

BIOSORPTION OF Pb (II) BY *Agave tequilana* Weber (AGAVE AZUL) BIOMASS

BIOSORCIÓN DE Pb (II) POR BIOMASA DE *Agave tequilana* Weber (AGAVE AZUL)

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Recibido 22 de Junio 2006; Aceptado 16 de Julio 2007

Abstract

In this study, the biomass produced from the industrial residues and agricultural waste of *Agave tequilana* Weber (Agave azul) generated in the production of tequila, demonstrated a high potential for Pb (II) removal from aqueous solution. The biosorption capacity of Agave azul leaves biomass was evaluated in batch experiments. These experiments included pH profile, time dependence, and the determination of adsorption capacity. Time profile experiments indicated that the adsorption of Pb ions by Agave azul biomass was time-dependent. Freundlich and Langmuir isotherms were used to describe the biosorption of Pb (II) onto the Agave azul leaves biomass at 298 K and pH 5.0. The correlation coefficient for the Freundlich isotherm was much higher than the coefficient for the Langmuir isotherm, indicating that only the Freundlich models fits the data. The maximum capacity (K_F) was $105.52 \cdot 10^{-2}$ mole/g for Pb (II). The adsorption capacity showed by Agave azul biomass was higher than the average values reported in the literature.

Keywords: biosorption, Pb(II), *Agave tequilana* Weber, Agave azul.

Resumen

En este estudio, la biomasa producida de los residuos industriales y el desecho agrícola del *Agave tequilana* Weber (Agave azul) generados en la producción de tequila, demostró un alto potencial para la remoción de Pb (II) de soluciones acuosas. La capacidad de biosorción de la biomasa de las hojas de Agave azul fue evaluada en experimentos en lote. Estos experimentos incluyeron perfil de pH, dependencia del tiempo y la determinación de la capacidad de adsorción. Los experimentos de dependencia del tiempo indicaron que la adsorción de los iones de Pb(II) por la biomasa de Agave azul fue dependiente del tiempo. Las isothermas de Freundlich y Langmuir fueron usadas para describir la biosorción del Pb (II) sobre la biomasa de las hojas del Agave azul a 298 K y un pH de 5.0. El coeficiente de correlación para la isoterma de Freundlich fue más alto que el respectivo coeficiente para la isoterma de Langmuir, indicando que solo el modelo de Freundlich describe los datos obtenidos. La máxima capacidad (K_F) fue $105.52 \cdot 10^{-2}$ moles/g para Pb (II). La capacidad de adsorción mostrada por la biomasa del Agave azul fue más alta que el valor promedio de los valores reportados en la literatura.

Palabras clave: biosorción, Pb (II), *Agave tequilana* Weber, Agave azul.

1. Introduction

Continuous discharges of heavy metals close to densely populated areas threat urban ecosystems and human health (Altindag and Yigit, 2005, Kar and Misra, 2004, Tylko *et al.*, 2005). Due to that, local and federal authorities derived resources to remove heavy metals and other pollutants from the environment. Scientists and engineers have recently found that several biomaterials can be used to

eliminate heavy metals from polluted soil and water (Davis *et al.*, 2003, Ahluwalia and Goyal, 2006, Goyal *et al.*, 2003). This technology has a significant connotation when the heavy metal contaminants exist at trace concentrations or where the current cleaning methods become inefficient and relatively expensive (Martínez *et al.*, 2000, Chuah *et al.*, 2005, Ahluwalia, and Goyal, 2005).

As observed with other materials, the biosorbent process reaches an equilibrium between

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the biosorbed metal and the bulk concentration of the metal (Martínez *et al.*, 2000, Altin *et al.*, 1998) This equilibrium depends on the type of available functional groups onto the biomaterial, the target metal and the characteristics of the matrix around the biosorbent species (Altin *et al.*, 1998, Chojnacka *et al.*, 2005, Krishna *et al.*, 2000). The biosorption can be controlled by physical attraction, chemical complexation with the biomass functional groups, ion-exchange, or hydrate formation at the surface (Davis *et al.*, 2003, Demirbas *et al.*, 2005).

The theoretical aspects of the sorption process have been extensively studied. Adsorption isotherms have been widely used to model the biosorption equilibrium, and to predict the binding at different metal concentrations and environmental conditions (Altin *et al.*, 1998, Volesky, 2001). The isotherms also produce many thermodynamic and kinetic parameters that could be used to better understand the mechanism involved in the biosorption (Lin and Juang, 2002, Volesky, 2003). The most common equations that are used to describe the experimental isotherm data are the Freundlich and the Langmuir isotherms, both are non-linear models that suggest metal monolayer coverage onto the surface of the biomass (Benhammou *et al.*, 2005, Romero-Gonzalez *et al.*, 2005a).

The present investigation includes the heavy metal Pb (II). Similar to other heavy metals, this metal is released to the environment mainly from industries, it is not biodegradable, and is accumulated in living organisms causing diseases, disorders, and other toxic effects (Fichet *et al.*, 1998, Volesky, 2001).

Previous studies have shown that similar biomasses have a high potential for the removal of cadmium and chromium (III) from aqueous solutions (Sawalha *et al.*, 2005). Experiments have also shown that these biomasses have the capacity to adsorb, Pb (II), from synthetic polluted waters (Contreras *et al.*, 2005). The current investigation proposes the use of the biomass produced from the industrial residues and agricultural waste of *Agave tequilana* Weber, commonly known as Agave azul, which is generated in the production of tequila for the removal of lead as an alternative in a cost-effective and environmentally friendly manner. The present manuscript reports on the Pb (II) biosorption capacity of the Agave azul leaves biomass.

2. Materials and methods.

2.1. Agave Azul collection

Agave azul (*Agave tequilana* Weber) leaves were collected from Centro de Propagación de Agave del Estado de Guanajuato (CEPAEG) of Instituto de Ciencias Agrícolas of Universidad de Guanajuato, with no previous report on metal contamination. The leaves were cut, washed with tap

water; oven dried at 70°C for 48 h, grounded using a Wiley-Mill, and sieved to pass through a 100-mesh (0.149 mm) screen to obtain a uniform particle size. The leaves were chosen because they represent the highest percentage of Agave azul plant.

2.2. Metal analyses

A flame atomic absorption spectrometer (FAAS) (Perkin-Elmer model 3110) was used to determine Pb (II) in samples. The analytical wavelength used was 283.3 nm with a slit width of 0.7 nm. The Pb hollow-cathode lamp current was 30 mA. An impact bead was used to improve instrument sensitivity. Standards were prepared by dilution of a 1000 mg/l stock solution and calibration curves were obtained using 6 points including the blank. The coefficients of the used models were computed with linear least-square fitting. The amount of metal bound was calculated from the difference between the amount of metal determined in the corresponding control solution and the amount of metal in the solution after treatment with the biomass.

2.3. pH profile studies for metal binding

This experiment was carried out using the pH profile method previously reported by Gardea-Torresdey *et al.* (1998). A 250-mg sample of Agave azul biomass, previously grounded, was washed four times with HCl 0.01M, using a centrifuge, to remove any debris or metals ions from the biomass. The sample was then washed three times with deionized water in order to remove soluble material or biomolecules that might interact with any sorbed metal ions. The washed biomass was resuspended in 50 ml of deionized water to obtain a concentration of 5 mg of Agave azul per ml of water. The suspension was adjusted to pH 2 using diluted solutions of HCl and NaOH. Six aliquots of 4 ml each of the biomass suspension were placed into six clean test tubes. The tubes were equilibrated for 60 min and then centrifuged at approximately 3000 rpm for 5 min (Fisher Scientific Marathon K 8). The biomass pellets were separated from the supernatants and saved for the next experiments. 0.1 mM solution of Pb (II) was prepared from the salt, $Pb(NO_3)_2$, and adjusted to pH 2. Three 4 ml aliquots of Pb (II) solution were transferred to the test tubes containing the Agave azul biomass pellets. Three more 4 ml aliquots were transferred to clean test tubes and set as control. The tubes were then equilibrated for 1 h and centrifuged. Similar procedure was followed for each of the following pH values: 3, 4, 5 and 6. The final pH of the supernatants was recorded and the lead content was determined using atomic absorption spectroscopy. Each experiment was performed in triplicate for quality control and statistical purposes.

2.4. Time dependence for Pb(II) sorption

The time dependence experiments were performed in a similar fashion to that previously reported by Gardea-Torresdey *et al.* (1998). A 250 mg sample of grounded biomass was washed in deionized water in order to remove any metal ions or soluble materials that might interfere with Pb (II) adsorption. The biomass was then re-suspended in 50 ml of deionized water to obtain a final biomass concentration of 5 mg/ml. The biomass suspension was then adjusted to the appropriate optimal pH, determined from the pH profile studies: pH 5 for Pb (II). Aliquots of 4 ml of 0.3 mM metal solution (Pb (II) at pH 5) were added to the 42 tubes containing biomass pellets and allowed to react for: 5, 10, 15, 30, 60, 90 and 120 min. At each time interval the test tubes were centrifuged and the supernatants were discarded. Three additional tubes containing just Pb (II) solution were maintained as control for each time period. The tubes, containing approximately 20 mg of biomass and 4 ml of 0.3 mM metal solution and the respective controls, were then equilibrated at the different time intervals and then centrifuged at 3,000 rpm for 5 min. The supernatants from all tubes were separated from the pellets and were transferred to clean test tubes for their posterior analysis of concentration Pb (II) using FAAS.

2.5. Adsorption capacity

The adsorption capacity of *Agave tequilana Weber* for Pb removal was determined with the isotherms experiments. These were performed as previously published (Romero-Gonzalez *et al.*, 2005b). A sample of 2.0 grams was taken from the ground Agave Azul leaves biomass, washed once with HCl 0.01M and twice with deionized water. After each washing, the biomass was centrifuged for 5 min at 3000 rpm (Fisher Scientific Marathon 6K). The biomass was suspended in deionized water to have a final concentration of 5 mg of biomass per ml with the pH previously adjusted to 5.0. Two ml of the biomass solution were placed in 5-ml test tubes, centrifuged, and the supernatants were discarded. Each tube was used at 0.0, 9.6, 19, 29, 38, 48, 58, 67 and 77×10^{-5} mol of Pb(II) · dm⁻³ (three replicates per Pb (II) concentration, adjusted to pH 5.0). Besides, a fourth tube containing only Pb (II) solution (no biomass) was set as a control. Aliquots of 2 ml of the Pb (II) solutions were transferred to the respective labeled biomass tubes. The tubes and controls were allowed to equilibrate for 60 min at room temperature (25 ± 2 °C), centrifuged, and the supernatants were saved for metal quantification.

3. Results and Discussion.

3.1. pH profile

The percentage binding of Pb (II) to Agave azul biomass is shown in Table 1. As one can see in this table, the binding of Pb (II) is pH dependent. First, the amount of Pb (II) bound to Agave azul biomass increased as pH increased from pH 1 to 5. At pH 5, the biomass showed a maximum binding of 93% of the Pb (II) present in the solution. On the other hand, the binding of Pb (II) to Agave azul biomass decreased as pH increased above 5. This trend in pH dependence suggests that the binding of the metals to the biomass is through an ion exchange mechanism. Solution pH influences both cell surface metal binding sites and metal chemistry in water. At low pH, cell wall ligands were closely associated with the hydronium ions H₃O⁺ and restricted the approach of metal cations as a result of the repulsive force. As the pH increased, more ligands such as carboxyl, phosphate and amino groups would be exposed and carried negative charges with subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface (Romero-Gonzalez *et al.*, 2005a).

Table 1. pH profile for Pb(II) binding by *Agave tequilana Weber* biomass.

pH	% metal bound
1	42
2	74
3	76
4	86
5	93
6	76
7	65

3.2. Adsorption kinetic parameters

The results of Pb (II) adsorption by Agave azul biomass, from the time dependence studies are shown in Table 2. These results indicate that the process of Pb (II) adsorption by Agave azul is time-dependent. The trend in Pb (II) adsorption suggests that the binding of this ion may be through interactions with functional groups such as carboxyl or hydroxyl groups located on the surface of Agave azul biomass.

In order to investigate the mechanism of Pb(II) biosorption, the experimental data of the time dependence studies were utilized in the first-order and pseudo second-order kinetic models. The first-order rate expression of Lagergren based on solid adsorption capacity is generally expressed as follows (Ho *et al.*, 1996):

$$dq / dt = K'_{ad} (q_e - q) \quad (1)$$

where q_e is the amounts of solute adsorbed at equilibrium per weight of adsorbent (mg/g), q the

amount of solute adsorbed at any time (mg/g), and K'_{ad} is the rate constant of first-order biosorption (min^{-1}). If equation (1) is integrated for the boundary conditions $t=0$ to $t > 0$ and $q=0$ to $q > 0$, the following linear time dependence function is obtained:

$$\log(q_e - q) = \log(q_e) - (K'_{ad}/2.302)t \quad (2)$$

Table 2. Time profile for Pb(II) biosorption by Agave azul biomass.

Time [min]	Metal in liquid	Metal onto biomass
5	23%	77%
10	21%	79%
15	19%	81%
30	10%	90%
45	10%	90%
60	10%	90%
90	10%	90%
120	9%	91%

The experimental data obtained from time dependence study was used in equation (2). The results of the appropriate calculations are shown in Fig. 1. The data shown in this figure were used to estimate the constants shown in Table 3.

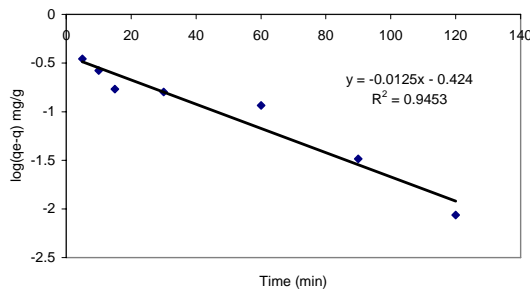


Fig. 1. Linear plot of first order for the adsorption of Pb(II) to Agave tequila Weber biomass.

Table 3. Comparative analysis of linear pseudo first order and pseudo second order rate equations, their constants and correlation coefficients (R^2 values), for the adsorption of Pb(II) to Agave tequilana Weber biomass.

Model type	Constant of pseudo reaction	q_e (mg/g)	R^2
Pseudo first order	$K'_{ad} = 0.035 \text{ min}^{-1}$	0.53	0.9453
Pseudo second order	$K''_{ad} = 0.572 \text{ (g mg}^{-1} \text{ min}^{-1})$	0.45	0.9895

The pseudo-second order model (Ho and McKay, 1999) is also based on the sorption capacity of the solid phase. The pseudo second-order chemisorption kinetic rate equation is expressed as the following:

$$dq/dt = K''_{ad}(q_e - q)^2 \quad (3)$$

where K''_{ad} is the rate constant of second-order biosorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), q and q_e represent the

variables explained before. Integrating Eq. (3) for the boundary conditions $t=0$ to $t > 0$ and $q=0$ to $q > 0$, the following linear time dependence function is obtained:

$$t/q = 1/2K''_{ad}q_e^2 + (1/q_e)t \quad (4)$$

The experimental data obtained from time dependence study was used in Eq. (4). The results of the appropriate calculations are shown in Fig. 2. The data shown in this figure were used to estimate the constants shown in Table 3.

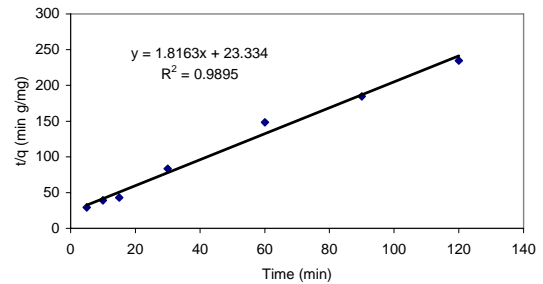


Fig. 2. Linear plot of pseudo second order for the adsorption of Pb(II) to Agave tequilana Weber biomass.

The comparative analysis of R^2 values shown in Table 3 indicates that a pseudo-second order ($R^2 > 0.9895$) reaction model explain better the kinetic data for Pb(II) sorption to Agave azul biomass. These results suggest that a rate-limiting step may be the chemical adsorption process of Pb(II) binding to Agave azul biomass. This process involves an exchange of electrons between the adsorbate and the surface of the adsorbing material. Similar results were reported by Ho and McKay (1999) for Pb(II) adsorption by cypress leaves and peat.

3.3 Sorption Isotherms

The Langmuir and Freundlich isotherms are the most widely used models for studying the sorption equilibrium between the metal solution and the solid biomass phase (Davis et al., 2003, Goyal et al., 2003, Martínez et al., 2000, Martínez et al., 1998, Krishna et al., 2000, Benhammou et al., 2005, Volesky, 2003). The Langmuir isotherm is a non-linear model that is based on a first order equilibrium kinetics. In this model the biosorbed metal covers a monolayer on the homogeneous solid surface, where all the superficial binding sites have uniform adsorption energies without any interaction between the adsorbed molecules (Goyal et al., 2003, Romero-Gonzalez et al., 2005a). This model is represented in Eq. (1).

$$q_e = \frac{Q_L b C_e}{(1 + b C_e)} \quad (5)$$

where q_e is the quantity of metal adsorbed at equilibrium over the mass of adsorbent biomass (mol g^{-1}); Q_L stands for the monolayer adsorption capacity, defined as the maximum amount of metal

Table 4. Freundlich and Langmuir isotherm parameters for the biosorption of Pb(II) onto *Agave tequilana Weber* biomass at 24±2 °C and pH 5.0

Metal	Freundlich			Langmuir			
	$K_F \cdot 10^{-2}$ mol·g ⁻¹	n	R^2	$Q_L \cdot 10^{-2}$ mol/g	$b \cdot 10^{-2}$ dm ³ ·mol ⁻¹	R_L	R^2
Pb(II)	105.52	0.87	0.9675	0.04	34.91	0.0221	0.1380

ion adsorbed forming a complete monolayer on the biomass surface per mass of adsorbent biomass (mol g⁻¹), and b is a constant related to the energy of adsorption (dm³ mol⁻¹). C_e is the concentration of the metal in the solution at equilibrium (mol dm⁻³). The Langmuir model is usually linearized as shown in Eq. (6). The biosorption data obtained for Pb(II), and were fitted into equation (2) by plotting C_e/q_e versus C_e ,

$$\frac{C_e}{q_e} = \frac{C_e}{Q_L} + \frac{1}{bQ_L} \quad (6)$$

The dimensionless adsorption intensity (R_L) is computed using the following equation (Lin and Juang, 2002).

$$R_L = \frac{1}{(1 + bC_o)} \quad (7)$$

where C_o is the initial metal concentration in the solution (mol dm⁻³); R_L indicates the type of isotherm; if it is irreversible $R_L = 0$, favorable $0 < R_L < 1$, linear $R_L = 1$, or unfavorable $R_L > 1$.

The adsorption behavior of the investigated metals onto the *Agave azul* was also fitted into the Freundlich isotherm. The Freundlich model is also a non-linear model that suggests a monolayer sorption of the metal on the biomass. Differing from the Langmuir, the Freundlich model assumes a heterogeneous energetic distribution of the active binding sites on the sorbate surface with interactions between the adsorbed molecules (Davis et al., 2003, Romero-Gonzalez et al., 2005a). In the Freundlich model, it is considered that the binding sites affinities on the biomass surface vary with the interactions between the adsorbed molecules. Consequently, the sites with stronger affinity are occupied first (Davis et al., 2003). The general equation and the linearized form for the Freundlich isotherm is expressed in eqs. (8) and (9) as follows,

$$q_e = K_F C_e^{1/n} \quad (8)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (9)$$

In eqs. (8) and (9), K_F is the maximum adsorption capacity (mol g⁻¹), and n is the adsorption intensity, which is related to the affinity or binding strength (Davis et al., 2003). K_F and $1/n$ are determined from the slope and intercept resulting from plotting $\ln q_e$ versus $\ln C_e$.

The parameters obtained from fitting the Langmuir and Freundlich models onto the data obtained from the binding of *Agave azul* biomass with Pb (II) are presented in Table 4. As shown in Table 4, the correlation coefficient (R^2) obtained

resulted from the Freundlich model was 0.9675 for Pb(II), while for the Langmuir model the R^2 value was 0.1380. This suggests that *Agave tequilana Weber* biomass sorbed Pb(II) following the Freundlich model ($R^2 > 0.95$). The result also suggests that the biosorption system of *Agave azul* biomass could have more than one functional group which is responsible for the metal binding such as it was suggested in the study of section 3.1, pH profile.

The K_F value obtained from the Freundlich model of $7.02 \cdot 10^{-2}$ mol g⁻¹ for Pb(II). It was hard to compare the maximum capacity with many reported studies due to differences in experimental conditions and models used to fit the data in each study. However, under similar conditions, the maximal capacities of African alfalfa biomass were reported to be $0.081 \cdot 10^{-2}$ mol g⁻¹ for Pb(II) (Gardea-Torresdey et al., 1998). In addition, it has been reported that the synthetic resin amberlite IR-120 has a maximal adsorption capacity of $1.96 \cdot 10^{-2}$ mol g⁻¹ for Pb(II) (Demirbas et al., 2005). The results from the present study clearly showed that the Pb (II) binding capacity of *Agave azul* leaves biomass is higher than the reported capacity for African alfalfa biomass and the amberlite IR-120 synthetic resin.

Conclusions

The results of this study demonstrated that the *Agave tequilana Weber* leaves biomass has the potential for the removal of Pb (II) from aqueous solution. Although, the maximum adsorption capacity was obtained at pH 5 (93%). The adsorption process was found to be time-dependent. Adsorption isotherms showed that the adsorption pattern for Pb (II) followed the Freundlich isotherm. The adsorption capacity showed by *Agave azul* biomass was higher than the average values reported in the literature.

Acknowledgment

The authors would like to acknowledge financial support from the University of Guanajuato at México and the Programa de Mejoramiento del Profesorado (PROMEP) (Agreement PROMEP/103.5/04/2921).

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