Environmental Health Engineering and Management Journal 2015, 2(4), 157–163

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Environmental Health Engineering and Management Journal

Original Article

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Cadmium removal from synthetic wastewater by using *Moringa oleifera* seed powder

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Abstract

Background: Cadmium (Cd) is a heavy metal that is widely utilized in industries and contaminates soil and groundwater. There are several environmental problems related to cadmium, therefore, the technical and economic methods of removing Cd are of great importance. So this study was conducted to evaluate the efficiency of a type of plant to remove the Cd from aqueous environments.

Methods: In this cross-sectional study, the adsorption of Cd examined from synthetic aqueous solutions was evaluated using the seed powder of Miracle tree (*Moringa oleifera*). In this order, 70 samples were prepared and tested. To determine the absorption of metals by this sorbent, different pH (5, 7 and 9), sorbent dose (1.5, 3 and 5 g), temperature (20, 30 and 45°C), concentrations of Cd (2, 5, 10 and 20 ppm) and exposure time (0, 30, 60, 120, 180 and 210, 240 minutes until reaching equilibrium) were experimented upon, using atomic absorption spectrometer (Varian-AA240FS), and the residual concentration of Cd was read.

Results: The highest removal efficiency of Cd under optimum condition (180 minutes and pH of 5) was 70%. The optimum sorbent dose was 1.5 g, which achieved a removal efficiency of 75%. The removal trend was an inverse of Cd concentration. The adsorption of Cd using *M. oleifera* fitted into both models (Freundlich and Langmuir), but was somewhat better fitted with the Freundlich model and followed pseudo second order kinetics.

Conclusion: The results indicated that under optimized absorption conditions (pH: 5, sorbent: 1.5 g, temperature of 45°C, Cd concentration of 2 ppm and exposure time of 180 minutes), the removal rate of Cd was 80% and thus the nature of the adsorption reaction was endothermic. Based on the results obtained, the studied sorbent could be introduced as a practical sorbent to the Industrial society. In some sorbents, for *M. oleifera*, the adsorption capacity was determined based on the results obtained, and the adsorption capacity was found to be 0.1 mg/g. This means that, in order to remove any pollutant (in this case Cd), 10 times of the sorbent weight need to be added.

Keywords: *Moringa oleifera*, cadmiun, adsorption

Citation: Abedini S, Alipour V. Cadmium removal from synthetic wastewater by using Moringa oleifera seed powder. Environmental Health Engineering and Management Journal 2015; 2(4): 157–163.

Article History:
Received: 13 September 2015
Accepted: 23 November 2015
ePublished: 6 December 2015

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Introduction

Industrial development has caused the release of various pollutants including heavy metals into the environment. These toxic compounds are extremely dangerous to organisms and the environment due to their non-biodegradability, severe toxicity, carcinogenicity, the ability to accumulate in nature and ability to contaminate groundwater and surface water (1). As a result of the toxic effects of cadmium (Cd) on man and animals, it is a highly important environmental pollutant. Cd is a toxic, nonessential transition metal and has been classified as a human carcinogen. There are several sources of human exposure to Cd, including working in metal industries, production of batteries, some electroplating processes, and consumption of tobacco products. Cd enters the environment through industrial wastes from plating processes, plastic production, mining, as well as the production of dye, alloys and batteries (2).

Due to the harmful effects of Cd, there are strict regulations on environmental exposure to this heavy metal. However, the removal of many pollution sources leads to removal of this heavy metal from the environment; ion exchange, chemical precipitation, membrane processes (electrodialysis and reverse osmosis), oxidation and reduction, electrochemical treatment, solvent extraction, adsorption and bio-absorption can be cited as conventional methods of removing heavy metals from the environment (3). Nowadays, absorption is known to be an important phenomenon in most physical, biological and chemical processes (4). This method in comparison with conventional types has advantages such as cost-effectiveness, selective absorption ability, metal recovery ability, high relative rate of the process and no sludge production, particularly in relation to natural absorbents that are inexpensive and readily available (5).

Moringa is a plant belonging to the family *Moringaceae* with 13 species. *M. oleifera* is a well known species among others. Romans, Greeks and Egyptians use the extracted oil from *Moringa* seeds as a skin lotion (6). This species grows in arid, semi-arid and humid areas and has been named "miracle tree" owing to its several benefits (7).

The drooping panicles of the tree are arranged 10-30 cm long. Flowers and fruits (pods) can be produced twice a year; though in many places, flowering and fruiting occur all year-round. The fruits are initially light green, slim and tender, which eventually turns dark green and becomes firm. Most are rectangular in cross-section, but a number are triangular while others are round. When fully mature, the dried seeds are surrounded by a lightly wooded shell with three papery wings (8). Several uses of *Moringa* have been determined: it can be used for nutritional and medicinal purposes (9), as antibacterial agent (10), and as material coagulant in water and wastewater (11).

Studies on heavy metal absorption using plant residues, mainly began in 1970 (12). A study was carried out by Al-Asheh and Duvnjak on the adsorption of Cd and other metals using pine bark, it was shown that pine bark can adsorb Cd ions from aqueous solution (13). The study of Bichi (8) on the use of *M. oleifera* seeds in water treatment showed that the results of removing oil from water by disinfection, using *M. oleifera* will be good. In the study of Malakootian and Haratinejad Torbati (14), it was shown that saffron leaf has more ability to adsorb lead from aqueous solution, compared with Cd and copper.

Due to the necessity of applying economic, efficient and eco-friendly methods, the objectives of this study are as follows: to measure Cd removal using *M. oleifera* seed powder, to study the absorption kinetics and adsorption isotherm models as important factors in designing adsorption systems, to determine the capacity of a sorbent and to optimize its usage. So this study was conducted to evaluate the efficiency of a *M. Olifera* to remove the Cd from aqueous environments.

Methods

This cross-sectional study, conducted over a period of 3 months, comprised of various stages, which include the preparation of absorbent and Cd stock solution, the study of adsorption equilibrium, kinetics and isotherm. In this study, a total of 70 samples, used as stock, were obtained and tested as thus explained.

Preparing absorbent and synthetic cadmium solution stock

At first, mature *M. oleifera* seed pods were collected, the intact seeds were then separated from the pod and thereafter, the seeds were washed using distilled water to eliminate dust and other particles, after which they were dried at ambient temperature. The crust of seeds was removed, powdered using mortar and placed on a flat surface. Finally, the powder was kept in the oven for 24 hours at 50°C (Figure 1).

To prepare Cd stock solution, the standard aqueous solution of Cd (Cd $(NO_3)_2$ in HNO_3 0.5 mol/L with a concentration of 1000 mg/L (Merck) was used. To adjust the pH, the two solutions (0.1 N HCl and 0.1 NaOH) were used.

Adsorption tests

To obtain the equilibrium time, 5 g of absorbent and 100 cc of soluble Cd with concentration of 2 mg/L were placed in the 250 cc flask at pH 7, and sampling was done at different times until an equilibrium time was achieved. To determine the optimal pH, 5, 7, and 9 were selected and tested. Also, to determine the optimum sorbent dose, 1.5, 3 and 5 g of sorbent were added to 100 cc of soluble Cd with concentration of 2 mg/L in optimum pH, in the equilibrium time. All tests were carried out at ambient temperature and mixing rate of 100 rpm. To determine the effect of temperature on Cd adsorption, soluble Cd with concentration of 2 mg/L under optimal pH and sorbent, was placed in a flask and tests were performed at 3 different temperatures (20, 30 and 45°C). Thereafter, sampling was performed in equilibrium time. To determine the effect of Cd concentration, for a Cd solution at a concentration of 2, 5, 10, 20 mg/L under optimum pH, sorbent measurement and temperature test were done at equilibrium time, using the atomic absorption spectrometer after filtering and the optimum concentration was determined after examination. In these tests, magnet was used for mixing. All the tests samples were injected into an atomic absorption spectrometer (Varian-AA240FS) and the residual concentration of Cd was read.

Adsorption equilibrium models

In this study, the non-linear models of Langmuir and Freundlich isotherms were evaluated. In these models, the

Figure 1. Removing crust of seeds (A), separated seeds (B), making powder (C), prepared sorbent (D).

adsorbed metal concentration in the sorbent phase, after balance, was calculated.

Reaction kinetics equations

To find the affective factors of the reaction rate, the evaluation of kinetics is necessary. Therefore, the design of the chemical processes is based on the determination of the best type of pollutant removal models. In this study, fitness to pseudo first order kinetics and pseudo second order kinetics were evaluated.

Analysis and statistical methods

Statistical analysis was done using SPSS software version 19 for windows, and analysis of variance (ANOVA) test in addition to least significant difference (LSD) post hoc test in the range of significance of 0.05, the graphs were drawn using excel software.

Results

In this section, the findings of this study are presented in the form of diagrams and tables. Figure 2 shows the different times of sampling, the concentration of Cd remaining and the adsorption balance time.

As shown in Figure 2, the removal efficiency increases in the time range of 0 to 180 minutes and becomes fixed and partly decreases at 180 to 240 minutes. Thus, the adsorption balance time was determined at 180 minutes in this test.

In Figure 3, the effect of pH on the removal of Cd is observed at 3 different pH (5, 7, and 9), with sorbent of 5 g/l and primary concentration of 2 mg/L.

Figure 3 shows the removal efficiency of Cd at the balance time and at 3 different pH (5, 7 and 9), which respectively equals to 70%, 67% and 50%. Therefore, it is apparent that the removal efficiency decreases by increasing the pH, thus the highest level of removal of Cd was observed at pH 5.

Figure 4 shows the effect of sorbent dose at different times on the rate of removal of Cd (pH: 5, primary concentration: 2 mg/L).

As shown in Figure 4, the removal efficiency of Cd with 1.5, 3 and 5 g of sorbent, respectively equals 75%, 74% and 69%. 1.5 g of sorbent was observed to have the highest level of removal of Cd.

Figure 5 shows the effect of temperature on the removal efficiency of Cd (pH: 5, amount of sorbent: 1.5 g/l, primary concentration: 2 mg/L).

As shown in Figure 5, the highest efficiency of Cd removal was at temperature of 45°C. Figure 6 shows the effect of different concentrations of Cd at different times on its removal efficiency (pH: 5, sorbent: 1.5 g/l, temperature: 45°C).

As shown in Figure 6, the removal efficiency of Cd with concentrations of 2, 5, 10 and 20 mg/L equals 80%, 51%,

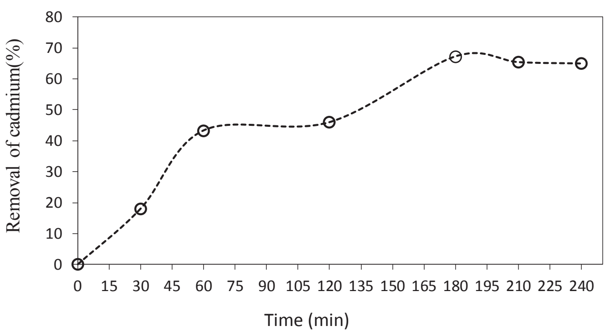

Figure 2. Efficiency of cadmium (Cd) removal at different times (C_0= 2 mg/l, C_{ab}= 5 g/l, pH = 7).

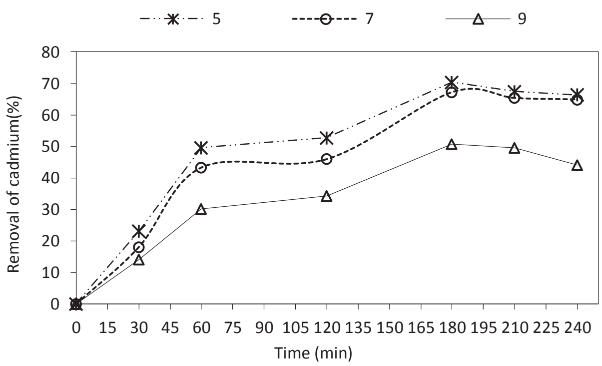

Figure 3. Effect of pH on the removal efficiency of cadmium (C_0= 2 mg/l , C_{ab}= 5 g/l).

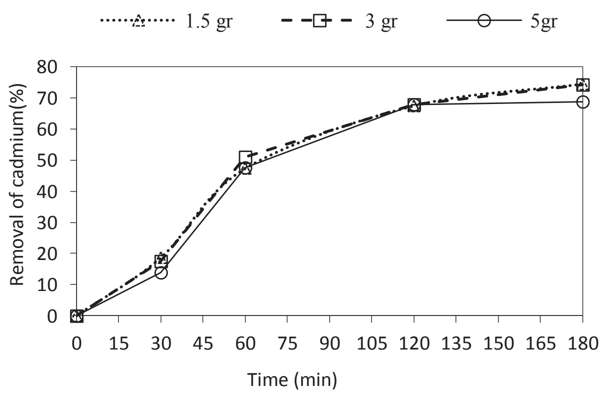

Figure 4. Effect of the amount of sorbent at different times on the rate of removal of cadmium (Cd).

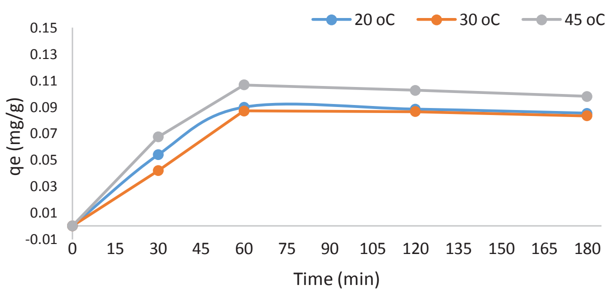

Figure 5. Effect of temperature on the removal efficiency of cadmium (C_0= 2 mgl, pH = 7, C_{ab}= 5).

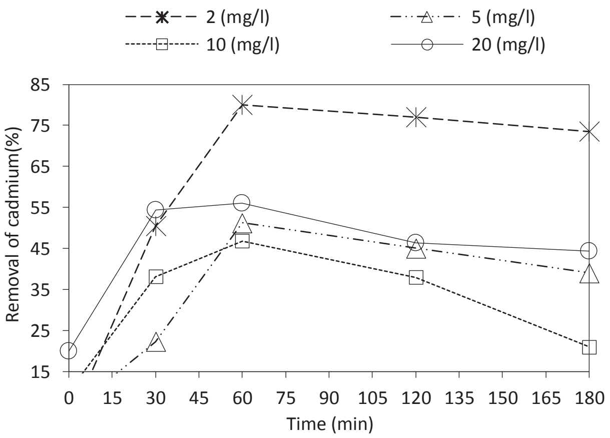

Figure 6. Effect of different concentrations of cadmium at different times on its removal efficiency (T = 45°C, pH = 5, C_{ab}= 5 gr/l).

46% and 56%, respectively. Thus, no linear relationship was observed between the primary concentration and Cd removal.

The adsorption isotherms of Cd by the sorbent is shown in Figure 7. In Figure 7, R^2= 0.95 in Langmuir model and R^2 = 0.996 in Freundlich model.

Figure 8 shows the adsorption kinetics of Cd using *M. oleifera*. Figure 8 shows that R^2=0.965 for the pseudo first order kinetics and R^2=0.75 for first order kinetics.

Thermodynamic parameters for adsorption

In order to fully understand the nature of adsorption, thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated (Table 1). It was possible to estimate these thermodynamic parameters for the adsorption reaction by considering the equilibrium constants under the several experimental conditions. These parameters can be calculated using the following equations (15). In general these parameters indicate whether the adsorption process is spontaneous or not and exothermic or endothermic. The standard ΔH for the adsorption process is as follows: (*i*) positive value indicates that the process is endothermic in nature. (*ii*) negative value indicate that the process is exothermic in nature and a given amount of heat is evolved during the binding metal ion on the surface of the sorbent. This could be obtained from the plot of percent of adsorption, against temperature (T). The percent of adsorption increased with increase in temperature, this indicates for the endothermic processes and the opposite is correct (16). The positive value of ΔS indicates an increase in the degree of freedom (or disorder) of the adsorbed species (15).

$\Delta G = \Delta H - T\Delta S$

These parameters were obtained during the experiments at various temperatures using the previous equations. The values of ΔH and ΔS were determined from the slope and intercept of the linear plot of (ln Kd) vs (1/T). To calculate (ln Kd), Arrhenius plot was used as shown in the equation:

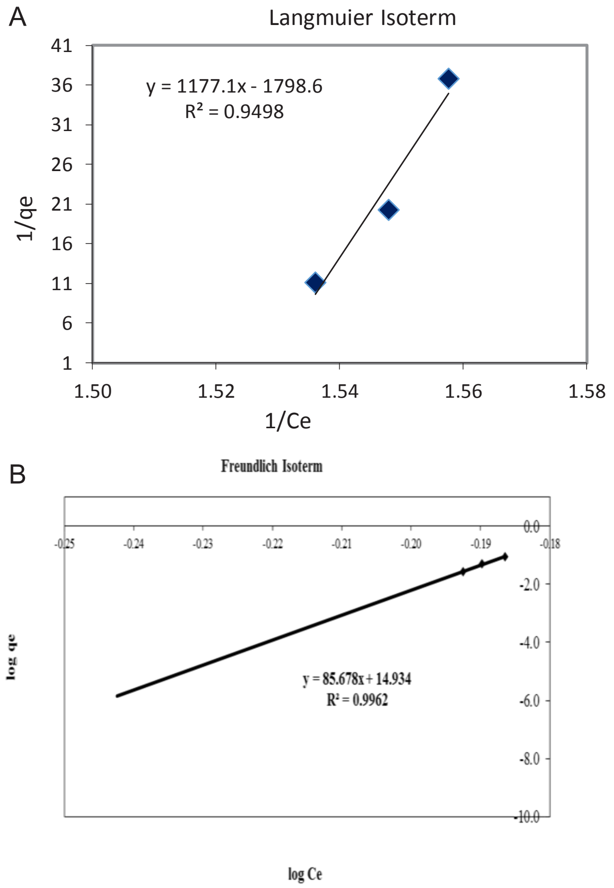

Figure 7. Langmuir (A) Freundlich (B) Removal of cadmium by *Moringa*.

$\text{Ln Kd} = \Delta S/R - \Delta H/RT$

where Kd value is the adsorption coefficient obtained from qe/ce (Figure 9). The slope was determined using the equation:

Slope = - ΔH/R and Intercept= ΔS/R.

In all equations, R is the universal gas constant (8.314).

Discussion

As shown in Figure 2, the highest removal efficiency of Cd was observed at 180 minutes and the exposure ranged from 0-180 minutes, the clash between sorbent and heavy metal (Cd) increased with exposure time. Cd in the aqueous solution required more time to be adsorbed, thereafter, the removal rate increased stopped and partly decreased due to the establishment of balance. The results of the studies of Mahvi et al (17) showed that the maximum level of absorption of lead and Cd was at balance time (180'), which is consistent with the balance time obtained in this study. The removal efficiency decreased when the pH was increased from 5 to 9 and the maximum level of removal was at pH: 5 and this could be attributed to the high performance of bio-sorbents in acidic environments. It could also be attributed to the metal ions absorbed on the defined bandages of the sorbent with H^+. The obtained results are in line with the findings of Malakootian and Haratinejad Torbati (14) on the removal efficiency of cop-

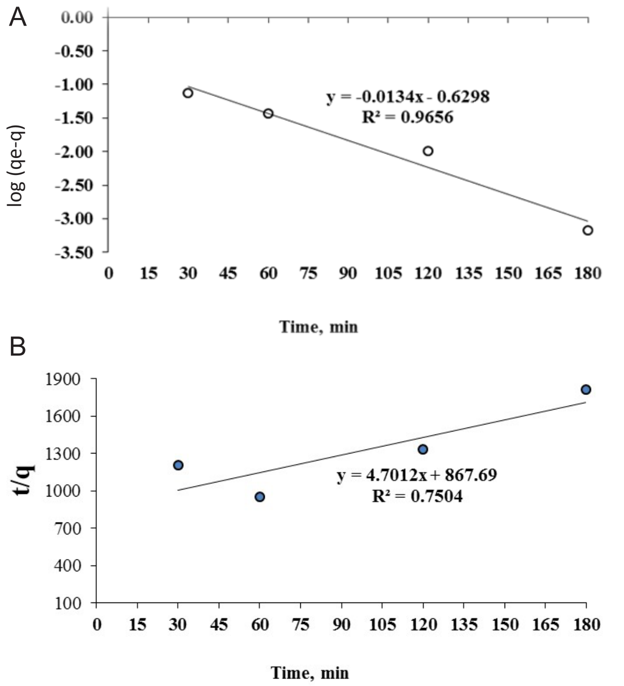

Figure 8. Pseudo first order (A) and second order (B) kinetics of cadmium adsorption by *Moringa*.

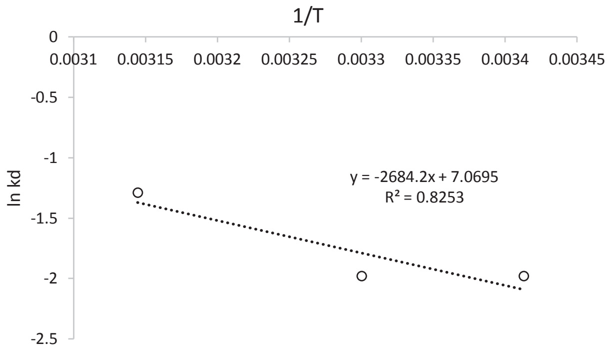

Figure 9. Arrhenius plot: ln(k) against 1/T.

Table 1. Thermodynamic parameters for the adsorption of cadmimum using *Moringa oleifera* seed powder

T (k°)	ΔG	ΔH	ΔS
293	252.3		
303	172.1	2692.5	58.7
318	24.3		

per, Cd and lead using saffron leaf in aqueous solutions and the determination of adsorption isotherms. Thus, the results are also in line with the study of Abdel-Ghani and Elchaghaby (18) on the removal of copper, Cd and lead using race pod and Indigo plant. As shown in Figure 4, the maximum removal efficiency of the Cd was in the sorbent dose of 1.5 g/100 cc. With increasing amount of sorbent, the amount of absorbed contaminants decreased. This phenomenon can be attributed to the use of available surface in an unsaturated type of absorbent. In a study by Malakootian and Haratinejad Torbati (14), on the removal efficiency of copper, Cd and lead using saffron leaf in aqueous solutions and the determination of adsorption isotherms, it was shown that the amount of optimal sorbent for the removal of Cd is 1.5 g/l and this is consistent with the result obtained in this study.

As shown in Figure 5, the maximum level of removal efficiency of the Cd is restively at temperatures of 20, 30 and 45°C. By increasing the temperature, the adsorption performance increased due to the intensification of interaction between the sorbent and heavy metal. At the temperature of 30°C, the adsorption was lower than 20°C and this is as a result of the physical adsorption. At 45°C, chemical adsorption occurred and the level of adsorption increased. The result of this study is confirmed by the result obtained in the study of Kamyab (19) on Cd removal from wastewater dyeing industry using magnetic nanoparticles modified at 23, 33 and 43°C. It was shown that by increasing temperature, the removal of Cd increased and the highest removal was observed at 43°C (19).

Furthermore, as shown in Figure 6, there is no linear relationship between the primary concentration of Cd and removal rate, and the maximum removal efficiency was observed at concentration of 2 mg/L. Increasing the Cd concentration creates the moving force for mass transfer, so the velocity of Cd molecules in capturing layer of sorbent will increase. The decreasing removal efficiency and the increasing initial concentration of Cd may be attributed to the reduced ion exchange bands between Cd and adsorbate.

Based on the study of Gholami Boroujeni and Najatzade Barandvzy (20) on the efficiency of waste urban green space and removal of Cd from aqueous solutions, the maximum removal efficiency of Cd under optimum condition (equilibrium time of 60 minutes at pH = 6) was achieved at the initial concentration of 2 mg/L (20). This result is in line with the result of the present study.

As shown in Figure 7, the Freundlich and Langmuir Isotherm models were studied to describe the relationship between the level of adsorption and the equilibrium concentration in liquid phase. This relationship and adsorption parameters for each model were as follows: $R^2 = 0.95$ in the Langmuir model and $R^2 = 0.996$ in the Freundlich model and based on the correlation coefficient, it was found that the absorption of Cd using *M. oleifera* is considered fit for both models (Freundlich and Langmuir). However, the amount of correlation coefficient (R^2) shows that the Freundlich model states a better relationship in this adsorption process. This could be that the active sites on the sorbent are uniformly distributed and of a multilayer.

The research by Bazrafshan et al (21) on the investigation of the removal of heavy metal Cd from aqueous solutions using ash trees Haloxylon, showed that the Freundlich model is a better fit in comparison with Langmuir (21). This result is in line with the result obtained in this study.

Based on the results presented in Figure 8; R^2 for the pseudo first and second order kinetics were 0.965 and 0.75, respectively, as such, there is a very high correlation coefficient between the adsorption kinetics of Cd and the sorbent of the pseudo first order model. This indicates that there was a near linear form of relationship between the concentration of Cd and the efficiency of its removal by the studied sorbent in this evaluation. In other words, this sorbent is able to remove Cd in a specific range of the Cd concentration and above this range, the removal rate is not economically cost-effective and technical.

Table 1 shows that the reaction process is endothermic in nature and as such, the ΔH for the adsorption process is positive value. The positive value of ΔS indicates an increase in the degree of freedom (or disorder) of the adsorbed species. Also, the percent of adsorption increase with increase in temperature, this indicates that the endothermic processes and the opposite are correct based on the fact that ΔS and ΔH are positive and can be found in spontaneous reaction at high temperatures. This result is in line with the result of Mobasherpour et al (22).

Conclusion

The results of this study showed that the seed of miracle tree (*M. oleifera*) is appropriate for the removal of Cd from aqueous solution and serves as bio sorbent under optimal absorption conditions (pH: 5, sorbent: 1.5 g, temperature: 450°C, concentration of Cd: 2 ppm and exposure time: 180 minutes). The removal rate of Cd was 80%. Adsorption of Cd using *M. oleifea* fitted both models (Freundlich and Langmuir), but is somewhat better fitted with the Freundlich model and follows the pseudo second order kinetics. The various thermodynamic factors are ΔS, ΔH and ΔG, respectively. The thermodynamic parameters, which measured the absorption system show that the absorption process is naturally spontaneous and endothermic.

Acknowledgements

The Natural Resources Department of Azad University, Bandar Abbas branch is gratefully acknowledged

Ethical issues

The authors hereby certify that all data collected during the study are as stated in this manuscript and no data from the study has been or will be published elsewhere separately.

Competing interests

The authors are committed to declare that they have no competing interests.

Authors' contributions

All authors contributed equally and were involved in designing the study, data collection, and article approval.

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