Removal of hexavalent chromium from aqueous environments using adsorbents (Lemna and Azolla): An Equilibrium and Kinetics Study

Mohammad Ali Zazouli [1]   Davood Balark [2]

Associate Professor Department of Environmental Health Engineering [1] , Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran. MSc of Environmental Health Engineering [2] , Health Promotion Research Center, Zahedan Universitgy of Medical Sciences, Zahedan, Iran.

Original Article

Abstract

Correspondence:
Davood Balark, MSc.
Health Sciences Research Center, Zahedan University of Medical Sciences.
Zahedan, Iran
Tel:+98 9388517121
Email:
dbalark2@gmail.com

Introduction: Chromium is among the important heavy metals which is found in most industrial wastes and is associated with both health and environmental risks. Therefore, this study tries to analyze the efficiency of lemna and azolla powders in removing hexavalent chromium from aqueous solutions.

Methods: As an experimental trial, this study was conducted experimentally in the lab scale. Initially, lemna and azolla were collected and washed three times with distilled water. They were desiccated in a dry heat, set on 105°C, for 24 hours and then were sieved with a 10-30-mesh sieve. Variation in pH, adsorbent dose, contact time, and initial metal ion concentration were investigated and the remaining concentration was analyzed using spectrophotometer (540 nm). [Equilibrium] Adsorption data were explained using the adsorption isotherms and kinetics.

Results: The results of the study indicated that increasing adsorbent dose and contact time will increase adsorption efficiency with both adsorbents (azolla and lemna), whereas the adsorption capacity will be decreased; also, efficiency of [chromium] removal was decreased with decreasing the initial concentration of chromium and the best pH that can be used for removing chromium was found 3. For adsorbents used in this study, the best type of isotherm was Langmuir and the best reaction kinetics was second order kinetics.

Conclusion: Generally, the adsorbents considered in this study, as inexpensive adsorbents, can be used successfully for treating industrial wastes and aqueous solutions.

Key words: Chromium (VI) – Azolla - Adsorption

Introduction:

Emission of heavy metals in the environment, as the result of industrial development and increasing population, is a major environmental problem in most countries (1). Such metals are not biodegradable and their toxic effects will survive in the body of living organisms (2,3). Chromium is used in various industrial processes including plating, electrical processes, leather industry, wood preservatives, dyeworks, print and paper, plastic

coatings, textiles industry, etc. (4,5). A great deal of wastes containing chromium is discharged from different industries into the environment (6). Chromium often is found, as trivalent and hexavalent forms, in the nature and since chromium is a non-degradable element with carcinogenic and mutagenic properties, it threatens natural life and general health and usually results in certain diseases such as dermatitis, respiratory tract congestion and nasal septum perforation (7). The hexavalent chromium is more toxic (about 500-1000 times) than its trivalent counterpart (8,9). Regarding the detrimental effects of this metal and its coaggregation property in body and the fact that it is not biodegradable, its removal from wastes is necessary (9). Different methods have been used so far for removing heavy metals from industrial wastes including chemical sequestration, ion exchange, adsorption, reverse osmosis, extraction with solvents (10,11). Thanks to its efficiency and easy-to-use nature, adsorption has been introduced as one of the most popular methods (12,13). In this technique, heavy metals are adsorbed across the pores of adsorbents, which are in fact insoluble compounds in water. Usually, adsorption works on the active carbon, which has a high capacity and surface area. However, active carbon is very expensive and its processing needs professional operators (14). Therefore, taking advantage of inexpensive and natural adsorbents instead of commercial active carbon was followed by researchers. There are plenty inexpensive adsorbents available in the nature and their preparation cost is very low. Today, researchers use natural adsorbents such as chitosan, fly ash, peach and olive kernel, charcoal, barley and wheat straw, sawdust to remove organic and inorganic contaminants (12). Lemna and azolla are two phytoplanktons that grow very quickly on ponds and creeks and cover water's surface; hence, they menace life of aquatic animals (because they prevent oxygen circulation) (15,16). Researchers are looking for a solution to remove azolla in Anzali Lagoons; however, regarding its absorbing properties, it is used in many countries as a high-efficient, quick and inexpensive adsorbent for removing organic materials such as dyes and heavy metals (e.g. chromium, zinc, plumb, copper and arsenic) and some good results have been achieved

after using the biomass of azolla and the percentage removal of chromium has been found over 90% in all cases (17-21). Thus, regarding the frequency of azolla and lemna in the environment, this study aims at analyzing contact time, pH, initial concentration of hexavalent chromium and adsorbent dose on efficiency of hexavalent chromium removal and determining the best isotherm model and kinetics of adsorption.

Methods:

Preparation of adsorbent: Initially, azolla and lemna were collected from irrigation canals and/or farms around the Mazandaran University of Medical Sciences complex and then were transported to its Medical School's lab. They were washed in order to remove the wastes stuck to them. Then, they were activated with 0.2 M sodium hydroxide and for removing the acid they were washed with the double-distilled water three times and were desiccated in a dry heat, set on 105°C, for 24 hours. The dried biomass was then grinded in mortar and sieved to a mesh size of 10-18 mm. The final biomass had 1-2 mm size which was proper for our target (22).

Properties of the adsorbent:
Specific surface area and the sealed porosity size of adsorbents were determined using BET test, performed by U.S. Micromeritics GEMINI 2375, while particles density was measured using U.S. Micromeritics AccuPyc 1330 Pycnometer in Materials and Energy Research Center. The apparent properties of biomass of azolla and lemna were analyzed by a SEM equipped with EDX (Plips Model). In order to achieve a general understanding on the biomass chemical structure, FTIR spectra of modified azolla and lemna was collected using the instrument (420, Jasco, Japan) set on wavelength of 400-4000 cm^{-1}.

Preparation of metal ion solution: The stock chromium ion solution (1000 mg/l) used in this study was prepared through solving potassium dichromate ion (made by German Merck Co.) in a double-distilled water. The stock solution is used for producing chromium solutions with different concentrations.

Adsorption experiments in continuous still: This trial was conducted experimentally in a lab scale. Reviewing previous literature showed that the most important variables which may affect the adsorption are pH, adsorbent dose, contact time and chromium concentration. Since chromium concentration in industrial waste varies from 1 to 100 mg/l, its initial concentrations (10-100 mgr/l) were selected for this study (3). Regarding the previous studies, the effect of pH, varies from 3 to 11, retention time (10, 20, 30, 45, 60, 90, 120, and 180), and adsorbent dose, varies from 0.2 to 1.4 g/100 cc, were selected (3) and were analyzed through separate phases during the study. A 250-ml Erlenmeyer flask was used for working in a batch system. In any adsorption experiment, a certain volume of chromium solution with certain concentration was added to the Erlenmeyer, the ideal condition was set and a certain dose of the adsorbent was added. A shaker (180 rpm) was used for mixing and making a proper contact between adsorbent and chromium and then was purified with a 3000 rpm centrifuge. All stages of the experiment were conducted in two steps in order to find the possible errors. Regarding the optimality of parameters and repeating tests for two adsorbents, a total of 120 samples were chosen (23). It is necessary to note that another 30 samples in different times and concentrations were carried out for resorption tests. Therefore, the total samples for adsorption and resorption tests were 150 samples. When all tests were completed, the significance level for all data was measured using SPSS18 and regression coefficient (28-30).

How to measure chromium: All concentrations of chromium were measured according to λmax, which was measured for chromium using DR4000 spectrophotometry as large as 540 nm (7,9). Chromium concentrations in both standard and unknown samples were measured according to the standard techniques used in water and wastewater tests relied on 1, 5-Diphenylcarbazide agent (9). 1N HCI or NaOH solution was used to set pH.

Desorption Tests: Containers which already used for conducting adsorption were filtered using a 0.45 micron filter, then the biomass collected over the filter was washed with distilled water and then was kept in contact with 0.5 M Hydrochloric acid and distilled water. The prepared sample was kept for 90 minutes, which is the optimal contact time, on the shaker. The sample was filtered again and spectrophotometry was used to read the sample's fluoride content (24). The resorption ratio was measured using the following equation (25):

Resorption percentage = resorbed chromium ion/ adsorbed chromium ion x 100

Isotherm Equations: In order to analyze the effect of adsorbent mass on chromium removal, which is necessary for extracting adsorption isotherms, initially the contact time is calculated through the primary kinetics test; hence, the equilibrium tests of adsorption operation will be possible. Data resulted from the equilibrium tests usually are recognized as the adsorption isotherms. The equilibrium data are considered as basic data used for designing adsorption systems. To do so, classic models of adsorption including Langmuir, Freundlich, Temkin and Bet were employed, which represent the equilibrium relations of concentration of the removing material between the adsorbent and the solution.

Table 1 summarizes isotherm equations. Adsorption isotherms and adsorption capacity were determined based on the results of kinetic batch tests of adsorption process. For determining adsorption capacity and removal efficiency, the following equation was used (26):

Table 1. Isotherm equations

Model	Equation
Langmuir Model	$\dfrac{ce}{qe} = \dfrac{1}{q_m K_L} + \dfrac{ce}{q_m}$
Freundlich Model	$\text{Log } \dfrac{x}{m} = \dfrac{1}{n} \log Ce + \log K_F$
Temkin	$q_e = B_l \ln(k_t) + B_l \ln(c_e)$
Dubinin-Radushkevich Model	$qe = exp(-k_{d-r}\,\varepsilon^2)$
Bet Model	$\dfrac{c_e}{(c_i - c_q)q} = \dfrac{1}{A(X_m)} + \dfrac{A-1}{AX_m}$

$$R = \frac{(Co - Ce) \times 100}{Co}$$

$$qe = \frac{(Co - Ce) \times V}{M}$$

Table 2. The equations of isotherms

Model	Equation
Pseudo first order	$\log(q_e - q) = \log q_e - k_1 t / 2.3$
Pseudo second order	$t/q = 1/k_2 q_e^2 + t/q_e$
Elovich	$q_e = (\frac{1}{\beta})\ln(\alpha\beta) + (\frac{1}{\beta})\ln t$
Intraparticle diffusion	$q_t = k_{dif} t\, 0.5 + c$

Where R is efficiency; qe is adsorption capacity (mg/g of adsorbent); C_0 is the initial concentration of chromium (mg/l); C_e is chromium concentration in time (t) (mg/l); M is the mass of adsorbent (g); and V is volume of initial sample (l).

Results:

Table 3 summarizes properties of biomass resulted from both azolla and lemna. The specific surface areas of biomasses of lemna and azolla are 34 and 28.5 sq-m/g, it shows their appropriate adsorption area. The total biomass porosity volumes of azolla and lemna are 0.168 and 0.145 sq-cm/g. Figure 1 and table 4 show EDX and SEM micrographs of the produced biomass. The weight percentage of elements in the biomass structure indicates that C, O_2, and Ca are three main elements of azolla and lemna and as SEM images show, the prepared adsorbent have a very high porosity and a heterogeneous surface. FTIR spectrum of azolla and lemna in the wavelength range of 400 to 4000 cm^{-1} was implemented and the results indicate that the spectra of 3320 to 3410 cm^{-1} belong to O-H functional group in which the hydrogen makes bond with polymer compounds. Thus, this wavelength represents hydroxyl functional group in the adsorption process (31); hence, the decreased adsorption intensity or the increased passage of infrared spectra in this bond may be due to a bond made between hydroxyl group and metals. Passage of 28-2917 cm^{-1} spectrum shows strips belong to C-H bond which are located in the aliphatic area. In spectrum 21-1709 cm^{-1}, there are carboxylic acids functional group (e.g. COOH, -$COOH_3$) which may make bond with carboxylic acid and other esters. 14-1609 cm^{-1} to 1395-1404 spectra are symmetrical and asymmetrical stretching of O=C, COO-, respectively. Spectrum of 25-1009 cm^{-1} shows strips belong to C-OH bond which binds with alcohol and carboxylic acid compounds (1).

Contact time: The effect of contact time on efficiency of chromium adsorption in this system was studied through increasing the contact time from 10 min to 180 min. As figure 3 indicates, increasing the contact time by 90 min for azolla and by 120 min for lemna, the removal efficiency will be increased; as the removal efficiency in minute 10 for azolla (10 mg/l) is equal to 41%, whereas in a 90-min sample it is equal to 98% and for lemna is less than that in azolla, as in minute 90 is equal to 92% in the latter. The contact times of 90 and 120 minutes were determined as the optimal contact time for azolla and lemna, respectively. Analyzing data using linear regression demonstrated that increasing the contact time as large as 1 unit, will decrease the removal efficiency as large as 0.032% and 0.029%, respectively (P≤0.001).

Effect of pH: Effect of pH on chromium adsorption efficiency in this system was studied by increasing pH from 3 to 11 and as figure 4 shows, in an acidic pH, the removal efficiency is high for both adsorbents and increasing pH may decrease, whereas increasing pH will decrease the removal efficiency. Therefore, an optimal pH for absorbing trivalent chromium is equal to 3. Analyzing data using linear regression significantly showed that increasing pH (more than 3) will decrease the removal efficiency as large as 0.037% and 0.031%, respectively (P≤ 0.001).
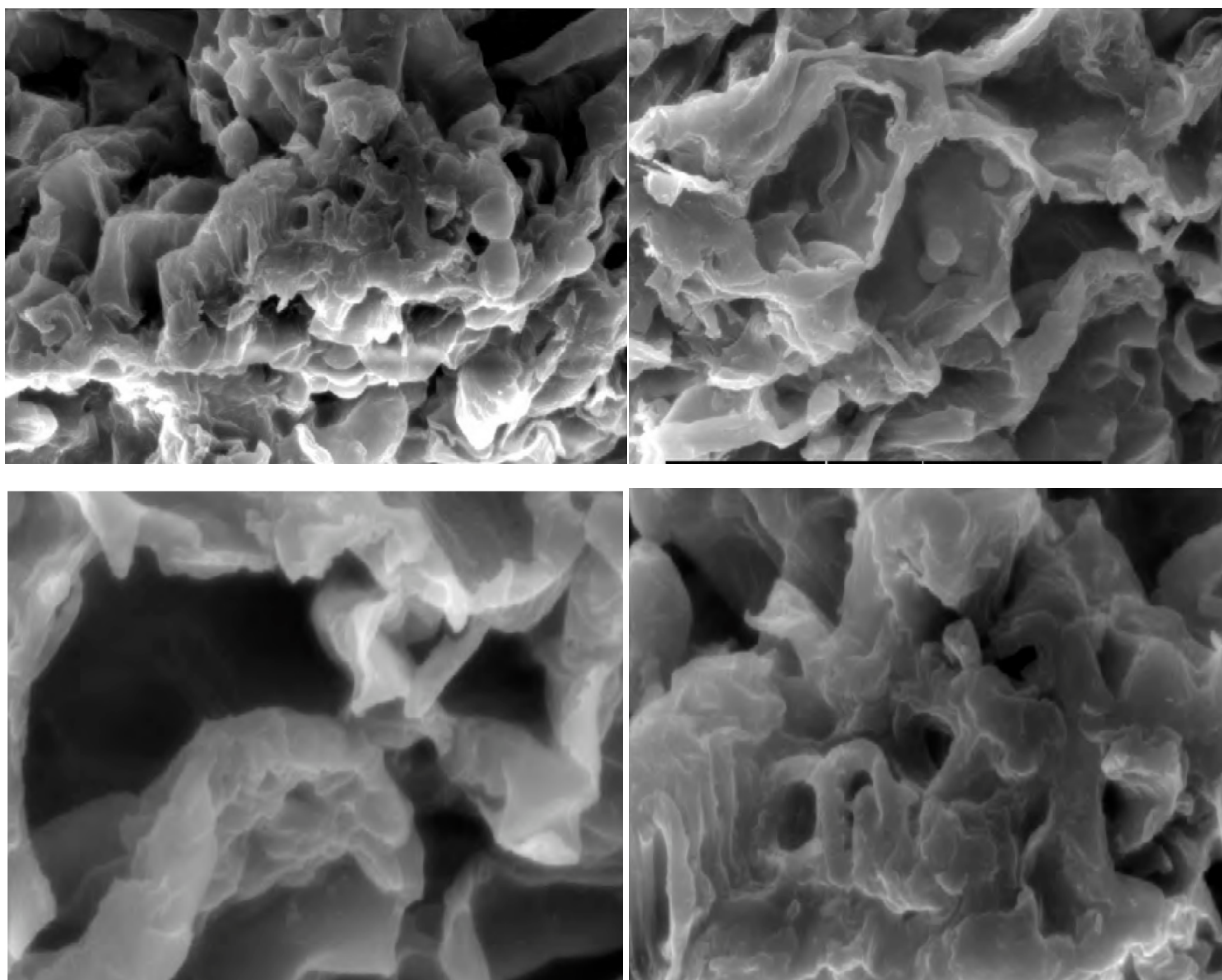
Figure 1: SEM image of biomass before and after usage A) azolla before usage B) azolla after usage C) lemna before usage D) lemna after usage
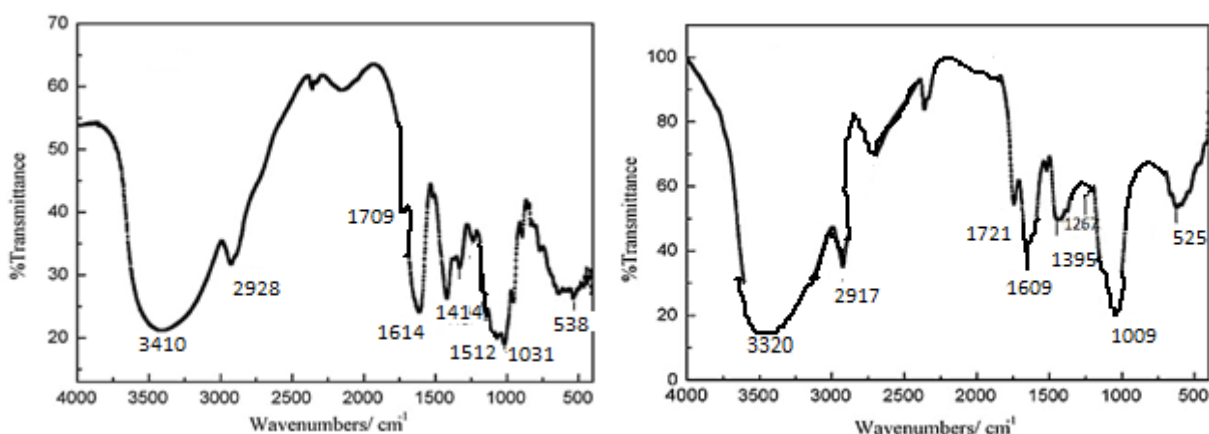

Figure 2. FTIR of biomass a) azolla; b) lemna

Effect of the initial concentration of chromium: The effect of initial concentration of chromium on chromium removal efficiency in this system was studied by changing the initial concentration of chromium in terms of g/l (100-1) and as figure 5 indicates changing chromium concentration will decrease the removal efficiency in both adsorbents, as for concentrations of 10

mg/l, (contact time=90 min), the removal efficiency for azolla and lemna is 98% and 92%. Analyzing data using linear regression indicated significantly that increasing the initial chromium concentration as large as 1 unit will decrease the removal efficiency as large as 0.036 and 0.041 in azolla and lemna, respectively ($P \leq 0.001$).
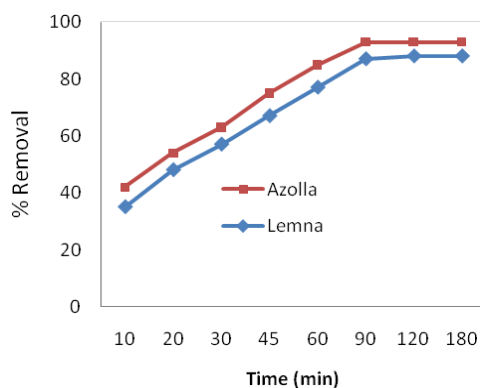

Figure 3. The effect of contact time of removal efficiency (adsorbent dose: 10 g/l, chromium concentration: 10 mg/l, pH: 3)
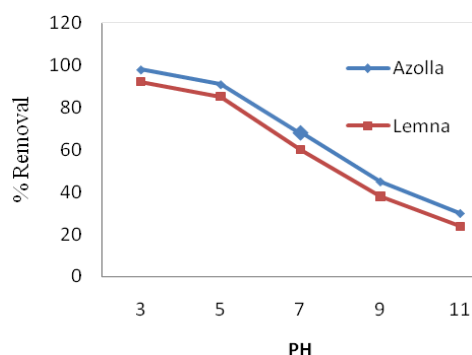

Figure 4. The effect of pH on removal efficiency (adsorbent dose: 10 g/l, chromium concentration: 10 mg/l, contact time: 90 min for azolla, 120 min for lemna)
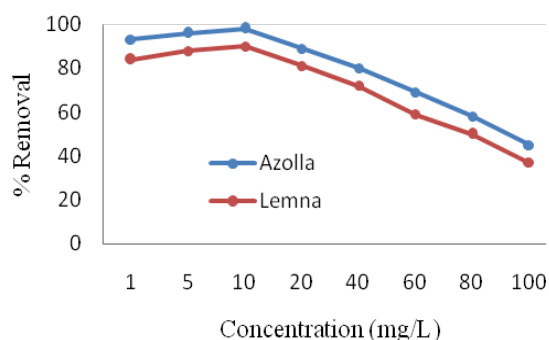

Figure 5. The effect of initial concentration of chromium on removal efficiency (adsorbent dose: 10 g/l, contact time: 90 min for azolla and lemna, pH= 3)
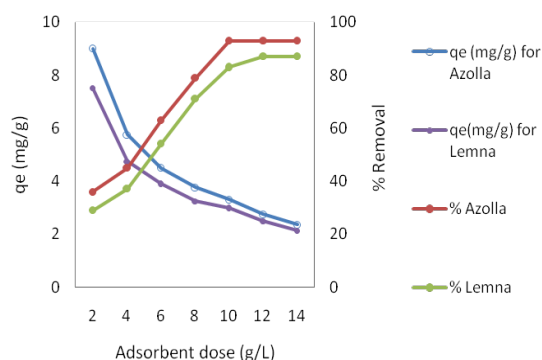
Figure 6. The effect of adsorbent dose on removal efficiency (chromium concentration: 10 mg/l, contact time: 90 min for azolla and 120 min for lemna, pH: 3)

Table 3. Properties of adsorbents

Parameter	Azolla's biomass	Lemna's biomass
Specific surface area (m²/g)	34	28.5
Single point specific surface area (m²/g)	36.5	29.8
Density (g/cm³)	1.14	1.04
Moisture (%)	Trivial	Trivial
Size of particle (mm)	1.1-1.6	1.45-1.05
Porosity volume (cm³/g)	0.168	0.145

Table 4. Weight percentage in biomass structure

Elements	Weight percent of azolla	Weight percent of lemna
C	57.58	53.61
O_2	35.7	37.8
Ca	4.4	5.7
Mg	1.2	1.7
Na	0.1	0.14
K	0.44	0.21
Al	0.37	0.51
Cl	0.11	0.28

Effect of adsorbent dose: The effect of the initial adsorbent dose on chromium removal efficiency in this system was studied by changing the initial adsorbent dose (2-14 g/l). As figure 6 shows, increasing the adsorbent dose will increase the chromium removal efficiency, as in dose of 2 g/l, the removal efficiency for azolla and lemna is 36% and 29%; however, in dose of 10 g/l, the removal efficiency is over 90% for both plants. However, in doses more than 10 g/l, the chromium removal gradient is very low and close to equilibrium. Although increasing the adsorbent dose will increase the removal efficiency, the chromium removal efficiency for each gram of adsorbent (qe) will be decreased.

Table 5. Results of desorption tests

Initial dose (mg/l)	Adsorbent dose (g/100cc)	Removal percent of azolla	Removal percent of lemna	Resorption with distilled water (azolla)	Resorption with distilled water (lemna)	Resorption with acid (azolla)	Resorption with acid (lemna)
10	0.5	54	47	19	17	31	28
	1	93	82	34	36	65	63
20	0.5	49	43	23	22	37	34
	1	81	72	39	34	69	67
50	0.5	36	29	28	24	45	41
	1	64	56	42	39	74	71

Table 6. Paramaters of isotherm models

Isotherm type	Isotherm parameter	Chromium concentration (mg/l) (azolla)		Chromium concentration (mg/l) (lemna)	
		10	20	10	20
Freundlich	N	0.78	0.92	0.71	0.85
	k_f	1.45	1.37	1.2	1.12
	R^2	0.977	0.948	0.981	0.967
Langmuir	K_L	0.016	0.021	0.014	0.019
	R^2	0.998	0.994	0.997	0.992
	q_m	16.2	13.1	15.9	12.2
Tekmin	A_T	5.39	5.05	5.24	4.85
	B_T	4.2	3.65	3.75	3.41
	R^2	0.987	0.982	0.979	0.984
Dubinin-Radushkevich	K_{D-R}	0.0000021	0.000002	0.0000018	0.00000016
	Q_m	9.82	12.92	8.4	11.7
	E	8.17	9.4	7.7	8.6
	R^2	0.964	0.942	0.971	0.951
Bet	K_G	69.45	64.4	62.4	59.12
	R^2	0.994	0.987	0.988	0.947
	q_m	29.4	24.2	26.1	21.9

Table 7. The adsorption kinetic model constants

Type of kinetic	Kinetic parameter	Fluoride concentration (azolla) (mg/l)		Fluoride concentration (lemna) (mg/l)	
		10	20	10	20
First order	K_1	0.89	0.84	0.8	0.76
	q_e	14.2	17.9	14.4	16.7
	R^2	0.841	0.945	0.932	0.962
Second order	K_2	0.0045	0.0034	0.0027	0.0034
	q_e	16.6	19.4	15.7	18.3
	H	1.27	2.65	1.2	2.49
	R^2	0.999	0.984	0.991	0.987
Elovich	A	2.9	4.7	2.4	4.1
	β	0.24	0.18	0.21	0.16
	R^2	0.91	0.982	0.945	0.967
Intra-partucle diffusion	K_{dif}	0.75	1.4	0.66	1.21
	C	4.17	8.5	11.4	8.5
	R^2	0.82	0.87	0.93	0.84

Conclusion:

As mentioned earlier, the specific surface area is a determining parameter for adsorption capacity of an adsorbent substance, because there is a direct relationship between specific surface area of a substance and its porosity; thus a higher contact surface with the absorbing substance will be developed. The specific surface area for azolla and lemna is 34 and 28.5 sq-m/g; hence, azolla has a better surface area rather lemna; however, both of them have a proper specific surface area in contrast to almond and walnut and were compatible completely with the results that already have been gained on such adsorbents (32). Infrared spectrophotometer analysis demonstrated the role of carboxyl and hydroxyl in bio-adsorption process (17). The importance of carboxyl groups in bonding with heavy metals has been demonstrated already, as we know that the decreased intensity of adsorption or the increased passage of infrared in such functional groups may be due to development of bonds between carboxyl and hydroxyl groups with metals (1,31). Naturally, increasing contact time will increase adsorption possibility, because of increasing the chance of contact between metal ions and adsorbent particles. Thus, when the contact time between adsorbent and solutions containing metal ions is increased, more metal ions are absorbed by adsorbent; such behavior is seen in contact times vary from 10 to 90 minutes. In other words, more metal ions are removed by increasing contact time and chromium removal efficiency by

adsorbent (azolla) will be fixed and after 90 minutes a equilibrium will be developed between the metal ions absorbed by the solid phase and the solution, which is in contact with that. However, the equilibrium time for lemna is achieved after 120 minutes and removal efficiency in equilibrium time of 120 minute is less than that in equilibrium time of 90 minutes. The results were compatible with Chonjnacka (Poland) (33). The different result of this study with other studies is due to structural difference of the used adsorbents. Adsorption in lemna and azolla is realized through diffusion across pores; whereas in studies in which equilibrium has been developed within 24 hours, diffusion is seen in the initial pores (27); however, in nanoparticles which has low equilibrium time, adsorption is seen in the superficial area, hence here we have a faster adsorption (34). Chromium removal starts very quickly, but it dwindles over time, which it would be due to decreasing the soluble chromium and decreasing the active points across the adsorbent surface, because there are many empty sites during the primary stages of adsorption, but they are filled with chromium molecules over time (23). As this study showed, the highest efficiency of chromium removal was reached in pH: 3, it can be explained based on the adsorbent loading and percentage of hydronium ions in solution. Reduction and adsorption are two important processes involved with removing hexavalent chromium in this system; as a result, adding biomass will reduce the initial yellow color

of the hexavalent chromium over time and it will become green because of reducing the hexavalent chromium to a trivalent one. Converting a neutral pH to an acidic one will improve the removal efficiency, because the dominant ion in neutral to acidic pH is cr_2o_7; formation of this ion will decrease the concentration of the initial chromium which in turn increases the removal efficiency. The decreased removal efficiency in high pHs is due to the increased OH^- ion in the environment and formation of metal hydroxide sediments including trivalent hydroxide cr $(oh)_3$ which is completely compatible with previous studies on this regard (7,35,36). Generally, the hexavalent chromium in this study is removed through pH variations according to equations 1-3 (37,38).

Under acidic pH condition: $Cr_2O_7^{2-} + 14H^+ + 6e^- \quad 2Cr(III) + 7H_2O$

Under neutral pH condition: $CrO_4^{2-} + 7H^+ + 3e^- \quad Cr(III) + 4H_2O$

Under basic pH condition: $CrO_4^{2-} + 4H_2O + 3e^- \quad Cr(OH)_3 + 5OH^-$

Similarly, increasing the adsorbent dose will increase the removal efficiency which is due to the increased active surface area of adsorbent to a certain efficiency of pollutant. The results shows that although there is a direct relationship between adsorbent dose and efficiency, the adsorbed chromium per each gram of adsorbent is decreased which is due to unsaturation of active points in adsorbing pollutant. Therefore, increasing adsorbent dose provides a condition in which the capacity of all active points across the adsorbent surface area are not used which in turn will result in the decreased removal efficiency per adsorbent's mass unit which is compatible with previous studies (8,39). Increasing the initial concentration of chromium will decrease the removal efficiency which is due to the fact that the adsorbent's surface area have limited site for adsorption, so when the chromium concentration is increased, the available surface area to the contaminant, which must be removed, is decreased which in turn decreases efficiency and chromium removal from water, as the results are compatible with Gupta's study on removing hexavalent chromium using sawdust (40). With regard to resorption tests, it can be concluded

that chromium removal on biomass of azolla and lemna is mostly superficial and adsorbent's surface area plays a key role in this process and the internal penetration is very low, because if the internal penetration occurs, the time required for performing resorption will be longer; whereas in this study the resorption was very well in the optimal time and was compatible with the previous studies (41). Regarding the correlation coefficients, it can be concluded that the equilibrium data of chromium adsorption on lemna and azolla mostly follow Freundlich, Bet and Dubinin-Radushkevich isotherms rather Langmuir and Temkin isotherms. Since adsorption with Freundlich and Bet isotherms is done in a multi-layered and heterogeneous, chromium removal using azolla and lemna is heterogeneous which is compatible with various previous studies (34,42). Dimensionless (R_L) and n coefficients are amongst key parameters that need to be determined in adsorption equations used to predict whether the adsorption is proper or not. They are measured by Langmuir and Freundlich curves, respectively. In Langmuir equation, if $R_L > 1$, it means that the adsorption is not proper, if $R_L = 1$, the adsorption is linear, if $R_l = 0$, the adsorption is irreversible and if $0 < R_L < 1$, the adsorption is proper [14], in this study R_L for biomass of azolla and lemna is 0.62 and 0.57, respectively. In Freundlich equation, n represents how the absorbing substance is diffused across the adsorbent surface area. Heterogeneity is seen in condition in which n is closer to zero (16), in this study n value for azolla and lemna is 0.32 and 0.46 and confirm the results of Freundlich isotherm which indicate heterogeneous adsorption (43). Although biomass of azolla and lemna are considered as two extraordinary adsorbents in removing contaminants from the aqueous environment, since they are only available in Northern Iran and regions with heavy rainfalls, other parts of the country cannot use them. A significant limitation is accessing these plants only during rainy seasons, thus, they cannot be used throughout the year. It is suggested that the biomass gained from these plants is used to remove other contaminants in a batch system.

Generally, removing chromium (VI) was increased after increasing contact time and adsorbent dose because of the increased collisions,

surface area and available adsorption points for the adsorbent. Similarly, increasing the initial concentration of chromium (VI) decreased the removal efficiency because of saturation of adsorbent's surface area in high concentrations. Generally, our results made it clear that adsorption process using biomass of lemna and azolla can be considered as an effective, inexpensive, fast and efficient method to remove heavy metals from the industrial wastes and removal efficiency depends on certain parameters such as contact time, pH, adsorbent's dose and initial concentration of heavy metals.

Acknowledgement:

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