RESEARCH ARTICLE

An evaluation of comparative biosorption study of Cadmium (II) and Chromium (VI) using Orange rind (*Citrus sinensis*), (L.) Osbeck, under optimized conditions

Poojari Anukthi C[1], Maind Sandip D[2] and Bhalerao Satish A[1]*

[1]Environmental Sciences Research Laboratory, Department of Botany, Wilson College, Mumbai-400007,
[2]Department of Chemistry, Bharatiya Vidya Bhavan's Hazarimal Somani College of Arts and Science,
Kulapati K.M. Munshi Marg, Chowpatty, Mumbai-400007, Maharashtra, India
*Corresponding Author Email : drsatishbhalerao55@gmail.com | drsatish16@rediffmail.com

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ABSTRACT

The present study investigated the comparative biosorption study of cadmium (II) and chromium (VI) using inexpensive biosorbentrind of orange (*Citrus sinensis*), (L.) Osbeck, under optimized conditions. A biosorption study was carried out in batch system from aqueous solutions. The biosorbent before and after biosorption was characterized by FTIR and SEM. The work considered the optimization of parameters such as solution pH, biosorbent dose, initial metal concentration, contact time and temperature. To assess the potential applicability of biosorbent, the experimental equilibrium data were analysed by Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin isotherms. Langmuir isotherm model provided a better fit with the experimental data for both cadmium (II) and chromium (VI). The maximum biosorption capacity of cadmium (II) and chromium (VI) which was determined from Langmuir isotherm was found to be 83.33mgg^{-1}and 10.74mg g^{-1}respectively. Simple kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and Weber & Morris intraparticle rate diffusion, were employed to determine the biosorption mechanism. A result clearly indicates that the pseudo-second-order kinetic model was found to be correlating the experimental data strongest for both cadmium (II) and chromium (VI), which suggests that chemical adsorption process was more dominant. 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 was found to remove cadmium (II) and chromium (VI) effective from aqueous solutions with uptake and selectivity in the order of cadmium (II) > chromium (VI).Thus biosorption have an advantages over other expensive cleanup technologies, can be used for waste water treatment for remediation of heavy metal contamination in industrial sectors.

Keywords: *Comparative study, Biosorption, Cadmium (II), Chromium. (VI), Orange (Citrus sinensis), (L.) Osbeck, FTIR, SEM, Adsorption isotherms, Adsorption kinetics, Thermodynamic study.*

INTRODUCTION

Heavy metal pollution of waste water, as a result of enormous industrial development and modernization is one of the most common environmental problems. Heavy metals are carcinogenic properties (Cimino and Caristi, 1990) and recalcitrant even at very low concentrations & they can pollute drinking water resources. Heavy metals (cadmium and chromium) are highly toxic, non-biodegrable and can accumulate along the food chain which results in serious ecological and health hazard. Cadmium (II) finds its way into water bodies through industries like metal production, phosphate fertilizers, pesticides, electroplating, textile operations, manufacture of batteries and pigments & dyes (Sharma, 2008; Perez-Marin *et al.*, 2007). Chromium (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).Cadmium (II) causes sterility and is harmful to human health. Cadmium (II) is likely to cause a number of acute and chronic disorders, such as itai-itai disease, renal damage, emphysema, hypertension, testicular atrophy, damage to the kidneys, lungs & liver, carcinogenesis etc. Diseases caused by chromium (VI) are bronchial asthma and lung cancer. When heavy metals (cadmium and chromium) are present in the wastewater beyond the permissible limits of concentration, it can have severe toxicological effects on both human and aquatic ecosystems. United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) have demarcated the permissible limit of cadmium and chromium in potable water as 0.003 mg/L and 0.05mg/L respectively (WHO, 2008). Hence, the removal of heavy metals becomes mandatory before the discharge of industrial effluents into main water stream.

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 (Bhalerao, 2011). Biosorption is the process based on the principle of metal binding capacities of biological materials. Biosorption is a process that utilizes low-cost biosorbents to sequester toxic heavy metals. Biosorption has distinct advantages over expensive clean up technologies which used in industrial sector. The major advantages of biosorption which include reusability of biomaterial, low operating cost, high efficiency of metal removal from dilute solution, no additional nutrient requirement, short operation time, no chemical and/or biological sludge and the possibility of metal recovery (Kratochvil and Volesky, 1998; Mungasavalli *et al.*, 2007).

In the recent years many low cost biosorbents materials have been utilized for heavy metal removal in waste water. We reported previously and investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions (Maind *et al.*, 2012; Maind *et al.*, 2013; Maind *et al.*, 2012; Maind and Bhalerao 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). Many low cost biosorbents have been intensively examined for their abilities to be applied for removal of cadmium (II) and chromium (VI) from aqueous solutions.

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 adsorption capacity, possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. which favours biosorption of heavy metals.

The aim of the present research wasto utilize the rind of orange (*Citrus sinensis*), (L.) Osbeck for the biosorption of cadmium (II) and chromium (VI) from aqueous solutions in a batch system. The objective of this study was to characterize biosorbent be four and after biosorption using FTIR and SEM. The study was extended with the objective for estimation and calculation of various parameters affecting the biosorption of metals such as solution pH, biosorbent dose, contact time, initial metal concentration and temperature. Adsorption isotherms (Langmuir, Freundlich, Dubinin-kaganer-Redushkevich (DKR) and Temkin) and kinetics models (pseudo-first-order, pseudo-second-order, Elovich equation and intraparticlerate diffusion) was employed to understand the probable biosorption mechanism. Thermodynamic studies was also carried out to estimate the standard Gibbs free 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 hydrochloric acid and dilute sodium hydroxide.

Preparation of cadmium (II) chromium (VI) solution

The stock solution of 1000 ppm of cadmium (II) ions was prepared by dissolving 0.1g cadmium metal in 1 ml concentrated nitric acid and diluted in 250 ml of double distilled water. 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^{0}C for one hour) in 250 ml of double distilled water. Further desired test solutions of cadmium (II) chromium (VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent

The oranges (*Citrus sinensis*), (L.)Osbeck was collected locally and the rind of oranges 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^{0}C 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 nitric 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.

Experimental procedure

The static (batch) method was employed at temperature (30^{0}C) to examine the biosorption of cadmium (II) and chromium (VI) by biosorbents. The method was used to determine the biosorption capacity, stability of biosorbent, and optimum biosorption conditions. The parameters were studied by combining biosorbent with solution of cadmium (II)and chromium (VI) in 250 ml separate reagent bottles. 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 cadmium (II) and chromium in the supernatant/filtrate solutions was determined using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820).The following equation was used to compute the percentage adsorption (% Ad) of cadmium (II) and chromium (VI) by the biosorbent,

$$\%\mathrm{Ad} = \frac{(Ci - Ce)}{C_i} \times 100 \qquad (1)$$

Where C_i and C_e are the initial concentrations and equilibrium concentrations of the cadmium (II) and chromium (VI) in mg/L.

The equilibrium cadmium (II) and chromium (VI) adsorptive quantity was determined by the following equation,

$$q_e = \frac{(Ci - Ce)}{w} \times V \qquad (2)$$

Where q_e (mg metal per g dry biosorbent) is the amount of cadmium (II) or chromium (VI) adsorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Estimations of cadmium (II) and chromium (VI) concentration

Quantitative estimations of cadmium (II) and chromium were carried out by UV-visible spectrophotometer using dithizone and 1,5-Diphenylcarbazide as a complex forming regent for cadmium (II) and chromium (VI) respectively.

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 Fig.1. (a, b and c). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The spectrums clearly showed the broad peak of -OH and -NH groups. The stretching of the –OH groups bound to methyl groups are clearly indicated in the spectrum. The characteristics peak of carbonyl group is present. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biomass. The peak of stretching and the stretching in aromatic rings are present. The peaks of C-H and C-O bonds observed. The –OH, NH, carbonyl and carboxyl groups are important sorption sites (Volesky, 2003). As compared to simple biosorbent, biosorbent loaded with metal, the broadening of -OH group peak and carbonyl group peak was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of metal.

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, b and c). 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 mictrographs 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

pH is considered as a very important parameter in biosorption process. The functional groups responsible for binding of metal ions in the biosorbent, affected by pH. It also affects the competition of metal ions that gets adsorb to active sites of biosorbent. The biosorption capacity of the biosorbent and speciation of metals in the solution is pH dependent. pH influences the chemical structure of the cadmium (II) and chromium (VI) in aqueous solution, hence influencing its bioavailability. The biosorption capacity of the cadmium (II) and chromium (VI) depends on the pH of the biosorption medium, which influences electrostatic binding of cadmium (II) and chromium (VI) ions to corresponding functional groups. The optimization of pH was done by varying the pH in the range of 2 to 10 for cadmium (II) and 1 to 8 for chromium (VI) and pH trend observed in this case is shown in Fig. 3. It was found that biosorption of cadmium (II) with biosorbent has increased by increasing pH and at pH 7 the biosorption process was maximum with 80.30 % and then decreases till pH 10. The lesser biosorption at lower pH was due to lesser surface sites are available for biosorption. pH 7 was chosen for all further biosorption studies for cadmium (II). It was found that at pH 2, biosorption of chromium (VI) with biosorbent was maximum with 71.01 % and after increasing pH, biosorption was decreases. According to the solubility equilibrium of chromium, $HCrO_4^-$ is the dominant species of chrmoium (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 bebiosorbed chrmoium (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 chromium (VI) & biosorbent and inhibits biosorption and resultantly percent chromium(VI) uptake may decrease.

Effect of biosorbent dose

Effect of biosorbent dose of biosorption of metal ions onto biosorbent which is an important parameter was studied while conducting batch biosorption studies. The biosorption capacity of cadmium (II) and chromium (VI) ontothe rind of orange (*Citrus sinensis*), (L.)Osbeck by varying biosorbent dose from 1.0mg/ml to 20 mg/mlfor zinc (II) and 1.0 mg/ml to 15 mg/ml for chromium (VI) is as shown in Fig. 4. From the results it was found that biosorption of cadmium (II) and chromium (VI) increases with increase in biosorbent dose 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 biosorption sites (Naiya *et al.*, 2009). The point of saturation for the rind of orange (*Citrus sinensis*), (L.) Osbeckwas found at 5 mg/mL of biosorbent dose with maximum removal efficiency for both cadmium (II) and chromium (VI). 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 *et al.*, 2007).The biosorbent dose 5mg/ml was chosen for all further studies.

Effect of initial cadmium (II)and chromium (VI) concentration

The effect of initial cadmium (II) concentration from 5 mg/L-300 mg/L and chromium (VI) concentration from 5 mg/L - 250 mg/L on the removal of cadmium (II) and chromium (VI) from aqueous solutions at biosorbent dose 5 mg/ml and at optimum pH at 30^{0}C temperature was studied. On increasing the initial cadmium (II) concentration, the total cadmium (II) uptake increased appreciably and the total chromium (VI) ions uptake decreased appreciably.

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 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 biosorbents. In order to optimize the contact time for the maximum uptake of cadmium (II), contact time was varied between 5 minutes–180 minutes and for chromium (VI), 10 minutes–180 minutes on the removal of metal ions from aqueous solutions in the concentration of metal ions10 mg/L, biosorbent dose 5mg/ml, at optimum pH and 30^{0}C temperature (Fig. 5). The results obtained from the biosorption capacity of cadmium (II) and chromium (VI) onto the 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 cadmium (II) and chromium (VI) onto the rind of orange (*Citrus sinensis*), (L.)Osbeck was 90 minutes and 150 minutes with maximum removal. The rapid uptake of cadmium (II) 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. So a contact time of 90 minutes and 150 minutes was fixed for cadmium (II) and chromium (VI) respectively 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 was applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm:

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by (Langmuir, 1918),

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

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 biosorbate.

Linearized Langmuir isotherm allows the calculation of biosorprtion capacities and Langmuir constants and is represented as,

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

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig. 6 (a). The 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 (q_m) of cadmium (II) and chromium (VI)is found to be83.33mg per gand 10.74mg per g, respectively.

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:

$$R_L = \frac{1}{1+bc_i} \qquad (5)$$

where b is the Langmuir constant and C_i is the maximum initial concentration of metal ions. 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 0.5181-0.9847 for concentration of 5 mg/L -300 mg/L with respect to cadmium (II) and 0.1503-0.8984 for concentration of 5 mg/L -250 mg/L with respect to chromium (VI). They are in the range of 0-1 which indicates favorable biosorption (Malkoc andNuhoglu, 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:

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

where θ is the suface area coverage. The θ was found to be 0.0152-0.4818 for concentration of 5 mg/L - 300 mg/L with respect to cadmium (II) and 0.1015-0.8496 for concentration of 5 mg/L - 250 mg/L with respect to chromium (VI).

Frenudlich adsorption isotherm:

Freundlich equation is represented by (Freundlich, 1906),

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

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 sorption data and is represented as,

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

Equilibrium data for the biosorption is plotted as log $q_e$vs log C_e, as shown in Fig. 6 (b). The 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 followes: 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 2.1505 and 2.7878 with respect to cadmium (II) and chromium (VI).Since n>1, this indicates the physical biosorption for both cadmium (II) and chromium (VI) onto the biosorbent. The higher value of K (10.423) for cadmium (II) and K (3.9801) for chromium (VI),indicates the higher biosorption capacity of the biosorbent.

***Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm*:**

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as (Dubinin and Radushkevich, 1947),

$$Inq_e = \text{In } q_m - \beta\varepsilon^2 \qquad (9)$$

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,

$$\varepsilon = RTIn\,(+\frac{\theta}{1-\theta}) \qquad (10)$$

Equilibrium data for the biosorption is plotted as ln$q_e$vsε^2, as shown in Fig. 6 (c). The constants β and q_m are calculated from the slope (β) and intercept (lnq_m) of the line, respectively. The values of adsorption energy E was obtained by the following relationship.

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (11)$$

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

Table 1: Adsorption isotherm constants for biosorption of cadmium (ii) and chromium (vi) byrind of orange (*citrus sinensis*), (l.)Osbeck

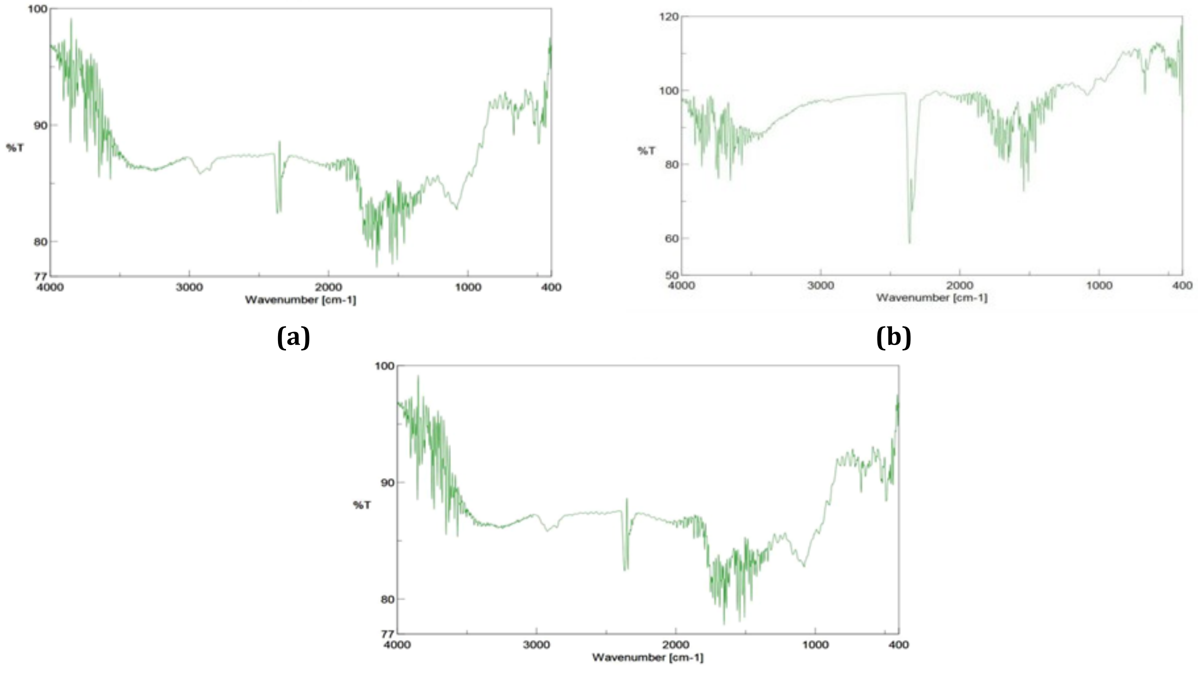
Metal	Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
	q_m	b	R^2	K	$1/n$	R^2	q_m	B	E	R^2	A_T	b_T	R^2
Cadmium (II)	83.33	0.0031	0.911	10.423	0.465	0.831	9.1614	-4E-7	1.4526	0.448	4.0212	294.34	0.654
Chromium (VI)	10.74	0.0226	0.998	3.9801	0.3587	0.915	5.3153	-3E-6	0.4082	0.741	2.2009	1364.94	0.890

Table 2: Adsorption kinetic data for biosorption of cadmium (ii) and chromium (vi) byrind of orange (*citrus sinensis*), (l.)Osbeck

Metal	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	a	B	R^2	ki	c	R^2
Cadmium (II)	2.3094	0.047	0.848	1.0729	4.599	0.998	1.3826	6.4935	0.713	0.044	0.584	0.537
Chromium (VI)	1.4605	0.0164	0.901	1.7111	0.0500	0.996	1.5000	4.3233	0.9313	0.062	0.9277	0.873

Table 3 : Thermodynamic parameters of biosorption of cadmium (ii) and chromium (vi) by rind of orange (*citrus sinensis*), (l.)Osbeck

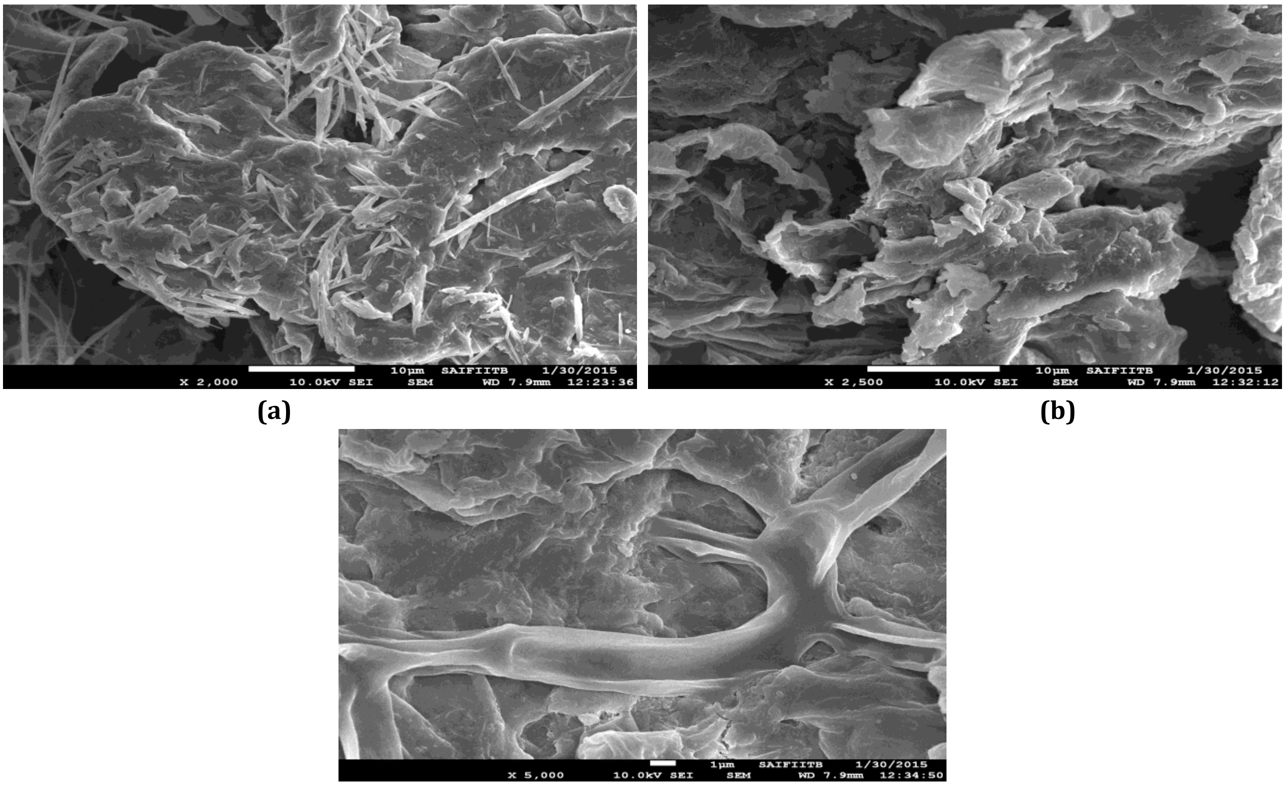
Metal	$-\Delta G^0$ (kJ/mol)				ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
	293 (Kelvin)	303 (Kelvin)	313 (Kelvin)	323 (Kelvin)		
Cadmium (II)		0.769	0.956	1.680	13.319	46.21
Chromium(VI)	0.211	0.810	0.837	1.185	8.839	30.27



(a) **(b)**

(c)

Fig. 1: FTIR spectra (a) biosorbent, rind of orange (*Citrus sinensis*), (L.)Osbeck (b) biosorbent, rind of orange (*Citrus sinensis*), (L.) Osbeck loaded with cadmium (II)(c) biosorbent, rind of orange (*Citrus sinensis*), (L.) Osbeck loaded with chromium (VI)



(a) **(b)**

(c)

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 cadmium (II)(b) biosorbent,rind of orange (*Citrus sinensis*), (L.) Osbeck loaded with chromium (VI)

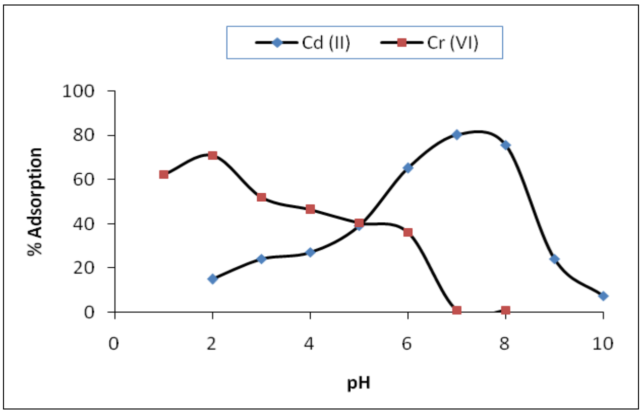


Fig. 3

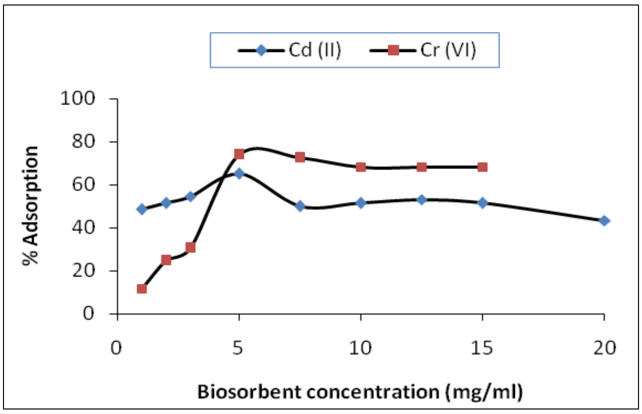


Fig. 4

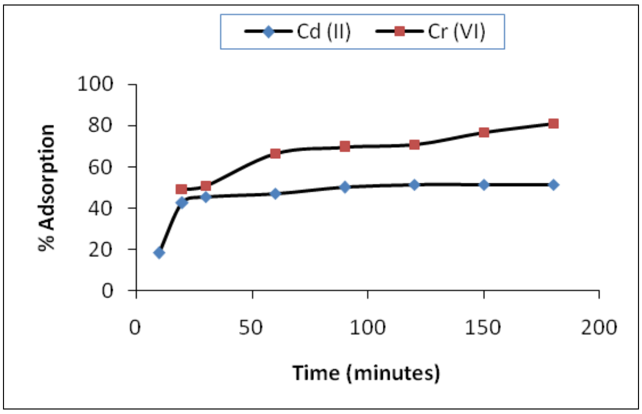
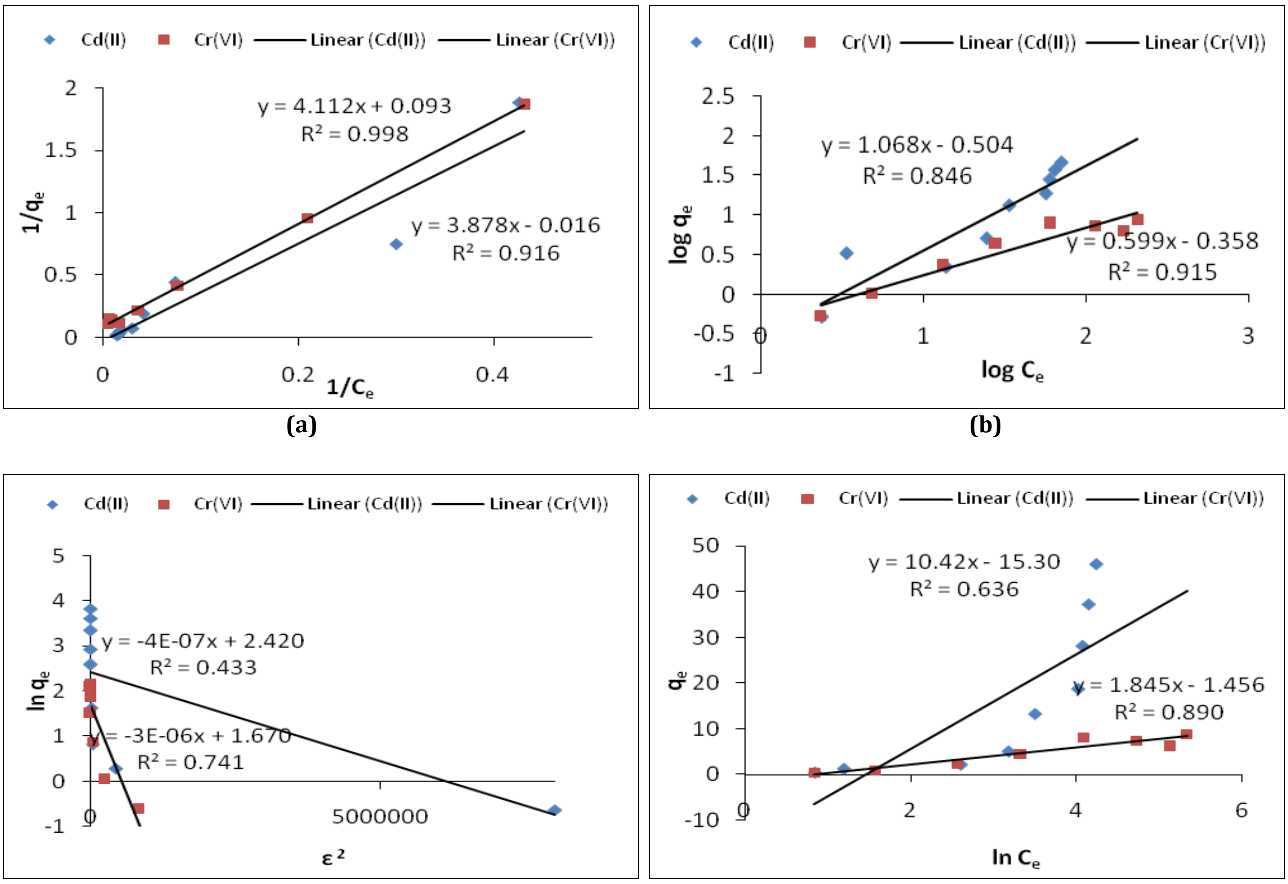


Fig. 3: Effect of pH on biosorption of cadmium (II) and chromium (VI)usingrind of orange (*Citrus sinensis*), (L.)Osbeck

Fig. 4: Effect of biosorbent dose concentration on biosorption of cadmium (II)and chromium (VI)using rind of orange (*Citrus sinensis*), (L.)Osbeck

Fig. 5: Effect of time on biosorption of cadmium (II)and chromium (VI) using rind of orange (*Citrus sinensis*), (L.)Osbeck



(a) **(b)**

(c) **(d)**

Fig. 6: Adsorption isotherm models (a) Langmuir (b) Freundlich (c) DKR and (d) Temkin, forbiosorption of cadmium (II) and chromium (VI) using rind of orange (*Citrus sinensis*), (L.) Osbeck

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 (1.118 KJ mol^{-1}) for cadmium (II) and (0.4082 KJ mol^{-1}) for chromium (VI) which is less than 8 KJ mol^{-1}, the biosorption of cadmium (II) and chromium (VI) onto biosorbent, is of physical in nature(Sawalha *et al.*, 2006).

Temkin adsorption isotherm:

Linearized Temkin adsorption isotherm is given by the equation (Temkinand Pyzhev, 1940),

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

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 $q_e$vslnC_e, as shown in Fig. 6 (d).The constants $b_T$and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot lnA_T$) of the line, respectively. The values of A_T,b_T and regression coefficient (R^2) are listed in Table 1.

Adsorption kinetics

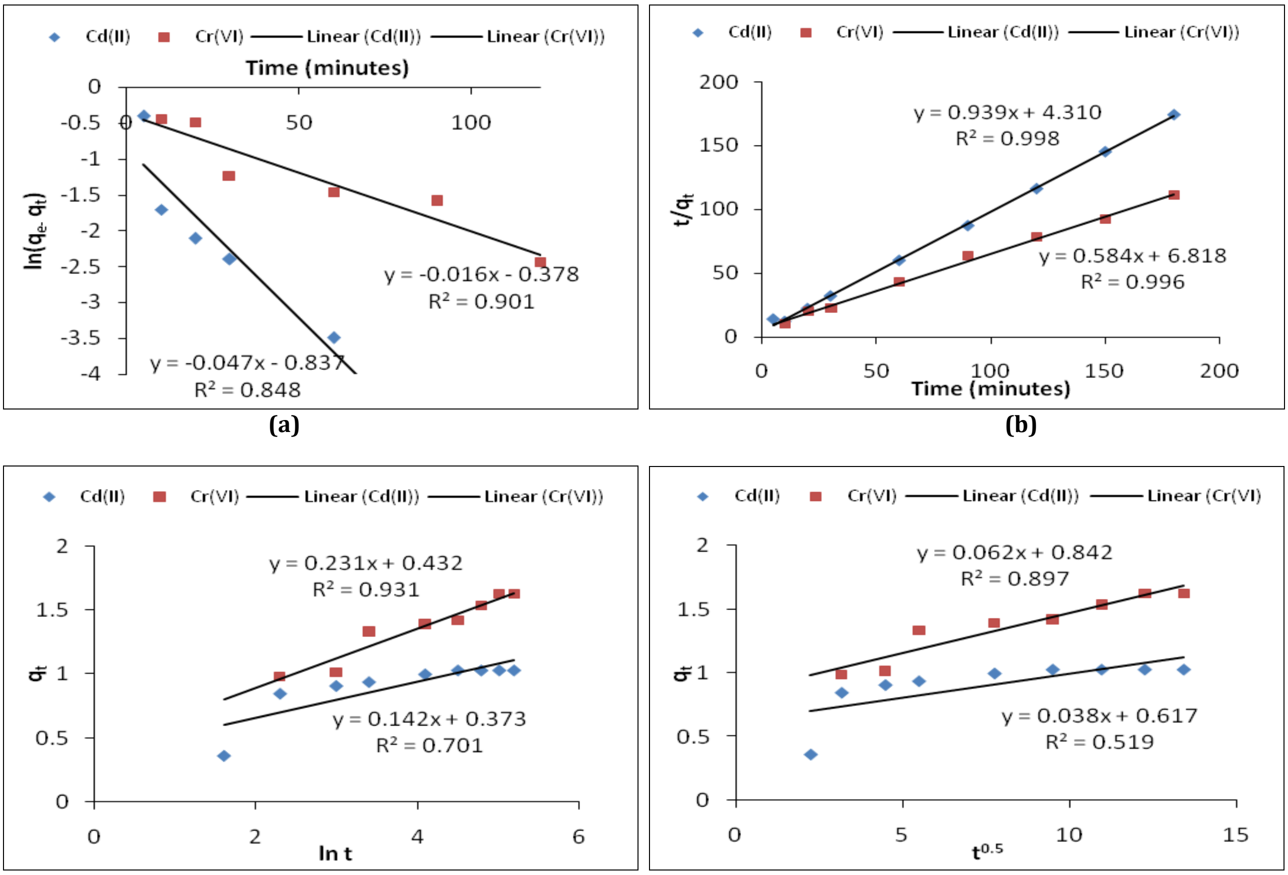
As aforementioned, a lumped analysis of biosorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first-order equation (Lagergren, 1898)(b) the pseudo-second-order equation (McKay, 1999)(c) Elovich(Chien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

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (14)$$

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

$$q_t = k_i t^{0.5} + c \qquad (16)$$



(a) (b) (c) (d)

Fig. 7: Adsorption kinetic models **(a)** pseudo-first-order **(b)** pseudo-second-order(c) Elovichand **(d)** Weber and Morris intraparticlerate diffusion, for biosorptionof cadmium (II) and chromium (VI) using rind of orange (*Citrus sinensis*), (L.) Osbeck

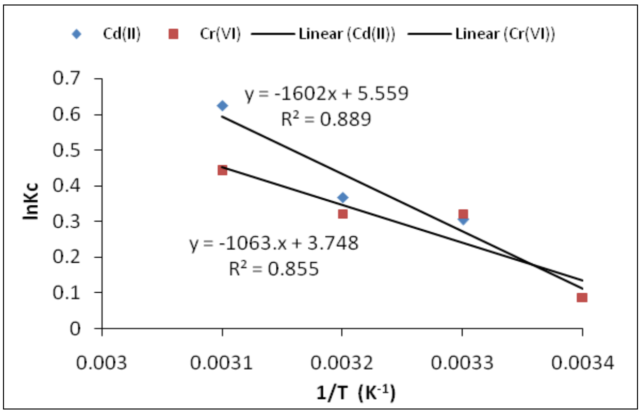


Fig. 8: Determination of thermodynamic parameters for biosorption of cadmium (II) and chromium (VI)using rind of orange (*Citrus sinensis*), (L.) Osbeck

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 biosorption rate and desorption constants, respectively. k_i (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant, c is intercept.

If the biosorption 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 biosorption process obeys the pseudo-second order rate equation. If the biosorption 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 biosorption process obeys the weber & Morris intra-particle diffusion rate equation.

Biosorption of metal ions on to biosorbent was monitored at different specific time interval. The metal ions uptake was calculated from the data obtained. From the metal ions 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 intra-particle diffusion rate equation. The pseudo-first-order equation was plotted for ln(q_e-q_t) against t (Fig. 7 (a)). The values of $q_e$and k_1 values were calculated from the slope (k_1) and intercept (lnq_e) of this plot. The values of q_e,$k_1$and regression coefficient (R^2) are listed 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 biosorbent and the metal ions biosorbed onto it (Septhum*et al.*, 2007). The pseudo-second-order equation was plotted for t/q_t against t (Fig. 7 (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. The valuesof q_e, $k_2$and regression coefficient (R^2) are listed in Table 2. This suggests that metal ions biosorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical biosorption is the rate-limiting step. Metal ions react chemically with the specific binding sites on the surface of biosorbent. The Elovich equation was plotted for $q_t$against ln$t$ (Fig. 7 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($\ln(\alpha\beta)/\beta$) of the plot. The values of β, α andregression coefficient (R^2) are listed in Table 2. The Elovich equation has been used to further explain the pseudo-second-order equation with the assumption that the actual adsorption surface is energetically heterogeneous. Therefore, this could be used to explain that the biosorption surface is energetically heterogeneous (Thomas and Thomas, 1997). The intraparticle diffusion rate equation was plotted for $q_t$against $t^{0.5}$ (Fig. 7 (d)). The value ofk_i and c are calculated from the slope (k_i) and intercept (c) of the plot. The values ofk_i, $c$and regression coefficient (R^2) are listed 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 intra-particle pore diffusion is not only rate-limiting step(Weber and Morris, 1963). The plot of intra-particle 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 biosorbent 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 metal ions from aqueous solutionsin the metal ions concentration 10 mg/L and biosorbentdose 5 mg/ml with optimized pH was studied. Experiments were carried out at different temperatures from 20^{0}C-70^{0}C. The samples were allowed to attain equilibrium. Sorption slightly increases from 30^{0}C-50^{0}C for cadmium (II) and 20^{0}C-50^{0}C for chromium (VI).The equilibrium constant(Catena and Bright, 1989)at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations,

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

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

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

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

Where K_c is the equilibrium constant, C_e is the equilibrium concentration of metal ions in solution (mg/L) and C_{Ae} is the metal ionsconcentration biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0, $\Delta H^0$and $\Delta S^0$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 lnKc versus $1/T$(Fig. 8.). The values of standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and the 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 (ΔG^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of Gibbs free energy (ΔG^0) were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of standard enthalpy change (ΔH^0) was positive, indicating the endothermic nature of the biosorption of metal ions onto the biosorbent. The positive values of standard entropy change (ΔS^0) shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

CONCLUSIONS

The present investigation revealed that the rind of orange (*Citrus sinensis*), (L.) Osbeck can be an inexpensive, excellent biosorbent for the removal of cadmium (II) and chromium (VI) from aqueous solutions.FTIR analysis of biosorbent confirmed that hydroxyl, carbonyl and carboxyl group, so that the cell wall surface of the biosorbent that may interact with the zinc (II) and chromium (VI). The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial metal ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of cadmium (II) and chromium (VI) ontothe rind of orange (*Citrus sinensis*), (L.) Osbeck.Langmuir isotherm model provided a better fit with the experimental datafor both cadmium (II) and chromium (VI). The maximum biosorption capacity of cadmium (II) and chromium (VI) which was determined from Langmuir isotherm was found to be 83.33 mg $g^{1}$and 10.74mg g^{-1}respectively.Results clearly indicates that the pseudo-second-order kinetic model was found to be correlate the experimental data strongest for both cadmium (II) and chromium (VI). The thermodynamic study confirmed thatreaction of biosorptionof cadmium (II) and chromium (VI) onto the rind of orange (*Citrus sinensis*), (L.) Osbeckis spontaneous, endothermicand increasing randomness of the solid solution interfaces. From these observations it can be concluded that the rind of orange (*Citrus sinensis*), (L.) Osbeck has considerable biosorption capacity, available in abundant, non-hazardous agro material could be used as an effective indigenous material for treatment of wastewater stream containing cadmium (II) and chromium (VI).

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