

## Evaluation of Cadmium Removal from the Water in Phytoremediation Process Using *Eichhornia crassipes*

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**ABSTRACT:** Conserving water resources and protecting them from pollution are of high account in the natural cycle of our life. This study has tried to determine the refining potential and capacity of water hyacinth (*Eichhornia crassipes*) in order to remove the cadmium from water, studying the influence of factors such as initial concentration of cadmium, contact time, adsorbent mass, and pH. Results have shown that the best efficiency of cadmium, more than 99%, was obtained in the optimum conditions (i.e. retention time of 30 hours, adsorbent dose of three plants (12 stems), and pH=6.6). By increasing the initial concentration of cadmium from 0.28 to 8.28 mg/L, the elimination efficiency did not change; moreover, by increasing the adsorbent mass, the elimination efficiency increased from 98.4 to 99.8 and the lowest retention time was obtained for the balance. All experiments have been repeated three times, showing in the end that water hyacinth is able to absorb cadmium up to 8.28 mg/L. This process follows Freundlich isotherm ( $R^2=0.98$ ). Results of this study indicate that this plant can grow well at high levels of cadmium and the growth of water hyacinth is better in the presence of cadmium than control conditions (city water). Finally, it can be concluded that it is necessary to provide a reliable, cheap, and fast method to eliminate pollution. *Eichhornia crassipes*, a promising plant with great functionality, can be used as a refiner in order to eliminate the heavy metals in wastewater (sewage) effluents, particularly industrial sewage.

**Keywords:** adsorbent, cadmium, phytoremediation, water hyacinth (*Eichhornia crassipes*).

### INTRODUCTION

Pollution is one of the most important factors, which leads to the loss of water resources. Limited water resources, lack of rainfall, risk of water shortage in the country, and the importance of water restoration on one hand, and increased pollution of surface water and groundwater by heavy metals and other pollutants as a result of industrial effluent on the other hand, makes it necessary to find an

environmental solution in order to eliminate these materials from the resources (Dermentzis et al., 2011). Curbing the pollution of the mentioned sources reduces the subsequent costs, such as refinement, purification, health care, and ultimately environmental protection, to a considerable level (Mohseni, 2008). The current status of water resources around the world is undesirable and critical, while we can prevent the expansion of global water crisis by taking advantage of the available technologies. High

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concentration of heavy metals leads to environmental health problems. Due to its negative impact on the environment along with its tendency to get accumulated throughout the food chain, cadmium is considered a serious threat to human health. This is a highly toxic metal, causing death, or at least a serious disease, the so-called Itai-Itai disease (arthritis or painful skeletal deformation). The main effects of cadmium toxicity are on the lungs, kidneys, and bones. Cadmium decreases the body resistance to bacteria and viruses (Ramezani, 2008). US environmental protection Agency has recommended a maximum amount of cadmium contamination, which is as little as 0.005 mg/L. Given the harmful and cumulative effects of this metal in the body not to mention its non-biodegradably characteristic, it is essential to eliminate this material from the effluents (sewages) (Asadi, 2001; Deen et al., 1972).

Phytoremediation is a process, in which the contaminants are purified via direct decomposition, indirect refinement by means of microbial population and absorption from the soil or water, and condensation in the plant's root or tissue (McCutcheon and Schnoor, 2003). Different crops (plants) have been used to eliminate the heavy metals and excess nitrate and phosphorus from the aqueous (water) environment (Sundaralingam and Gnanavelrajah, 2014).

In phytoremediation, the deployed roots of the plants, absorb the metal elements from the soil or aqueous environment, conducting them to the shoots for accumulation. Once the plants have sufficiently grown, upper surface extremities are removed and eliminated, and then the permanent metal elimination will be possible (Nanda Kumar et al., 1995). At least 45 families of plants with excessive accumulative potential of heavy metals have been known (Baker and Walker, 1989), which can reduce the heavy metals of drainage water, occasionally accumulating some trace elements (Ismail

et al., 1996). *Eichhornia crassipes* is an aquatic plant that can float on water surface, using deformed and sponged petioles (Center and Spencer, 1981). The use of this plant as a refiner can help solve environmental problems. The plant also has a high ornamental value. *E. Crassipes* is the native of tropical regions of the world, and has been distributed from the Amazon in Brazil to other regions such as Venezuela, parts of South and Central America among Caribbean islands (Edwards and Musil, 1975). Mosleh Arani et al. (2014) in a research on the two plants of *Myrtus* and *Pine* have investigated cadmium accumulation. Their results showed that the maximum amount of cadmium absorbed by *Myrtus* is 1000 mg per 1 kg soil (Mosleh Arani et al., 2014).

By investigating the efficiency of Rape wastes from the aqueous solution, it has been shown that the removal efficiency of cadmium after 24 hours is 95% (Asghar Zadeh et al., 2013a).

One investigation has studied the elimination of heavy metals from water resources by efficiently separating cadmium II from water solution through carbonic shells of dried Hazelnuts. Finally, a single-phase sucker has been designed to treat wastewater and the model of the solution has been studied as well. Results have shown that dry hazelnut shells can be useful as an adsorbent for separating cadmium (II) from wastewater (Imamoglu et al., 2015). In a research, conducted by Kutty (2012), nutrient removal from wastewater treatment plants have been evaluated by using the water hyacinth. Plant has been observed based on their scale weight, absorption, and stem improvements. Water hyacinth has proven to be capable of effectively removing roughly 49% COD, 81% ammonia, 67% phosphorus, and 92% nitrate (Kutty, 2012). A study has investigated nitrate removal from water by using sunflower and corn stalks, wherein crushed sunflower and corn stalks have been used for this purpose and

after conducting the experiment, nitrate removal by corn and sunflower has proven to be 84% and 91% respectively (Sedaghat, 2013).

The current research has been carried out in order to evaluate the potential of *Eichhornia Crassipes* for Cadmium removal. The methodology in this research differs from the previous implemented methods, with economic justification. Therefore, the study can be considered as the first method for purification of polluted resources and effluents in Iran.

## **MATERIALS AND METHODS**

### **Experiments**

The *Eichhornia crassipes*, used in this study, are of Iranian origin, being planted in ancient Iran during New Year, their bulbs often brought from the north of the country. From living plants, the root refining method of phytoremediation has been used in this study to remove cadmium.

### **Cadmium removal mechanism by phytoremediation**

Phytoremediation consists of one of the operations, to be explained below. Overall, the plant uses six main processes to purify the environment, namely extraction plants, evaporator plants, consolidation plant, phyto-stimulation, accumulation in microenvironment of the plant through the activities of soil microorganisms, and root refining which is plants' treatment of water from the root mass. According to the type of contamination and the type of purifying plant, various phytoremediation methods can be used to reduce heavy metals (consolidation plant, refining root) or to remove heavy metals out of the area (extraction plants, evaporation plants). Each of these methods has its own specific mechanism. Among them, the root treatment method is conceptually similar to extraction plant, though this method is used for refining the contaminated water, not the contaminated soil.

This method has received greater attention for treating industrial wastewater, agricultural runoff, and deposits of mineral acids, being used both as point and non-point method for the remediation of contaminated areas. The roots or seeds of plants are used to absorb metal contaminants from surface water or groundwater. Plant or sapling of the desired seeds grow in the contaminated area and concentrate pollutants in their roots. Root exudates and pH changes of rhizosphere area deposit these metals on the surface of the root. Most researchers believe that refining plants should accumulate metals only in their roots (Bhatt, 1997)

First, in order to eliminate the pollutions from the surface, the plant's root was washed several times with tap water and distilled water. Afterwards the output washing water was measured, using a conductivity meter to ensure that the plant's root has been cleaned. Then its water was taken completely and was used to prepare various absorbent doses. The samples of water, contaminated with cadmium, were diluted using the cadmium reference standards of Kem Lab, Belgium and distilled water (to prepare solution of cadmium with different concentrations, standard guidelines of water and wastewater laboratory was used). Some of the prepared solutions were excluded as the standard control sample. The solution pH was prepared using 1 mol/L HCL and 1 mol/L soda. The effects of the above-mentioned variables were investigated by keeping one and changing the other. For example, to evaluate the effect of pH (3.1, 4.1, 5.3, 6.6, 7.6, 8.5, and 11) the experiments were done in a beaker with 1000 cc cadmium with a certain concentration equal to 1.03 mg/L and 400 ml volume for 24 hours. Once the optimum pH was determined, in order to evaluate the effect of contact time, experiments were done in 5 levels for dummy solution with a certain cadmium concentration equal to 1.03 mg/L and 400 ml of the volume for 30 hours in optimum absorbent mass. The experiment was

conducted with different masses of *Eichhornia crassipes*: i.e. 1, 2, and 3 plants, and also with a certain cadmium concentration equal to 1.03 mg/L and volume of 400 ml in optimum time and pH, in order to calculate the optimum absorbent mass. To determine the standard optimum cadmium concentration, absorption tests were conducted with initial concentrations equal to 0.28, 1.03, 2.05, 3.01, 4.35, 5.13, 6.15, 7.1, and 8.28 mg/L in optimum pH, time, and absorbent mass. All experiments were repeated three times (one plant was used once to ensure high accuracy of the experiment and elimination of likely errors).

All samples passed through a 0.45-micrometer Wattman filter paper at regular intervals and then the concentration of metal ions in solutions were measured before and after the absorption, using the atomic absorption spectrophotometer device model PU 9400, product of Phillips Company. The cadmium amount was measured by the device, the elimination percentage was calculated, and the optimum amount was obtained. The experimental data were compared to Langmuir and Freundlich absorption model as a function of initial cadmium concentration. To calculate the equilibrium (balance) absorption capacity of absorbent, Equation (1) was used.

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where  $q_e$  is mg amount of absorbed cadmium per 1 gram of absorbent;  $V$ , the experimental sample,  $C_0$ ; initial concentration of cadmium in mg/L;  $C_e$ , the concentration of remained cadmium in mg/L; and  $m$ , the absorbent mass of *Eichhornia Crassipes* in gram.

Equation (2) and (3) show the Langmuir and Freundlich models, respectively (Heidari et al., 2009).

$$q_e = (q_m \cdot b \cdot C_e) / (1 + b \cdot C_e) \quad (2)$$

$$q_e = K_F \cdot C_e^{1/n} \quad (3)$$

where  $C_e$ , is equilibrium concentration of metal ions in mg/L;  $q_e$ , the amount of

absorbed ion in mg per gram;  $q_m$ , the maximum capacity of metal ion absorption in mg per gram; and  $b$ , the equilibrium constant of Langmuir absorption mg per mg. The coefficient  $k_f$  and the Freundlich constants  $n$  are indices of capacity and absorption rate, respectively.

## RESULTS AND DISCUSSION

This section deals with the effect of pH, contact time, absorbent mass, and initial concentration of the effluent in terms of cadmium absorption, using the *Eichhornia Crassipes*.

### Effect of pH on nitrate removal

One of the important parameters in the absorption process is the initial pH of the solution. The solution pH plays an important role when determining the concentration of cation in the solution, itself. This section elaborates on the effect of artificial effluent's pH on the absorption capacity of *Eichhornia Crassipes* for elimination or reduction of cadmium ion at the stable temperature of 25°C, cadmium concentration of 1.03 mg/L, solution volume of 400 ml for a duration of 24 h. Considering the effect of pH on the elimination efficiency of cadmium by *Eichhornia Crassipes*, the pH range was considered from 3.1 to 11. Table 1 shows the variations of the absorbed cadmium value as a function of preliminary pH. As can be seen, elimination efficiency differs at various pHs. The percentage of cadmium elimination increases as pH value rises (following the ascending inclination though in a weak manner), and by approaching the neutral pH the maximum value of the absorption will occur. Then, as pH rises, absorption percentage is reduced (after that we saw a decline in the removal percentage). It should be noted that the declining half is faster than the other half. As it can be seen, in specified cadmium concentration equal to 1.03 mg/L, after 24 h and pH=6.6, the elimination value was equal to 98.15%, i.e. the maximum

amount. In optimum pH, Eichhornia Crassipes showed more capacity and capability to absorb cadmium and the absorption efficiency reached its maximum rate. To justify this problem, we can refer to the high level of Eichhornia Crassipes and the increase in factorial groups in them (The results of optimum pH were based on three iterations with an average of 6.6 and a standard deviation of 0.5. On the other hand, suitable pH for the growth of Eichhornia Crassipes is in neutral range). By reducing the pH, the hydrogen ion is released into the solution, so due to the small size of hydrogen ion, compared with

cadmium ion, it can be absorbed faster than cadmium, decreasing the absorption capacity. By increasing the pH due to the release of hydroxide ion, the ability to absorb cadmium is reduced.

With respect to the fact that in pH below 7 (Table 1), cadmium ion is dominant; therefore, the omission of cadmium in high pH is due to the formation of cadmium hydroxide and cadmium sediment, not the omission of cadmium by Eichhornia crassipes. Similar results have been reported by Broujeni (Gholami Boroujeni and Nejat Zadeh, 2010).

**Table1. Cadmium removal percentage in concentration of 1.03 mg/L based on pH variation for 24 h**

pH	3.1	4.1	5.3	6.6	7.6	8.5	11
The observed amount of cadmium (mg/L)	0.0730	0.0700	0.0266	0.0190	0.0196	0.0198	0.1940
cadmium removal percentage	92.91%	93.2%	97.41%	98.15%	98.09%	98.07%	81.16%

#### Effect of reaction contact time on nitrate removal

After determining the optimized pH in the previous step, the influence of balance time on the cadmium absorption by Eichhornia crassipes was investigated. At this stage, the absorbent mass included as one plant (with 4 stems), with a cadmium concentration of 1.03 mg, and an optimum pH, equal to 6.6. The retention time was changed from 4 to 30 h. Table 2 shows the variations of cadmium absorption efficiency and the variations of contact time by Eichhornia crassipes as well as the direct relationship between the retention time and elimination percentage of cadmium. According to this diagram, by increasing the retention time, the elimination percentage in specified cadmium concentration, equal to 1.03 mg/L, increased, which is due to the increased contact of Eichhornia Crassipes roots with the solution along with more ion exchange between the solution and Eichhornia Crassipes. At the end of this stage, the maximum percentage of cadmium elimination occurred in the optimum pH equal to 6.6 and retention time

of 30 h, in which this the cadmium value is equal to 0.0162 mg/L, i.e. 98.42% of cadmium elimination. Therefore we can consider the period of 30 h as the optimum time.

The project came to an abrupt cancellation, based on the following reasons:

1. The remaining cadmium value was less than the allowed maximum standard of fresh water.

2. The balance time of absorption process and absorption efficiency, as economic parameters, were of the greatest account for knowledge development and water treatment technology, based on natural absorption.

3. The results of phytoremediation studies showed that increasing absorbent dosage can also increase elimination percentage; therefore, optimum time of 30 hours was considered. (The results of optimum retention time were based on three iterations, its average being equal to 29.7 and standard deviation, to 0.57).

According to the data, the elimination percentage of cadmium had an increasing

trend over the time. The maximum value of absorption occurred in the first 12 h that was equal to 98.21%, and after that, this ascending trend continued with less speed without any significant variation in the cadmium elimination after 12 h (Table 2). It is due to the completion of the absorption capacity of absorbent that is compatible with the results of Lu et al. (2004) and Shah Mohammadi Heidari (2013).

#### Effect of absorbent dose on the absorption amount

Table 3 shows the elimination percentage of cadmium, based on the plant weight (in optimum conditions of time and pH). As it can be seen, by increasing the absorbent dosage from one plant to three plants, cadmium absorption efficiency increases. Based on Table 3, the maximum amount of cadmium elimination in the three plants with specified concentration of 1.03 mg/L of cadmium is 98.8%. (The results of optimum absorbent dosage were based on three iterations with a mean equal to 3 and standard deviation of zero) The reason behind this phenomenon is that by increasing the absorbent dose, the number of competing active surface sites or metal ions also increased and more ions were eliminated from the solution. The results showed that variations in absorbent value have a meaningful effect on the elimination efficiency, illustrating that the absorbent dose is an effective factor in elimination efficiency. Similar results have been reported by Asghar Zadeh et al. (2013).

#### Effect of initial effluent concentration on the absorption value

Solution concentration is an influential factor in balance time and absorption efficiency. The influence of initial cadmium concentration on the absorption of cadmium ions by means of absorbent as cadmium concentrations changes (0.28, 1.03, 2.05, 3.01, 4.35, 5.13, 6.15, 7.1, and 8.28 mg/L) and by considering optimum conditions of the previous stages (pH=6.6, retention time of 30 hours, and absorbent dose of 3 plants (12 stems), the absorption capacity was examined in various initial concentrations. Based on Table 4, which shows the effect of initial concentration of cadmium on its elimination efficiency by *Eichhornia Crassipes*, it can be concluded that by increasing the initial concentration of cadmium, elimination percentage does not have any significant change, and in the initial cadmium concentrations of 0.28, 1.03, 2.05, 3.01, 4.35, 5.13, 6.15, 7.1, and 8.28 mg/L, the elimination value is equal to 99.8%. This is due to the fact that by increasing the concentration, because of the increased number of metal ions and absorbent collision (hit), the ions are eliminated from the solution, indicating the tendency and ability of *Eichhornia Crassipes* to accumulate the cadmium in its roots at 8 mg/L concentration. It also shows the plant's resistance to cadmium. Similar results have been achieved by Mosleh Arani (Mosleh Arani et al., 2014).

**Table 2. Cadmium removal percentage in concentration of 1.03 mg/L based on contact time variations**

Retention time	4h	8h	12h	24h	30h
The observed amount of cadmium (mg/L)	0.0361	0.0333	0.0184	0.0173	0.0162
cadmium removal percentage	96.49%	96.76%	98.21%	98.32%	98.42%

**Table 3. The effect of absorbent dose in cadmium removal at concentration of 1.03 mg/L after 30h**

Absorbent dose	One plant (4 stems)	Two plants (8 stems)	Three plants (12 stems)
The observed amount of cadmium (mg/L) after 30 h	0.0162	0.0044	0.0020
cadmium removal percentage	98.4%	99.57%	99.8%

**Table 4. The elimination percentage of cadmium according to the concentration variations in optimum conditions**

Cadmium concentration (mg/L)	0.28	1.03	2.05	3.01	4.35	5.13	6.15	7.1	8.28
The observed amount of cadmium (mg/L)	0.0003	0.0020	0.0040	0.0040	0.0110	0.0130	0.0140	0.0150	0.0150
cadmium removal percentage	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%	99.8%

**Absorbent isotherms**

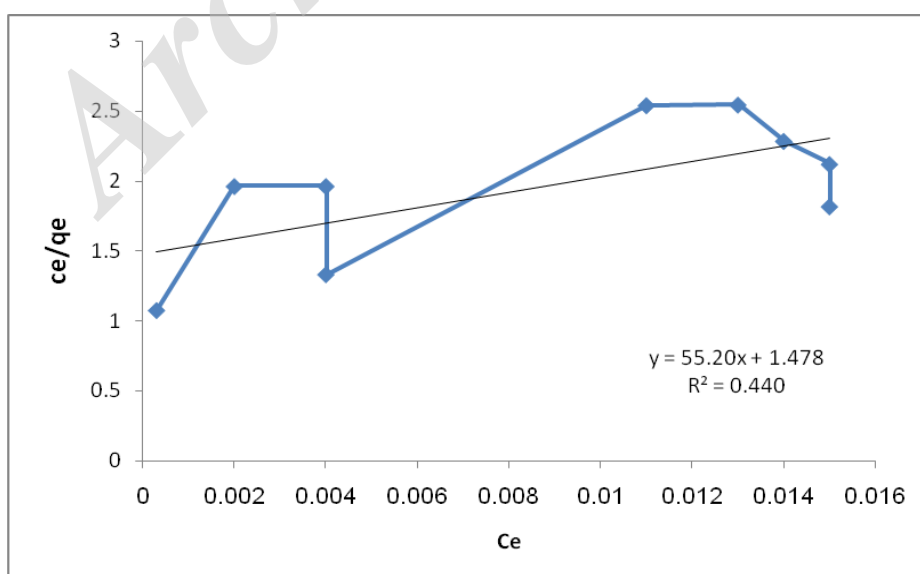
A suitable method to determine absorbent capabilities is to gain absorption isotherm. Absorption isotherm curves are able to quantitatively evaluate the absorption behavior and performance concerning natural absorbents for a metal at a time.

Another hypothesis, proposed in this study is that whether cadmium absorption isotherm by the *Eichhornia Crassipes*

complies with Langmuir and Freundlich isotherms or not. Considering the above-mentioned relations and calculations, it can be concluded that the cadmium elimination process using the *Eichhornia Crassipes* complies Freundlich isotherm with a coefficient correlation of  $R^2=0.98$  (approaching 1) and  $n=1.2$  (a value more than one shows efficient absorption). (Tables 5, 6 and Figs. 1, 2).

**Table 5. Data of Langmuir isotherm for cadmium removal**

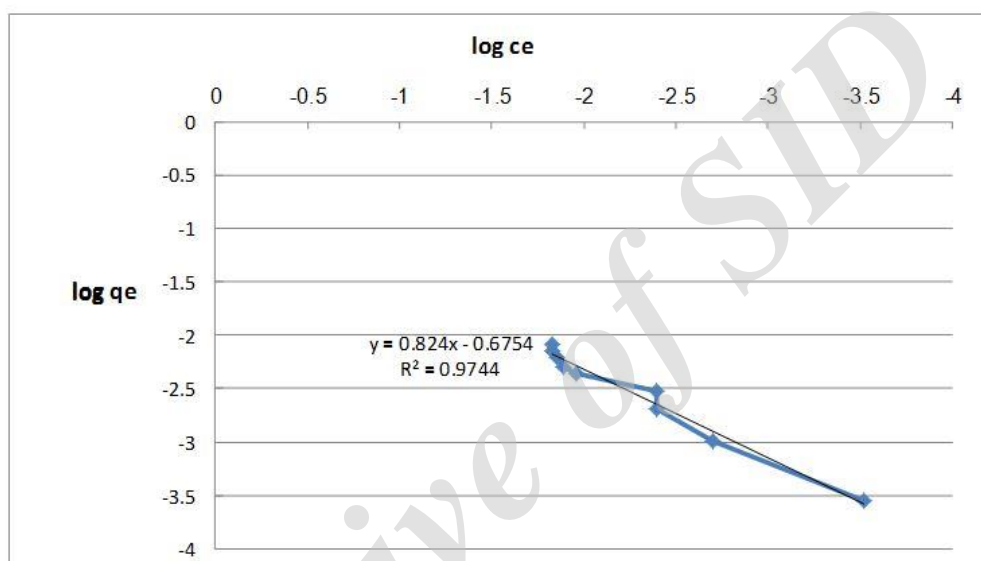
$R^2$	$q_e$	$C_e/q_e$	$C_e$	$C_0$
0.27	0.00028	1.073	0.0003	0.28
	0.00102	1.961	0.0020	1.03
	0.00204	1.961	0.0040	2.05
	0.00300	1.333	0.0040	3.01
	0.00433	2.540	0.0110	4.35
	0.00511	2.544	0.0130	5.13
	0.00613	2.284	0.0140	6.15
	0.00708	2.119	0.0150	7.1
	0.00826	1.816	0.0150	8.28



**Fig. 1. Langmuir isotherm for cadmium removal**

**Table 6. Data related to Freundlich isotherm for cadmium removal**

$R^2$	$\log q_e$	$\log C_e$	$q_e$	$C_e/q_e$	$C_e$	$C_0$
0.98	-3.553	-3.523	0.00028	1.073	0.0003	0.28
	-2.991	-2.699	0.00102	1.961	0.0020	1.03
	-2.690	-2.398	0.00204	1.961	0.0040	2.05
	-2.523	-2.398	0.00300	1.333	0.0040	3.01
	-2.364	-1.959	0.00433	2.540	0.0110	4.35
	-2.292	-1.886	0.00511	2.544	0.0130	5.13
	-2.213	-1.854	0.00613	2.284	0.0140	6.15
	-2.150	-1.824	0.00708	2.119	0.0150	7.1
	-2.083	-1.824	0.00826	1.816	0.0150	8.28

**Fig. 2. Freundlich isotherm for cadmium removal**

## CONCLUSION

Expanding influential technologies, compatible with the environment for refining soil and wastewater pollution with toxic materials is an interesting universal subject. On one hand, the balance time of the absorption process as well as the absorption performance (yield), as the economic parameters, have the most importance for the development of knowledge and technology concerning water purification, based on natural absorbents. The solution concentration and absorbent capacity are two effective factors on balance time and absorbent performance. This study has investigated the ability (potential) of cadmium removal by means of *Eichhornia crassipes* under such performance parameters

as pH, contact time, absorbent mass, and the initial concentration of the effluent on cadmium elimination. Based on the results, the best conditions for cadmium removal by *Eichhornia crassipes* were obtained at pH=6.6, 30 h retention time, and absorbent mass of three plants. The results obtained from absorption experiments totally confirm Freundlich surface absorption isotherm. By using regression analysis (correlation coefficient  $R^2$ ) regarding the influence of pH on the cadmium elimination value and also with regard to the  $R^2=0.31$ , there is no significant relation between cadmium removal percentage and pH. Also, in order to examine the effect of time variation on cadmium removal, it can be concluded that with regards to  $R^2=0.84$ , there is a significant



relationship between cadmium removal percentage and time lapse, i.e. by increasing the contact time, the absorption percentage increases as well, which is due to more contact of *Eichhornia Crassipes*' root with the solution and also greater ion exchange between *Eichhornia Crassipes* and the solution. By increasing the absorbent mass, removal percentage increased and less retention time was obtained for the balance. Based on the results of  $R^2=0.87$ , there is a significant relation between rising absorbent mass and cadmium removal percentage. By increasing the initial cadmium concentration, the removal percentage did not change considerably and there was no significant relation between cadmium removal percentage and the initial cadmium concentration. By increasing the concentration, the contact between metal and absorbent ions increased, and then the ions were eliminated from the solution. This indicates the tendency and ability of *Eichhornia Crassipes* to accumulate cadmium in its roots.

The present study revealed that *Eichhornia Crassipes* had the ability to accumulate cadmium in its root at the concentration of 8.28 mg/L. These findings did not agree with the findings of Lu et al. (2004) who reported that the best value of bio-concentration factor would be obtained when cadmium value is in a 2 mg/L solution. According to the findings of Lu et al. (2004), cadmium absorption value in *Eichhornia Crassipes* rose as time increased and these results were in agreement with our results (Lu et al., 2004). Asghar Zadeh et al. (2013b) used sunflower plant to remove cadmium from aqua environments, their results showing that by increasing the solution's pH from 2 to 6, the efficiency of cadmium elimination increased and pH=6 saw the highest elimination possible. The efficiency of cadmium elimination also increased as absorbent mass and contact time grew. These results were in agreement with those

of the present study (Asghar Zadeh et al., 2013b). Similar results have been reported by Mahvi et al. (2007), Alipour (2010) and Heidari (2009).

According to previous studies, accumulation of metals in plants' roots is more than their leaves; hence *Eichhornia Crassipes* can play an important role as biological absorbent in the elimination of metals from polluted water and wastewater of factories and agriculture. Of course, using this plant and similar marine plants in wastewater systems in scientific scale needs more research in the field of creating appropriate conditions for the plant growth, the kind of wastewater, and the time of their application. Since natural purification systems need less energy and are cheaper, there have been lots of studies in this field globally. This method is a cheap and stable method which is developing as a suitable alternative for current purification methods in developing countries. Moreover, increased studies in the field, lets us contribute to solving the problem of water shortage in our country.

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