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BIOSORPTION STUDIES OF CADMIUM (II) IONS FROM AQUEOUS SOLUTIONS ONTO ORANGE RIND (CITRUS SINENSIS L. OSBECK)

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Abstract: The biosorption studies for effective removal of cadmium (II) ions from aqueous solutions using orange rind (*Citrus sinensis* L. Osbeck), cost effective biosorbent, was carried out in batch system. FTIR analysis of biosorbent confirmed that carboxyl, hydroxyl, carbonyl group which was responsible for biosorption of cadmium (II) ions. The SEM represents porous structure with surface area. The effects of operational factors including solution pH, biosorbent dose, initial cadmium (II) ions concentration, contact time and temperature were studied. The optimum solution pH for cadmium (II) ions biosorption by biosorbent was 7.0 with the optimal removal 80.30 %. The biosorbent dose 5 mg/ml was enough for optimal removal of 65.15 %. The biosorption process was relatively fast and equilibrium was achieved after 90 minutes of contact. The experimental equilibrium biosorption data were analysed by four widely used two-parameters Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin isotherm models. Langmuir isotherm model provided a better fit with the experimental data than Freundlich, Temkin and Dubinin-Kaganer-Redushkevich (DKR) isotherm models by high correlation coefficient value (R^2 = 0.911). The maximum adsorption capacity determined from Langmuir isotherm was found to be 83.33 mg/g of biosorbent. Simple kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intra-particle diffusion rate equation were employed to determine the adsorption mechanism. Results clearly indicates that the pseudo-second-order kinetic model (R^2 = 0.998) was found to be correlate the experimental data strongest than other three kinetic models and this 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. Orange rind (*Citrus sinensis* L. Osbeck) was successfully used for the biosorption studies of cadmium (II) ions from aqueous solutions and can be applied in waste water technology for remediation of heavy metal contamination.

Keywords: Adsorption isotherms; Adsorption kinetics; FTIR; SEM; Thermodynamic study.

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INTRODUCTION

The increase in environmental pollution due to discharge of industrial effluents containing heavy metals into the open landscapes and water bodies is one of the most serious issues of the country. Heavy metals are a sanitary and ecological threat. They are highly toxic, carcinogenic properties (Cimino and Caristi, 1990) and recalcitrant even at very low concentrations and they can pollute drinking water resources. Strict environmental protection legislation and public environmental concerns lead the search for novel techniques to remove of heavy metals from industrial waste water. Research is therefore important to fully understand systems and technologies for heavy metal removal. Cadmium is a toxic heavy metal of significant environmental and occupational concern (Waalkes, 2000). Cadmium is one of the heavy metal, considered as toxic pollutants which find its way to the water bodies through industries like metal production, phosphate fertilizers, pesticides, electroplating, textile operations, manufacture of batteries and pigments and dyes (Sharma, 2008; Perez-Marin *et. al.,* 2007). Cadmium is non-biodegradable and can accumulate along the food chain which results in serious ecological and health hazard. Cadmium causes sterility and is harmful to human health. Cadmium 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 and liver, carcinogenesis etc. Therefore, the maximum concentration limit for cadmium (II) ions in drinking water has been strictly regulated. The World Health Organization (WHO) set a maximum guideline concentration of 0.003 mg/L for Cadmium (II) ions in drinking water (WHO, 2008). Hence, there is great interest regarding the removal of cadmium from waste water streams.

Various treatment processes in removal of cadmium from waste water has been extensively studied by many authors. A variety of suitable treatment methods can be used for removal of metal pollutants such as reverse osmosis, electrodialysis, ultrafiltration, ion exchange, chemical precipitation, phytoremediation etc. (Rich and cherry, 1987). However, less efficiency, time consuming, disposal, high operational cost and input of chemicals often make these processes impractical and results in further environmental damage (Han et al., 2006). Treatment of industrial effluent with sorbents of biological origin is simple, comparatively inexpensive and friendly to the environment. Biosorption is a powerful, most efficient and cost effective technique which is based on the principle of metal binding capacities of various biological materials, which is very useful method for removal of metal pollutant from wastewater (Bhalerao, 2011; Ahalya *et al.,* 2003; Maind et al., 2012; Maind *et al.,* 2013).

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions. 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 rice husks (Kumar and Bandopadhyay, 2006; Ajmal *et al.,* 2003), ulmus leaves and ulmus leaves ash (Mahvi et al, 2008), banana peel (Anwar *et al.,* 2010), mangosteen shell (Zein et al., 2010) brown alga (Mata et al., 2009), loquat leaves (Awwad and Salem 2011), orange waste (Perez-Marin *et al.,* 2006), coconut shell powder (Pino *et al.,* 2006), coconut copra meal (Ofomaja and Ho 2007), nano zerovalent iron particles (Boparai et al., 2010), olive stones (Blazquez *et al.,* 2005), dried sludge (Choi and Yun 2006), fungi- *Aspergillus niger* (Yun-Guo et al., 2006), sugarcane bagasse (Ibrahim *et al.,* 2006), pomelo peel (Saikaew *et al.,* 2009), *sea urchin test* (John *et al.,* 2014), red alga (*Osmundea pinnatifida*) (Hassoun et *al.,* 2014), *Chlorella vulgaris* (Edris *et al.,* 2014), clays, zeolites, activated carbon have been used for cadmium removal.

Orange (*Citrus sinensis* L. Osbeck) belongs to Rutaceae family being one of the highest production fruit in Maharastra state of India and during production of orange juice, produced a large amounts of waste which has no commercial value.it has chemical constituents like alkaloids, tannins,resins, saponins etc. Orange (*Citrus sinensis* L. Osbeck) rind was selected because of a low cost, higher adsorption capacity, possibility of availability of function groups such as hydroxyl, carboxylic etc. The focus of this work is to study the possible use of Orange rind (*Citrus sinensis* L. Osbeck) as an efficient biosorbent for cadmium (II) ions from aqueous solutions by conducting batch experiments as a function of solution pH, biosorbent dose, initial cadmium (II) ions concentration, contact times and temperature. Adsorption isotherm models (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) and 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).

EXPERIMENTAL

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) ions solution

The stock solution of 1000 ppm of cadmium (II) ions was prepared by dissolving 0.1 g cadmium metal (AR grade) in 1 ml concentrated nitric acid and then diluted in 100 ml of double distilled water and further desired test solutions of cadmium (II) ions were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of adsorbent

The Orange (*Citrus sinensis* L. Osbeck) was purchased from local market. The outer cover which is called as rind of orange removed from fruit and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material and water soluble impurities and water was squeezed out. Biosorbent was then dried at 50^{0}C overnight and crushed. It was sieved to select particles 100 µm in size 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.

Procedure

The static (batch) method was employed at temperature (30^{0}C) to examine the sorption of cadmium (II) ions by biosorbents. The method was used to determine the biosorption capacity, stability of biosorbent and optimum sorption conditions. The parameters were studied by combining adsorbent with solution of cadmium (II) ions 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 cadmium (II) ions 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) ions by the biosorbent,

$$\%\ \mathrm{Ad} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \textbf{(i)}$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the cadmium (II) ions in mg/L.

The equilibrium cadmium (II) ions adsorptive quantity was determined by the following equation:

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

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

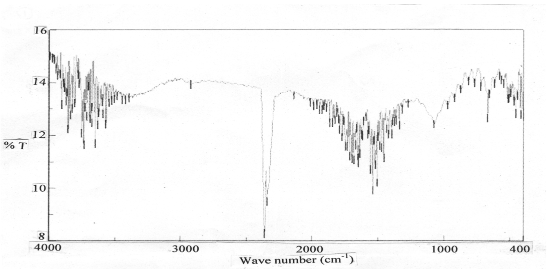
Estimation of cadmium (II) ions concentration

A 0.002 % w/v solution of dithizone (H_2Dz) was prepared in carbon tetra chloride (CCl_4). Known volume of sample solution containing cadmium (II) ions, was pipette out into 250 mL separating funnel and sufficient NaOH was added to get a minimum final NaOH concentration ~5%. To the solution, dithizone (H_2Dz) in carbon tetra chloride (CCl_4) was added until no longer pink color appears. The pink color carbon tetra chloride (CCl_4) layer was separated and washed with 0.1 M NaOH solution. The pink color solution was diluted with carbon tetra chloride (CCl_4) to the 25 ml standard measuring flask. Cadmium (II) ions concentration was estimated by measuring absorbance of the pink color, cadmium-dithizone complex at 520-nm against carbon tetra chloride (CCl_4) as a blank using a UV-visible spectrophotometer. A linear plot for standard cadmium (II) ions solution was obtained indicating adherence to the Beers Lamberts law in the concentration range studies and amount of cadmium (II) ions 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 cadmium (II) ions was tested and results shows that no any appreciable signal of intensity at wavelength 520-nm obtained.

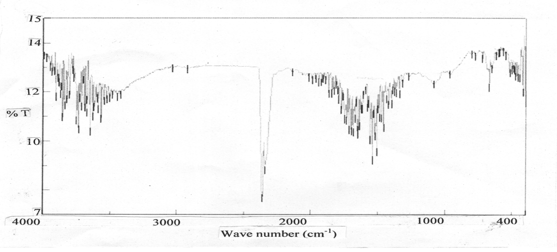
RESULTS AND DISCUSSION

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 biomass. 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. To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in Figure1. 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. As compared to simple biosorbent, biosorbent loaded with cadmium (II) 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 cadmium (II) ions.



(a)

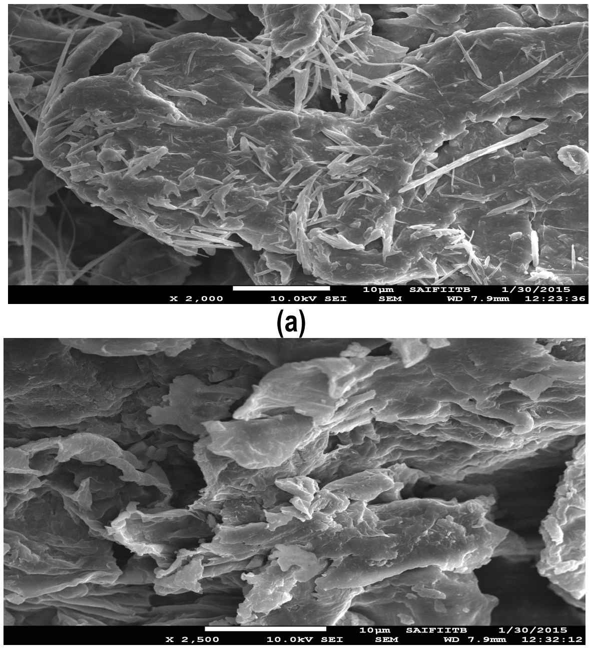


(b)

Figure 1. FTIR spectra (a) biosorbent Orange rind (*Citrus sinensis* L. Osbeck) (b biosorbent Orange rind (*Citrus sinensis L. Osbeck*) loaded with Cd (II) ions.

SEM analysis

The surface morphology of Orange rind (*Citrus sinensis* L. Osbeck) was examine using scanning Electron Microscope (SEM), before and after adsorption and the corresponding SEM micro graphs were obtained by accelerating voltage of 10.0 kv at 2000x for before and 2500x for after adsorption magnification and are presented in Figure 2. At such magnification, the Orange rind (*Citrus sinensis* L. Osbeck) particles showed rod shape and rough areas of within which micro pores were clearly identified.



(a)

(b)

Figure 2. SEM Analysis (a) biosorbent Orange rind (*Citrus sinensis L. Osbeck*) (b) biosorbent Orange rind (*Citrus sinensis* L. Osbeck) loaded with Cd (II) ions.

Effect of pH

The 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. pH influences the chemical structure of the cadmium (II) ions in aqueous solution, hence influencing its bioavailability (Ozacar, 2005). The sorption capacity of the cadmium (II) ions depends on the pH of the adsorption medium, which influences electrostatic binding of cadmium (II) ions to corresponding functional groups. The optimization of pH was done by varying the pH in the range of 2-10 for cadmium (II) ions and pH trend observed in this case is shown in Figure 3. It was found that adsorption increased by increasing pH and at pH 7 the adsorption process was maximum with 80.30 % and then drastically decreases till pH 10. The lesser adsorption at lower pH was due to lesser surface sites are available for sorption. The pH 7 was chosen for all further biosorption studies. Similar observations have been observed for the adsorption of cadmium (II) ions by watermelon (*Citrullus lanatus*) rind (Lakshmipathy *et al.,* 2013).

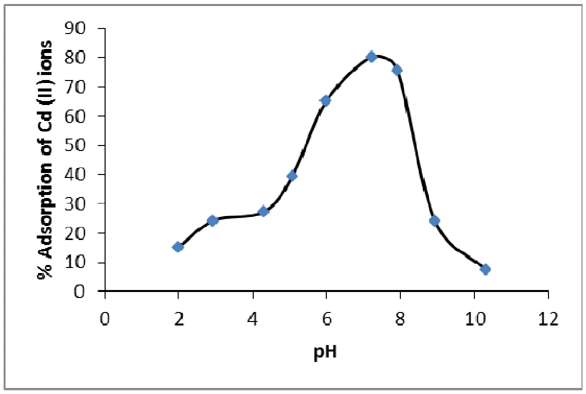


Figure 3. Effect of pH on cadmium (II) ions biosorption by Orange *rind* (*Citrus sinensis* L. Osbeck) (biosorbent dose concentration: 5 mg/ml, cadmium (II) ions concentration: 10 mg/L, contact time: 90 minutes, temperature: 30⁰C).

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 adsorption studies. The sorption capacity of cadmium (II) ions on to orange rind (*Citrus sinensis* L. Osbeck) by varying biosorbent dose from 1.0 mg/ml to 20 mg/ml is as shown in Figure 4. From the results it was found that adsorption of cadmium (II) ions increases with increase in biosorbent dose and is highly dependent on adsorbent 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 orange rind (*Citrus sinensis L. Osbeck*) was found at 5 mg/ml of biosorbent dose with 65.15 % of removal efficiency.

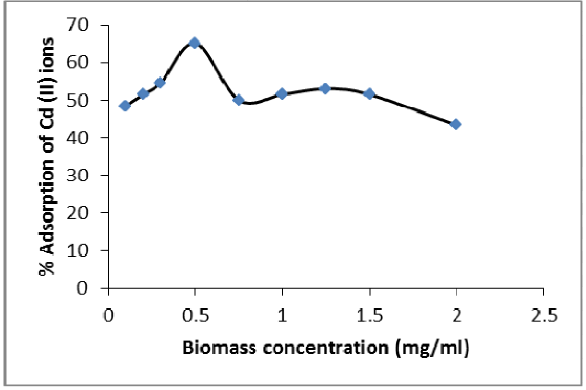


Figure 4. Effect of biosorbent dose concentration on cadmium (II) ions biosorption by Orange rind (*Citrus sinensis* L. Osbeck) (pH: 7, cadmium (II) ions concentration: 10mg/L, contact time: 90 minutes, temperature: 30⁰C).

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 5 mg/ml was chosen for all further studies.

Effect of initial cadmium (II) concentration

The effect of initial cadmium (II) ions concentration from 5 mg/L-300 mg/L on the removal of cadmium (II) ions from aqueous solutions at adsorbent dose 5 mg/ml and at optimum pH 7.0 at 30⁰C temperature was studied. On increasing the initial cadmium (II) ions concentration, the total cadmium (II) ions uptake increased appreciably 53.00 % to 76.76 % at cadmium (II) ions concentration ranges from 5 mg/L-300 mg/L with slight fluctuations.

Effect of contact time

Contact time plays an important role in affecting efficiency of adsorption. 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 cadmium (II) ions, contact time was varied between 5 minute –180 minute on the removal of cadmium (II) ions from aqueous solutions in the concentration of cadmium (II) ions 10 mg/L, biosorbent dose 5 mg/ml, optimum pH 7.0 and 30^0C temperature. The results obtained from the adsorption capacity of cadmium (II) ions onto Orange rind (*Citrus sinensis* L. Osbeck) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for adsorption of cadmium (II) ions onto Orange rind (*Citrus sinensis* L. Osbeck) was 90 minutes with 51.51 % removal. The rapid uptake of cadmium (II) ions 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 cadmium (II) ions biosorption. So a contact time of 90 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 (Bhalerao, 2011).

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:

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

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 adsorprtion capacities and Langmuir constants and is represented as:

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

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Figure. 5 (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 83.33 mg per g of biosorbent which is higher than the other adsorbents used by many authors like rice husks (8.58 mg/g) (Kumar and Bandyopadhyay, 2006), ulmus leaves (6.94 mg/g) and ulmus leaves ash (8.44 mg/g) (Mahvi *et al.,* 2008), sugar cane bagasse (6.79 mg/g) (Ibrahim *et al.,* 2006), banana peel (5.471 mg/g) (Anwar *et al.,* 2010), mangosteen shell (3.15 mg/g) (Zein *et al.,* 2010). 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:

$$R_L = \frac{1}{1+bC_i} \qquad \textbf{(v)}$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of cadmium (II) ions. 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 0.5181-0.9847 for concentration of 5 mg/L -300 mg/L of cadmium (II) ions. 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:

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

Where θ is the surface area coverage. The θ was found to be 0.0152-0.4818 for concentration of 5 mg/L -300 mg/L of cadmium (II) ions.

Frenudlich adsorption isotherm (Frenudlich, 1906)

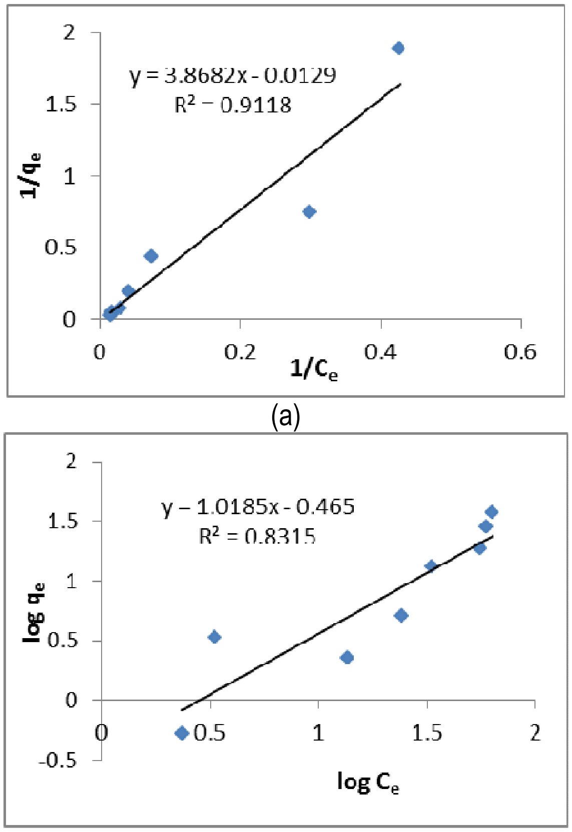
Freundlich equation is represented by:

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

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

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

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad \textbf{(viii)}$$



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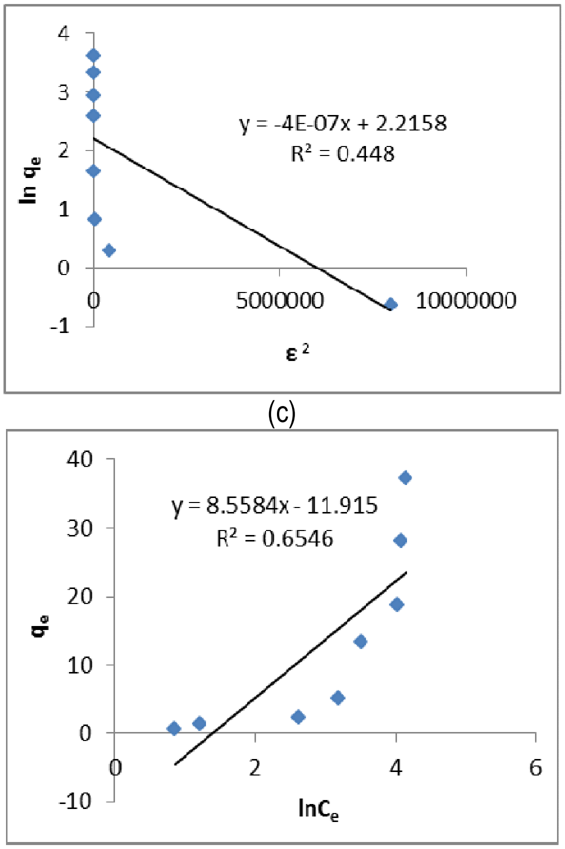


(c)

(d)

Figure 5. Adsorption isotherm models: (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of cadmium (II) ions by Orange *rind* (*Citrus sinensis* L. Osbeck). (pH: 7.0, biosorbent dose concentration: 5 mg/ml, contact time: 90 minute, temperature: 30^{0}C).

Equilibrium data for the biosorption is plotted as log q_e vs log C_e, as shown in Figure 5 (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 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. Since *n* > 1, this indicates the physical biosorption of cadmium (II) ions onto Orange rind (*Citrus sinensis* L. Osbeck). Similar results was obtained by other authors (Awwad and Salem, 2011; Perez-Marin *et al.,* 2006; Pino et al., 2006; Yun-Guo *et al.,* 2006; Ibrahim *et al.,* 2006). The higher value of *K* (10.423) 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:

$$lnq_e = \ln q_m - \beta\, \varepsilon^2 \qquad \textbf{(ix)}$$

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:

$$\varepsilon = RT ln\,(1 + \frac{1}{C_e}) \qquad \textbf{(x)}$$

Equilibrium data for the adsorption is plotted as ln q_e vs ε^2, as shown in Figure 5c. 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.

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

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 (1.118 KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of cadmium (II) ions 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:

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

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 Figure 5 (d). The two 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.

Table 1. Adsorption isotherm constants for biosorption of cadmium (II) ions by orange rind (*Citrus sinensis* L. Osbeck)

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
83.33	0.0031	0.911	10.423	0.465	0.831	9.1614	-4 E-7	1.4526	0.448	4.0212	294.34	0.654

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 et al., 1999) (c) Elovich equation (Chien and Clayton, 1980) (d) Weber and Morris intraparticle diffusion rate equation (Weber and Morris, 1963) are presented below.

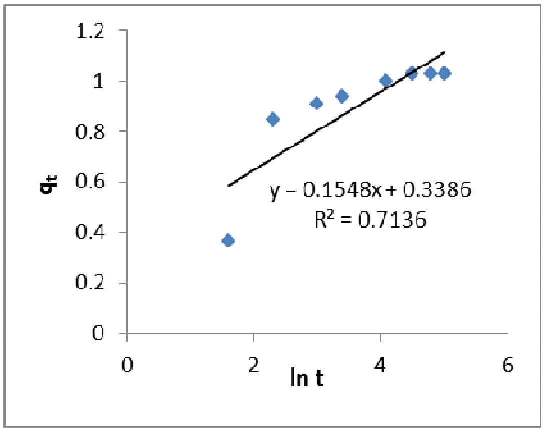
$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \textbf{(xii)}$$

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

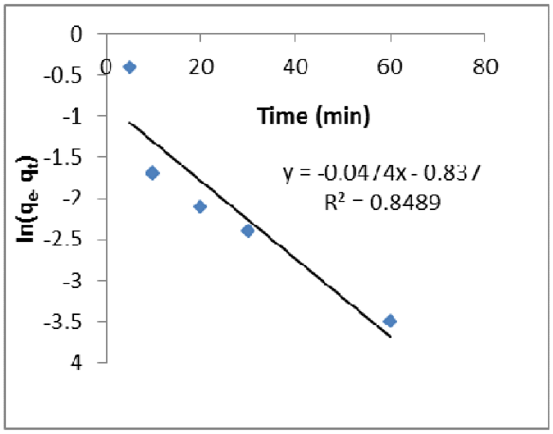
$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad \textbf{(xv)}$$

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

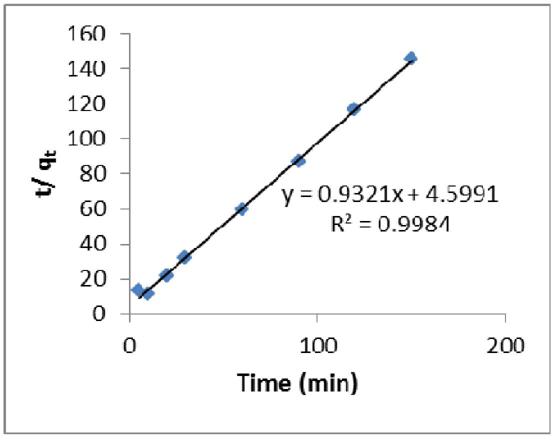
Where q_e (mg/g) is the solid phase concentration at equilibrium, q_t (mg/g) is the average solid phase concentration at time t (min), K_1 (min^{-1}) and K_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α (mg/g/min) and β (g/mg) are Elovich coefficients representing initial sorption rate and desorption constants, respectively. K_i (mg/g/min^2) is the intraparticle diffusion rate constant, c is intercept. If the biosorption follows the pseudo-first-order rate equation, a plot of ln $(q_e\text{-}q_t)$ 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 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 biosorption process obeys the Weber and Morris intraparticle diffusion rate equation. Biosorption of cadmium (II) ions on to biosorbent was monitored at different specific time interval. The cadmium (II) ions uptake was calculated from the data obtained. From the cadmium (II) 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 and Morris intraparticle diffusion rate equation. The pseudo-first-order equation was plotted for ln $(q_e\text{-}q_t)$ against t (Figure 6a). The values of q_e and K_1 values were calculated from the slope (K_1) and intercept (ln q_e) of this plot and shown in Table 2. Pseudo-first-order kinetic model showered the correlation value ($R^2 = 0.848$) being lower than the correlation coefficient for the pseudo-second-order equation. Kinetic adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions sorbed onto it (Septhum *et. al.*, 2007). The pseudo-second-order equation was plotted for t/q_t against t (Figure 6 (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. Pseudo-second-order kinetic model showered the strongest correlation ($R^2 = 0.998$). This suggests that cadmium (II) ions adsorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical biosorption is the rate-limiting step. Cadmium (II) ions react chemically with the specific binding sites on the surface of biosorbent. The Elovich equation was plotted for q_t against ln t (Figure 6c). 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 to further explain the pseudo-second-order equation with the assumption that the actual biosorption surface is energetically heterogeneous. Elovich equation showed a correlation value ($R^2 = 0.713$) being lower than the correlation coefficient for the pseudo-first-order and pseudo-second-order equation. 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 $t^{0.5}$ (Figure 6d). 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.



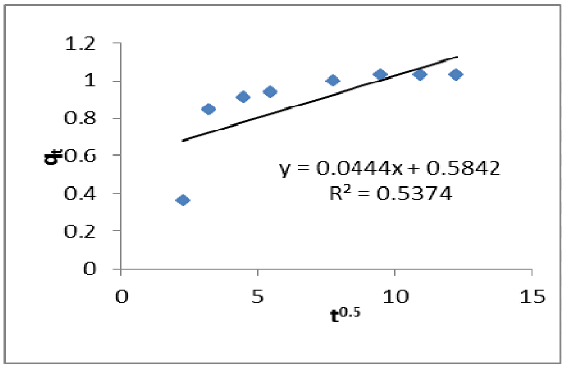
a.



b.



c.



d.

Figure 6. Adsorption kinetic models: (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intra-particle diffusion rate equation, for biosorption of cadmium (II) ions by Orange rind (*Citrus sinensis* L. Osbeck) (pH: 7.0, biosorbent dose concentration: 5 mg/ml, cadmium (II) ions concentration: 10 mg/L, temperature: 30^0C).

Table 2. Adsorption Kinetic data for Biosorption of cadmium (II) ions by Orange rind (*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	a	β	R^2	Ki	C	R^2
2.3094	0.047	0.848	1.0729	4.599	0.998	1.3826	6.4935	0.713	0.044	0.584	0.537

The Weber and Morris intra particle diffusion rate equation showed a lowest correlation value (R^2 = 0.537) being lower than the correlation coefficient for the Elovich equation, pseudo-first-order 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, 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 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 adsorption (Panday *et al.,* 1986).

Thermodynamic study

The effect of temperature on removal of cadmium (II) ions from aqueous solutions in the cadmium (II) ions concentration 10 mg/L and biosorbent dose 5 mg/ml with optimum pH 7.0 was studied. Experiments were carried out at different temperatures from 30^0C-70^0C. The samples were allowed to attain equilibrium. Sorption slightly increases from 30^0C-50^0C. The equilibrium constant (Catena and Bright, 1989) at various temperatures and thermodynamic parameters of biosorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \qquad \text{(xvii)}$$

$$\Delta G^0 = -RT\ \ln K_c \qquad \text{(xviii)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{(xix)}$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad \text{(xx)}$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration of the cadmium (II) ions in solution (mg/L) and C_{Ae} is the cadmium (II) ions 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).

Table 3. Thermodynamic parameters of biosorption of Cadmium (II) ions by orange rind (*Citrus sinensis* L. Osbeck)

T (K)	Kc	$-\Delta G^0$ (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
303	1.3571	0.769	13.319	46.2
313	1.4444	0.956		
323	1.8696	1.680		

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 7).

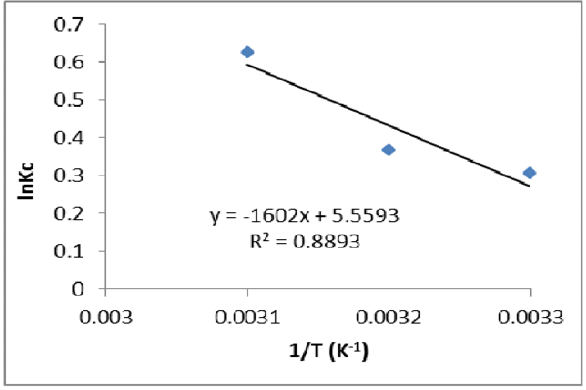


Figure 7. Determination of thermodynamic parameters for biosorption of cadmium (II) ions by Orange rind (*Citrus sinensis* L. Osbeck) (pH: 7.0, biosorbent dose concentration: 10 mg/ml, cadmium (II) ions concentration: 10 mg/L, contact time: 90 minutes).

The values of equilibrium constant (*Kc*), 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 rate. The standard Gibbs free energy (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 value of ΔH^0 was positive, indicating the endothermic nature of the biosorption of cadmium (II) ions onto Orange rind (*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.

CONCLUSION

The present investigation reveals that Orange rind (*Citrus sinensis* L. Osbeck) can be an inexpensive, excellent biosorbent for the removal of cadmium (II) ions from aqueous solutions. The biosorbent characterized by FTIR analysis, it was confirmed that functional groups like hydroxyl, carbonyl and carboxyl present which was responsible for biosorption of cadmium (II) ions. The SEM represents porous structure with surface area. The optimal parameters such as solution pH, biosorbent dose, initial cadmium (II) ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of cadmium (II) ions onto Orange rind (*Citrus sinensis* L. Osbeck). The maximum cadmium (II) ion loading capacity (q_e) of Orange rind (*Citrus sinensis* L. Osbeck) was found to be 83.33 mg g^{-1} with perfect fit to Langmuir isotherm model and follows pseudo-second order kinetics. The thermodynamic study confirmed that reaction of biosorption of cadmium (II) ions onto Orange rind (*Citrus sinensis* L. Osbeck) is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that Orange rind (*Citrus sinensis* L. Osbeck) has considerable biosorption capacity, available in abundant, non-hazardous material could be used as an effective indigenous material for treatment of wastewater stream containing cadmium (II) ions.

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