



Cr(VI) ADSORPTION BY *LEMNA MINOR* CONSIDERING OPERATIONAL, CHEMICAL AND BIOLOGICAL FACTORS

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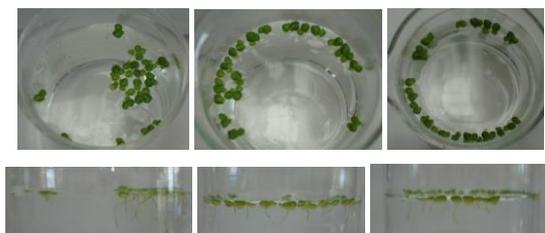
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The conditions for Cr(VI) adsorption by *Lemna minor* (LM) were analyzed. Regarding the macrophyte the parameters were: growth rate and calcination temperature. Adsorption capacity of LM was measured as a function of the Cr(VI) concentration, stirring contact time, stirring speed, temperature, and pH; as well as considering the quantity of LM units and the LM root length. The data were well adjusted to the kinetic pseudo second order model and to the Langmuir isotherm model. Acid pH enhanced the adsorption because of the negative charge Cr (VI) and the protonated surface of the adsorbent material. Experiments by using a rinse water from the chromium plating process showed that chromium was successfully removed by LM. The best conditions were found for the adsorption process of Cr(VI) by LM.



INTRODUCTION

Today, pollution is a major environmental problem that affects ecosystems and human health. Heavy metals are among the most worrying contaminants that significantly affect the environment.¹ Metals are naturally subject to biogeochemical cycles that determine their presence and concentration in environmental compartments, such as soil, groundwater and surface water, air and living beings. The intervention of man can considerably change the concentrations of metals in these compartments and modify their distribution.

Chromium is used as catalyst for the synthesis of ammonia, chrome and stainless steels

manufacturing, for alloys containing chromium and for galvanic chromium plating. Organic complexes are used as dyes in the coloured reliefs; inorganic compounds of chromium are used as pigments for paints. The salts of chromium (VI) are widely used for wood preservation and for leather tanning. Chromium is present in the environment almost exclusively forming chemical compounds, the most important chromium mineral is chromite. On the other hand, pure chromium is obtained through the reduction of chromium oxide (III) with aluminum by electrolysis or using chromic iodide.

The metallic chrome is non-toxic in water due to its low solubility. Divers hexavalent compounds

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represent a high threat due to their genetic effects. Chromium (VI) compounds are active in the majority of the model systems designed to determine their mutagenic effects. Chronic poisoning can cause mutations in the gastrointestinal tract and deposits in the liver, kidneys, thyroid and bone marrow.^{2,3}

The removal of Cr (VI) from water is mainly achieved by hydroxide precipitation. The reduction of chromium (VI) to chromium (III) is required prior to the hydroxide formation, then the hydroxide is precipitated and separated from the liquid solution in form of sewage sludge. In addition to the disadvantage of sludge generation, this process requires the addition of a reducing agent to proceed.

Alternatives for chromium removal are electrochemical processes,⁴ photocatalytic oxidation, electrocoagulation, bioremediation, bioadsorption⁵ and vitrification.⁶

Phytoremediation is an emerging technology that uses plants and rhizosphere microbiota to remove, transform the contaminants contained in

soils, sediments, aquifers, bodies of water and even in the atmosphere (Table 1).^{7,8}

Aquatic macrophytes develop in the transition zone between terrestrial environments and water or in areas flooded during certain times of the year.⁹ The macrophytes of the family *Lemnaceae* belong to the family of monocotyledons that are aquatic or floating herbs with very simple structures that lack stems or leaves, and its vegetative apparatus is reduced to lenticular fronds, sometimes with small threadlike roots on its underside. Reproduction is mostly by sprouts.¹⁰

Aquatic macrophytes have been used in recent decades for the monitoring of heavy metals or other aquatic pollutants and for heavy metals removal, competing with expensive treatments and technologies with low stability.¹¹ The interest of biological removal of chromium is increasing and may replace conventional methods.¹²⁻¹⁷

This work aims to optimize the adsorption of Cr(VI) by *Lemna minor* (*LM*) considering operational, chemical and biological factors to provide an sustainable alternative for metals removal in water.

Table 1

Plants as heavy metals accumulating systems

Plants (Scientific name)	Elements accumulated
<i>Azolla filiculoides</i>	Cu, Ni, Mn, Pb
<i>Bacopa monnieri</i>	Cd, Cr, Cu, Hg, Pb
<i>Lemna minor</i>	Cd, Cu, Pb, Zn
<i>Eichornia crassipes</i>	Cd, Cr, Cu, Hg, Pb, Zn
<i>Hydrilla verticillata</i>	Cd, Cr, Hg, Pb
<i>Pistia stratiotes</i>	Cd, Cr, Cu, Hg
<i>Salvina molesta</i>	Cr, Ni, Pb, Zn
<i>Spirodela polyrrhiza</i>	Cd, Cr, Ni, Pb, Zn
<i>Vallisneria americana</i>	Cd, Cr, Cu, Pb
<i>Brassica juncea</i>	Cd, Cr, Cu, Ni, Pb, U, Zn
<i>Helianthus annuus</i>	Cs, Pb, Sr, U
<i>Agrostis castellana</i>	Al, As, Mn, Pb, Zn
<i>Thlaspi caerulescens</i>	Cd, Co, Cr, Cu, Ni, Pb, Zn

MATERIALS AND METHODS

The aquatic macrophytes *LM* were collected from a pond in the Queretaro Municipality, Mexico (latitude of 20°46'34.16"N; longitude of 100°3'10.47"O), washed with and conserved in well water using containers of 1 m x 0.5 m x 0.31 m. The containers were connected in series and maintained at 20 °C – 25 °C with an isothermal bath (Thermo Scientific, U.S.A.).

The plant growth rate was determined by monitoring the increase in the number of *LM* along the time. Twenty *LM* were placed by triplicated in a 250 mL beaker with 200 mL of underground water (Fig. 1) and supplemented with Sulfamin 45 fertilizer (ammoniacal nitrogen 21 % and sulfur 24%), then the increase in the number of plants was observed in samples at different periods with a microscope (Leica EZ4 D, Leica Microsystems, U.S.A.).

The plant growth rate (μ) was determined by the equation (1):

$$\mu = \frac{\ln x_2 - \ln x_1}{t_2 - t_1} \quad \text{Eq. 1}$$

where x correspond to the number of aquatic plants determined at the time t .

Biosorption kinetics were obtained as a function of operational, chemical, and biological parameters at times of 1, 2, 3, 4, 5, 8 and 15 h. The chrome concentrations were run in 2.5, 5, and 7.5 mg L⁻¹, with 200 *LM* equivalent to 2.83 g dry weight (dw), the solutions were placed at 45 °C, pH 5 and a stir speed of 90 rpm. Temperature was evaluated at 25, 40, 45, 50 and 60 °C, with 200 *LM* (2.8 g dw), Cr(IV) solution of 5 mgL⁻¹, at pH 5 and a stirring speed of 90 rpm for 1 h to 15 h. The pH was tested at values of 2, 5, 6, and 10, with 200 *LM*

(2.8 g), Cr(IV) solution of 5 mgL⁻¹, at 45 °C and stirring speed of 90 rpm. The biological parameters were the number of *LM*: 50, 100, 150, 200 and 300, and the root sizes tested were 1, 2, 4 and 5 cm, with Cr(IV) solution of 5 mgL⁻¹, pH 5, at 45 °C and stirring speed of 90 rpm for 1 h to 15 h. The stirring speed was run at 50, 75, 90, and 150 rpm, with 200 *LM*, in Cr(IV) solution of 5 mgL⁻¹, at 45 °C and pH 5. Experiments was carried out in a 250 mL Erlenmeyer beaker with 100 mL of Cr(IV) solution, in Batch runs.

The Cr(VI) was analyzed using a method based on an oxide-reduction reaction, briefly the hexavalent chromium Cr(VI) reacts with 1, 5-diphenylcarbazide in an acid medium to form Cr³⁺ and 1,5-diphenylcarbazone, thus developing a violet colour intensity is measured spectrophotometrically at 540 nm. The colour intensity is directly proportional to the concentration of hexavalent chromium.

A potassium dichromate stock solution (1000 mg Cr(VI) L⁻¹) was used for adsorption experiments.

Adsorption capacities of *LM* (q_e) were calculated as a function the operational parameters with the equation (2).

$$q_e = \frac{m_i - m_f}{m_L} \quad \text{Eq. 2}$$

where m is the chromium (VI) mass in the initial solution and in the solution after biosorption process, and m_L is the mass of *LM*.

The adsorption percentage was calculated using the equation 3.

$$\% \text{Cr(VI)}_{\text{adsorbed}} = \frac{m_{\text{ads}}}{m_i} * 100 \quad \text{Eq. 3}$$

where m_{ads} is the adsorbed chromium (VI) mass.



Fig. 1 – *Lemna minor* placed in a beaker by triplicated.

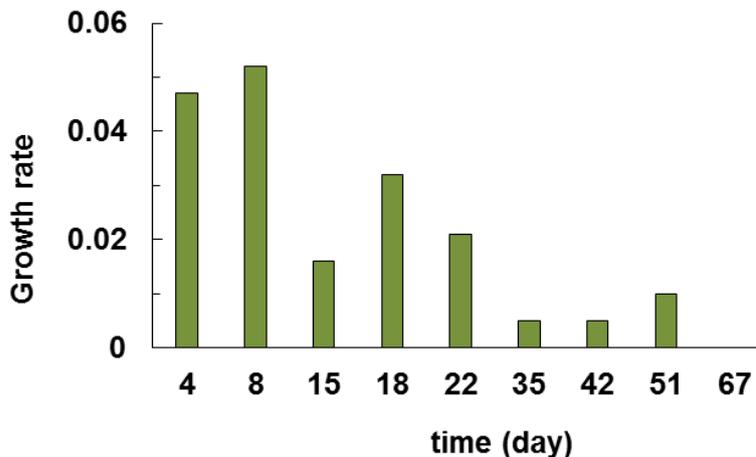


Fig. 2 – Growth rate of *LM* in well water supplemented with fertilizer.

Rinse water from a chromium plating process was used as model wastewater. The total chrome concentration in the wastewater was 4.38 mg/L from which 3.81 mg/L correspond to Cr(VI); The pH in the wastewater was 6.76. Experiments were carried out in a Erlenmeyer beaker of 250 mL with 100 mL of wastewater and 200 plants of *LM*, in an isothermic bath with orbital stirring fixed at 90 rpm (MAX Q 4000). The samples were filtered and the filtrate was analyzed for adsorbed Cr(VI) at the end of each test.

The wastes generated by the *LM* plants, after the bioadsorption process was estimated by the total solids method. The wet weight of 50, 100, 200 and 300 *LM* was registered, then the plants were dried to reach a constant weight by heating at 100 °C for 2 h, thereafter the plants were heated again at 100 °C, 200 °C, 300 °C and 400 °C in a furnace for one hour to obtain the ashes. The total, fixed, and volatile solids were determined by comparing the mass of the sample before and after each drying step.¹⁸

RESULTS AND DISCUSSION

Plant growth rate

Plant growth rate was determined in laboratory at various culture periods along 67 days (Fig. 2). The highest growth rate of *LM* occur in the first 8 days, with a rate of 0.0521 plants/day. This indicated that the aquatic macrophytes adapted and efficiently assimilated the nutrients from the fertilizer used, which caused them to reach an adult stage and reproductive age in 8 days of culture. The growth rate descended to 0.0161 plants/day at 15 days, this decay was explained by a death

period after a rapid growth. This growth-death cycle was confirmed for the measures at 18 and 22 days (0.0331 plant/day). However, the growth-death cycles stopped after 35 days, which might be a plant ecological response to the artificial conditions in laboratory; even that, the period of rapid plant production was established as 8 days of culture.

Effect of initial concentration of Cr(VI) and pH

The adsorption isotherm was obtained from data of the concentration of Cr(VI) in the liquid phase (C_e , mg L⁻¹) and the solid phase q_e (mg g⁻¹) using three points for different contact time with stirring. The data were modeled with the Langmuir model as indicated in equation 4.

$$\frac{C_e}{q_e} = \frac{1}{q_0} C_e + \frac{1}{q_0} K_L \quad \text{Eq. 4}$$

where K_L is the constant of the Langmuir isotherm and q_0 is the maximum adsorption capacity.

The Langmuir model assumes that sorption takes place at defined sites on the surface of the adsorbent, forming a monolayer, and that the energy of adsorption is the same in all adsorption sites, so the adsorbent material is considered homogeneous.¹⁹

The viability of the process and the characteristic of the Langmuir isotherm can be expressed through the non-dimensional term R_L (equation 5).

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq. 5}$$

where C_0 is the initial concentration of Cr(VI).

Fig. 3 shows Langmuir isotherms at different stirring times.

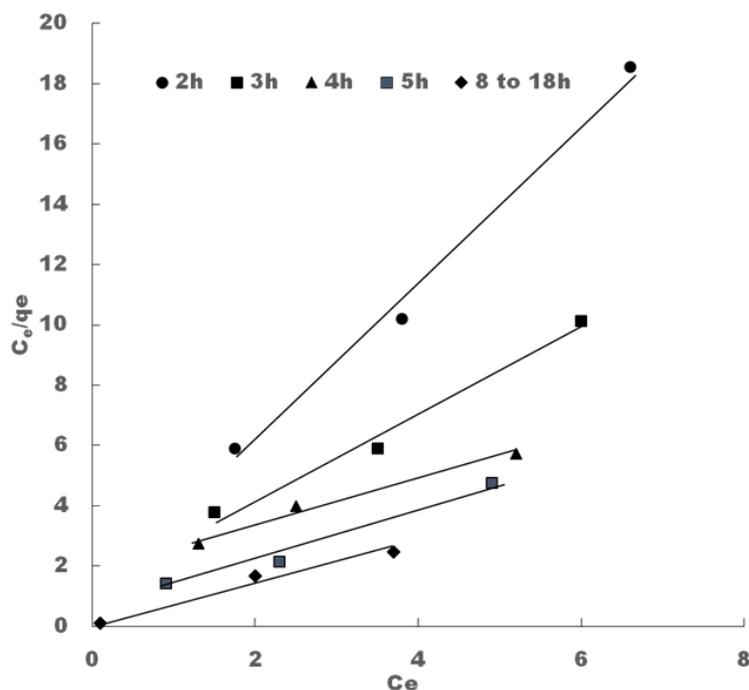


Fig. 3 – Adsorption isotherm of Cr(VI) by LM. Data adjusted to the Langmuir model for a stirring time of 5 h.

Table 2

Langmuir model, equations and parameters for Cr(VI) adsorption by LM

Time (h)	$C_e/q_e = m C_e + b$			Parameters	
	m	b	R ²	q ₀ (mg g ⁻¹)	K _L
2	2.6±0.2	0.9±1	0.99	0.38	1.95
3	1.4±0.2	1.4±0.7	0.98	0.71	1.0
4	0.7±0.1	1.9±0.3	0.99	1.31	0.44
5	0.9±0.1	0.5±0.3	0.98	1.17	1.84
8 and 15	0.7±0.1	0.14±0.2	0.97	1.52	4.53

The equations and parameters of the Langmuir model are given in Table 2. Good fits were found for stirring times longer than 2 h. The average value of maximum adsorption capacity, q_0 , for stirring times between 4 h and 15 h (1.3 ± 0.2 mg Cr(VI) g⁻¹ plant) was similar to q_{max} obtained for temperatures from 45 °C to 60 °C as explained later (Table 3).

The R_L values ranged from 0.9 to 0.03 for initial concentration C_0 from 2.5 mg L⁻¹ to 7.5 mg L⁻¹ which indicated favorable conditions for Cr(VI) adsorption by LM.

The effect of pH on adsorption is shown in Fig. 4. The highest adsorption percentage was

$91 \pm 4\%$ obtained in a medium with pH 2 and from 1 h of contact of LM with the Cr(VI) solution under stirring. Adsorption diminishes for higher values of pH, 5, 6 and 10. Species of Cr (VI) have a negative charge at pH 2, whereas the surface of the adsorbent has a positive charge due to the protonation of the active groups;²⁰ therefore, a strong attraction between the opposite charges of Cr (VI) atoms and LM as adsorbent occurred. As the pH increases, the H⁺ concentration decreases and the charge on the surface of the adsorbent becomes negative, which likely prevented the retention of the chromium species by LM.²¹

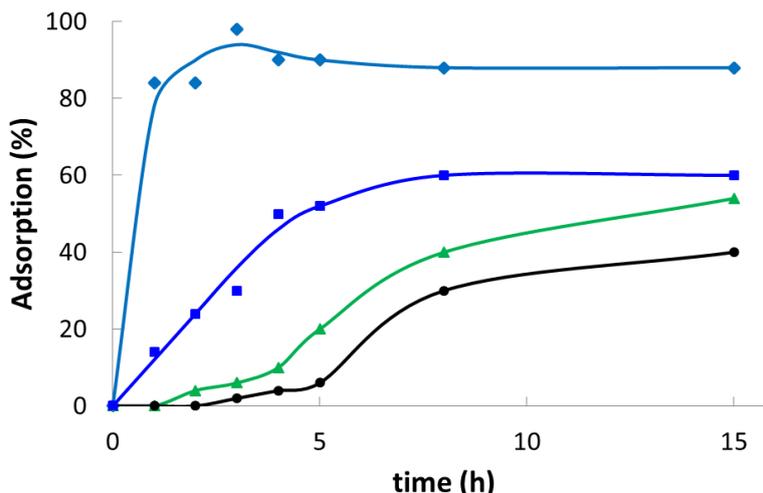


Fig. 4 – Adsorption of Cr(VI) by LM at different pH values and contact time with stirring (♦2, ■5, ▲6, and ●10 pH).

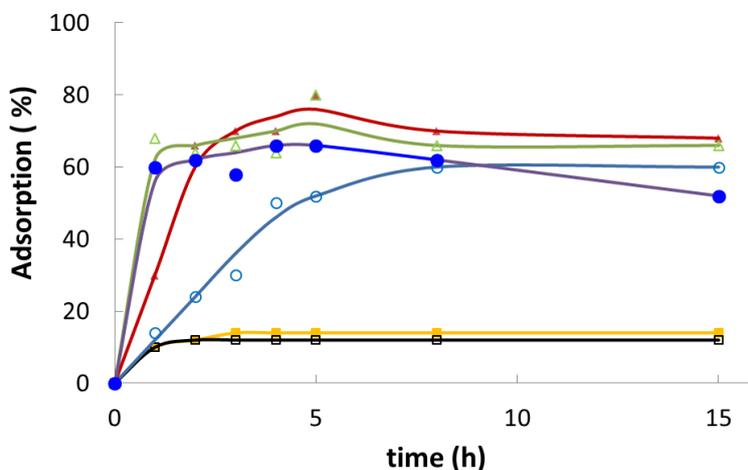


Fig. 5 – Adsorption of Cr(VI) by LM at different temperatures and contact time (■25, □40, ○45, ▲50, ▲55, and ●60 °C).

Effect of the temperature

The adsorption of Cr(VI) by LM at 25 °C and 40 °C was minimal, whereas adsorption increased by $66 \pm 9\%$ for the range of temperature from 45 °C to 60 °C (Fig. 5). The increase in adsorption with the temperature was explained by the heat stress caused to LM; the stress increased the assimilation of Cr ions via the LM metabolism. On the other hand, the slight decline in Cr(VI) adsorption for longer contact time with stirring and the highest temperature (60 °C) was due to the prolonged heat stress at which was submitted LM, then likely the physical integrity of LM was affected and chromium leaching occurred.²²

The experimental data of adsorption coefficients were treated with the pseudo-second order model, which is based on the adsorption

capacity of a solid phase and can be described using the equation (6). The pseudo-second order model assumes that the rate-limiting step can involve chemisorption or can be achieved via involving valence forces with sharing or exchange of electrons between sorbent and sorbate.²³

$$\frac{t}{q_t} = \frac{1}{K_2 q_{max}^2} + \frac{1}{q_{max}} t \quad \text{Eq. 6}$$

where q_t , q_{max} (mg g^{-1}) correspond to the amount of Cr(VI) adsorbed at t time and the equilibrium state respectively, and K_2 is the pseudo-second order rate constant ($\text{g mg}^{-1} \text{h}^{-1}$).

As it was expected, the q_{max} value increased with temperature and good fits for the adsorption model were found for all temperatures tested as shown in Figure 6 and the kinetic parameters listed in Table 3.

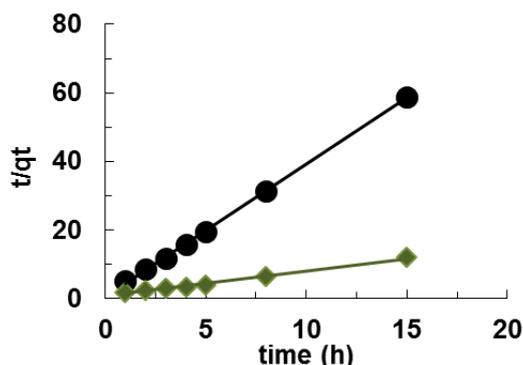


Fig. 6 – Fitting of kinetic data at different temperatures to the pseudo-second order model (● 25 °C to 40 °C; ♦ 45 °C to 60 °C).

Table 3

Parameters obtained from the experimental data and the pseudo-second order model for the adsorption of Cr(VI) by *LM* at different temperatures

Temperature (°C)	Equations	R ²	Parameters	
			q _{max} (mg g ⁻¹)	K _m (g mg ⁻¹ h ⁻¹)
25, 40	$t/q_t = 3.86 \pm 0.04 t + 0.5 \pm 0.2$	0.999	0.26	28.1
45, 50, 55, 60	$t/q_t = 0.73 \pm 0.04 t + 0.6 \pm 0.2$	0.99	1.4	0.9

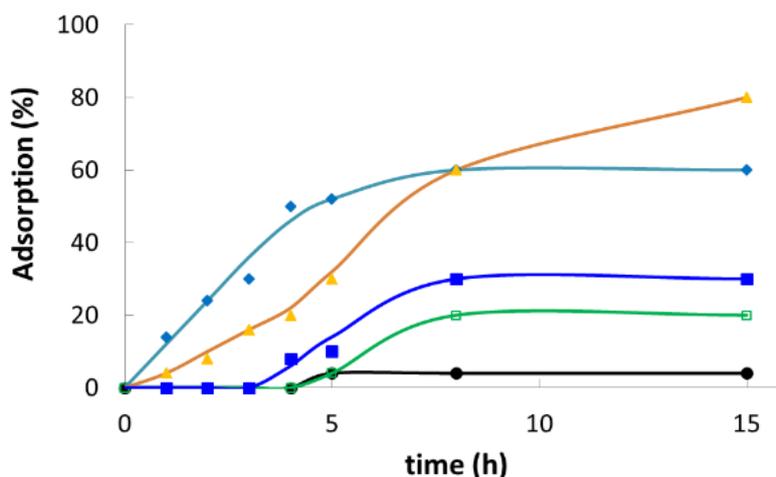


Fig. 7 – Adsorption percentages of Cr(VI) by different quantity of units of *LM* and stirring contact times (●50; □100; ■150; ◆200; ▲300).

Effect of the number of plants and root size

According to data in Fig. 7, retention of Cr(VI) was a function of the quantity of plants or units. The chromium adsorption was minimum for less than 100 units of the macrophyte, but the adsorption increased when more than 100 units were put in contact with the Cr(VI) solution. The adsorption percentage was lower with 300 units than with 200 units; this contradictory result was explained by the entanglement of the roots which disrupted the contact of the whole plants with the metal in solution.

The adsorption of Cr(VI) by *LM* depends on the size of the roots because this plant feature is related to the age of the macrophyte (Fig. 8). Root length from 1 cm to 2 cm corresponded to still growing young plants; at this age the plants presented slow and low Cr(VI) adsorption. Root length of 4 cm showed an optimal plant age with an efficient, rapid and high, Cr(VI) adsorption. Finally, plants with root length of 5 cm showed slow adsorption rate at the first period (5 h) of contact with the metal solution because the plants were older thus they could not adsorb rapidly the ions in solution.

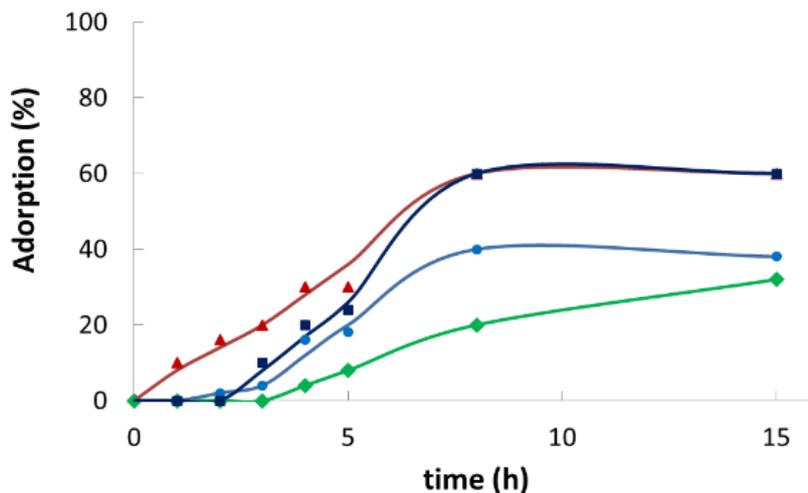


Fig. 8 – Adsorption of Cr(VI) by *LM* with various root length and contact time. (◆1; ●2; ▲4; ■5 cm root length).

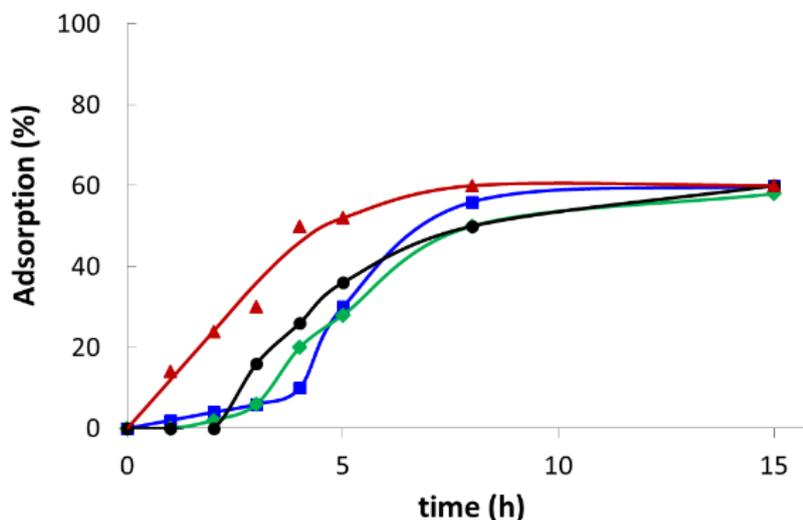


Fig. 9 – Adsorption of Cr(VI) by *LM* at different stirring speeds and contact times. (■50; ◆75; ▲90; ●150 rpm).

The relation between root size and metal adsorption capability depends on the plant species. *Medicago sativa* (alfalfa) plants present high tolerance to Cd (II), Cu (II) and Zn (II) when they have long roots in a mature stage,²⁴ while *Helianthus annuus* (sunflower) is more tolerant to Cr (III) at younger ages, *i. e.* having short roots.²⁵ In the present research, the adsorption process by *LM* verified the feasibility of metals adsorption by plants in a mature stage.

Effect of stirring speed

The adsorption percentage was higher for 90 rpm stirring speed and increased with the contact time for all the speeds tested (Fig. 9). The adsorption showed similar behavior ($57 \pm 5\%$) for 50 rpm, 75 rpm, and 150 rpm of stirring speed. This result indicated that diffusion limitations

were negligible at the conditions indicated in the experimental section and enabled to select the stirring speed for the experiments described above.

Rinsing water from the chromium plating process

The *LM* plants were immersed in rinse water from a chromium plating process. The Cr(VI) concentration diminished by absorption on *LM* plants during the contact time. Differences of chromium removal were observed as a function of the temperature (Fig. 10).

At 25°C, the concentration of Cr(VI) remained stable after 5 h of contact, and a similar trend was observed at 30 °C. An improvement in Cr(VI) removal was observed at 45°C; Cr(VI) concentration shifted near to zero within approximately 8 h of contact time.

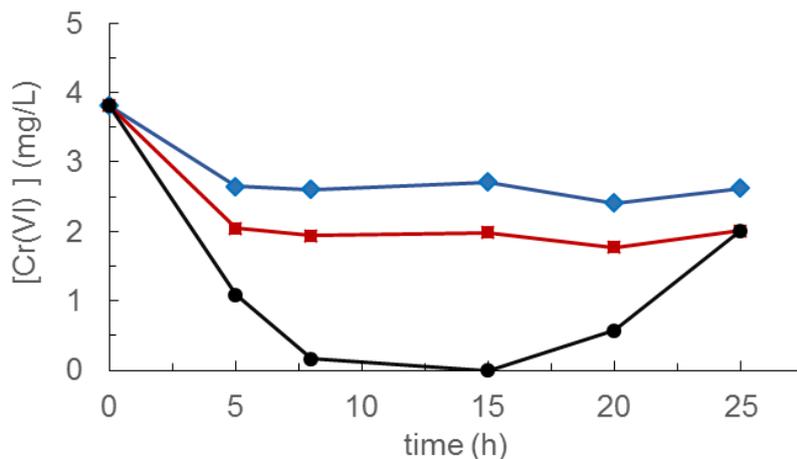


Fig. 10 – Removal of Cr (VI) in real wastewater at different temperatures and contact time. (◆25; ■35; ● 45 °C).

At the highest temperature, the adsorption processes seemed to be reversible. The Cr(VI) concentration in the solution started to increase from 15 h of contact time and continued until 25 h. This behavior was explained by heat stress for longer periods at which were submitted the LM units.

This result confirmed the decline in adsorption percentage at high temperature showed in Fig. 5. In resume, the physico-chemical process parameters that included chromium concentration, pH, temperature, and stirring speed, in addition to the biological conditions such as number of plant units and the root length enabled establish the appropriate conditions to perform Cr(VI) adsorption by LM.

The values of each operation parameter to optimize the adsorption process are: 2.5 mg L⁻¹ to

7.5 mg L⁻¹ for chromium concentration; 8 h for contact time, 90 rpm for stirring speed, a temperature of 45 °C, pH 2, and an amount of LM greater than 200 plant units with roots of 4 cm length.

Thermal treatment of LM wastes

Thermal treatment of LM plants was carried out and the LM dehydration occur at 100°C (Fig. 11), while the LM plants were calcined to ash like carbon at 200°C. After heat the LM plants at 200, 300 y 400 °C the amount of residue obtained was almost the same; therefore, the temperature required to reduce the LM mass to ashes was stated at 200 °C.

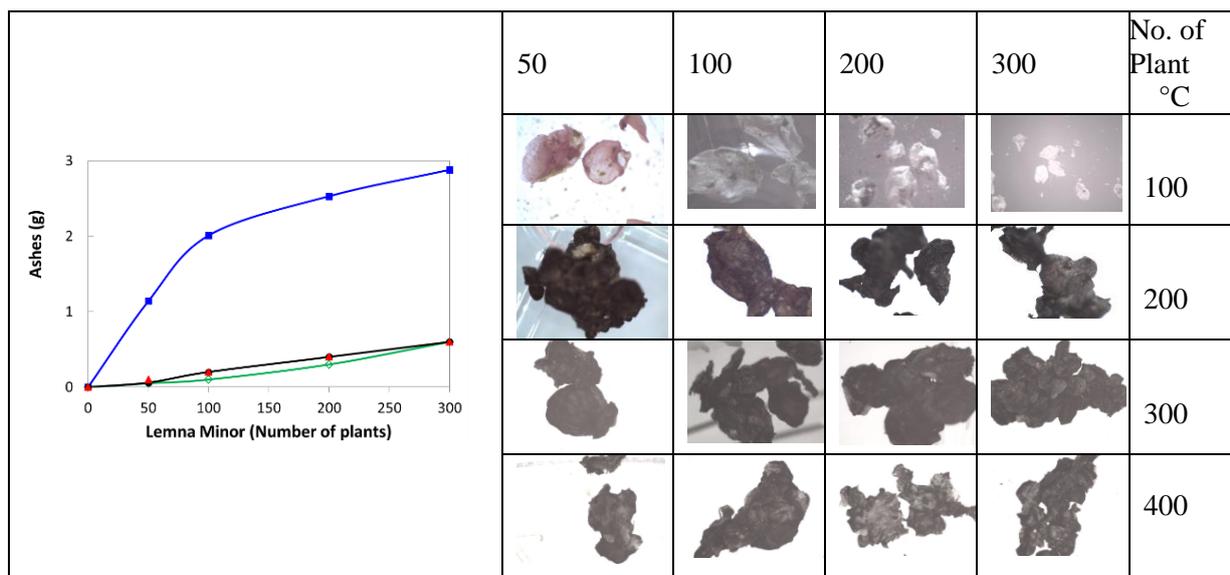


Fig. 11 – Mass of ashes (g) obtained from 50-300 plant units after 1 h of thermal treatment at different furnace temperatures (■100, ◆ 200, ▲ 300, ●400 °C).

CONCLUSIONS

The best stage of the *LM* to bioadsorb the Cr(VI) is when it is in mature age, that is, when its root measures approximately 4 cm, which reaches in a few days according to the life cycle studied. The results suggest that the adhesion of Cr(VI) to the *LM* is carried out by bioadsorption since when the *LM* dies from the combination of heating and Cr(VI) poisoning, Cr(VI) is returned into solution. The bioadsorption kinetics data conform to the pseudo-second order model and the process follows the Langmuir isotherm model. Slightly acidic conditions, high temperatures with low exposure times, the number of *LM* and long roots are conditions that promote bioadsorption, while the kinetics of the bioadsorption of Cr(VI) remains almost the same with the increase in agitation, indicating that the process is not dependent on diffusion to the conditions studied. It was obtained that the *LM* is reduced to ash at 200°C with one hour of exposure, which is one more factor to consider the *LM* as a bioadsorbent of Cr(VI).

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