

## Removal of Cadmium from Aqueous Solution by Spinach (*Ipomoea aquatica*)

Nguyen Van Suc and Nguyen My Linh

Ho Chi Minh City University of Technical Education, 01 Vo Van Ngan,  
Thu duc, Ho Chi Minh City, Vietnam

**Abstract:** The use of batch method to study the adsorption ability of spinach for removal of Cd(II) from aqueous solution was carried out. Results obtained shown that the pH and contact time for maximum removal efficiency percentage of Cd<sup>2+</sup> was found to be from 4.5 to 6.5 and 30 min, respectively. The experimental data fitted the pseudo second order model with correction coefficients  $R^2 \geq 0.98$  for all Cd<sup>2+</sup> concentrations in the range of 5, 10 and 15 mg/l and the adsorption rate was controlled by intraparticle and boundary layer diffusions. The Langmuir model was found to be an appropriate model for describing the equilibrium adsorption process and the maximum adsorption capacity was found to be 9.54 mg Cd<sup>2+</sup>/g adsorbent. With three cycles of de-adsorption/adsorption without changing the adsorption efficiency, it could be concluded that spinach is a potential material for removal of Cd<sup>2+</sup> from contaminated water.

**Key words:** Spinach • Cadmium • Adsorption • Kinetic models • Isotherm models

### INTRODUCTION

Because of high toxicity, contamination of water by cadmium causes adverse effects to human health and survival of aquatic animals. Chronic exposure to cadmium even at very low doses leads to kidney damage, renal disorder, bone fracture and destruction of red blood [1-3].

Cadmium may enter surface and ground water systems indirectly via run off from solid waste disposal sites and agriculture fields or directly through effluent from mines, fertilizer production and electroplating, etc. [2-4]. Concentration of cadmium in drinking water under the guidance of the World Health Organization is 3 ppb [5]. However, there are several natural water sources that contain Cd<sup>2+</sup> high concentration exceeding the permitted level. Therefore, it is necessary to remove this metal from contaminated water down to permitted level to protect human health.

In order to remove cadmium from contaminated water, a number of technologies have been used such as precipitation, adsorption, ion exchange, etc [4, 6]. However, these technologies are still expensive and it is less common in developing countries. Therefore, the need to find an alternative technology which can effectively remove cadmium as well as low cost. Currently, adsorption technology is considered a suitable solution for the remediation-contaminated water. Further, if adsorption technology

using adsorbents which are available in nature with high adsorption capacity, it will significantly reduce the cost of treatment [7].

Recently, the study of the adsorption materials derived from plants have been extensively conducted. Because of the diversity and availability in nature, these materials can be considered a replacement for other costly materials used in the adsorption technology to remove pollutants from contaminated water [6, 8-16].

The objective of this research was the determination of the adsorption characteristics of Cd<sup>2+</sup> by spinach, a plant species is fairly common in Vietnam and other countries in Asia, for utilizing in the adsorption technology. The results obtained will be reported here including the effect of parameters such as pH, contact time, adsorbent dose. The experimental data were also fit the kinetic and isotherm models to clarify the adsorption process for Cd<sup>2+</sup> by this new material.

### MATERIALS AND METHODS

The spinach used in this study was collected from Ho Chi Minh City of Vietnam. The fresh spinach was cut into small pieces and dried in oven at 80°C for three hours. The resulting dried spinach were then crushed and sieved. The fraction of 0.25 mm was selected for adsorption study. The FT-IR spectra of raw dried spinach was obtained using JASCO FTIR-3500 model.

**Corresponding Author:** Nguyen Van Suc, Ho Chi Minh City University of Technical Education, 01 Vo Van Ngan,  
Thu duc, Ho Chi Minh City, Vietnam, E-mail: sucnv@hcmute.edu.vn,  
Tel: (84.8) 38968641, Fax: (84.8) 38964922 .

**Adsorption Experiment:** Batch experimental method was set up to investigate effects of pH, contact time, adsorbent dose on the adsorption process. To determine the effect of contact time, experiments were conducted in Erlenmeyer flasks containing 0.1 g of spinach powder, 50 ml of Cd<sup>2+</sup> solution with concentration in the range of 5.0, 10.0 and 15.0 mg/l. pH of the solution was adjusted to pH 5 using either with diluted solution of HNO<sub>3</sub> or NaOH. The adsorption solution was shaken at speed of 200 rpm for predetermined time intervals at room temperature 28 ± 1°C. After shaking, the mixture was filtered and Cd<sup>2+</sup> concentration in the liquid phase was determined by the voltammetric method [17] using polargraph instrumental 797 VA Computrace from Metrohm company. Effect of the pH on the adsorption was determined by varying pH of the adsorption solution from 1-7 while keeping contact time and Cd<sup>2+</sup> concentration constant. Effect of the adsorbent dose was determined by changing the dose of adsorbent in the optimum conditions of pH and contact time which were selected in the previous experiments.

For recovery of Cd<sup>2+</sup> and assessment of reuse ability of adsorbent, the adsorption / de-sorption cycles were investigated with the exhausted adsorbents using different concentrations of nitric acid as an elution solution.

The amount of Cd<sup>2+</sup> adsorbed at equilibrium ( $q_e$ , mg/g) and the removal percentage ( $R\%$ ) were calculated by relationships:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium Cd<sup>2+</sup> concentration (mg/l) respectively,  $V$  is the solution volume (l) and  $m$  is the mass of adsorbent (g).

## RESULTS AND DISCUSSION

**FT-IR Spectra:** FT-IR spectra of the spinach is given in fig. 1. There are characteristic peaks of functional groups such as CO, OH, CH appearing in the spectra. These functional groups are considered as active sites for metal ion adsorption. The bands appearing at 3200 to 3600 cm<sup>-1</sup> were assigned to OH stretching, characteristic of the presence of H<sub>2</sub>O, phenol or amino acids. The group of CH was recognized at peak of 2935 cm<sup>-1</sup> indicative of the chlorophyll groups. The peaks at 1637 and 1053 cm<sup>-1</sup> and peak at 1412 cm<sup>-1</sup> were assigned to CO stretching characteristic of compounds containing CO groups.

The peak at 1411 cm<sup>-1</sup> represent the bending vibrations of CH groups [11]. As results shown in fig 1. The adsorption intensity of peaks presenting for CO groups in the spinach is relative stronger than that of OH groups. This indicated that the adsorption of metal cations by spinach is mostly due to involving the CO groups.

**Effect of PH:** pH of the solution is one of the most important parameters for the adsorption process. pH of the solution controls the sorption capacity through its influence on the surface properties of the adsorbent and species of adsorbate in solution [18]. Effect of pH was studied in the pH range of 1 -7 and results obtained are shown in fig 3. From results, it was found that the removal efficiency of Cd<sup>2+</sup> was low at pH ≤ 2 and increased with increasing pH and reached maximum value at pH from 4.5 to 7.0. The change of the removal efficiency by pH variation can be explained by the competition of hydrogen ion for adsorption sites on the adsorbent surface. At pH 2-3, all the adsorption sites occupied by H<sup>+</sup> ions. At higher pH, the concentration of H<sup>+</sup> reduced and Cd<sup>2+</sup> are freely attracted to the adsorption sites, leading to the removal efficiency increases. On the other hand, the maximum removal efficiency at pH > 4 due to the involvement of the deprotonation of carboxylic groups in spinach [11]. It was found that the pKa value of the carboxylic group which is 3.3-4.8. At pH > 4, the carboxylic group is deprotonated and became negatively charged, hence increasing the availability of binding sites for positively charged of Cd<sup>2+</sup> ions. Thus, CO function groups in spinach has a decisive role for the adsorption of Cd<sup>2+</sup>. A similar trend was observed when studying the absorption Cd<sup>2+</sup> by juniper bark and wood [11], adsorption of Cr<sup>3+</sup> by banana peel [18], etc. The increase of the Cd<sup>2+</sup> removal efficiency was observed at pH >7. This phenomenon can be explained by the contribution of the precipitation of Cd(OH)<sub>2</sub> [10]. Thus, pH from 5 -6.5 can be selected for the next Cd(II) adsorption studies.

### Effect of Contact Time and Initial Concentration:

Figure 1 shows the dependence of the removal efficiency of Cd<sup>2+</sup> on the contact time at pH 5. As can be seen in the results, the adsorption rate increased rapidly with increasing the contact time and reached the equilibrium adsorption after 30 min. The initial faster rate observed can be explained by the presence of the available uncovered surface areas of the adsorbent. According to Badmus *et al.* [19], when contact time increases, the active sites on the adsorbent surface are gradually filled and the adsorption process becomes more difficult. Hence, the removal efficiency almost did not increase and it is represented as a flat line in the plot.

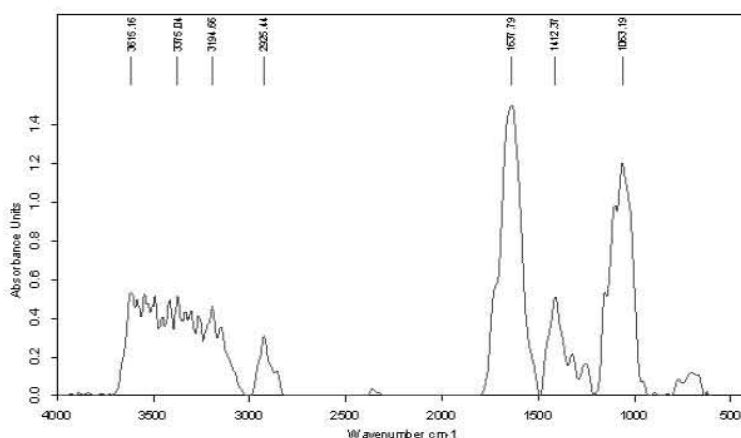


Fig. 1: FT-IR spectra of spinach

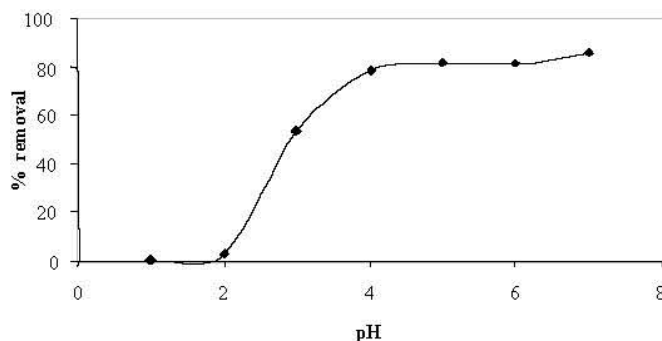


Fig. 2: Effect of pH on the adsorption of Cd<sup>2+</sup> by spinach

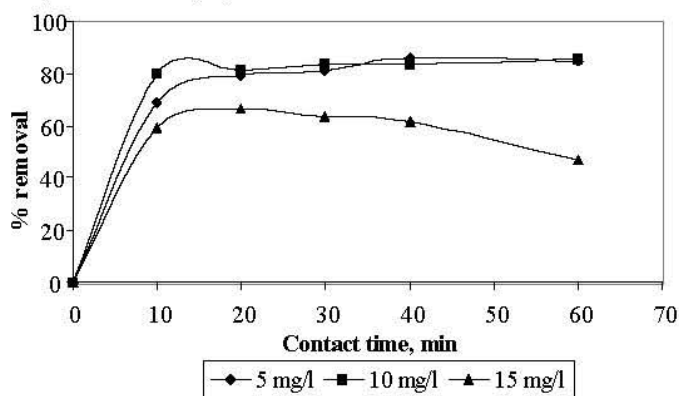


Fig. 3: Effect of contact time on the adsorption efficiency of Cd<sup>2+</sup> by spinach

Effect of the contact time to the removal efficiency of different concentrations of Cd<sup>2+</sup> ranging from 5 to 15 mg/l is also represented in fig. 3. The obtained results show that the adsorption rate was depended on the initial concentration of Cd<sup>2+</sup>. The higher initial Cd(II) concentration, the fatter initial adsorption rate to reach adsorption equilibrium. However, the removal efficiency was decreased from 86.7 to 62.3% as initial concentration of Cd<sup>2+</sup> increased from 5 to 15 mg/l. The removal efficiency decreased with increasing concentration is due

to the fixed number of adsorption sites on the adsorbent surface was saturated with adsorbed Cd<sup>2+</sup> while the surplus of Cd<sup>2+</sup> in the solution.

**Effect of Adsorbent Dose:** The effect of adsorbent dose on adsorption capacity of Cd<sup>2+</sup> was studied by varying the adsorbent dose of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 g in 50 ml of Cd<sup>2+</sup> solution of 10 mg/l at pH 5. The obtained results are presented in Fig. 6. The maximum adsorption capacity reached 2.3 mg/g at 0.2 g of adsorbent and then decreased

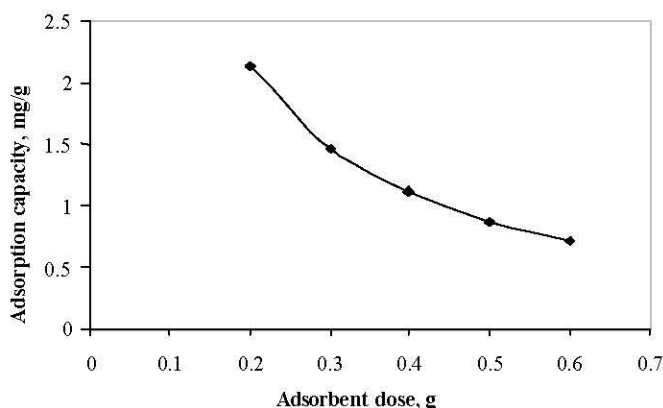


Fig. 4: Effect of adsorbent dose

Table 1: Parameters of pseudo second order model for Cd(II) adsorption by ;spinach

Concentration of Cd (mg/l)	$q_e$ (mg/g)	$h$ (mg.g <sup>-1</sup> .min <sup>-1</sup> )	$k$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	R <sup>2</sup>	$q_e$ (experimental)
5	2.238	0.828	0.199	0.998	1.978
10	3.885	3.575	0.066	0.999	3.743
15	4.783	9.505	0.038	0.999	4.737

with increasing the adsorbent dose. Such adsorption behavior is related to the specific surface adsorption of adsorbent. When adsorbent dose was low, the active sites on the adsorbent surface utilized effectively. On the reverse, increasing the adsorbent dose while maintaining Cd<sup>2+</sup> concentration constant leads to surplus of the adsorption sites [7].

**Adsorption Kinetic:** Adsorption kinetic investigation is to find out the stage which plays a decisive role to the adsorption reaction rate. Therefore, the use of kinetic models to fit the time dependent experimental data is one of important steps for the adsorption study.

In this research, two kinetic models used for fitting data are pseudo second order model and intraparticle diffusion rate model.

**The Second Order Equation:** The sorption kinetics following pseudo second order model [11,14, 20, 21] is expressed in the linear equation as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{3}$$

$$h = kq_e^2 \tag{4}$$

where  $q_e$  is the amount of Cd<sup>2+</sup> adsorbed at equilibrium (mg/g),  $k$  is the equilibrium rate constant (g/mg.min),  $q_t$  is the amount of Cd<sup>2+</sup> adsorbed at time  $t$  (mg/g).  $h$  is the

initial adsorption rate as  $t \rightarrow 0$ . The plot  $t/q_t$  against  $t$  should give a straight line with the slope of  $1/q_e$  and intercept of  $1/h$ .

The pseudo second plots from Eq. (3) and results of parameters computed from plot of for different concentration of Cd<sup>2+</sup> is presented in Fig. 4 and Table 1. The plot shows good straight lines with the correction coefficient R<sup>2</sup> 0.998, 0.999 and 0.999 for concentrations of 5, 10 and 15 mg/l, respectively. The pseudo second order the equilibrium rate constants,  $k$  were in the range of 0.199 to 0.038. The initial adsorption rate,  $h$  calculated from Eq. (4) for concentrations of 5, 10 and 15 mg/l was found to be 0.083, 3.57 and 9.50 respectively. Values of  $q_e$  obtained from experiments were found to be good agreement with those has been predicted from the pseudo-second order.

**The Intraparticle Diffusion Equation:** The adsorption process of solutes onto the solid surfaces is a process of mass transfer characterized by either external mass transfer or intraparticle diffusion or both. Thus, the adsorption rate will be determined by one or both processes. However, for experiments carrying out by the batch method with a good mixing condition, the rate of the external mass transfer usually is negligible. Therefore, the adsorption rate is determined primarily by intraparticle diffusion [26].

The relation between the amount of adsorbate on the adsorbent surface varies proportionately with a function of retention time is given by Weber and Morris [22]:

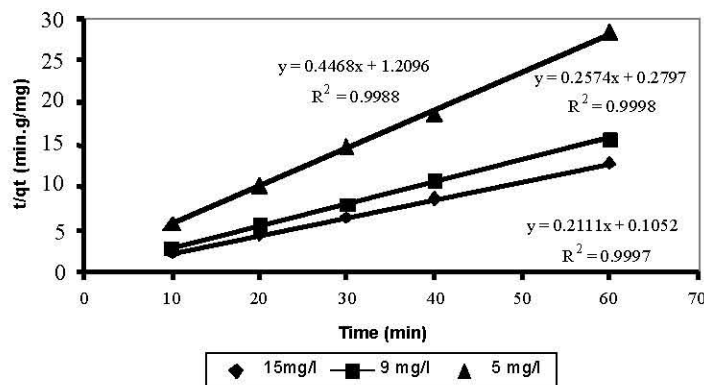


Fig. 5: Plot of pseudo second order equation for Cd (II) adsorption by spinach

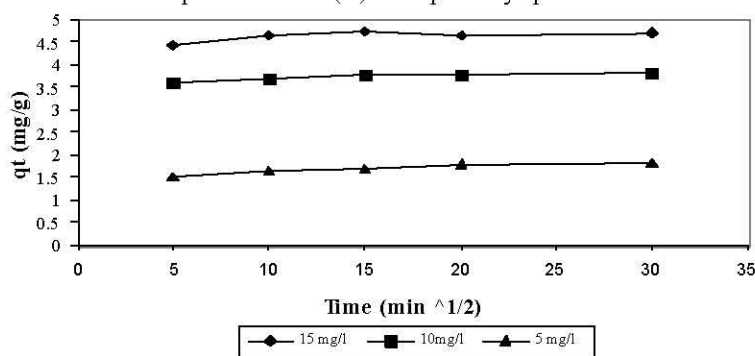


Fig. 6: Plot of intraparticle diffusion model for Cd<sup>2+</sup> adsorption by spinach

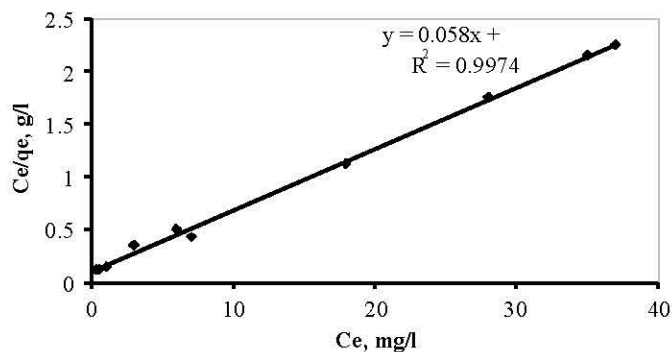


Fig.7: Langmuir isotherm linear plot of Cd<sup>2+</sup> adsorption by spinach

$$q_t = K_{id}t^{1/2} \quad (5)$$

where  $K_{id}$  is the rate constant of intraparticle diffusion (mg/g.min).

The plot of  $q_t$  against  $t^{1/2}$  in the Eq.(5) is presented in the Fig. 5 that will yield a straight line which should pass through the origin and diffusion constants  $K_{id}$  was calculated by the slope of the plot.

The  $K_{id}$  values obtained from the plots are  $1.23 \times 10^{-2}$ ,  $9.3 \times 10^{-3}$ ,  $8.2 \times 10^{-3}$  mg/g.min for Cd<sup>2+</sup> concentrations of 5, 10 and 15 mg/l, respectively. However, the intercept of the plot showed in Fig. 5 did not pass through the origin. It indicates that besides the intraparticle diffusion, the rate

of adsorption process was contributed by the mass transport mechanism of the Cd<sup>2+</sup> from the solution through liquid film to the adsorbent exterior surface [23].

**Adsorption Isotherm:** The Cd<sup>2+</sup> adsorption at room temperature has been studied with the Cd<sup>2+</sup> concentrations ranging from 5-80 mg/l at pH 5 and 30 min of contact time, The experimental data for adsorption of Cd<sup>2+</sup> by spinach were processed in accordance with the Langmuir and Freundlich models that are most widely used to describe the adsorption equilibrium [21-24]. Linear equations of Langmuir and Freundlich models are presented as follows:

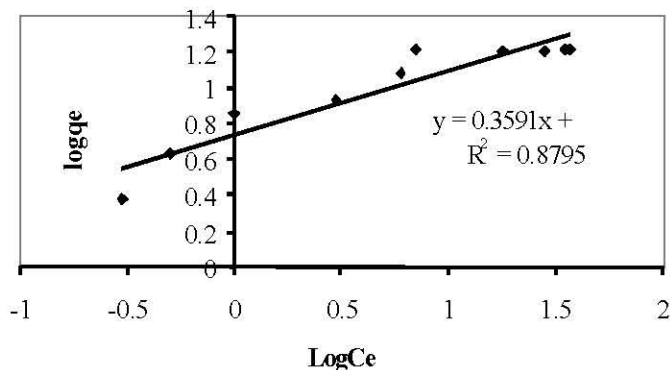


Fig. 8: Freundlich isotherm linear plot of Cd<sup>2+</sup> adsorption by spinach

Table 2: Parameters of Langmuir and Freundlich models

Langmuir model		Freundlich model	
K <sub>l</sub> (l/g)	1.80	K <sub>f</sub> (mg/g)	5.447
q <sub>m</sub> (mg/g)	9.54	1/n	0.3591
R <sup>2</sup>	0.997	R <sup>2</sup>	0.879

The Langmuir Equation:

$$\frac{C_e}{q_e} = \frac{1}{K_l q_m} + \frac{C_e}{q_m} \quad (6)$$

The Freundlich equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

where C<sub>e</sub> is the concentration of metal ions in the liquid phase at equilibrium (mg/l), q<sub>e</sub> is the adsorption capacity at equilibrium (mg/g), K<sub>l</sub> is Langmuir constant (l/g), q<sub>m</sub> is the maximum adsorption capacity (mg/g), 1/n is constant, K<sub>f</sub> is Freundlich constant.

The plots of C<sub>e</sub>/q<sub>e</sub> against C<sub>e</sub> from Eq. (6) and lnq<sub>e</sub> against lnC<sub>e</sub> from Eq. (7) are presented in Fig.7 and Fig. 8. The values of K<sub>l</sub>, q<sub>m</sub>, K<sub>f</sub> and, 1/n in the Langmuir and Freundlich equations were determined from the slopes and intercept of the plots and are reported in table 2. Comparing the correction value, R<sup>2</sup> = 0.9974 for Langmuir and R<sup>2</sup> = 0.8795 for Freundlich model, it can be concluded that the Langmuir isotherm model is appropriate to describe the adsorption process of Cd<sup>2+</sup> by spinach. From the Langmuir equation, the maximum adsorption capacity was found to be 9.54 mg Cd<sup>2+</sup>/g spinach.

#### Cadmium Recovery and Reusable of Adsorbent:

To avoid the decomposition of the adsorbent and release cadmium back into the environment duration storing, it is necessary to recover cadmium from the exhausted adsorbent. The experiment was conducted in each 10 ml HNO<sub>3</sub> solutions with concentrations of 0.1, 0.5 and 0.7 M. 1.0 g of the exhausted adsorbent were added into each

HNO<sub>3</sub> acid solutions. The mixtures were shaken for 5 min. After shaking, a volume aliquot of the adsorption solution were taken and the liquid phase was separated from solid phase by centrifugation. Determination of Cd<sup>2+</sup> concentration the liquid phase by voltammetric method. The recovery yield (%) was determined by the formula:

$$\%RE = \frac{C_R}{C_{Ex}} \times 100 \quad (8)$$

where RE is recovery efficiency (%), C<sub>R</sub> is amount of Cd<sup>2+</sup> from solid phase entering into the solution (mg/g), C<sub>Ex</sub> is initial amount of Cd<sup>2+</sup> in the solid phase, i.e. in the exhausted spinach (mg/g).

Recovery efficiencies of cadmium with different concentrations of HNO<sub>3</sub> was found to be 99.9% for all concentrations of HNO<sub>3</sub>. From the results, the solution of HNO<sub>3</sub> 0.1 M was selected as an elution for recovery of cadmium.

Three adsorption/de-adsorption cycles were carried out to evaluate the possibility of reuse of the adsorbent. In each cycle, Cd<sup>2+</sup> was removed from the exhausted adsorbent, using the solution of HNO<sub>3</sub> 0.1 M then the adsorbent was washed several times with distilled water until pH 5. The adsorption procedure was repeated. Results obtained showed that after three cycles, the adsorption efficiency of spinach was found to be unchanged. This indicates that, spinach can be multiple used for removal of Cd<sup>2+</sup> from aqueous solution.

In conclusion, the results obtained in this study show that spinach is a potential material for removal of Cd<sup>2+</sup> from contaminated water. The adsorption process was described by using the kinetic and isotherm models. The results obtained indicated that the adsorption of Cd<sup>2+</sup> followed the pseudo second order kinetic model and Langmuir isotherm model. From the Langmuir model, the maximum adsorption capacity for Cd<sup>2+</sup> was found to be 9.54 mg/g spinach powder.

## REFERENCES

1. David, A.W. and P. Welbourn, 2003. Environmental toxicology, Cambridge University press.
2. Johannes, G., S. Franziska, G.S. Christian, E. Vera, B. Paul, R. Andrea and A.G. David, 2006. J. Occupational Medicine and Toxicol., 1: 22.
3. Krishna Murti, C.R., *et al.* 1987. "Group Report: cadmium." in T.C. Hutchinson and K.M. Meema, eds., New York: John Wiley and Sons.
4. Izanloo, H. and S. Nasseri, 2005. Cadmium removal from aqueous solutions by ground pine cone, Iranian J Env Health Sci., 2(1): 33-42.
5. World Health Organization (WHO), 2004. Recommendations, Geneva, 1: 317.
6. Mahvi, A.H., R. Nabizadeh, F. Gholami, J. Nuri and A. Kaeiri, 2010. Biosorption of Cadmium from Aqueous Solution by ULMUS Leaves and their Ash, European J. Technology and Advanced Engineering Res., 1: 4-11.
7. Megat Hanafiah, M.A.K., M.Z.A. Yahya, H. Zakaria and S.C. Ibrahim, 2007. Adsorption of (Cd(II) from aqueous solution by lalang (*Imperata cylindrica*) leaf powder: effect of physicochemical environmental, J. Applied Sci., 7(4): 489-493.
8. Mataka, L.M., S.M.I. Sajidu, W.R.L. Masamba and J.F. Mwatseteza, 2010. Cadmium sorption by *Moringa stenopetala* and *Moringa oleifera* seed powders: Batch, time, temperature, pH and adsorption isotherm studies. International J. Water Resources and Environmental Engineering, 2(3): 50-59.
9. Ho, Y.S. and C.C. Wang, 2004. Pseudo-isotherms for the sorption of cadmium ion onto tree fern, Process Biochemistry, 39: 759-763.
10. Ibrahim, S.C., M.A.K.M. Hanafiah and M.Z.A. Yahya, 2006. Removal of cadmium from aqueous solution by adsorption onto sugarcane bagasae, American-Eurasian J. Agric and Environ. Sci., 1(3): 179-184.
11. Shin, E.W., K.G. Karthikeyan and A.M. Tshabalala, 2008. Adsorption mechanism of cadmium on juniper bark and wood, Bioresource Technol., 98: 588-594.
12. Zheng, L., Z. Dang, C. Zhu, X. Yi, H. Zhang and C. Liu, 2010. Removal of cadmium(II) from aqueous solution by corn stalk graft copolymers, Bioresour Technol., Aug., 101(15): 5820-6.
13. Wang, F.Y., H. Wang and J.W. Ma, 2010. Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent--bamboo charcoal, J. Hazard. Mater., 177(1-3): 300-6.
14. L. Zheng, Z. Dang, X. Yi and H. Zhang, 2010. Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk, J. Hazard. Mater. 176(1-3): 650-656.
15. U.Garg, M.P. Kaur, G. Jawa, D. Sud and V.K. Garg, 2008. Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. J. Hazard. Mater., 154(1-3): 1149-57.
16. Horsfall, M.J.R. and A.A. Abia, 2003. Adsorption of cadmium(II) and zinc(II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta* Cranz), Water Res., 37(20): 4913-4923.
17. Sana, A. and A. Alshikh, 2010. Voltammetry determination of some trace elements in tap water samples of Jeddah area in the Kingdom of Saudi Arabia, J. American Sci., 6(10): 1026-1032.
18. Memon, J.R., Q. Saima, Memon, I.M. Bhanger and Y.M. Khuhawar, 2008. Banana Peel: A Green and Economical Sorbent for Cr(III) Removal, Pak. J. Anal. Environ. Chem., 9(1): 20-25.
19. Badmus, M.A.O., T.O.K. Audu and B.U. Anyata, 2007. Removal of lead from industrial wastewater by activated carbon prepared from periwinkle shell (*Typanotonus fuscatus*), Turkish J. Eng. Env. Sci., 31: 251-263.
20. Kumar, K.V. and K. Porkodi, 2008. Pseudo second order kinetics for the sorption of auramine O onto activated carbon, Indian Chemical Engineer, 50(3): 227-238.
21. Benhima, H., M. Chiban, F. Sinan, P. Seta and M. Persin, 2008. Removal of lead and cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants. J. Colloids and Surfaces, 61(1): 10-16.
22. Sahmoune, M.N., K. Louhab and A. Boukhiar, 2009. Biosorption of Cr (III) from Aqueous Solutions Using Bacterium Biomass *Streptomyces rimosus*, Int. J. Environ. Res., 3(2): 229-238.
23. Kushwaha, S. S. Sodaye and P. Padmaja, 2008. Equilibrium, Kinetics and Thermodynamic Studies for Adsorption of Hg (II) on Palm Shell Powder, World Academy of Science, Engineering and Technol., 43: 600-606.
24. Mahvi, A.H., J. Nouri, G.A. Omrani and F. Gholami, 2007. Application of *platanus orientalis* leaves in removal of cadmium from aqueous solution, World Appl. Sci. J., 2(1): 40-44.