Asian Journal of Water, Environment and Pollution, Vol. 14, No. 1 (2017), pp. 69–74.
DOI 10.3233/AJW-170008

Study of Nitrate Removal from the Water by Using *Eichhornia crassipes*

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Received November 16, 2015; revised and accepted December 7, 2016

Abstract: Conserving water resources and protecting them from the pollution are of high importance in natural cycle of our life. Nitrate, as one of the important sources of water pollution, is a serious threat to aquatic ecosystems, and due to its high solubility, its extraction from the water is a costly process. Providing a reliable, low cost and fast method is necessary for eliminating pollution. This study tried to determine the refining potential and capacity of *Eichhornia crassipes* for removing nitrate from the water. Factors such as initial concentration of nitrate, contact time, absorbent mass, pH and the presence of other competing ions such as sulfate on nitrate absorption have been studied. The results showed that the best efficiency of nitrate removal, more than 99%, in the optimum condition (the retention time of 30 hours, absorbent dose three plants (15 stems) and pH = 6.4) occurred. In addition, the efficiency of nitrate removal in the presence of sulfate ions did not reduce. By increasing the initial nitrate concentration, from 30 to 150 mg/L, there was no significant change in removal efficiency. Actually, by increasing absorbent mass, removal time increased from 67.96% to 100%. The process of nitrate absorption followed Langmuir isotherm ($R^2 = 1$). However, the results showed that *Eichhornia crassipes*, a promising plant with great functionality, can be used as a refiner for removing nitrate and it is a simple, efficient and low cost method.

Key words: Absorbent, *Eichhornia crassipes*, nitrate, phytoremediation.

Introduction

Pollution is one of the most important factors that lead to the loss of water resources (Dermentzis et al., 2011). Population growth, industrial expansion, the increment of water consumption and also growing pollution of water resources due to the lack of control of wastewaters effluent has resulted into lower water quality. Curbing the pollution of above-mentioned resources reduces subsequent costs such as refinement, purification, health care and ultimately the costs of environmental protection to a considerable level (Mohseni, 1996). One of the nowadays' environmental problems is the existence (presence) of nitrate in ground waters and also the water contacted with domestic and industrial effluents (Madahi Arefi and Darvish, 1995). As one of the most important resources of water pollution, nitrate is considered as a serious threat for water ecosystems. Eutrophication, groundwater pollution, toxicity for creatures and public health are considered as its negative effects (Nolan, 2001; WHO, 2006). The US Environmental Protection Agency declared the maximum amount of nitrate pollution equal to 10 mg/L of NO_3-N (50 mg/L of nitrate) (World Health Organization, 2008; Gilchrist et al., 2010). Phytoremediation is a process during which the pollutions are purified through the direct analysis, indirect refinement and also by the support of microbial population and absorbing from the soil or water and concentrating in plant's root (McCutcheon and Schnoor, 2003).

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Erichhornia crassipes is an important part of aquatic ecosystem that is easily and successfully used in wastewaters and improves the water quality with the reduction of organic and inorganic materials (Brix, 1993). This plant can reduce the heavy metals of drainage water. Some trace elements may accumulate by the plant (Ismail et al., 1996). Water hyacinth (*Eichhornia crassipes*) is an aquatic plant that can float on the water surface suing the deformed and sponged petioles (Center and Spencer, 1981). The use of this plant as the refiner can help to solve environmental problems. The plant has also 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, ports of south and Central America, Caribbean islands (Edwards and Musil, 1975).

Eichhornia crassipes is effective in the significant elimination of heavy metals such as cadmium, chromium, copper, manganese, lead, nickel and zinc, from the fresh water at low concentration (Sultan and Rashed, 2003). Planting poplar trees in buffer strips and the rows of coast trees in the USA, and also the rows of coast poplar trees between a river and a corn farm in Australia so that its flow entered in the river, have successful results to eliminate the nitrate (Pivetz, 2001).

Ayyasamy et al. (2009) have examined the potential of submerged water plants such as *Eichhornia crassipes*, water lettuce and pennywort, in nitrate removal at five concentrations, 200, 300, 400, 500 and 100 mg/L. The removal amount by the *Eichhornia crassipes* in the concentrations of 100 mg/L was 64 percent, in concentrations of 200 to 300 mg/L was 80 to 83 percent, and in higher concentrations was zero, and also in the two other plants were very little (negligible) (Ayyasamy, 2009).

In the study of Ferasati et al. (2011) nitrate removal using the plant nano-absorbent and also modified Dunnage of cane and straw, the removal percentages were 87 and 90%, respectively for each of them. Based on studies of Fox et al. (2008) on *Eichhornia crassipes*, about 60 to 85 percent of nitrogen was eliminated from the modified Hoagland solution and it has been caused to increase the plant canopy cover. In artificial wetland created in Shoosh refinery of Tehran with different loadings of Kjeldahl and total nitrogen, the removal equal to 86 and 80 percent, respectively, were performed (Sadeghpour et al., 2000).

In order for nitrate elimination from the water, a research was done using the stalks of sunflower and corn. To this end, it has been used to chopped stalks of sunflower and corn and after the implementation of the plan, the removal amount of nitrate using the corn and sunflower were calculated that were equal to 84% and 91% respectively (Sedaghat, 2013). This research was implemented to evaluate the potential of *Eichhornia crassipes* for nitrate removal. Based on conducted studies, so far, no study has been done in this area in Iran, and only very limited studies have been done in the world. Furthermore, the studied method in this research is differing from the previous conducted methods, and it has economic justification. Therefore, this study can be treated as the first method for purification of polluted resources and effluents in Iran.

Materials and Methods

First, in order to eliminate the pollutions from the surface, the plant's root was washed several times with tap water and distilled water and then the output water of washing 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 for preparation of different absorbent doses. The samples of contaminated water were diluted using the nitrate reference standards of Kem Lab, Belgium, and distilled water (to prepare nitrate solutions with different concentrations, standard guidelines of water and wastewater laboratory were used). Some of the made solutions were excluded as the standard control sample pHs of solution. Solution pHs were prepared using the 1µ HCl and 1µ soda. The effects of above-mentioned variables were investigated by keeping each and changing the other one. For example, to evaluate the effect of pH (2.3, 4.6, 6.4, 9.3 and 11.9) the experiments were done in a beaker with 1000 cc nitrate by the certain concentration equal to 51.2 mg/L and volume of 400 ml for 24 hours. After determining the optimum pH, in order to evaluate the effect of contact time, experiments were done in nine levels for dummy solution by the certain concentration of cadmium equal to 51.2 mg/L and the volume of 400 ml for 30 hours in optimum absorbent mass. The experiment was done by the different masses of *Eichhornia crassipes*, 1, 2 and 3 plants respectively and also by the certain concentration of cadmium equal to 51.2 mg/L and the volume of 400 ml in optimum time and pH to calculate the optimum absorbent mass. To determine the standard optimum concentration of cadmium absorption tests were done by the initial concentrations of 31.7, 51.2, 71.2, 101.5 and 151.2 mg/L and also the optimum pH, time and absorbent mass.

In order to examine the interference effect of sulfate ion on the removal efficiency, the standard solutions by concentrations of 100, 250, 350 and 400 mg/L were prepared and then their effects were investigated on the concentration of 51.2 mg/L of nitrate, in the optimum conditions (retention time, pH and absorbent mass). All samples were passed through 0.45 micrometer Watman filter paper at regular intervals and then nitrate amount was measured in wavelength of 275 nanometer (UV range) using the spectrophotometer Dr 5000 device, and the elimination (removal) percentage was also calculated to obtain the optimum amount. The experimental data were compared to Langmuir and Freundlich absorption model as a function of initial concentration of nitrate. To calculate the equilibrium (balance) absorption capacity of absorbent, the relation (1) was used.

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

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

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

$$q_e = (q_m.b.C_e)/(1 + b.C_e) \qquad (2)$$

$$q_e = k_F.C_e^{1/n} \qquad (3)$$

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 also b is the equilibrium constant of Langmuir absorption mg per mg. The k_f and n coefficients and Freundlich constants are indexes of capacity and absorption rate, respectively.

Results and Discussion

In this section, the effect of pH, contact time, absorbent mass and initial concentration of effluent on amount of cadmium absorption using the *Eichhornia crassipes* are investigated.

Effect of pH on Nitrate Removal

One of the important parameters in the absorption process is the initial pH of solution. Solution pH has an important role in determining the concentration of ion in solution. In this section, the pH effect of artificial effluent on the absorption capacity of *Eichhornia crassipes* in the elimination or reduction process of nitrate ion, in constant conditions, at 25^o Celsius, nitrate concentration equal to 51.2 mg/L, solution volume equal to 400 ml and for 24h, will be discussed. Regarding the effect of pH on the nitrate removal efficiency by *Eichhornia crassipes*, the pH range was considered between 2.3 and 11.9. Table 1 shows that the elimination (removal) efficiency is different at various pHs. The percentage of nitrate elimination is increased by increment of pH value, and maximum amount of absorption will occur by approaching to neutral pH. Then by increasing pH, absorption percentage is reduced. As it can be seen, in specified concentration for cadmium, equal to 51.2 mg/L, after 24 hours and pH = 6.4, the elimination value was equal to 66.17 percent i.e. the maximum amount. On the other hand, an appropriate pH for *Eichhornia crassipes* is in neutral range. In pH = 2.3 and pH = 11.9 there was no elimination that in general it is due to that by increasing the electrostatic interactions between negative load of absorbent and ammonium group with positive load, the nitrate absorption by the absorbent is increased. Since absorbent load was neutralized in higher and very low pHs, it had a constant absorption to nitrate ions with negative load; so no absorption was seen in high and low pHs and these results are consistent with the ones prepared by Hamidi et al. (2008) and Tehrani et al. (2011).

Effect of Reaction Contact Time on Nitrate Removal

To investigate the effect of time on elimination (removal) process, the optimized pH in previous step should be considered. Table 2 shows the direct relationship between the retention time and removal percentage of nitrate. According to Table 1, by increasing the retention time, the removal percentage in specified concentration that was equal to 51.2 mg/L of nitrate, is increased, that it is due to the contact increment of *Eichhornia crassipes* with the nitrate-water solution and also increasing the ion exchange between the nitrate-water solution and *Eichhornia crassipes* (It is obvious that after eight hours a faster upward process occurred, while before that we could see a gradual process). At the end of this stage, the maximum percentage of nitrate elimination (removal) is in the optimum pH equal to 6.4 and retention time of 30 hours; in this value the nitrate amount is equal to 16.4 mg/L, that is equivalent to 67.96 percent of nitrate removal. Therefore we can consider the time of 30 hours as the optimum time. Similar results were presented by Zarei et al. (2008).

Table 1: Nitrate removal percentage based on pH variation for 24 hours

pH	*2.3*	*4.6*	*6.4*	*9.3*	*11.9*
Nitrate amount (mg/L)	65.8	19.25	17.32	32.17	117
Nitrate removal percentage	error	62.4%	66.17%	32.17%	error

Table 2: Nitrate removal percentage based on contact time variations

Retention time	*0.5 h*	*1 h*	*2 h*	*3 h*	*6 h*	*8 h*	*21 h*	*24 h*	*30 h*
Nitrate amount (mg/L)	43.6	43	42.3	41.3	40.7	40	33.1	20.62	16.4
Nitrate removal percentage	14.84%	16%	17.38%	19.33%	20.5%	21.87%	35.35%	59.72%	67.96%

Effect of Absorbent Dose on the Absorption Amount

Table 3 shows the nitrate removal percentage based on the plant weight (in optimum conditions of time and pH). As it can be seen, by increasing the plant's weight, the removal amount is increased. Given Table 3, the maximum amount of nitrate removal in the three plants by the specified concentration equal to 51.2 mg/L of cadmium is 100% (Note: by increasing the absorbent dose, balance retention time is also decreased (Table 4). It is because by increasing the absorbent dose, the numbers of competing active surface sites or metal ions have also increased and more ions were eliminated from the solution. This showed that the absorbent dose is an effective factor on elimination (removal) efficiency. These results are consistent with the ones prepared by Shahmoradi et al. (2012) and Farasati (2012).

Table 3: The effect of absorbent dose in nitrate removal at concentration of 51.2 mg/L after 30 h

Absorbent	*One plant (5 stems)*	*Two plants (10 stems)*	*Three plants (15 stems)*
Nitrate amount (mg/L) after 30 h	16.4	2.46	0
Nitrate removal percentage	67.96%	95.19%	100%

Table 4: The effect of absorbent dose in nitrate removal at concentration of 51.2 mg/L after 24 h

Absorbent dose	*One plant (5 stems)*	*Two plants (10 stems)*	*Three plants (15 stems)*
Nitrate amount (mg/L)	20.62	6	0
Nitrate removal percentage	59.72%	88.28%	100%

Effect of Initial Effluent Concentration on the Absorption Value

In this stage, considering the optimum conditions of previous stages (pH = 6.4, retention time of 30 hours, absorbent dose of three plants (15 stems), the absorption capacity was examined in various initial concentrations. Given Table 5, that showed the effect of initial concentration of nitrate, it can be concluded that by increasing the initial concentration of nitrate, removal percentage does not have any significant variation, and in the initial concentrations of 31.7, 51.2, 71.2 and 101.5 mg/L of nitrate, the elimination (removal) value is equal to 100 percent and in concentration of 151.2 mg/L, the removal value is equal to 99.27 percent. The reason of this phenomenon is that by increasing the concentration, due to the increased number of metal ions and absorbent hit, the ions are eliminated from the solution. This showed trend and ability of *Eichhornia crassipes* to accumulate the nitrate in the root at the concentration of 8 mg/L, and also the resistance of plant to cadmium. Similar results were presented by Shahmoradi et al. (2012).

Effect of Interfering Sulfates Ion Concentration on Absorption Amount

Given the results of previous studies and also with regard to the fact that one of the proposed assumptions is the probability of sulfate ion interfering effect in the process of nitrate absorption, the results of nitrate removal experiments using *Eichhornia crassipes* and by the presence of sulfate ions in optimum conditions of previous stage and the nitrate concentration equal to 51.2 mg/L were studied, and it can be seen that in Table 6, the removal efficiency of nitrate by the presence of abovementioned ions does not have a significant reduction and at concentration of 51.2 mg/L without interferer was 100 percent and by the presence of interfering sulfate ion at concentration of 400 mg/L (the highest concentration that tested) is 99 percent.

Table 5: Nitrate removal percentage based on concentration variations in the optimum conditions

Nitrate concentration (mg/L)	*31.7*	*51.2*	*71.2*	*101.5*	*151.2*
Nitrate amount (mg/L)	0	0	0	0	1.1
Nitrate removal percentage	100%	100%	100%	100%	99.27%

Table 6: Nitrate removal percentage in concentration of 51.2 mg/L based on concentration variations of interfering sulfate ion (optimum conditions)

Nitrate concentration (mg/L)	*100*	*250*	*350*	*400*
Nitrate amount (mg/L)	0.1	0.09	0.06	0.05
Nitrate removal percentage	99.8%	99.82%	99.88%	99.9%

Absorption Isotherms

Another hypothesis proposed in this study is the adherence of nitrate absorption isotherm by the *Eichhornia crassipes* to Langmuir and Freundlich isotherms or not, that given the above-mentioned relations and calculations, it can be concluded that the process of nitrate removal using the *Eichhornia crassipes*, adherence to Langmuir isotherm by the coefficient of correlation equal to R^2 = 1. Since the Langmuir isotherm is related to monolayer absorption, and assumes that the absorbent surface has locations with equal energy in which each absorbed molecule is allocated to only one location, then it probably explains the uniform distribution of active surface sites of *Eichhornia crassipes* (Tables 7 and 8).

Table 7: Langmuir isotherm data for nitrate removal

R^2	q_e	C_e/q_e	C_e	C_0
1	0.0317	0	0	31.7
	0.0512	0	0	51.2
	0.0712	0	0	71.2
	0.1015	0	0	101.5
	0.1501	7.328	1.1	151.2

Table 8: Freundlich isotherm for nitrate removal

R^2	$Log\ q_e$	$Log\ C_e$	q_e	C_e/q_e	C_e	C_0
	-1.489	*	0.0317	0	0	31.7
0.49	-1.290	*	0.0512	0	0	51.2
	-1.147	*	0.0712	0	0	71.2
	-0.993	*	0.1015	0	0	101.5
	-0.823	0.0413	0.1501	7.3284	1.1	151.2

Conclusion

The balance time of absorption process and also absorption efficiency, as the economic parameters, have the most importance for developing the knowledge and technology of water purification (treatment) based on natural absorbents. Solution concentration and absorbent capacity are the two effective factors on balance time and absorption performance. In this study the potential (ability) of nitrate removal using the *Eichhornia crassipes* and by influencing the functional parameters such as pH, contact time, absorbent mass and initial concentration of effluent on nitrate absorption were examined using the Regression instrument (R^2 coefficient of correlation). Based on the results, regarding the pH effect on nitrate removal and also with regard to the R^2 = 0.03 amount, there is no significant relationship between nitrate removal percentage and pH amount. Also, to evaluate the time variation on nitrate removal amount, it can be concluded that given the R^2 = 0.76 amount, there is almost significant relationship between nitrate removal percentage and time lapse, that is, by increasing the contact time, the absorption percentage is increased which is due to the increment of *Eichhornia crassipes*'s root contact with the water-nitrate solution and also the increment of ion exchange between *Eichhornia crassipes* and water-nitrate solution. By increasing the absorbent mass, the removal performance (efficiency) is increased from 67.96% to 100%, and the less retention time is obtained for balance and based on the results of R^2 = 0.85, there is a significant relationship between absorbent mass increment and nitrate removal percentage.

By increasing the initial concentration of nitrate, the removal percentage does not have significant change and there is no significant relationship between nitrate removal percentage and initial concentration of nitrate. It is due to that by increasing the concentration because of increasing the hit number of metal ions and absorbent, the ions are eliminated from the solution, and it showed the trend and ability of *Eichhornia crassipes* in collecting nitrate at root. In addition, the removal efficiency of nitrate is not reduced by the presence of sulfate ions. Then there is no significant relationship between the concentration of sulfate ion and nitrate removal percentage. Ultimately, *Eichhornia crassipes* had the ability to accumulate nitrate in the root at concentration of 151 mg/L; that it shows the resistance of the plant to the nitrate. Based on previous studies, the accumulation of metals in the plant's root was more than the shoots and results showed that *Eichhornia crassipes* is advisable for refinement of waters up to concentration of 151 mg/L.

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