REMOVAL OF TOXIC METALS FROM AQUEOUS SOLUTION BY DUCKWEED (*Lemna minor L*): ROLE OF HARVESTING AND ADSORPTION ISOTHERMS

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الخلاصـة :

تمت دراسة امتصاص عشب البط لعناصر الكروم (٦) والنحاس (٢) والكادميوم (٢) من محاليل مائية ، وقد تم استعمال ثلاثة مفاعلات في هذه الدراسة التجريبية ، حيث لم يتم قطف الأعشاب من المفاعل الأول ، بينما تم قطف الأعشاب في المفاعل الثاني مرة كل أربعة أيام ، وتم قطف الأعشاب في المفاعل الثالث مرة كل يومين . وكانت فترة الاحتجاز ثمانية أيام ، وقد اتضح من التجربة إمكانية إزالة أيونات المعادن من السوائل إذا تم قطف الأعشاب بصورة متكررة أكثر .

وحين كان يتم قطف الأعشاب مرة كل يومين ، كان التركيز الابتدائي للكروم (٦) يساوي خمسة ملغ / لتر، فأصبح ٠,٥ ملغ / لتر ، بينما كانت مستويات النحاس (٢) والكادميوم (٢) تحت الحد الأدنى للقياس . وحين كان التركيز الابتدائي للكروم (٦) يساوي ١٠ ملغ / لتر ، كان التركيز النهائي للكروم (٦) يساوي ٠,٩٠ ، وللنحاس (٢) ٠,٩٤ ، وللكادميوم (٢) ٢,١٠ ملغ / لتر . وفي دراسات التوازن الحراري تم حساب معاملات لانغموار وفرندليتش للمعلومات التي تم جمعها أثناء فترة الاحتجاز التي استمرت أربعة أيام في المفاعل الثاني . وقد كانت المعلومات الناتجة متوافقة مع معامل فرندليتش .

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ABSTRACT

The sorption of Cr(VI), Cu(II) and Cd(II) ions from aqueous solutions into duckweed has been investigated. Three reactors have been used in the experimental studies. Whereas duckweed was not harvested in the first reactor, it was harvested once every four days and once every two days in the second and the third reactors, respectively. The detention time was 8 days. For all the metal ions, the results show that heavy metals can be successfully removed from solutions if duckweed is frequently harvested. When duckweed was harvested every two days, while, for initial concentrations of 5 mg l^{-1}, Cr(VI) ions were measured at 0.5 mg l^{-1} and the levels of Cu(II) and Cd(II) were not detectable, for initial concentrations of 10 mg l^{-1}, final concentrations were: Cr(VI) 0.90; Cu(II) 0.94; and Cd(II) 2.10 mg l^{-1}. In the isotherm studies, the Langmuir and Freundlich constants have been calculated for the results obtained during the detention time of four days in the second reactor. The experimental adsorption data fitted reasonably well the Freundlich isotherm.

Keywords: Duckweed, harvesting, removal, sorption, heavy metal, Langmuir, Freundlich.

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1. INTRODUCTION

Removal of toxic pollutants such as phenol, ammonia, and toxic metals from sewage and industrial wastewater has received much attention [1–3], since the number of health problems associated with environmental contamination continues to rise.

Heavy metals have toxic effects and must be removed from wastewater before it is discharged into the receiving environment. Treatment processes for metal removal involve generally advanced treatment processes such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, and activated carbon adsorption. These processes are effective for treatment of wastewater, but they are often unsuitable for the mass removal of toxic pollutants because of their high cost. This has motivated researchers to investigate alternative treatment technologies.

Adsorption is still found to be economically appealing for the removal of toxic metals from wastewater by using some adsorbents under optimum operation conditions. It has been reported that some plants such as algal biomass [4], seaweed [5], aquatic macrophytes [6], alfalfa [7], water hyacinth [8], and duckweed [9], agricultural residues such as coconut husk [10, 11], rice husk [1], tea leaf [12], and almond husk [13], and by-products such as alumina [14], all have the capacity to adsorb and accumulate heavy metals.

The use of aquatic plants for wastewater treatment becomes interesting and beneficial for small communities where wastewater cannot be sewered to a centralized wastewater treatment system in a cost effective way. These treatments must be reliable and easy to operate and must have low capital and operating costs.

Duckweed is a small floating aquatic plant, well known for its high productivity and high protein content. In temperate climates, it can offer a good possibility of use, unlike water hyacinth, which is more resistant to low temperatures [15, 16].

Duckweed is a family of floating monocotyledons consisting of four genera (*Lemna, Spirodela, Wolffia, and Wolffiella*) and 28 species [17]. They are green, small in size (1–3 mm), and have short but dense roots (1–3 cm).

Duckweed is able to grow at water temperatures as low as 5–7°C and at atmospheric temperatures of 1–3°C [18, 19]. Because duckweed grows at temperatures of 7–30°C, it is among the most vigorously growing plants on earth [20]. Optimal temperatures are 20–30°C. It is shown that duckweed reached a doubling of frond numbers every four days under laboratory conditions, that is: constant temperature of 24°C and 12 hour dark and light photoperiod [19]. Its growth rate decreased at natural weather climates. Typical pH range is 4.5–7.5. Its growth is completely inhibited only at a pH greater than 10 [15].

Typical water content of duckweed is 94–95% [19]. Apart from having high productivity, duckweed has a high protein content and low fiber content. It has been found to have a protein content of 240–410 g.$(kgDW)^{-1}$, a nitrogen content of 40–60 gN.$(kgDW)^{-1}$, a phosphorus content of 13–29 gP.$(kgDW)^{-1}$, and a fiber content of 60–90 g.$(kgDW)^{-1}$, for duckweed harvested from wastewater ponds [21].

In this study, the harvesting has been done at differential time periods to increase the efficiency of heavy metal removal by duckweed (*Lemna minor*) and the role of frequent harvesting has been investigated, with regard to the treatment capacity.

2. MATERIAL AND METHOD

2.1. Adsorbate Solution

All reagents used were of analytical grade. Aqueous standard solutions of metal chlorides, namely Cr(VI), Cu(II), Cd(II), were prepared from stock solutions containing 1000 mg l^{-1} of each metal.

2.2. Procedure

Duckweed used in this study was collected from the secondary settling tank in Elazığ City Domestic Wastewater Treatment Facility. The duckweed was washed with an excess of pure water. Thirty g of wet duckweed was applied to 1.5 liters of solution having a known concentration of heavy metal ions. The reactor surface was covered to prevent evaporation and cross contamination.

Three reactors were used in the experimental studies. These reactors were made of plexiglass with dimensions of 10 cm × 40 cm × 10 cm. The experiments were carried out as batches under laboratory conditions (summer temperature of 27 ± 0.4°C and 12 hour dark and light photoperiod), for eight days. The water samples collected from reactors were analyzed to determine the metal concentration for each day.

Detention times of duckweed were eight days for the first reactor, four days for the second reactor, and 2 days for the third reactor. While duckweed was not harvested in the first reactor, it was completely harvested once every four days in the second reactor and once every two days in the third reactor. After harvesting, other duckweed washed with pure water was inserted into the reactors and subsequently the surface was covered. To account for the volume reduction from volatilization, the same amount of pure water as the reduced volume was added to the reactors.

The concentration of heavy metal ions were determined everyday by using a Unicam 929 Model Atomic Absorption Spectrometer. The percentage removal of heavy metals was found by calculating the differences between the concentration of metals in the initial and final samples.

2.3. Adsorption Isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several mathematical model equations, such as the standard Langmuir model and the Freundlich model [22]. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules. The model takes the following form:

$$\frac{C_e}{A_m} = \frac{1}{k}\frac{1}{b} + \frac{C_e}{b}\,, \tag{1}$$

where C_e is the equilibrium concentration (mg l^{-1}), A_m is the amount adsorbed per specified amount of adsorbent (mg.g^{-1}), k is the equilibrium constant, and b is the amount of adsorbate required to form a monolayer.

The Freundlich model assumes that the uptake of metal ions is heterogeneous and by monolayer adsorption. The model is described by the following equation:

$$Am = k.Ce^{1/n} \tag{2}$$

or

$$\log(A_m) = \log(k) + \frac{1}{n}\log(C_e)\,. \tag{3}$$

The common terms in Equations (1) and (2) were described earlier and n is an empirical constant.

3. RESULTS AND DISCUSSION

3.1. Adsorption Studies

The initial pH of the solution in the experimental studies was adjusted to 6.0 before addition of the duckweed, since duckweed can tolerate a wide pH range, but works best at 4.5 to 7.5. Figure 1 indicates the removal of Cr(VI), Cu(II), and Cd(II) from aqueous solutions at the detention time of eight days, without harvesting. Figure 1(*a*) and (*b*) contain the data from solutions having initial heavy metals concentrations of 5 mg l^{-1} and 10 mg l^{-1}, respectively. At the end of four days, it is observed that the concentrations of Cr(VI) decreased from 5 to 2.72 mg l^{-1} and from 10 to 5.93 mg l^{-1}, the concentration of Cu(II) decreased from 5 to 2.47 mg l^{-1} and from 10 to 5.48 mg l^{-1}, and the concentration of Cd(II) decreased from 5 to 2.09 mg l^{-1} and from 10 to 6.74 mg l^{-1}. At the end of the eighth day, the concentrations of Cr(VI), Cu(II), and Cd(II) ions increased to 4.36, 4.62, and 3.41 mg l^{-1} in the experiments for the initial concentration of 5 mg l^{-1}, and up to 8.43, 8.25, and 9.56 mg l^{-1} in the experiments for the initial concentration of 10 mg l^{-1}, respectively. Thus, the experiments were run for only eight days. From as detention time of five days for an initial concentrations of 5 mg l^{-1} and four days for an initial concentrations of 10 mg l^{-1}, the concentration of all heavy metals in the solutions started to increase with time, because of heavy metal toxicity. When the initial concentrations were increased from 5 to 10 mg l^{-1}, it was observed that the decrease of duckweed also occurred and started rather early.

Figure 2 shows the removal of Cr(VI), Cu(II), and Cd(II) with time at initial concentrations of 5 and 10 mg l^{-1}, with one harvest in four days. At the end of four days, heavy metal ions have decreased from 5 to 2.57 mg l^{-1} and from 10 to 6.90 mg l^{-1} for Cr(VI), from 5 to 1.97 mg l^{-1} and from 10 to 5.94 mg l^{-1} for Cu(II), and from 5 to 2.89 mg l^{-1} and from 10 to 6.73 mg l^{-1} for Cd(II), respectively. After harvesting was performed at the end of four days, the concentrations of heavy metals in the solution have continued to reduce. At the end of eight days, Cr(VI), Cu(II), and Cd(II) have decreased from 5 and 10 mg l^{-1} to 1.08 and 3.46 mg l^{-1}, 0.86 and 2.15 mg l^{-1}, and 0.72 and 3.31 mg l^{-1}, respectively. With a change in initial concentration of heavy metal in the solutions from 5 to 10 mg l^{-1}, it is shown that the removal efficiency for Cr(VI), Cu(II), and Cd(II) decreased from 78.4% to 65.4%, from 82.8% to 78.5%, and from 85.6% to 66.9%, respectively.

Figure 3 illustrates the removal of heavy metals from aqueous solutions using duckweed through harvesting once every two days. When the detention time was two days, it is shown that Cr(VI), Cu(II), and Cd(II) ions having initial concentrations of 5 and 10 decreased to 2.77 and 6.79 mg l^{-1}, 2.34 and 6.70 mg l^{-1}, and 2.64 and 7.13 mg l^{-1},

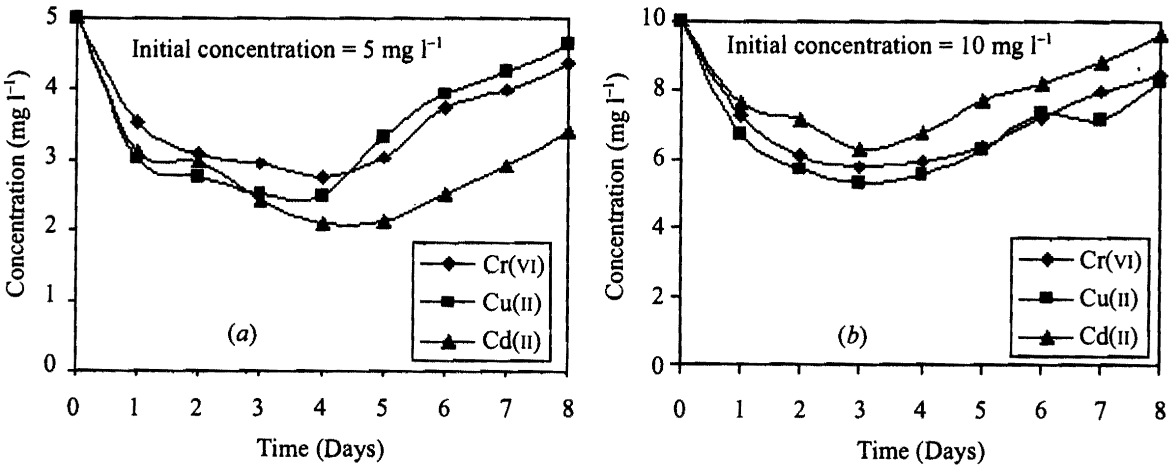

Figure 1. Uptake of heavy metals by duckweed without harvesting.

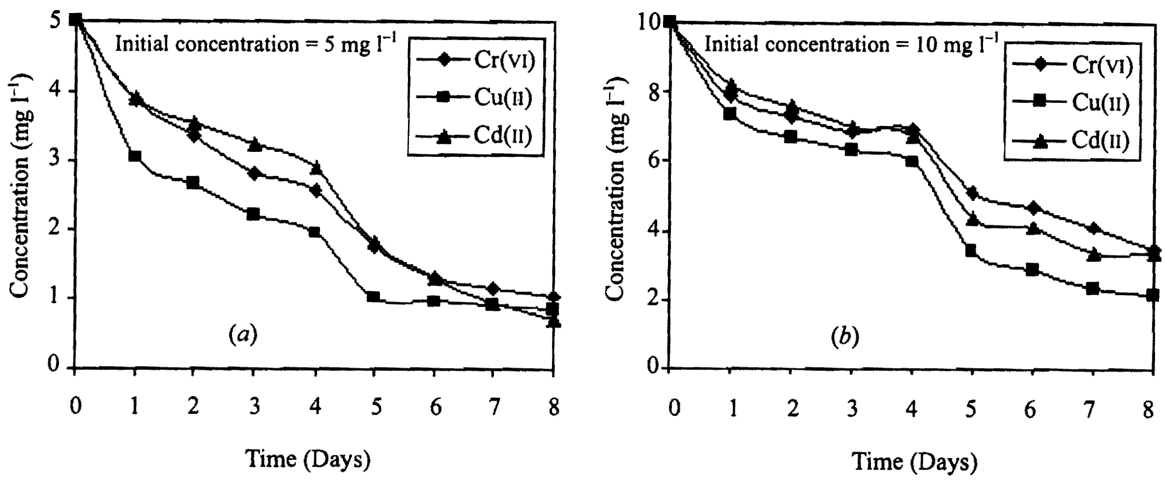

Figure 2. Uptake of heavy metals by duckweed with harvesting once every four days.

respectively. When the detention time of solution in the reactors was eight days, for an initial concentration of 5 mg l^{-1}, while Cr(VI) ions were measured to be 0.5 mg l^{-1}, the final concentration of Cu(II) and Cd(II) ions were at levels not detectable by atomic absorption spectrometry (AAS); the detection limits for heavy metals are 0.2, 0.2, and 0.5 ppm for Cr(VI), Cd(II), and Cu(II), respectively. For an initial concentration of 10 mg l^{-1}, Cr(VI), Cu(II), and Cd(II) ions at the end of eight days were measured at 0.90 mg l^{-1}, 0.94 mg l^{-1}, and 2.10 mg l^{-1}, respectively. The experiments were ceased because of the above results and, for the case in Figure 1, at the end of the eighth day.

3.2. Adsorption Isotherm Studies

Batch sorption tests were carried out on the obtained data with harvesting once every four days at the initial concentrations of 5, 10, 15, 20, and 25 mg l^{-1} and during a detention time of four days. Because duckweed sorbing metals were removed from the reactors at the end of each harvesting, reliable results for adsorption kinetics can be received through data obtained during harvesting made once every four days. It was assumed that the dry weight of duckweed is 5 % of its wet weight, since its typical water content is 94–95%.

The plot of $\log(A_m)$ against $\log(C_e)$ gives straight lines (Figure 4*a*), showing the applicability of the Freundlich isotherm. The values of k and $1/n$ for each metal ion have been determined from the slopes and intercepts of these lines, and are listed in Table 1. The Freundlich correlation coefficients, r, were found to be higher than 0.99, which indicates that there is strong positive relationship in the data. The Freundlich type adsorption isotherm is an indication of surface

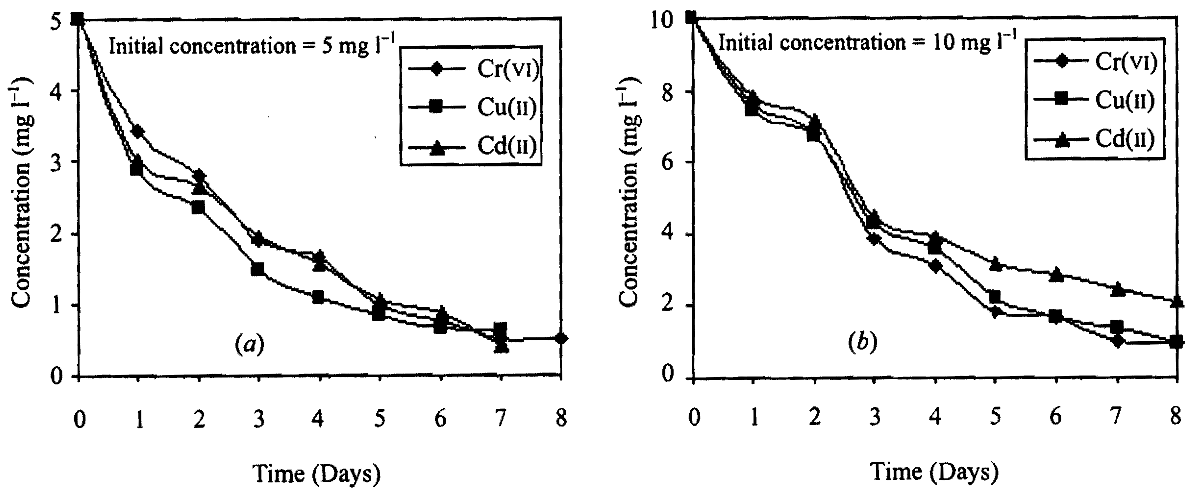

Figure 3. Uptake of heavy metals by duckweed with harvesting once every two days.

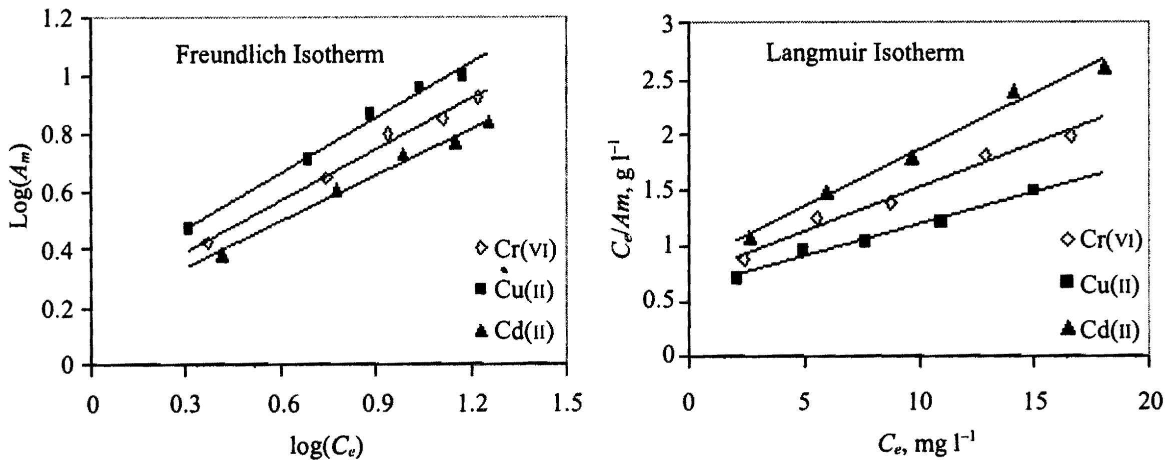

Figure 4. The adsorption isotherms for removal of metals ions by duckweed.

heterogeneity of the adsorbent, while the Langmuir type isotherm hints at surface homogeneity of the adsorbent [3]. This leads to the conclusion that the surface of duckweed is made up of small heterogeneous adsorption patches, which are very similar to each in respect of adsorption phenomenon. As can be seen the results of the Freundlich isotherm, the values of k are 1.632, 1.881, and 1.495, and the values of $1/n$ are 0.589, 0.642, and 0.537 for Cr(VI), Cu(II), and Cd(II), respectively. The Freundlich equation is suitable because the values of $0.1 < 1/n < 1.0$ show that adsorption of heavy metals on the anion exchanger is favorable [23]. The values of k, which is a measure of adsorption capacity, and $1/b$ have been determined by the plot of C_e/A_m *versus* C_e (Figure 4*b*) and listed in Table 1. The intercept which gives the value of k and b is calculated from the slope.

As may be seen in all the figures, the adsorption density rate decreased with contact time. While the adsorption density rate was high in the start of experimental studies and after harvesting, it is shown that this value decreased on other days. This demonstrates that duckweed is restricted in the removal of heavy metals, and that the solution of this problem relays in frequent harvesting.

Table 1. Isotherm Constants for The Freunlich and Langmuir Models.

Metal Ions	Freundlich Isotherm			Langmuir Isotherm		
	r	k(mg.g^{-1})	$1/n$	r	k(l.mg^{-1})	b(mg.g^{-1})
Cr(VI)	0.995	1.632	0.589	0.991	0.103	12.987
Cu(II)	0.995	1.881	0.642	0.988	0.093	17.422
Cd(II)	0.993	1.495	0.537	0.994	0.121	9.814

4. CONCLUSION

Metals removal was found to occur through duckweed uptake. High metal concentrations inhibit *Lemna minor* growth. It could be used as a potential adsorbent for removal of toxic metals from wastewater when it is frequently harvested. Since the use of duckweed is an inexpensive method for removing heavy metals, it may be potentially useful for treatment of wastewater containing low concentrations of metal. The Freundlich equation is better obeyed by the system than the Langmuir one, as is evident from the values of regression coefficients and slope. The contaminated duckweed is disposed of on hazardous waste land.

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