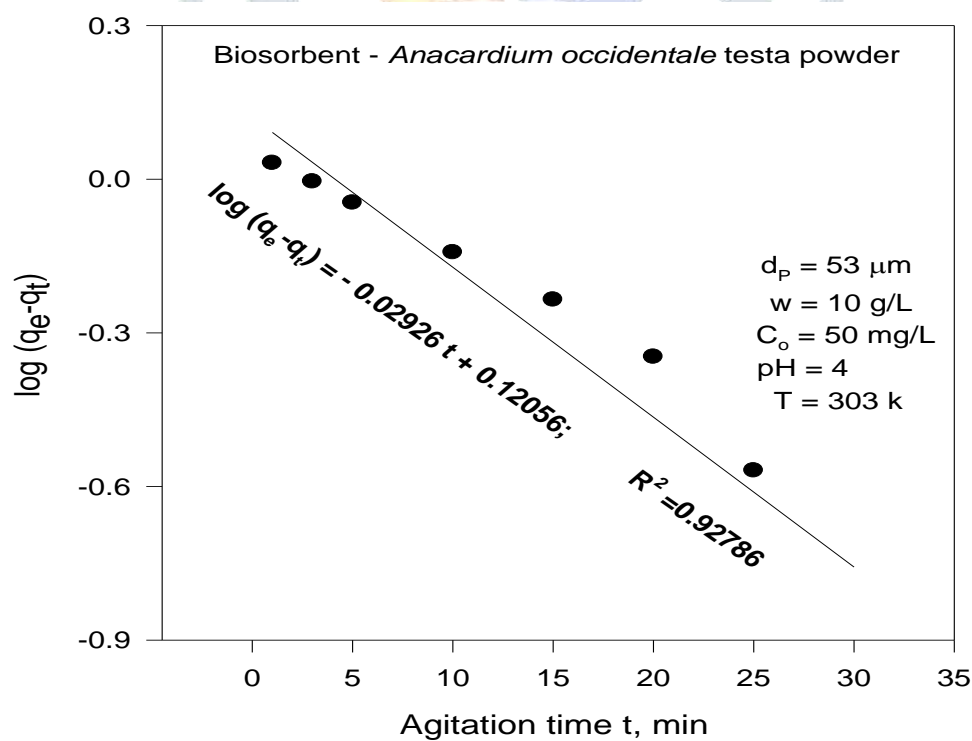


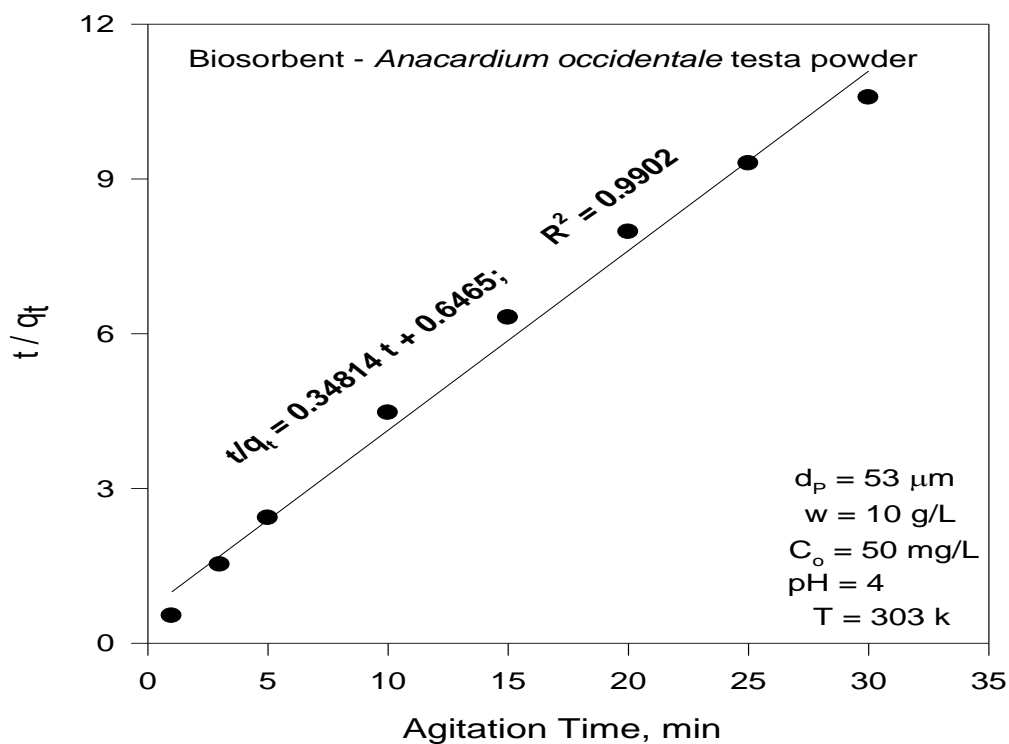**Fig.12** First order kinetics for biosorption of chromium

**Fig.13** Second order Kinetics for biosorption of chromium

**Table2**

**Equations and rate constants**

| Order | Equation | Rate constants | $R^2$ |
|---|---|---|---|
| Lagergren first order | $\log(q_e-q_t)=-0.02926\,t-0.12056$ | $0.06738\ min^{-1}$ | 0.9278 |
| Pseudo second order | $t/q_t=0.3481\,t+0.6465$ | $0.1874\ g/(mg\text{-}min)$ | 0.9902 |

As the correlation coefficient value for the pseudo second order kinetics **[39]** is 0.9902, we can say that the pseudo second order kinetics describes the mechanism of chromium using *Anacardium occidentale* testa powder interactions are better.
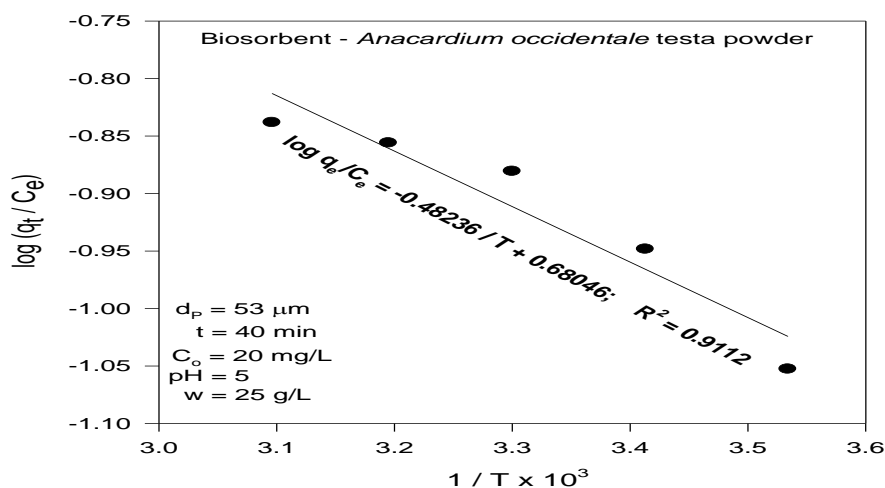
**Thermodynamics of biosorption**



**Fig.14** Van'thoff plot for biosorption

Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The Van'thoff plot indicating the effect of temperature on biosorption of chromium is shown in Fig.14. In the present investigation, $\Delta H$ = 9.2358 J/mole, $\Delta S$ = 13.0288 J/mole-K and $\Delta G$ = –3938.50876 J/mole.$\Delta H$ is positive indicating that the biosorption is endothermic. The negative value of $\Delta G$ indicates the spontaneity of biosorption. As $\Delta S$ is more than zero, it indicates the irreversibility of biosorption.

## IV.Conclusion

The *Anacardium occidentale* testa powder was used as an effective low cost biosorbent for the removal of chromium in aqueous solution. The equilibrium agitation time for chromium biosorption was 40 minutes. The percentage removal of chromium increased significantly with an increase in biosorbent dosage from 5 to 25 g/L at pH 5 and with an increase in the initial concentration of chromium in the aqueous solution, the percentage removal of chromium from the aqueous solution is decreased. In the range of variables optimized, percentage removal of chromium increased from 37.64 % (1.882 mg/g) to 78.4 % (0.6272 mg/g). The maximum uptake capacity of 14.613 mg/g is obtained at 303 K. Langmuir equilibrium isotherm model proved to be good fit for the experimental data of chromium biosorption on *Anacardium occidentale* testa powder. The kinetics of the biosorption of chromium described by a pseudo-second-order kinetic model with $R^2$0.9927. Free energy change (D$G°$) with negative sign reflectsthe feasibility and spontaneous nature of the process. The positive enthalpy values indicate endothermic in nature. *Anacardium occidentale* testa powder can be used in cleaning chromium polluted water and it is eco-friendly, effective, affordable.

## Acknowledgments

## Competing interests

The authors declare no competing interests.

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