ISSN: 0976-3376

Available Online at http://www.journalajst.com

ASIAN JOURNAL OF
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 6, Issue 05, pp. 1425-1435, May, 2015

RESEARCH ARTICLE

STUDIES ON CR (VI) BIOSORPTION USING COST EFFECTIVE BIOSORBENT: PEANUT HULLS (*ARACHIS HYPOGAEA* LINN.)

[1]Amit S. Sharma, [2]Sandip D. Maind and [1]*Satish A. Bhalerao

[1]Environmental Sciences Research Laboratory, Department of Botany, Wilson College, Mumbai-400007, University of Mumbai, M.S., India
[2]Department of Chemistry, BharatiyaVidya Bhavan's Hazarimal Somani college of Arts and Science, Mumbai-400007, University of Mumbai, M.S., India

ARTICLE INFO

Article History:
Received 28th February, 2015
Received in revised form
10th March, 2015
Accepted 18th April, 2015
Published online 31st May, 2015

Key words:

Biosorption,
Chromium (VI),
Peanut hulls *(Arachis hypogaea* Linn.*)*,
FTIR,
SEM,
Adsorption isotherms,
Adsorption kinetics,
Thermodynamic study.

ABSTRACT

The effectiveness of low-cost biosorbent: peanut hulls (*Arachis hypogaea* Linn.), was studied for Cr (VI) biosorption from aqueous solutions in a batch system. 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 chromium (VI) concentration, contact time and temperature were studied. The optimum solution pH for chromium (VI) adsorption by biosorbent was 2.0 with the optimal removal 50.63 %. The adsorbent dose 5 mg/ml was enough for optimal removal of 60.70 %. 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 ($R^2 = 0.997$) than Freundlich isotherm ($R^2 = 0.991$), Temkin isotherm ($R^2 = 0.825$) and Dubinin-Kaganer-Redushkevich (DKR) isotherm ($R^2 = 0.569$). The maximum adsorption capacity determined from Langmuir isotherm was found to be 6.535 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-particulate mixing equation. Results clearly indicates that the Weber & Morris intra-particulate mixing 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 peanut hulls (*Arachis hypogaea* Linn.) used successfully for biosorption studies of Cr (VI) from aqueous solutions, can be used very promisingly for industrial wastewater treatment.

INTRODUCTION

Discharge of industrial effluents containing heavy metals into the open landscapes and water bodies due to industrial activities is one of the most serious problems that need to be solved. Heavy metals are toxic to all forms of life including humans. Heavy metals are non-biodegrable and can accumulate along the food chain which results in serious ecological and health hazard. Chromium is listed among top pollutants and is ranked 16th harmful pollutant due to its carcinogenic and teratogenic characteristics on the community (Selomuya *et al.,* 1999: Geleel *et al.,* 2013). Chromium occurs frequently as Cr (VI) and Cr (III) in aqueous solutions (Daikiky *et al.,* 2002).

Hexavalent chromium, which is primary present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) possesses significantly higher level of toxicity than the other valence states (Smith and LECd, 1972: Sharma and Forster, 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

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***Corresponding author: Satish A. Bhalerao**
Environmental Sciences Research Laboratory, Department of Botany, Wilson College, Mumbai-400007, University of Mumbai, M.S., India

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 adsorbent 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 adsorbents, including leaf mould (Sharma *et al.,* 1994), pongamia leaf (Sivamani 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: Quintellas *et al.,* 2008: Saran *et al.,* 2013), rice husks (Srinivasan *et al.,* 1988), quarternised rise husk (Low and Lee, 1992), hazelnut shell (Kobya, 2004), almond shell (Candela *et al.,* 1995), corn cob (Bosico *et al.,* 1996), quaternised wood (Low *et al.,* 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 *et al.,* 2013), have been used for chromium (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.

Peanut (*Arachis hypogaea* Linn.) belonging to leguminaceae family and sub family papilionioceae is being one of the highest production food in India and during processing of food, produced a large amounts of waste which has no commercial value. Peanut hulls (*Arachis hypogaea* Linn.) was selected because of a low cost, higher adsorption capacity, possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. due to high cellulose (44.8%) and lignin (36.1%) content, which favours biosorption of heavy metals (olivereira *et al.,* 2010). The aim of this study is to characterize the biosorbent: peanut hulls (*Arachis hypogaea* Linn.) by FTIR and SEM to find out the functional groups and porosity which is responsible biosorption of Cr (VI). The main objective of this work was to evaluate the adsorption capacity of peanut hulls (*Arachis hypogaea* Linn.) 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 peanut hulls (*Arachis hypogaea Linn.*) were described. Kinetic models (pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intra-particulate mixing 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 chromium (VI) was prepared by dissolving 0.7072 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) (previously dried at 50^0C for one hour) in 250 ml of double distilled water and further desired test solutions of chromium (VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent: The peanut hulls (*Arachis hypogaea* Linn.) was collected locally and 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 50^0C 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 µm 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 105ºC for 1-2 hrs. For further use, the dried biomass was stored in air tighten 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-4100typeA) 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.

Biosorption studies: The static (batch) method was employed at temperature (30^0C) to examine the sorption of Cr (VI) by adsorbents. The method was used to determine the adsorption capacity, stability of adsorbent and optimum sorption conditions. The parameters were studied by combining adsorbent 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 adsorbents by filtration, using Whatmann filter paper and amount of Cr (VI) in the supernatant/filtrate solutions was determined.

Estimation of Cr (VI) concentration: 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 dropwise. 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 Lamberts 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 adsorbent 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 adsorption studies were used to calculate the percentage adsorption of Cr (VI) by using the mass balance relationship. The Cr (VI) concentrations adsorbed on the solid were calculated from the difference between initial Cr (VI) content (C_i) and Cr (VI) content after adsorption (C_e). The following equation was used to compute the percentage adsorption (% Ad) of Cr (VI) by the adsorbent,

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

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 adsorption studies were done at 30^0C to check the applicability of the adsorption isotherms under the specified condition, the solution pH of 2.0, adsorbent dose of 5 mg/ml, an initial Cr (VI) concentration range 5 mg/L - 250 mg/L and contact time 150 minutes. Analysis of Cr (VI) content in various solutions were performed by UV-Visible spectrophotometer method. The data obtained in batch adsorption studies was used to calculate the equilibrium Cr (VI) adsorptive quantity by the following equation:

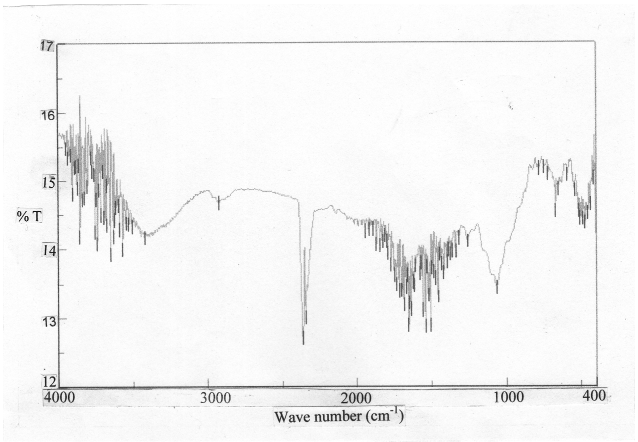
$$q_e = \frac{(C_i - C_e)}{w} \times \text{V} \qquad (2)$$

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

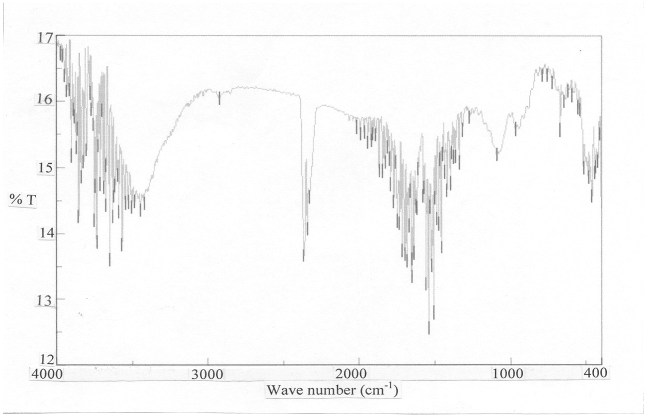
Adsorption kinetics: The kinetic measurements were conducted by employing adsorption dose of 5 mg/ml of adsorbent contacted with 10 mg/L of a Cr (VI) solution with optimum pH 2.0 and temperature 30^0C in a rotary shaker. The concentration of Cr (VI) in the solution was determined at known time intervals. Analysis of Cr (VI) content in various solutions was performed by UV-visible spectrophotometer. The amount of Cr (VI) adsorbed q_t (mg/g) at time t was calculated by Eq. (2).

RESULTS 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 Figure 1 (a and b).



(a)

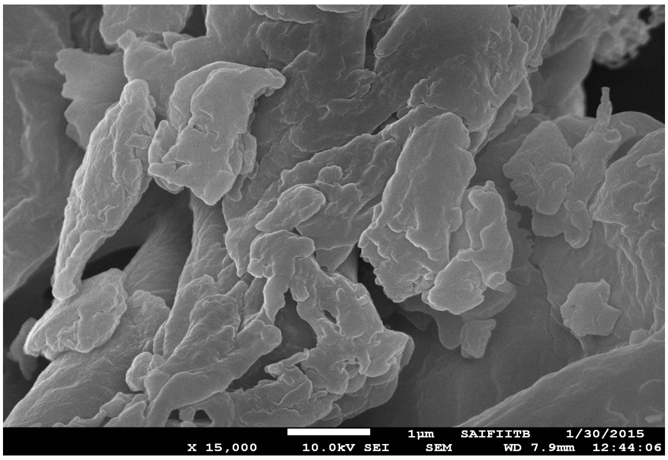


(b)

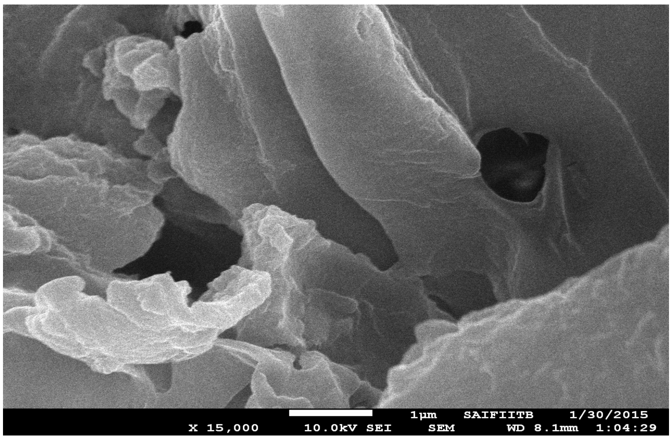
Figure 1. FTIR spectra (a) biosorbent peanut hulls (*Arachis hypogaea* Linn.) (b) biosorbent peanut hulls (*Arachis hypogaea* Linn.) loaded with Cr (VI)

As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The broad peak at 3422 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 2366 cm^{-1} and 2345 cm^{-1} are stretching peaks. The peaks located at 1735 cm^{-1} and 1637 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 1066 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), the broadening of -OH peak at 3422 cm^{-1} and carbonyl group peak at 1637 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 Figure 2 (a and b).



(a)



(b)

Figure 2. Scanning Electron Microscope (SEM) analysis (a) biosorbent peanut hulls (*Arachis hypogaea* Linn.) (b) biosorbent peanut hulls (*Arachis hypogaea* Linn.) loaded with Cr (VI)

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 adsorbed. 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 adsorption capacity of the biosorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 2-9 for bisorption of chromium (VI) and pH trend observed in this case is shown in Figure 3.

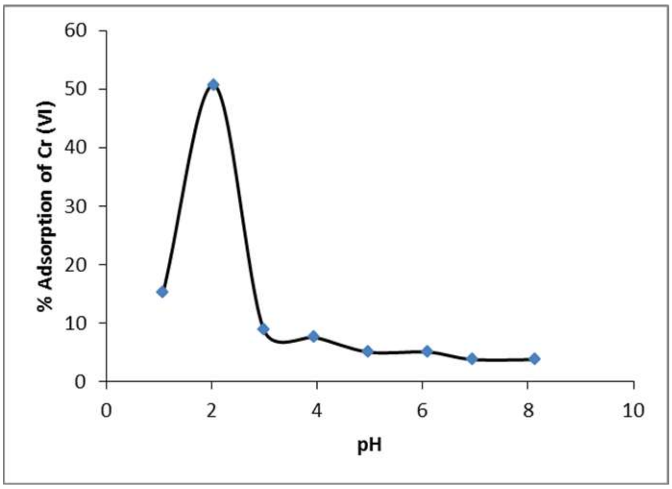


Figure 3. Effect of pH on chromium (VI) biosorption by peanut hulls (*Arachis hypogaea* Linn.) (biosorbent dose concentration: 5 mg/ml, chromium (VI) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^0C)

It was found that at pH 2 the adsorption process was maximum with 50.63 % and after increasing pH, adsorption was decreases. 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 $Cr_2O_7^{2-}$. Furthermore, the surface of biosorbent may be positively charged at pH 2. Therefore, at this pH it is likely to be adsorbed 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 sorption 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 adsorption 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 chromium (VI) on to peanut hulls (*Arachis hypogaea* Linn.) by varying adsorbent dose from 1.0 mg/ml to 15.00 mg/ml is as shown in Figure 4. From the results it was found that adsorption of chromium (VI) increases with increase in adsorbent dosage and is highly dependent on adsorbent concentration. Increase in adsorption 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 peanut hulls (*Arachis hypogaea* Linn.) was found at 5 mg/ml of biosorbent dose with 60.75 % of removal efficiency. The decrease in efficiency at higher adsorbent concentration could be explained as a consequence of partial aggregation of adsorbent which results in a decrease in effective surface area for metal uptake (Karthikeyan *et al.,* 2007). The biosorbent dose 5 mg/ml was chosen for all further studies.

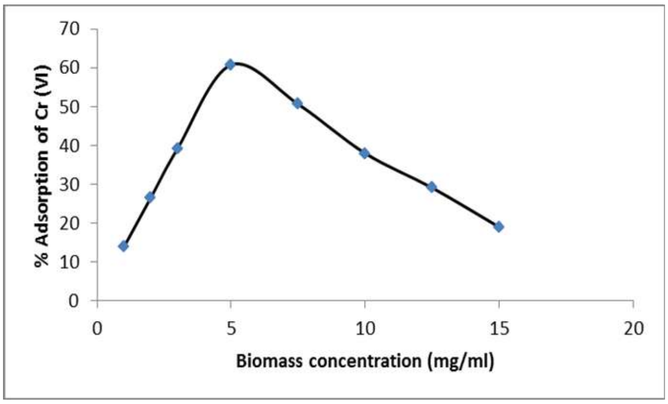


Figure 4. Effect of biosorbent dose concentration on chromium (VI) biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2, chromium (VI) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^0C)

Effect of initial chromium (VI) concentration

The effect of initial chromium (VI) concentration from 5 mg/L - 250 mg/L on the removal of chromium (VI) from aqueous solutions at adsorbent dose 5 mg/ml and at optimum pH 2.0 at 30^0C temperature was studied and shown in Figure 5. On increasing the initial chromium (VI) concentration, the total chromium (VI) ions uptake decreased appreciably when chromium (VI) concentration increases from 5 mg/L - 250 mg/L.

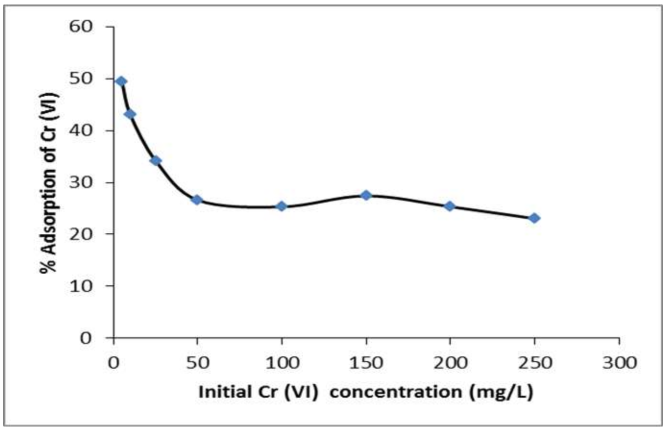


Figure 5. Effect of chromium (VI) concentration on chromium (VI) biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2, biosorbent dose concentration: 5 mg/L, contact time: 150 minutes, temperature: 30^0C)

Effect of contact time: Contact time plays an important role in affecting efficiency of adsorption. Contact time is the time needed for adsorption process to achieve equilibrium when no more changes in adsorptive 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 adsorbents. In order to optimize the contact time for the maximum uptake of chromium (VI), contact time was varied between 10 minutes – 180 minutes on the removal of chromium (VI) from aqueous solutions in the concentration of chromium (VI) 10 mg/L, biosorbent dose 5 mg/ml, optimum pH 2.0 and 30^0C temperature (Figure 6).

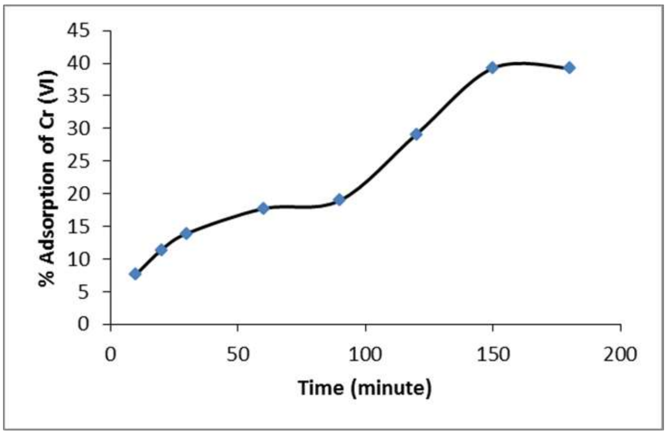


Figure 6. Effect of contact time on chromium (VI) biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2, biosorbent dose concentration: 5 mg/L, initial chromium (VI) concentration: 10 mg/ml, temperature: 30^0C)

The results obtained from the adsorption capacity of chromium (VI) onto peanut hulls (*Arachis hypogaea* Linn.) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for adsorption of chromium (VI) onto peanut hulls (*Arachis hypogaea Linn*.) was 150 minutes with maximum adsorption. The rapid uptake of chromium (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 chromium (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 adsorbent (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 adsorprtion capacities and Langmuir constants and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m\, b\, C_e} + \frac{1}{q_m} \tag{4}$$

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Figure 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 biosorbent (q_m) is found to be 6.535 mg per g of biosorbent which is higher than the other adsorbents used by many authors. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation:

$$R_L = \frac{1}{1+bC_i} \tag{5}$$

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 adsorption. 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 0.1149-0.8665 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 Nahoglu, 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:

$$bC_i = \frac{\theta}{1-\theta} \tag{6}$$

where θ is the suface area coverage. The θ was found to be 0.4153-0.9726 for concentration of 5 mg/L -250 mg/L of Cr (VI).

Frenudlich adsorption isotherm (Freundlich, 1906)

Freundlich equation is represented by:

$$q = KC_e^{1/n} \tag{7}$$

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

Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{8}$$

Equilibrium data for the adsorption is plotted as log q_e vs log C_e, as shown in Figure 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.

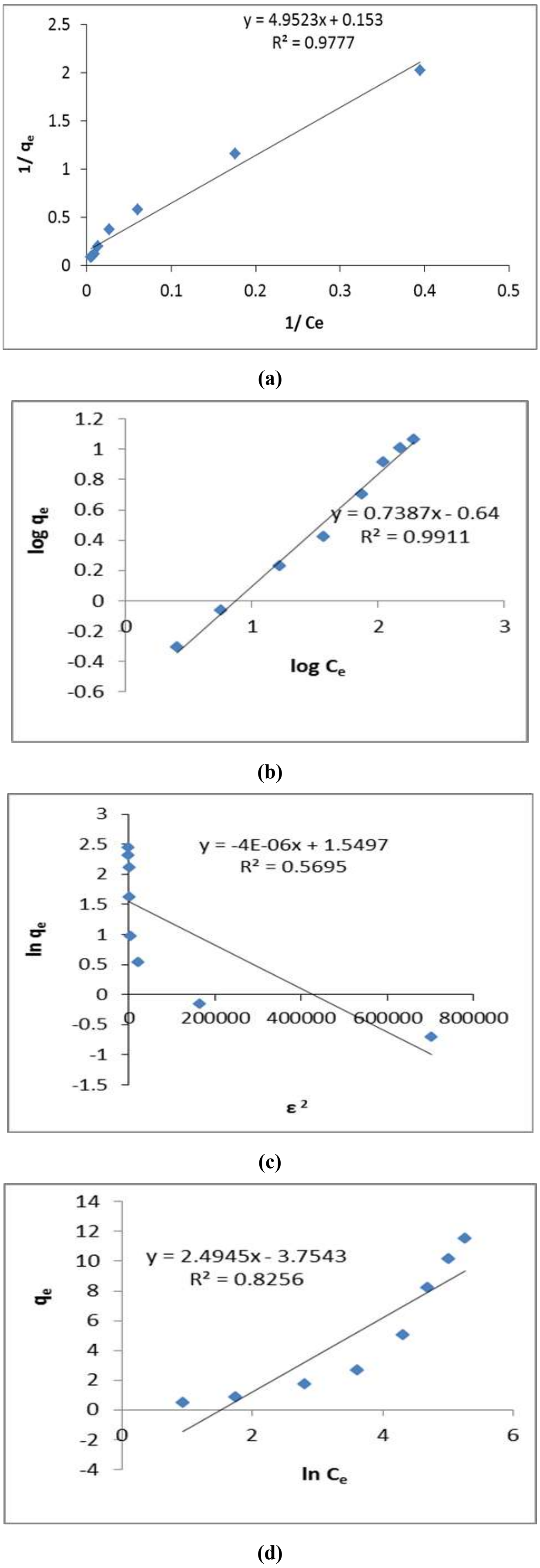


Figure 7. Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for bisorption of Cr (VI) by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2.0, biosorbent dose concentration: 5 mg/ml, contact time: 150 minutes, temperature: 30°C)

Table 1. Adsorption isotherm constants for biosorption of Cr (VI) ions by peanut hulls (*Arachis hypogaea* Linn.)

Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
q_m	b	R^2	K	1/n	R^2	q_m	β	E	R^2	A_T	b_T	R^2
6.535	0.0308	0.997	5.470	0.640	0.991	4.7100	-4E-6	0.3536	0.569	4.505	1010.08	0.825

The n value indicates the degree of non-linearity between solution concentration and adsorption as followes: if n = 1, then adsorption is linear; if n < 1, then adsorption is chemical process; if n > 1, then adsorption 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 1.5625. Since n > 1, this indicates the physical biosorption of Cr (VI) onto peanut hulls (*Arachis hypogaea* Linn.). The higher value of K (5.470) indicates the higher adsorption capacity of the adsorbent.

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

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

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

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

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

Equilibrium data for the adsorption is plotted as ln q_e vs ε^2, as shown in Figure 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 adsorption 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 (0.3536 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 sorption (J/mol) and A_T is the Temkin isotherm constant (L/g).

Equilibrium data for the adsorption is plotted as q_e vs ln C_e, as shown in Figure 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 adsorption 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, 1898) (b) the pseudo-second-order equation (McKay *et al.,* 1999) (c) Elovich equation (Chien and Layton, 1980) (d) Weber and Morris intraparticle diffusion rate equation (Weber and Morris, 1963) are presented below.

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

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

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

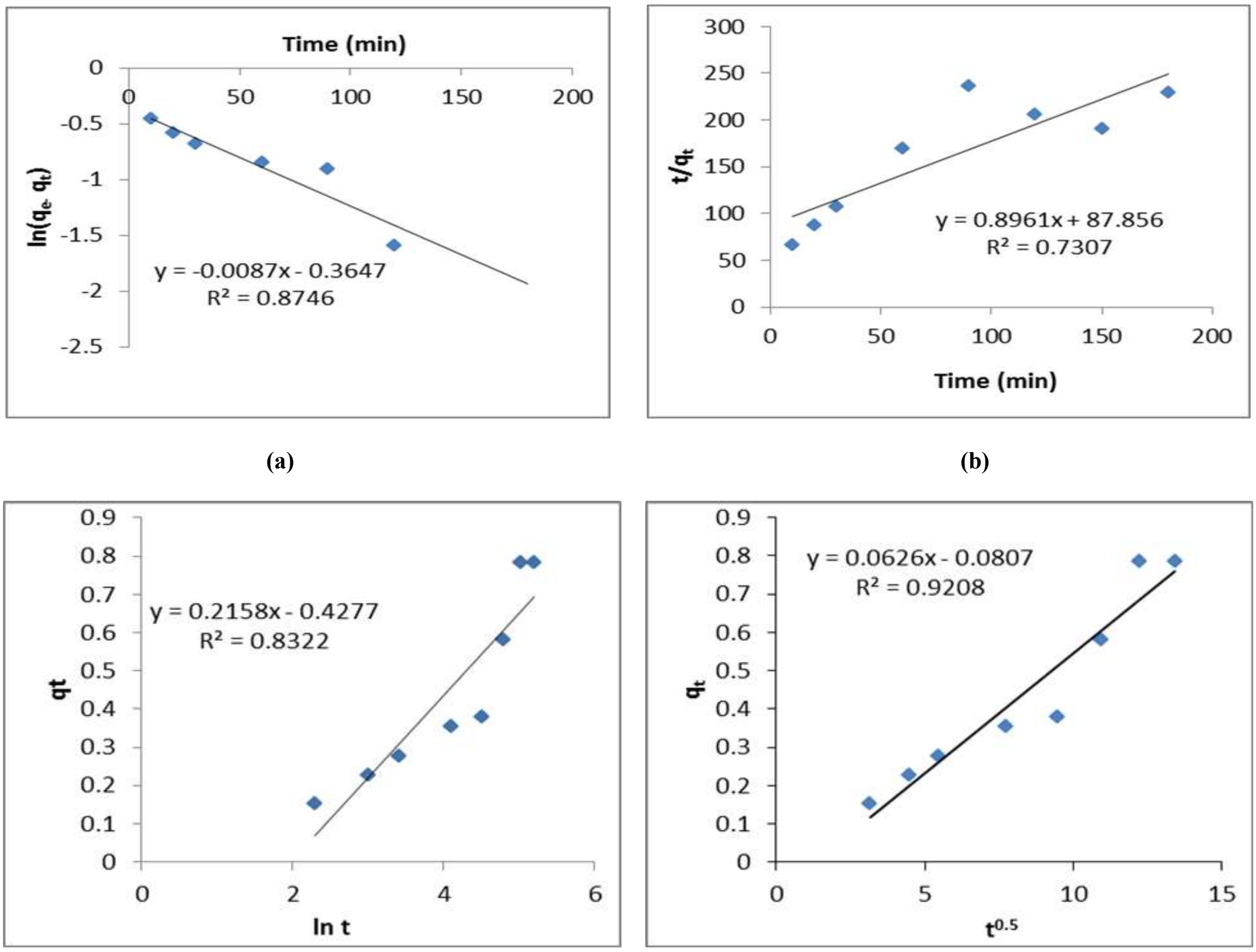
$$q_t = k_i t^{0.5} + c \tag{16}$$

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 (mg g^{-1} min^{-1}) and β (g mg^{-1}) are Elovich coefficients representing initial sorption rate and desorption constants, respectively. K_i (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion 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 lineally with time t if the adsorption 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 lineally the adsorption process obeys the Weber & 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 adsorption 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 (Figure 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 adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the

Table 2. Adsorption kinetic data for biosorption of Cr (VI) ions by peanut hulls (*Arachis hypogaea* Linn.)

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra particle diffusion rate model		
q_e	K_1	R^2	q_e	K_2	R^2	α	β	R^2	Ki	c	R^2
1.008	0.008	0.874	1.1160	0.009	0.730	1.556	4.651	0.832	0.062	0.080	0.920



(a) **(b)**

(c) **(d)**

Figure 8. Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intraparticle diffussion rate equation, for biosorption of Cr (VI) by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2.0, biosorbent dose concentration: 5 mg/ml, initial Cr (VI) concentration: 10 mg/L, temperature: 30^0C)

adsorbent and the ions adsorbed onto it (Septhum *et al.,* 2007). The pseudo-second-order equation was plotted for t/q_t against t (Figure 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 Elovich equation was plotted for q_t against ln t (Figure 8 (c)). The values of β and α are calculated from the slope (1/ β) and the intercept (ln (α β)/ β) of the plot and values are shown in Table 2. The Elovich equation has been used with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas and Thomas, 1997). The Weber & Morris intraparticle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Figure 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 Weber and Morris intra particle diffusion rate equation showed a strongest correlation value ($R^2 = 0.920$) being higher than the correlation coefficient for the pseudo-first-order, Elovich equation and pseudo-second-order equation. 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, 1964). The plot of intraparticle rate diffusion equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate 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 5 mg/L and biosorbent dose 5 mg/ml with optimum pH 2.0 was studied. Experiments were carried out at different temperatures from 20^0C-50^0C. The samples were allowed to attain equilibrium. Sorption slightly increases from 20^{0}C-40^{0}C and decreases after 40^{0}C. The equilibrium constant (Cantena and Bright, 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{17}$$

$$\Delta G^0 = -RT \ln K_c \tag{18}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{19}$$

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

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 chromium (VI) concentration adsorbed 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) and 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 Kc versus 1/T (Figure 9.). The values of equilibrium constant (Kc), 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 (Kc) 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 decreases 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 peanut hulls (*Arachis hypogaea* Linn.). The positive values of ΔS^0, shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

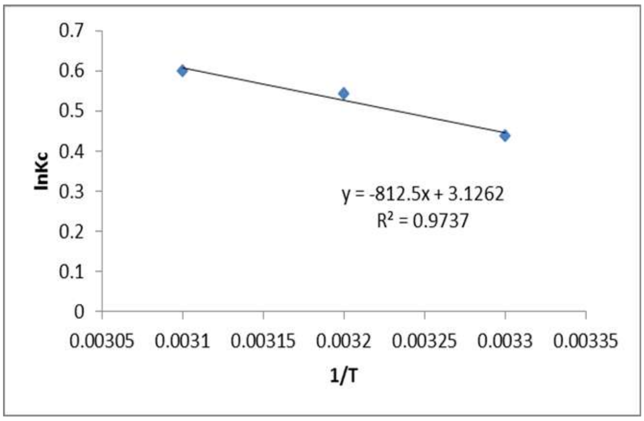


Figure 9. Plot of lnKc against 1/T for determination of thermodynamic parameters for biosorption of Cr (VI) by peanut hulls (*Arachis hypogaea* Linn.) (pH: 2.0, biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, contact time: 150 minutes)

Table 3. Thermodynamic parameters of biosorption of Cr (VI) by peanut hulls (*Arachis hypogaea* Linn.)

T (K)	Kc	$-\Delta G^0$ (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
283	1.5484	1.065	6.750	25.98
293	1.7188	1.364		
303	1.8216	1.560		
313	1.6322	1.315		

Conclusions

The present investigation revealed that peanut hulls (*Arachis hypogaea* Linn.) used as inexpensive, excellent biosorbent for the removal of chromium (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 chromium (VI) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of chromium (VI) onto peanut hulls (*Arachis hypogaea* Linn.). Sorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Temkin isotherm and Dubinin-Kaganer-Redushkevich (DKR) isotherm. The maximum chromium (VI) loading capacity (q_e) of peanut hulls (*Arachis hypogaea* Linn.) determined from Langmuir adsorption isotherm was found to be 6.535 mg g^{-1}. The Weber & Morris intraparticle diffusion rate model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of chromium (VI) onto peanut hulls (*Arachis hypogaea* Linn.) is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that peanut hulls (*Arachis hypogaea* Linn.) 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 chromium (VI).

Acknowledgements

The authors are very much thankful to Principal Dr. V.J. Sirwaiya for administrative support, cooperation and help. Thanks to Viva College for FTIR analysis and IIT, Mumbai for SEM analysis.

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