

Original Research Article

Effective removal of Cr (VI) from aqueous solutions using rind of Orange (*Citrus sinensis*), (L.) Osbeck

Anukthi C. Poojari¹, Sandip D. Maind² and Satish A. Bhalerao^{1*}

¹Environmental Sciences Research Laboratory, Department of Botany, Wilson College, Mumbai-400007, University of Mumbai, Maharashtra, India

²Department of Chemistry, Bhavan's Hazarimal Somani college of Arts and Science, Kulapati K.M. Munshi Marg, Chowpatty, Mumbai-400007, University of Mumbai, Maharashtra, India

*Corresponding author

A B S T R A C T

The effective removal of Cr (VI) from aqueous solutions in a batch system using of low-cost biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck was studied. The FTIR study of acid treated biosorbent showed that the possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The SEM represents a porous structure with large surface area. The effects of operational factors including solution pH, biosorbent dose, initial Cr (VI) concentration, contact time and temperature were studied. The optimum solution pH for Cr (VI) biosorption by biosorbent was 2.0 with the optimal removal 71.01 %. The adsorbent dose 5 mg/ml was enough for optimal removal of 73.91 %. The equilibrium was achieved after 150 minutes of contact. The equilibrium data were well described by typical Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin adsorption isotherms. Sorption equilibrium exhibited better fit to Langmuir isotherm ($R = 0.9986$) than Freundlich isotherm ($R = 0.9153$), Temkin isotherm ($R = 0.8903$) and Dubinin-Kaganer-Redushkevich (DKR) isotherm ($R = 0.7413$). The maximum adsorption capacity determined from Langmuir isotherm was found to be 10.7411 mg per g of biosorbent. Furthermore, to determine the adsorption mechanism, a detailed analysis has been conducted by testing kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber & Morris intra-particle diffusion rate equation. Results clearly indicates that the pseudo-second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. Thermodynamic study revealed that the biosorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. The rind of Orange (*Citrus sinensis*), (L.) Osbeck used successfully for removal of Cr (VI) from aqueous solutions, can be used very promisingly for industrial wastewater treatment.

Keywords

Effective removal, Chromium (VI), Rind of Orange (*Citrus sinensis*), (L.) Osbeck FTIR, SEM, Adsorption isotherms, Adsorption kinetics, Thermodynamic study

Introduction

Environmental pollution by heavy metals due to industrial activities tends to persist indefinitely circulating and eventually accumulating throughout the food chain which results in serious ecological and health hazard. This problem that needs to be solved. Heavy metals are non-biodegradable and toxic to all forms of life including humans. Chromium is listed among top pollutants and is ranked 16th harmful pollutant due to its carcinogenic and teratogenic characteristics on the community (Selomulya et al 1999; Geleel et al 2013). Chromium occurs frequently as Cr (VI) and Cr (III) in aqueous solutions (Dakiky et al 2002). Hexavalent chromium, which is primary present in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) possesses significantly higher level of toxicity than the other valence states (Smith and Lec 1972; Sharma et al 1995). Cr (VI) discharge into the environment can be due to various large numbers of industrial functions like dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, etc (Patterson 1985). Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lung cancer. Due to the several toxicity of Cr (VI), the EU Directive, WHO and US EPA have set the maximum contaminant concentration level for Cr(VI) in domestic water supplies as 0.05 ppm (Directive 98/83/EC). So, the removal of Cr (VI) from water and wastewater is important to protect environment.

The conventional methods for removing heavy metal ions from industrial effluents include oxidation/reduction, filtration by membranes, chemical precipitation, coagulation, solvent extraction, cementation, freeze separation, reverse osmosis, ion-

exchange, electro-dialysis, electro-winning and electro-coagulation (Ahluwalia and Goyal 2007). These methods have found limited application because they often involve high capital and operational cost. Treatment of industrial effluent with sorbents of biological origin is simple, comparatively inexpensive and friendly to the environment. Biosorption of heavy metals is very effective, versatile, powerful, most efficient and cost effective technologies involved in the removal of heavy metals from industrial effluents. Biosorption is the process based on the principle of metal binding capacities of biological materials.

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions. Use of low cost biosorbent for biosorption study of heavy metals is very advantageous (Maind et al 2012 ;Maind et al 2013). Among the various resources in biological waste, both dead and live biomass, exhibit particularly interesting metal-binding capacities. The use of dead biomass eliminates the problem of toxicity and the economics aspects of nutrient supply and culture maintenance (Pino et al 2006). A variety of biosorbents, including leaf mould (Sharma and Forster 1994), pongamia leaf (Shivamani and Prince 2008), algae (Gupta et al 2001), bacteria (Loukidou et al 2004), tamarindus indica seeds (Agarwal et al 2006), activated carbon (Selvi et al 2001, Quintelas et al 2008; Saran et al 2013), rice husks (Srinivasan et al 1988), quarternised rice husk (Low and Lee 1999), hazelnut shell (Koby 2004), almond shell (Candela et al 1995), corn cob (Bosico et al 1996), quaternised wood (Low and Lee 2001), groundnut husk (Periasamy et al 1991), coconut husk and palm pressed fibers (Tan et al 1993), coconut shell (Alaerts et al

1989), coconut jute (Chand et al 1994), coconut tree sawdust (Selvi et al 2001), native and immobilized sugarcane bagasse (Ullah et al 2013), synthetic material (Yu et al 2013), inorganic materials (Rosales-Landeros 2013), have been used for Cr (VI) removal.

Natural materials that are available in large quantities or certain waste products from industrial and agricultural operations may have potential as inexpensive sorbents. The rind of Orange (*Citrus sinensis*), (L.) Osbeck being one of the highest production fruit in Maharashtra state of India and in juice making industry produced large amounts of waste which has no commercial value. The rind of Orange (*Citrus sinensis*), (L.) Osbeck was selected because of a low cost, higher biosorption capacity, possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. due to high cellulose, pectin, hemicellulose and lignin content, which favours biosorption of heavy metals.

The aim of this study is to characterize the biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck by FTIR and SEM which helps to find out the functional groups which is responsible biosorption of Cr (VI) and porosity of the biosorbent. The main objective of this work was to evaluate the biosorption capacity of rind of Orange (*Citrus sinensis*), (L.) Osbeck for the effective removal of Cr (VI) from aqueous solutions by varying solution pH, biosorbent dose, initial Cr (VI) concentration, contact time and temperature. Equilibrium adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) for adsorption of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck were described. Kinetic models (pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intra-

particle diffusion rate equation) were employed to understand the probable adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0).

Materials and Methods

Chemicals and reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute sulphuric acid and dilute sodium hydroxide.

Preparation of Cr (VI) solution

The stock solution of 1000 ppm of Cr (VI) was prepared by dissolving 0.7072 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) (previously dried at 50⁰C for one hour) in 250 ml of double distilled water and further desired test solutions of Cr(VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent

The Orange (*Citrus sinensis*), (L.) Osbeck was collected locally and rind of Orange washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material & water soluble impurities and water was squeezed out. The washed biosorbent was then dried at 50⁰C overnight and grounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 μ m will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M sulphuric acid for 1 hour.

The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This filtered biomass was first dried, at room temperature and then in an oven at 105°C for 1-2 hrs. For further use, the dried biomass was stored in air tight plastic bottle to protect it from moisture.

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biomass samples were examined using FTIR spectrometer (model: FT/IR-4100 type A) within range of 400-4000 cm^{-1} . All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure.

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis:

The Scanning Electron Microscope (SEM) was used to see the porosity of the biosorbent. The samples were covered with a thin layer of gold and an electron acceleration voltage of 10 KV was applied and then Scanning Electron Micrograph was recorded.

Experimental procedure

The static (batch) method was employed at temperature (30°C) to examine the biosorption of Cr (VI) by biosorbent. The method was used to determine the biosorption capacity, stability of biosorbent and optimum sorption conditions. The parameters were studied by combining 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, centrifuged, the content was separated from the biosorbents by filtration, using Whatmann filter paper and amount of Cr (VI) in the supernatant/filtrate solutions was determined.

Estimation of Cr (VI) concentration

A 0.2 % w/v solution of 1,5-Diphenylcarbazide was prepared in acetone containing 1 ml of H_2SO_4 (1:9). Known volume of sample solution containing Cr (VI), was pipetted out into 250 ml beaker and 3 to 4 drops of 0.02 % KMnO_4 solution added and covered the beaker with watch glass. The solution was heated without boiling for 15 minute. The acidity of the solution was made 0.05 M to 0.1 M by H_2SO_4 . If the pink color disappears in the course of heating, more KMnO_4 solution was added. The excess of oxidant was reduced by adding 1 % sodium azide solution drop wise. The solution was cooled and transferred in a 50 ml volumetric flask and 5 ml of 0.2 % w/v solution of 1,5-Diphenylcarbazide was added. The solution was diluted with water to 50 ml standard measuring flask. Cr (VI) concentration was estimated by measuring absorbance of the pink color, Cr-diphenylcarbazide complex at 545-nm against water as a blank using a UV-visible spectrophotometer. A linear plot for standard Cr (VI) solution was obtained indicating adherence to the Beers Lambert's law in the concentration range studies and amount of Cr (VI) in the samples were estimated. The amount determined was a mean of triplicate sample analysis with standard deviation less than 5 %. The blank solution i.e. solution containing biosorbent without Cr (VI) was tested and results shows that no any appreciable signal of intensity at wavelength 545-nm obtained.

Instrumentation and data analysis

The concentration of Cr (VI) in the solutions before and after equilibrium was determined by measuring absorbance using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820). The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode.

The data obtained in the batch biosorption studies were used to calculate the percentage biosorption of Cr (VI) by using the mass balance relationship. The Cr (VI) concentrations biosorbed on the solid 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 adsorption (% Ad) of Cr (VI) by the biosorbent,

$$\% \text{ Ad} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the Cr (VI) in mg/L.

Adsorption isotherms

A series of solutions containing different initial concentrations of Cr (VI) were prepared and the batch biosorption studies were done at 30°C to check the applicability of the adsorption isotherms under the specified condition, the solution pH of 2.0, biosorbent dose of 5 mg/ml, an initial Cr (VI) concentration range 5 mg/L - 250 mg/L and contact time 180 min. Analysis of Cr (VI) content in various solutions were performed by UV-Visible spectrophotometer method. The data obtained in batch biosorption studies was used to calculate the equilibrium Cr (VI)

biosorptive quantity by the following equation:

$$q_e = \frac{(C_i - C_e)}{w} \times V \quad (2)$$

where q_e (mg metal per g dry biosorbent) is the amount of Cr (VI) biosorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Adsorption kinetics

The kinetic measurements were conducted by employing biosorption dose of 5 mg/ml of biosorbent contacted with 10 mg/L of a Cr (VI) solution with optimum pH 2.0 and temperature 30°C in a rotary shaker. The concentration of Cr (VI) in the solution was determined at known time intervals. Analysis of Cr (VI) content in various solutions was performed by UV-visible spectrophotometer. The amount of Cr (VI) biosorbed q_t (mg/g) at time t was calculated by Eq. (2).

Result and Discussion

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in Fig.1. (a and b). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The broad peak at 3421 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the -OH groups bound to methyl groups presented in the signal at 2924 cm^{-1} . The peaks at 2361 cm^{-1} and 2343 cm^{-1} are stretching peaks. The peaks located at 1733 cm^{-1} and 1636 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the

presence of carboxyl acid groups in the biomass. The peak at 1508 cm^{-1} is associated with the stretching in aromatic rings. The peaks observed at 1074 cm^{-1} are due to C-H and C-O bonds. The -OH, NH, carbonyl and carboxyl groups are important sorption sites (Volesky 2003). As compared to simple biosorbent, biosorbent loaded with Cr (VI) ions, the broadening of -OH peak at 3421 cm^{-1} and carbonyl group peak at 1636 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of Cr (VI).

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface characteristics, structure and particle size distribution of biosorbent before and after biosorption was examined using Scanning Electron Microscope (SEM). The SEM micrographs are shown in Fig. 2. (a and b). These micrographs represent a porous structure with large surface area. The SEM clearly demonstrated that there is more uniformity after biosorption on metal ions in comparison to before biosorption. It was evident from the micrographs that the biosorbent presents an unequal structure before metal biosorbed. The number of canals in the biosorbent was higher in the initial case. The metal ions adsorbed on the cell wall matrix and created stronger cross linking and uniformity on the surface of biosorbent.

Effect of pH

The biosorption capacity of the adsorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 1-8 for biosorption of Cr(VI) and pH trend observed in this case is shown in Fig. 3. It was found that at pH 2 the biosorption

process was maximum with 71.01 % and after increasing pH, adsorption was decreased. According to the solubility equilibrium of chromium, HCrO_4^- is the dominant species of Cr (VI) at a pH 2. As the pH increases, the dominant form of chromium becomes CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Furthermore, the surface of biosorbent may be positively charged at pH 2. Therefore, at this pH it is likely to be biosorbed Cr (VI) onto biosorbent through electrostatic attraction and /or by the binding of HCrO_4^- to acidic functional groups on the surface of biosorbent. Also at pH 2, the number of protons available on the surface of biosorbent increases, which increases the attraction between HCrO_4^- & biosorbent and increases the biosorption capacity (Rao et al 1992). As the pH of the solution increases, charges on the surface of biosorbent becomes negative, this leads to generation of repulsive forces between Cr (VI) & biosorbent and inhibits biosorption and resultantly percent Cr(VI) uptake may decrease.

Effect of biosorbent dose

Effect of biosorbent dose of metal ions biosorption onto biosorbent which is an important parameter was studied while conducting batch adsorption studies. The sorption capacity of Cr (VI) on to the rind of Orange (*Citrus sinensis*), (L.) Osbeck by varying biosorbent dose from 1.0 mg/ml to 15.00 mg/ml is as shown in Fig. 4. From the results it was found that biosorption of Cr (VI) increases with increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available adsorption sites (Naiya et al 2009). The point of saturation for rind of Orange (*Citrus sinensis*), (L.) Osbeck was found at 5

mg/ml of biosorbent dose with 73.91 % of removal efficiency. The decrease in efficiency at higher biosorbent concentration could be explained as a consequence of partial aggregation of biosorbent which results in a decrease in effective surface area for metal uptake (Karthikeyan 2007). The biosorbent dose 5 mg/ml was chosen for all further studies.

Effect of initial chromium (VI) concentration

The effect of initial Cr (VI) concentration from 5 mg/L - 250 mg/L on the removal of Cr (VI) from aqueous solutions at biosorbent dose 5 mg/ml and at optimum pH 2.0 at 30°C temperature was studied and shown in Fig. 5. On increasing the initial Cr (VI) concentration, the total Cr (VI) ions uptake decreased appreciably when Cr (VI) concentration increases from 5 mg/L - 250 mg/L.

Effect of contact time

Contact time plays an important role in affecting efficiency of biosorption. Contact time is the time needed for biosorption process to achieve equilibrium when no more changes in biosorptive concentration were observed after a certain period of time. The contact time which is required to achieve equilibrium depends on the differences in the characteristics properties of the biosorbents. In order to optimize the contact time for the maximum uptake of Cr (VI), contact time was varied between 10 minutes– 180 minutes on the removal of Cr (VI) from aqueous solutions in the concentration of Cr (VI) 10 mg/L, biosorbent dose 5 mg/ml, optimum pH 2.0 and 30°C temperature (Fig. 6.). The results obtained from the biosorption capacity of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck showed that the biosorption

increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of Cr (VI) onto the rind of Orange (*Citrus sinensis*), (L.) Osbeck was 150 minutes with maximum biosorption. The rapid uptake of Cr (VI) is due to the availability of ample active sites for sorption. A further increase in the contact time has a negligible effect on the biosorption capacity of Cr (VI) biosorption. So a contact time of 150 minutes was fixed for further experiments.

Adsorption isotherms

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm (Langmuir 1918)

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by;

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where q_m is the maximum biosorption capacity of biosorbent (mg g⁻¹). b is the Langmuir biosorption constant (L mg⁻¹) related to the affinity between the biosorbent and sorbate.

Linearized Langmuir isotherm allows the calculation of biosorption capacities and Langmuir constants and is represented as;

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (4)$$

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig. 7 (a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m , b and regression coefficient (R^2) are listed in Table 1.

Maximum biosorption capacity of adsorbent (q_m) is found to be 10.7411 mg per g of biosorbent which is higher than the other biosorbents used by many authors.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation;

$$R_L = \frac{1}{1 + bC_i} \quad (5)$$

where b is the Langmuir constant and C_i is the maximum initial concentration of Cr (VI). The value of separation parameters R_L provides important information about the nature of biosorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.1503-0.8984 for concentration of 5 mg/L -250 mg/L of Cr (VI). They are in the range of 0-1 which indicates favorable biosorption (Malkoc and Nuhoglu 2005).

Biosorption can also be interpreted in terms of surface area coverage against initial metal ion concentration and separation factor. Langmuir model for surface area of biosorbent surface has been represented in the following equation:

$$bC_i = \frac{\theta}{1 - \theta} \quad (6)$$

where θ is the surface area coverage. The θ was found to be 0.1015-0.8496 for

concentration of 5 mg/L -250 mg/L of Cr (VI).

Freundlich adsorption isotherm (Freundlich 1906)

Freundlich equation is represented by;

$$q = KC_e^{1/n} \quad (7)$$

where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.

Linearized Freundlich adsorption isotherm was used to evaluate the biosorption data and is represented as,

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (8)$$

Equilibrium data for the biosorption is plotted as $\log q_e$ vs $\log C_e$, as shown in Fig. 7 (b). The two constants n and K are calculated from the slope ($1/n$) and intercept ($\log K$) of the line, respectively. The values of K , $1/n$ and regression coefficient (R^2) are listed in Table 1.

The n value indicates the degree of non-linearity between solution concentration and biosorption as follows: if $n = 1$, then biosorption is linear; if $n < 1$, then biosorption is chemical process; if $n > 1$, then biosorption is a physical process. A relatively slight slope and a small value of $1/n$ indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 2.7878. Since $n > 1$, this indicates the physical biosorption of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck. The higher value of K (3.9801) indicates the higher biosorption capacity of the biosorbent.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich 1947)

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{9}$$

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;

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{10}$$

Equilibrium data for the biosorption is plotted as $\ln q_e$ vs ε^2 , as shown in Fig. 7 (c). The two constants β and q_m are 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.

$$E = \frac{1}{\sqrt{-2\beta}} \tag{11}$$

The values of q_m , β , E and regression coefficient (R^2) are listed in Table 1.

The mean free energy gives information about biosorption mechanism, whether it is physical or chemical biosorption. If E value lies between 8 KJ mol⁻¹ and 16 KJ mol⁻¹, the biosorption process take place chemically and $E < 8$ KJ mol⁻¹, the biosorption process of the physical in nature (Olivieri and Brittenham 1997).

In the present work, E value (0.4082 KJ mol⁻¹) which is less than 8 KJ mol⁻¹, the biosorption of Cr (VI) onto biosorbent is of physical in nature (Sawalha et al 2006).

Temkin adsorption isotherm (Temkin and Pyzhev 1940):

Linearized Temkin adsorption isotherm is given by the equation:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{12}$$

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. 7 (d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot \ln A_T$) of the line, respectively. The values of A_T , b_T and regression coefficient (R^2) are listed in Table 1.

Adsorption kinetics:

As aforementioned, a lumped analysis of biosorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first-order equation (Lagergren et al 1898) (b) the pseudo-second-order equation (McKay et al 1999) (c) Elovich equation (Chein and Layton 1980) (d) Weber and Morris intraparticle diffusion rate equation (Weber and Morris 1963) are presented below.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{13}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{15}$$

$$q_t = k_i t^{0.5} + c \tag{16}$$

where q_e (mg g⁻¹) is the solid phase concentration at equilibrium, q_t (mg g⁻¹) is the average solid phase concentration at time t (min), K_1 (min⁻¹) and K_2 (g mg⁻¹ min⁻¹) are

the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. K_i ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra particle diffusion rate constant, c is intercept.

If the adsorption follows the pseudo-first-order rate equation, a plot of $\ln (q_e - q_t)$ against time t should be a straight line. Similarly, t/q_t should change linearly with time t if the biosorption process obeys the pseudo-second order rate equation. If the adsorption process obeys Elovich rate equation, a plot of q_t against $\ln t$ should be a straight line. Also a plot of q_t against $t^{0.5}$ changes linearly the biosorption process obeys the Weber and Morris intraparticle diffusion rate equation.

Biosorption of Cr (VI) onto biosorbent was monitored at different specific time interval. The Cr (VI) uptake was calculated from the data obtained. From the Cr (VI) uptake was plotted against time to determine a suitable kinetic model, the biosorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich equation and the Weber & Morris intraparticle diffusion rate equation. The pseudo-first-order equation was plotted for $\ln (q_e - q_t)$ against t (Fig. 8 (a)). The values of q_e and K_1 values were calculated from the slope (K_1) and intercept ($\ln q_e$) of the plot and shown in Table 2. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the adsorbent and the ions adsorbed onto it (Septum et al 2007). The pseudo-second-order equation was plotted for t/q_t against t (Fig. 8 (b)). The values of q_e and K_2 are calculated from the slope ($1/q_e$) and intercept ($1/K_2 q_e^2$) of the plot and values are

shown in Table 2. The pseudo-second-order equation showed a strongest correlation value ($R^2 = 0.9963$) being higher than the correlation coefficient for the Elovich equation, pseudo-first-order and Weber and Morris intraparticle diffusion rate equation. The Elovich equation was plotted for q_t against $\ln t$ (Fig. 8 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($\ln (\alpha \beta)/\beta$) of the plot and values are shown in Table 2. The Elovich equation has been used with the assumption that the actual biosorption surface is energetically heterogeneous (Thomas and Thomas 19970). The Weber & Morris intraparticle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Fig. 8 (d)). The value of k_i and c are calculated from the slope (K_i) and intercept (c) of the plot and values are shown in Table 2. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle pore diffusion is not only rate-limiting step (Weber and Morris 1963). The plot of intraparticle diffusion rate equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of biosorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption (Panday et al 1986).

Thermodynamic study

The effect of temperature on removal of Cr (VI) from aqueous solutions in the Cr (VI) concentration 10 mg/L and biosorbent dose

5 mg/ml with optimum pH 2.0 was studied. Experiments were carried out at different temperatures from 20⁰C-50⁰C. The samples were allowed to attain equilibrium. Biosorption slightly increases from 20⁰C-50⁰C. The equilibrium constant (Catena and Bright 1989) at various temperatures and thermodynamic parameters of biosorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad (17)$$

$$\Delta G^0 = -RT \ln K_c \quad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (19)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration of Cr (VI) in solution (mg/L) and C_{Ae} is the Cr (VI) concentration biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0 , ΔH^0 and ΔS^0 are changes in standard, Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K), T is the temperature (Kelvin). The values of ΔH^0 and ΔS^0 were determined from the slope ($\Delta H^0/R$) and the intercept ($\Delta S^0/R$) from the plot of $\ln K_c$ versus $1/T$ (Fig. 9.). The values of equilibrium constant (K_c), standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) calculated in this work were presented in Table 3. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intraparticle diffusion. The standard Gibbs free energy change (ΔG^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of ΔG^0 were found to decrease as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The positive values of ΔH^0 , indicating the endothermic nature of

the biosorption of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck. The positive values of ΔS^0 , shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

The present investigation revealed that rind of Orange (*Citrus sinensis*), (L.) Osbeck used as inexpensive, excellent biosorbent for the removal of Cr (VI) from aqueous solutions. The FTIR study of acid treated biosorbent showed that the possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial Cr (VI) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck. biosorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Dubinin-Kaganer-Redushkevich (DKR) isotherm and Temkin isotherm. The maximum chromium (VI) loading capacity (q_e) of rind of Orange (*Citrus sinensis*), (L.) Osbeck. determined from Langmuir adsorption isotherm was found to be 10.7411 mg g⁻¹. The pseudo-second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of Cr (VI) onto rind of Orange (*Citrus sinensis*), (L.) Osbeck is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that rind of Orange (*Citrus sinensis*), (L.) Osbeck has considerable biosorption capacity, available in abundant, non-hazardous agro material can be used as an effective indigenous material for treatment of wastewater stream containing Cr (VI).

Table.1 Adsorption isotherm constants for biosorption of Cr (VI) by rind of Orange]
(*Citrus sinensis*), (L.) Osbeck

Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
q_m	B	R^2	K	$1/n$	R^2	q_m	b	E	R^2	A_T	b_T	R^2
10.7411	0.0226	0.9986	3.9801	0.3587	0.9153	5.3153	-3E-6	0.4082	0.7413	2.2009	1364.94	0.8903

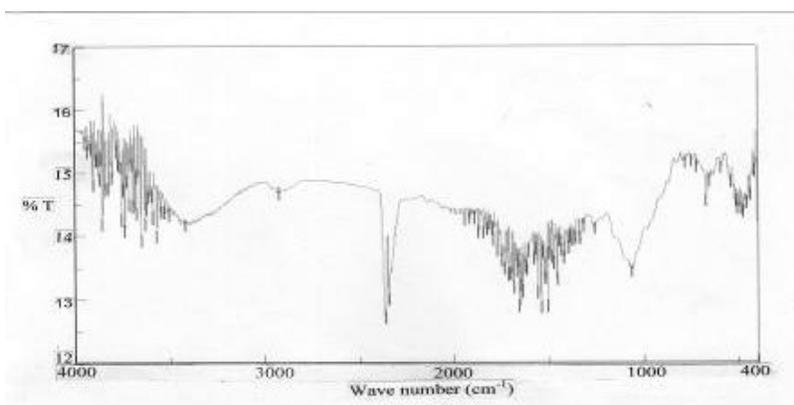
Table.2 Adsorption kinetic data for biosorption of Cr (VI) by rind of Orange
(*Citrus sinensis*), (L.) Osbeck

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra particle diffusion model		
q_e	K_1	R^2	q_e	K_2	R^2	α	β	R^2	K_i	C	R^2
1.4605	0.0164	0.9016	1.7111	0.0500	0.9963	1.5000	4.3233	0.9313	0.0629	0.9277	0.8736

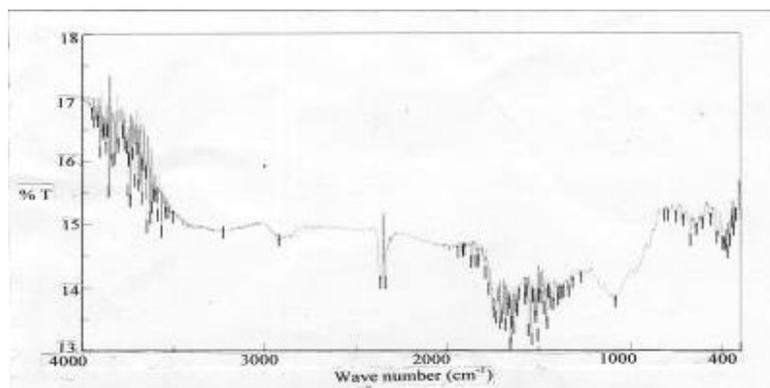
Table.3 Thermodynamic parameters of biosorption of Cr(VI) by rind of Orange (*Citrus sinensis*), (L.) Osbeck

T (K)	Kc	$-\Delta G^0$ (kJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
293	1.0909	0.211	8.839	30.27
303	1.3795	0.810		
313	1.3795	0.837		
323	1.5550	1.185		

Fig.1 FTIR spectra (a) biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck (b) biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck loaded with Cr (VI)

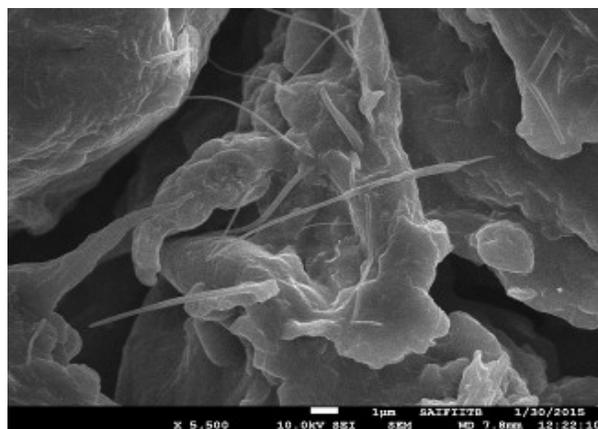


(a)

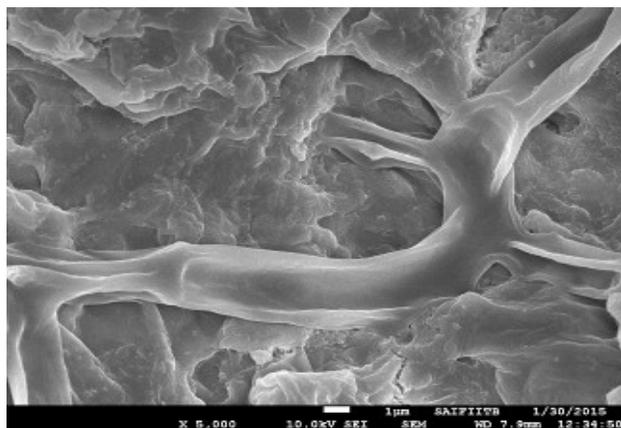


(b)

Fig.2 Scanning Electron Microscope (SEM) analysis (a) biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck (b) biosorbent rind of Orange (*Citrus sinensis*), (L.) Osbeck loaded with Cr (VI)



(a)



(b)

Fig.3 Effect of pH on Cr (VI) biosorption by rind of Orange (*Citrus sinensis*), (L.) Osbeck (biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, contact time: 150 minutes, temperature: 300C)

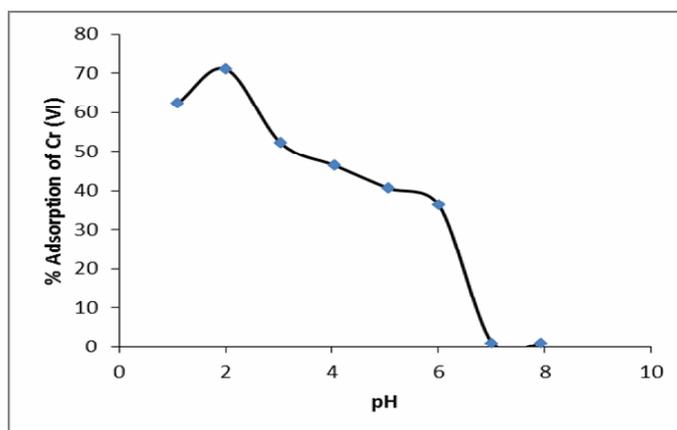


Fig.4 Effect of biosorbent dose concentration on Cr (VI) biosorption by rind of Orange (*Citrus sinensis*), (*L.*) Osbeck (pH: 2, Cr (VI) concentration: 10 mg/L, contact time: 150 minute, temperature: 300C)

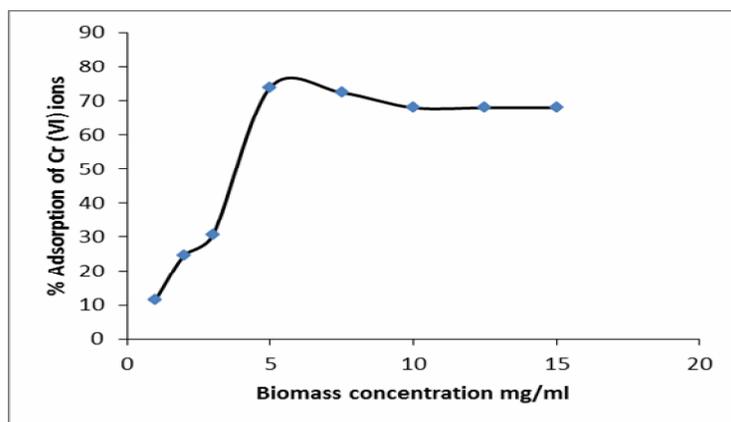


Fig.5 Effect of Cr (VI) concentration on Cr (VI) biosorption by rind of Orange (*Citrus sinensis*), (*L.*) Osbeck (pH: 2, biosorbent dose concentration: 5 mg/L, contact time: 150 minutes, temperature: 300C)

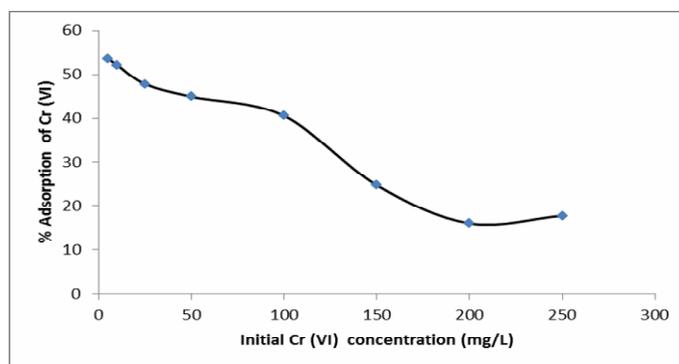


Fig.6 Effect of contact time on Cr (VI) biosorption by rind of Orange (*Citrus sinensis*), (*L.*) Osbeck pH: 2, biosorbent dose concentration: 5 mg/L, initial Cr (VI) concentration: 10 mg/ml, temperature: 300C)

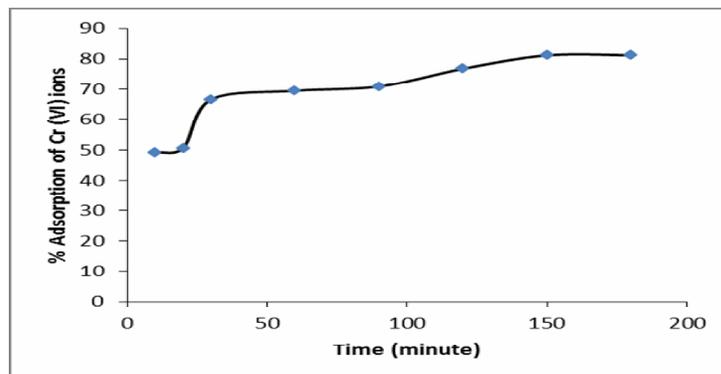


Fig.7 Adsorption isotherm models (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of Cr (VI) by rind of Orange (*Citrus sinensis*), (L.) Osbeck (pH: 2.0, biosorbent dose concentration: 5 mg/ml, contact time: 150 minutes, temperature: 300C)

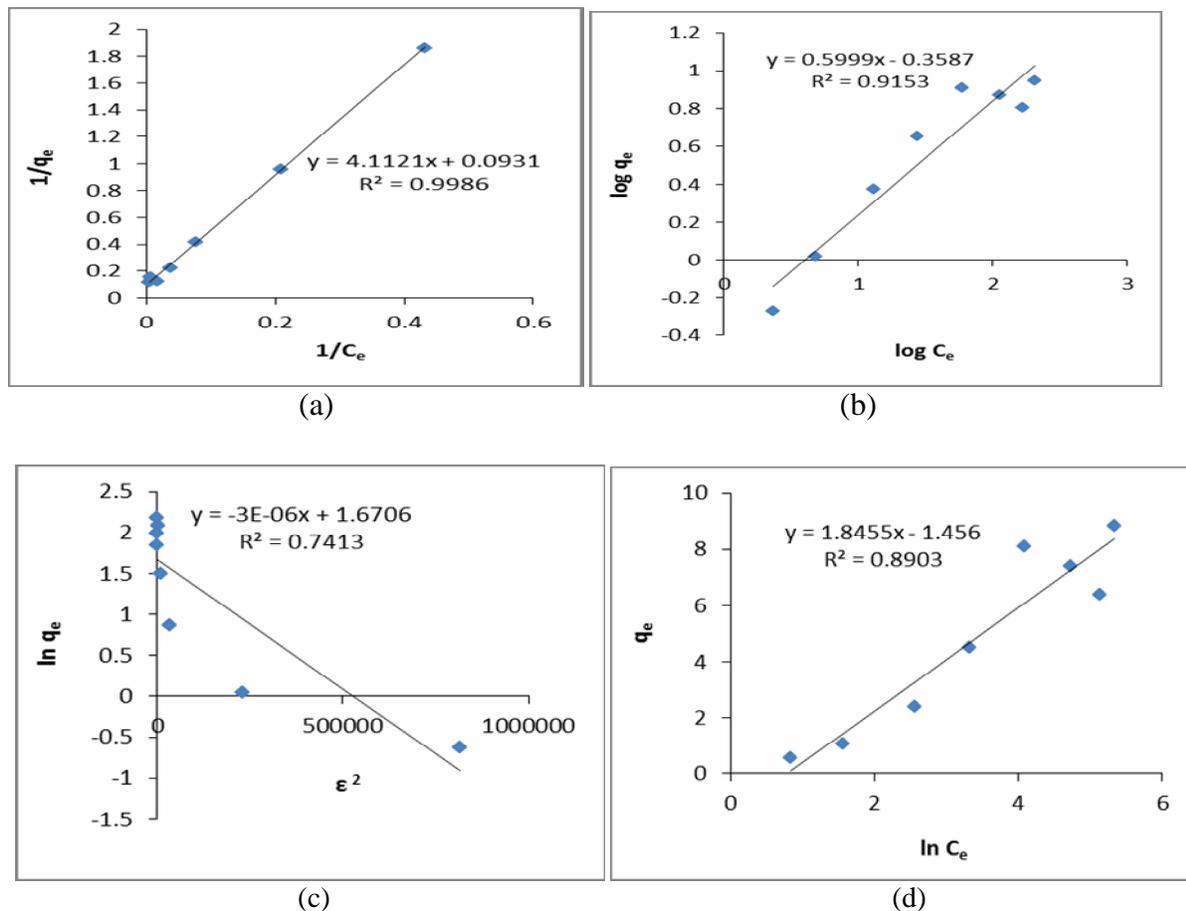
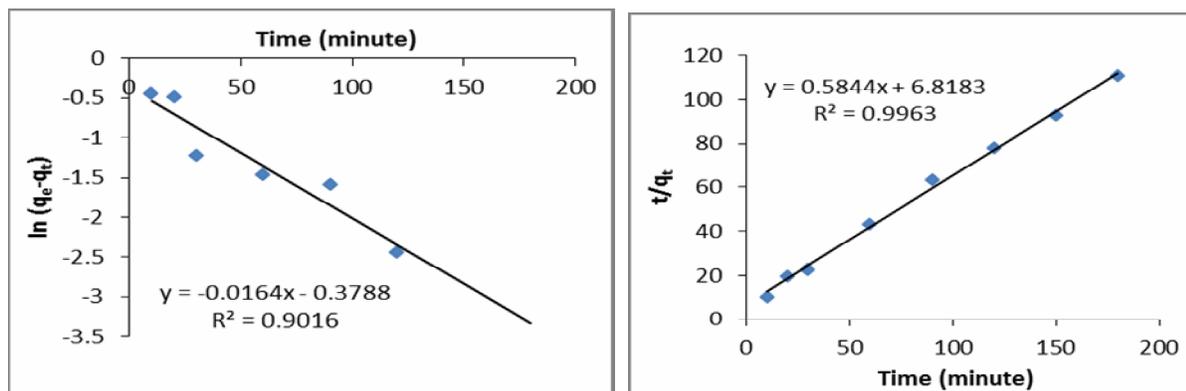


Fig.8 Adsorption kinetic models (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intraparticulate mixing equation, for biosorption of Cr (VI) by rind of Orange (*Citrus sinensis*), (L.) Osbeck pH: 2.0, biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, temperature: 300C)



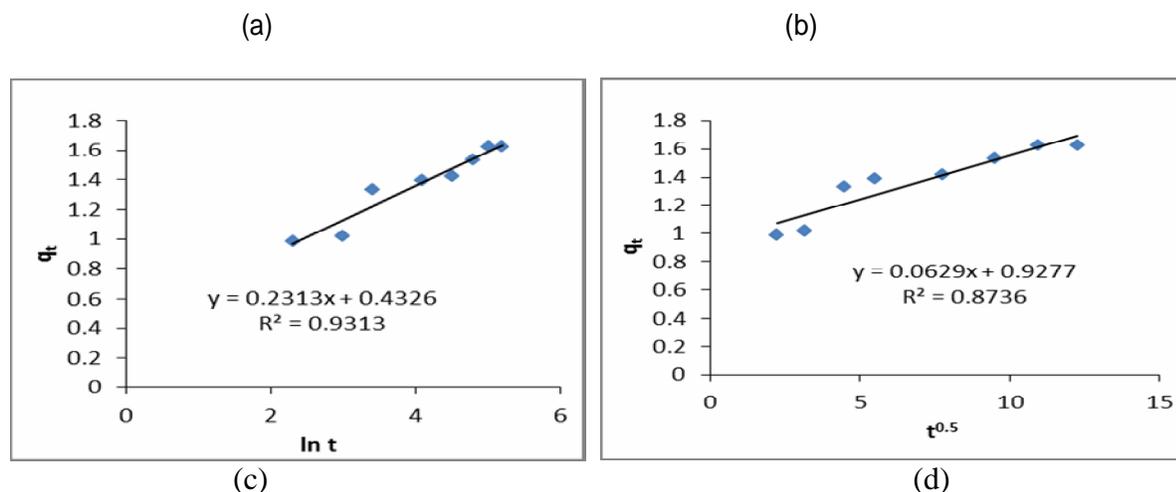
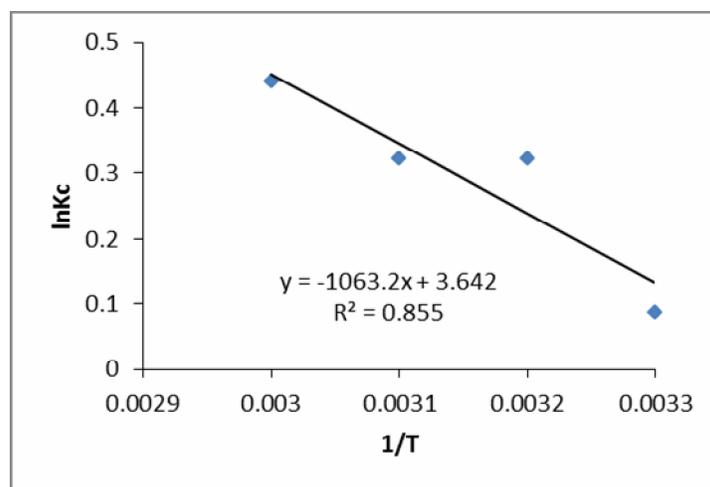


Fig.9 Plot of $\ln K_c$ against $1/T$ for determination of thermodynamic parameters for biosorption of Cr (VI) by rind of Orange (*Citrus sinensis*), (L.) Osbeck (pH: 2.0, biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, contact time: 150 minute)



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