



## BIO-SORPTION OF NICKEL ON MODIFIED PHOENIX DACTYLIFERA L. SEEDS

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### Abstract

This study reveals the potential of modified Phoenix Dactylifera L. seeds as a bio-sorbent to adsorb Ni (II) ions present in simulated wastewater. The effect of initial pH and contact time on the uptake of Ni (II) ions were studied. Pore diffusion model was fitted to determine the rate limiting step (RLS). Increase in pH from 3 to 5 increased the removal efficiency from 7.68 to 24.8 %. The maximum uptake of Ni(II) ions was 4.18 and 12.4 mg/g at pH 3 and 5 respectively. The Pseudo 2<sup>nd</sup> order (PSO) model was found most suitable in kinetic studies, showing value of correlation coefficient  $R^2$  close to unity. Most of the bio-sorption process was completed in first 20 minutes at pH 3 and 5 after that no substantial change was observed and system remained at equilibrium. Weber and Moris model showed multi linearity, indicating chemisorption to be rate limiting step (RLS) in bio-sorption of Ni (II) ions on modified Phoenix Dactylifera L. seeds.

**Keywords:** Biosorption, Phoenix Dactylifera L.seeds, pH, Kinetic study

### 1. Introduction

Increased industrialization and technology development has raised heavy metals release in the environment. Many Industries like electroplating, dyeing, metal finishing, mining, battery manufacturing and metal processing releases wastewater that contains toxic heavy metals such as Ni, Cd, Pb, Cu, and Cr etc. These heavy metals possess non-biodegradable and bio accumulating properties which can cause serious health issues to humans. Nickel is one of a heavy metal toxicant at higher concentration and its excessive exposure can pose serious damage to lungs, kidneys and skin dermatitis [1]. Nickel compounds creates tumor in animals which leads to cancer. Human and rodent's cells are transformed in vitro by insoluble nickel compounds. Nickel compounds are also declared carcinogenic in nature by International Agency for Research on Cancer (IARC) in 1990 [2]. These toxicological concerns have resulted in various studies for the removal of nickel in wastewater.

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Many techniques are currently in practice in order to purify industrial wastewater from heavy metals such as chemical precipitation, chemical reduction, adsorption, reverse osmosis, chemical precipitation, electro-coagulation and neutralization [3]. Most of these techniques are expensive and requires operational expertise, which limits their industrial applications. The choice of technique is based on heavy metal concentration in wastewater and cost associated with the treatment technique. Recently bio sorption technology using inactive and dead biomasses to remove toxic heavy metals is attaining importance day by day [4, 5]. Bio sorbents have high specific metal binding ability in complex media which makes them efficient for purification of wastewater from heavy metals [6]. In order to remove heavy metals ions from wastewater many agricultural wastes have been applied in recent years such as banana peel [7], corn cobs, corn stalks, wheat straw and soybean straw [8], neem bark and saw dust [9], Cinnamomum camphora leaves powder [10], cashew nut shell [11], coffee husks [12] etc. Although metal binding capacity of these agricultural waste is low compared to activated carbon or ion exchange resins commercially available in the market but slight modifications (acid, base or heat treatment) have enhanced biosorption capacity for heavy metals [13]. As a result, low cost agricultural waste can be used economically in replacement of commercially available adsorbents.

Phoenix dactylifera L. is a widely cultivated plant in Asia, North Africa and the Middle East. It is usually known as date palm plant. The plant is usually cultivated in dry and partly dried regions of the world. Countries like Saudi Arabia and Iraq are high date cultivating countries, the number of date palm trees are over 4,000,000 and approximately 100,000 tons of dates pits are available per year. Seeds of date palm plant are an agriculture waste and can be utilized for various benefits as they contain substantial amounts of nutrients [14, 15]. They can also be used as a sorbent to biosorb heavy metals present in wastewater. In recent years various studies have been conducted on date palm's wastes including sorption of anionic dye [16], Cu (II) ions [17,18], Pb (II) ions [19, 20, 21],  $\text{PO}_4^{3-}$  [22], Heavy metals ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ) ions [23] and Uranium (VI) ions [24].

Current study focuses on the potential of date palm seeds as low cost sorbent. In this study date palm seeds were modified by treating them with dilute  $\text{HNO}_3$  acid and effects of pH, contact time were investigated in order to adsorb Ni (II) ions present in simulated wastewater.

## 2. Materials and Methods

Date palm seeds were collected from different juice shops in Lahore, Pakistan and water-washed repetitively to eradicate soluble and insoluble impurities. The seeds were exposed in sunlight and dried for at least 24 h and grounded to fine powder of size range between 170-300  $\mu\text{m}$ . The modification process was done by treating date seeds powder with 0.1M  $\text{HNO}_3$  at room temperature for 24 h. Treated powder was then filtered and neutralized to pH 7 by thoroughly washing with distilled water. The biosorbent was then dried and preserved for further use. Weighted amount of analytical grade  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  salt was dissolved in distilled water to prepare 1000 mg/L Ni (II) ions stock solution. Stock solution was further diluted with distilled water in order to prepare sorption experiments solutions. Batch experiments were executed to investigate the factors effecting adsorption rate and uptake capacity. A weighted amount of biosorbent was mixed with 100 ml solution carrying 100 mg/L of Ni (II) ions in Erlenmeyer flask at room temperature. The flasks were shaken at 150 rpm constant shaking rate in orbital shaker. The effect of initial pH and contact time was investigated under optimized conditions

from 0 to 90 min at different pH values. At the beginning of sorption experiments, samples were withdrawn at 1-5 min intervals and at 10-20 min intervals after reaching equilibrium. 0.1M HCL and 0.1M NaOH was used to adjust the pH of solutions. Mean values of three independent experiments were used to present data of sorption experiments. Whatman filter paper (No.42) was used to filter the samples and Ni (II) ions concentration in the filtrate was checked by using Agilent 240FS AA. The Ni (II) ions uptake was determined from the mass balance equation

$$q_e = \frac{(C_i - C_f)V}{W} \quad (1)$$

Where  $C_i$  (initial concentration (mg/L)),  $C_f$ (instantaneous Ni (II) concentration (mg/L)),  $V$ (Ni (II) analyte volume (L)),  $W$  (biosorbent weight (g)),  $q_e$  (uptake (mg/g)).

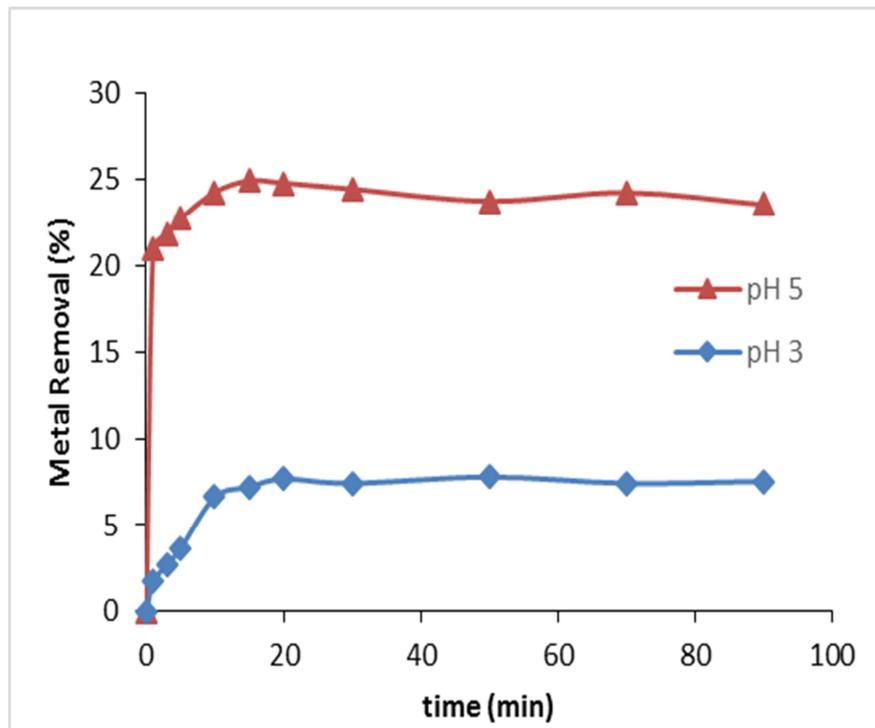
Removal (%) of Ni (II) ions in samples was determined from percent equation

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

### 3. Results and Discussion

#### 3.1 Effect of pH

One of the utmost precarious parameter, in the discussion of metal ions biosorption, is initial pH



**Figure 1: Effect of Initial pH and Contact time on sorption of Ni (II) ions on Phoenix Dactylifera L.seeds**

of biosorption medium as it influences biosorbent sites dissociation and solution chemistry [25, 26]. In this study effect of initial pH on sorption of Ni (II) ions was carried out on pH 3 and pH 5 at constant initial concentration of Ni (II) ions and dosage of biosorbent. Removal (%) of Ni (II) ions was remarkably greater at pH 5 than at pH 3 (Figure 1). It directly showed that number of

sites for biosorption of Ni (II) ions at pH 5 were greater than at pH 3. This increase in removal (%) of Ni (II) ions at pH 5 was due to increase in electrostatic forces as total negative charges on surface of biosorbent increased at higher pH. Furthermore, total number of negatively charged functional groups present at surface of biosorbent for binding of Ni (II) ions increased at higher pH which greatly reduced the competition between protons and metal ions [27].

### 3.2 Effect of Contact Time

Time required for metal biosorption strongly depends on nature of biosorbent. Batch kinetics experiments were performed from 0 to 90 min under optimized conditions. Figure 1 shows metal removal initially increased rapidly and equilibrium was achieved within 20 minutes as no improvement in metal removal was observed after this length of contact time. The sorption process can be understood by three common step. The first step is the mass transfer from bulk solution to thin liquid film layer surrounding the surface of the particle. In second step sorption process takes place at individual sites on surface of particle. This step is presumed to be rapid in nature and energy contents of the binding process depends on whether it is physical or chemical sorption. This step is assumed to be rapid in nature. The third step is intraparticle diffusion in which adsorbate molecules diffuses on adsorbent sites by solid surface diffusion or by pore diffusion mechanism [28]. One or more than one step could be responsible in describing the rate controlling mechanism. Biosorption of Ni (II) ions onto modified Phoenix Dactylifera L. seeds involves multiple steps as can be examined in Figure 1. Initial rapid biosorption of Ni (II) ions could be due to the availability of vacant binding sites on the surface of modified Phoenix Dactylifera L. seeds while intra particle diffusion (IPD) could be reason of slower step [29].

Pseudo 1<sup>st</sup> order (PFO) and pseudo 2<sup>nd</sup> order (PSO) models were used to investigate kinetic experimental data. The PFO Lagergan equation in linear form is represented as follows

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

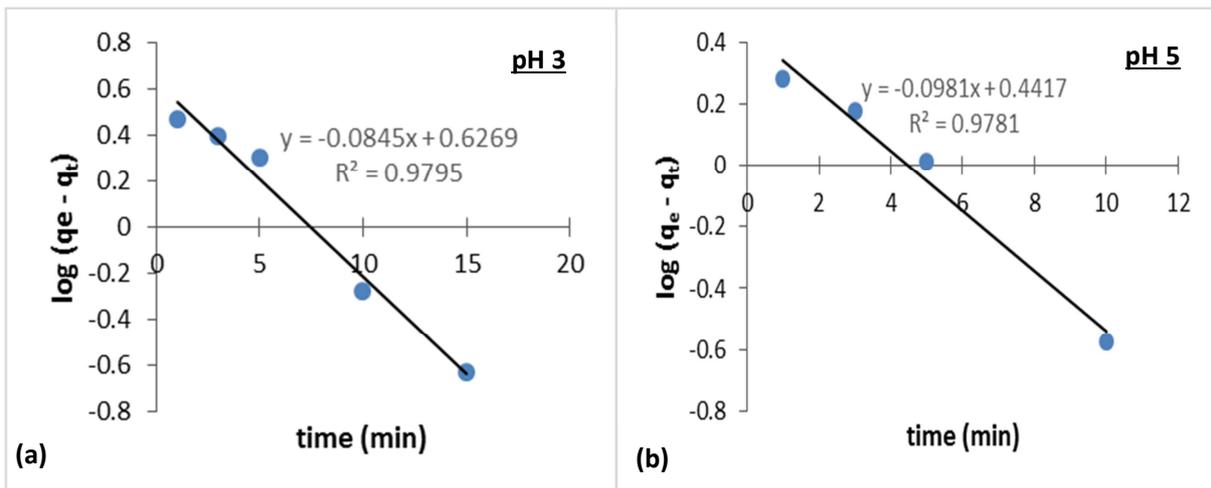


Figure 2: Pseudo 1<sup>st</sup>Order Plots at(a) pH 3 and (b) pH 5 of Ni (II) ions sorption on modified *Phoenix Dactylifera L.* seeds

Where  $q_t$ (Instantaneous Ni (II) uptake (mg/g)),  $q_e$ (equilibrium Ni (II) uptake (mg/g)),  $k_1$ (rate constant of PFO sorption process ( $\text{min}^{-1}$ )). Plots of  $\log(q_e - q_t)$  against  $t$  are presented in Figure. 2a and 2b. PFO equilibrium uptake  $q_e$  and rate constant  $k_1$  calculated by intercepts and slopes of plots are provided in Table 1. The correlation coefficient  $R^2$  were 0.979 and 0.978 for pH 3 and pH 5 respectively. The  $q_{e,cal}$  calculated and  $q_{e,exp}$  experimental values were not similar which showed that biosorption kinetics did not comply with the PFO model.

The PSO kinetic model equation in linear form is expressed as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where  $k_2$ (equilibrium rate constant of PSO sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ )). Plots of  $t/q_t$  against  $t$  generates straight lines as shown in Figure. 3a and 3b. PSO equilibrium uptake  $q_e$  and rate constant  $k_2$  calculated by intercepts and slopes of plots are provided in Table 1. The correlation coefficients ( $R^2$ ) were approximately unity. Moreover the  $q_{e,cal}$  calculated values were in good agreement with experimental values. Thus PSO kinetic model is more appropriate for biosorption of Ni (II) ions on modified *Phoenix Dactylifera L.* seeds [30].

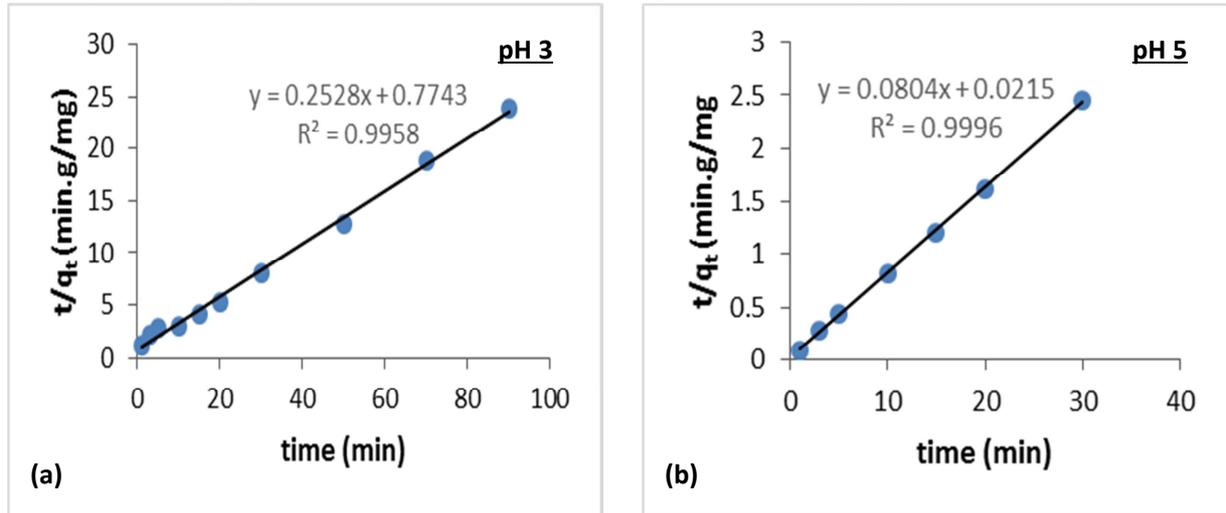


Figure 3: Pseudo 2<sup>nd</sup> Order Plots at (a) pH 3 and (b) pH 5 of Ni (II) ions sorption on modified *Phoenix Dactylifera L.* seeds

Table 1: Kinetic Models Regression Parameters

Kinetic Model		Ni (II)	
		3	5
pH			
	$q_{e,experimental}$	3.8417	12.400
Pseudo 1 <sup>st</sup> order	$k_1$	0.1946	0.2259
	$q_{e,cal}$	4.2350	2.7650
	$R^2$	0.9795	0.9781
Pseudo 2 <sup>nd</sup> order	$k_2$	0.0825	0.3006
	$q_{e,cal}$	3.9556	12.430

$R^2$ 

0.9958

0.9996

To find rate limiting step, Weber and Morris model was applied which is represented by following equation [31].

$$q_t = k_{diff}t^{0.5} + B \quad (5)$$

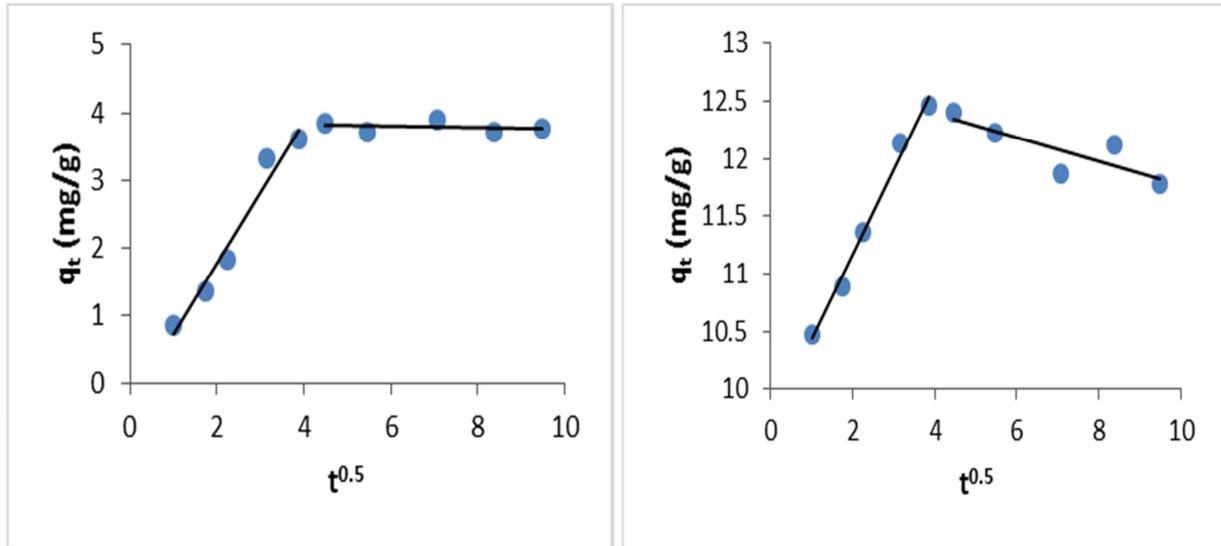


Figure 4: Pore diffusion model at (a) pH 3 and (b) pH 5 of Ni (II) ions sorption on modified *Phoenix Dactylifera L.* seeds

Where  $k_{diff}$  (rate constant of intra particle diffusion ( $\text{mg g}^{-1} \text{min}^{-1}$ )),  $B$  (boundary layer thickness ( $\text{mg g}^{-1}$ )). Straight line plotting between  $q_t$  against  $t^{1/2}$  indicates that the intraparticle diffusion (IPD) is the rate limiting step. However, plots in Fig. 4a and 4b showed multi-linearity, indicating intraparticle diffusion (IPD) is not the rate limiting step (RLS). It may be suggested that chemisorption is the RLS in biosorption of Ni (II) ions on modified Phoenix Dactylifera L. seeds.

In Table 2, comparison between Ni(II) ions uptake on modified date palm seeds (MDPS) and other biosorbents is provided. It shows that metal binding ability of MDPS is good as compared to other biosorbents used previously.

Table 2 Comparison of Ni(II) ions uptake on MDPS with literature

Biosorbent	$q_{max}$ (mg/g)	Reference
Cochlospermum gossypium	50.5	[32]
Oedogonium hatei	44.2	[33]
Undaria pinnatifida	24.71	[34]
Modified Date palm seeds	12.4	This Study

Baker's yeast	11.4	[35]
Rhodococcus opacus	7.63	[36]
Aspergillus niger	4.82	[37]
Chlorella miniata	1.37	[38]
Chlorella vulgaris	0.64	[38]

#### 4. Conclusions

The metal binding ability of modified *Phoenix Dactylifera* L. seeds for biosorption of Ni (II) ions was examined in simulated wastewater. Effect of initial pH and contact time clearly affected removal (%). Increase in pH from 3 to 5 increased the removal (%) from 7.68 to 24.8 %. Pseudo 2<sup>nd</sup> order (PSO) model was found most suitable in kinetic studies and equilibrium was reached rapidly within first 20 minutes at pH 3 and pH 5. Chemisorption was proved to be rate limiting step in sorption process. These results suggested that modified *Phoenix Dactylifera* L. seeds can exhibit as a potential biosorbent for Ni (II) ions removal from wastewater.

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#### References

- [1] E. Denkhaus and K. Salnikow, Nickel essentiality, toxicity, and carcinogenicity, *Critical Reviews in Oncology/Hematology* 42(2002) 35–56.
- [2] International Agency for Research on Cancer. IARC monographs on the evaluation of carcinogenic risks to humans. Chromium, nickel and welding. 49. IARC, Lyon; 1990
- [3] I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium (II) ions from aqueous phase by eucalyptus bark, *Journal of Hazardous Materials* 152(2008) 148–158.
- [4] G. H. Pino, L. M. S. De Mesquita, M. L. Torem, and G. A. S. Pinto, "Biosorption of heavy metals by powder of green coconut shell," *Separation Science and Technology*, vol. 41, no. 14, pp. 3141–3153, 2006.
- [5] G. H. Pino, L. M. Souza De Mesquita, M. L. Torem, and G. A. S. Pinto, "Biosorption of cadmium by green coconut shell powder," *Minerals Engineering*, vol. 19, no. 5, pp. 380–387, 2006.
- [6] V. K. Gupta and A. Rastogi, "Biosorption of lead (II) from aqueous solutions by non-living algal biomass *Oedogonium* sp. and *Nostoc* sp.: a comparative study," *Colloids and Surfaces B*, vol. 64, no. 2, pp. 170–178, 2008.
- [7] J. R. Memon, S. Q. Memon, M. I. Bhanger, A. Adel El-Turki, K. R. Hallam, G. C. Allen, Banana peel: A green and economical sorbent for the selective removal of Cr(VI) from industrial wastewater, *Colloids and Surfaces B: Biointerfaces* 70 (2009) 232–237.
- [8] M. Šæiban, M. Klačnja, B. Škrbiæ, Adsorption of copper ions from water by modified agricultural by-products, *Desalination* 229 (2008) 170–180.

- [9] T. K. Naiya, P. Chowdhury, A. K. Bhattacharya, S. K. Das, Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn (II) and Cd (II) ions from aqueous solutions, *Chemical Engineering Journal* 148 (2009) 68–79.
- [10] H. Chen, G. Dai, J. Zhao, A. Zhong, J. Wu, H. Yan, Removal of copper(II) ions by a biosorbent-Cinnamomum camphora leaves powder. *J. Hazard. Mater.* 2010, 177, 228.
- [11] P.S. Kumar, S. Ramalingam; V. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination* 2011, 266, 63.
- [12] W.E. Oliveira, A.S. Franca, L.S. Oliveira, S.D. Rocha, Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *J. Hazard. Mater.* 2008, 152, 1073.
- [13] D. Mohana and J. C .U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *Journal of Hazardous Materials B137* (2006) 762–811.
- [14] M.S. Baliga, B. R. V. Baliga, S.M. Kandathil, H.P. Bhat, P.K. Vayalil, A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera L.*). *Food Res. Int.* 2011, 44, 1812.
- [15] S. Besbes, C. Blecker, C. Deroanne, N.E.; Drira, H. Attia, Date seeds: chemical composition and characteristic profiles of the lipid fraction. *Food Chem.* 2004, 84, 577.
- [16] A.E. Ofomaja, Y.S. Ho, Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent. *Dyes Pigm.* 2007, 74, 60.
- [17] Y.S. Ho, A.E. Ofomaja Kinetic studies of copper ion adsorption on palm kernel fibre. *J. Hazard. Mater.* 2006, B137, 1796.
- [18] A.E. Ofomaja, Equilibrium studies of copper ion adsorption onto palm kernel fibre. *J. Environ. Manage.* 2010, 91, 1491.
- [19] Y.S. Ho, A.E. Ofomaja, Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber. *J. Hazard. Mater.* 2006, B129, 137.
- [20] Y.S. Ho, A.E. Ofomaja Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution. *Process Biochem.* 2005, 40, 3455.
- [21] Y.S. Ho, A.E. Ofomaja, Effects of calcium competition on lead sorption by palm kernel fibre. *J. Hazard. Mater.* 2005, B120, 157.
- [22] K. Riahi, B.B. Thayer, A.B. Mammou, A.B. Ammar, M.H. Jaafoura, Biosorption characteristics of phosphates from aqueous solution onto *Phoenix dactylifera L.* date palm fibers. *J. Hazard. Mater.* 2009, 170, 511.
- [23] L.A.A. Ahmed, Removal of heavy metals from waste water by date palm tree wastes. *Eng. Tech. J.* 2010, 28 (1), 119.
- [24] E.M. Saad, R.A. Mansour, A. El-Asmy, M.S. El-Shahawi, Sorption profile and chromatographic separation of uranium (VI) ions from aqueous solutions onto date pits solid sorbent. *Talanta* 2008, 76, 1041.
- [25] Q. Yu and P. Kaewsarn, *Korean J. Chem. Eng.*, 16(6), 753 (1999).
- [26] G. Li, P. Xue, C. Yan and Q. Li, *Korean J. Chem. Eng.*, 27(4), 1239 (2010).
- [27] S. S. Zamil, S. Ahmad, M. H. Choi, J. Y. Park, S. C. Yoon, correlating metal ionic characteristics with biosorption capacity of *Staphylococcus saprophyticus* BMSZ711 using QICAR model, *Bioresource Technology* 100 (2009) 1895–1902.

- [28] T. A. Kurniawan, G. Y. S. Chan, W. H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, *Journal Science of the Total Environment* 366 (2006) 409– 426.
- [29] M. Kazmi, N. Feroze, S. Naveed and S. H. Javed, *Korean J. Chem. Eng.*, 28(10), 2033 (2011)
- [30] L. Guo, C. M. Sun, G. Y. Li, C. P. Liu, C. N. Ji, Thermodynamics and kinetics of Zn (II) adsorption on crosslinked starch phosphates, *Journal of Hazardous Materials* 161 (2009) 510–515.
- [31] M. Kazmi, N. Feroze, S. Naveed and S. H. Javed, *Korean J. Chem. Eng.*, 28(10), 2033 (2011).
- [32] V.T.P. Vinod, R.B. Sashidhar, B. Sreedhar, Biosorption of nickel and total chromium from aqueous solution by gum kondagogu (*Cochlospermum gossypium*): A carbohydrate biopolymer. *Journal of Hazardous Materials* 2010; 178:851.
- [33] V.K. Gupta, A. Rastogi, A. Nayak, Biosorption of nickel onto treated alga (*Oedogonium hatei*): application of isotherm and kinetic models. *Journal of Colloid and Interface Science* 2010; 342:533.
- [34] Z. Chen, W. Ma, M. Han, Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): application of isotherm and kinetic models. *Journal of hazardous materials* 2008; 155:327.
- [35] V. Padmavathy, P. Vasudevan, S. Dhingra, Biosorption of nickel (II) ions on Baker's yeast. *Process Biochemistry* 2003; 38:1389.
- [36] J.E.B. Cayllahua, R.J. Carvalho, M.L. Torem, Evaluation of equilibrium, kinetic and thermodynamic parameters for biosorption of nickel (II) ions onto bacteria strain, *Rhodococcus opacus*. *Minerals Engineering* 2009; 22:1318.
- [37] A. Kapoor, T. Viraraghavan, Biosorption of heavy metals on *Aspergillus niger*: effect of pretreatment. *Bioresource Technology* 1998; 63:109.