



**LEAD REMOVAL FROM AQUEOUS SOLUTION BY SPHERICAL AGGLOMERATION USING AN EXTRACT OF *Agave lechuguilla* Torr. AS BIOSURFACTANT**  
**REMOCIÓN DE PLOMO EN SOLUCIÓN ACUOSA POR LA TÉCNICA DE AGLOMERACIÓN ESFÉRICA USANDO EXTRACTO DE *Agave lechuguilla* Torr. COMO BIOSURFACTANTE**

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### Abstract

This study focused on determining the optimal conditions for lead removal in aqueous solution models, by the spherical agglomeration technique (SAT), modifying the dose of *Agave lechuguilla* Torr. (lechuguilla) extract, used as biosurfactant. The SAT operating conditions at room temperature were: Initial pH 9, and constant agitation  $\omega = 600$  rpm. Experiments were performed under a 5x3 factorial design with five lechuguilla extract doses (0.3 - 2.0 g extract/g of pollutant), three different lead concentrations (1, 5 and 10 mg/L) and, for the SAT last stage, two different dosage ratio of CaCl<sub>2</sub> (10:1 and 20:1 parts of Ca<sup>2+</sup> by part of pollutant). Residual lead, sodium and calcium were determined by atomic absorption spectroscopy. According to statistical analysis, significant effects were observed for calcium dosages, initial lead concentration, extract dose and their interaction. Highest lead removal efficiency was achieved when applying the lower CaCl<sub>2</sub> dose and lechuguilla extract below 1 g extract/g of pollutant, such removal reached 99.8%.

**Keywords:** *Agave lechuguilla*, biosurfactants, saponins, hydrophobization, spherical agglomeration, residual lead.

### Resumen

El estudio se enfoca a la determinación de las condiciones óptimas para la remoción de plomo en soluciones acuosas modelo, por la técnica de aglomeración esférica (TAE), al modificar la dosis de extracto de *Agave lechuguilla* Torr. (lechuguilla), usado en la técnica como biosurfactante. Las condiciones de operación de la TAE a temperatura ambiente fueron: pH inicial de 9 y agitación constante de 600 rpm. Los experimentos se realizaron siguiendo un diseño factorial 5x3, con 5 dosis de extracto de lechuguilla (0.3-2.0 g extracto/g contaminante), tres concentraciones iniciales de plomo (1, 5 y 10 mg/L) y, para la última etapa de la TAE, dosis de CaCl<sub>2</sub> en diferentes radios (10:1 y 20:1 partes de Ca<sup>2+</sup> por parte de contaminante). Plomo, sodio y calcio residuales se midieron por espectrofotometría de absorción atómica. De acuerdo con el análisis estadístico, los factores dosis de calcio, concentración inicial de plomo, dosis de extracto y sus interacciones, provocan efectos significativos sobre el proceso. La máxima eficiencia de remoción se logró al aplicar la menor dosis de CaCl<sub>2</sub> y dosis de extracto de lechuguilla por debajo de 1 g extracto/g contaminante, tal remoción alcanzó 99.8%.

**Palabras clave:** *Agave lechuguilla*, biosurfactantes, saponinas, hidrofobización, aglomeración esférica, plomo residual.

## 1 Introduction

Lead is a potentially dangerous and non-biodegradable metal, whose geochemical cycle has been affected by human activities (Jalbani and Soyak, 2015). Lead is an important material in battery, paint, and other

industries, it can be deposited in the air, soil and water, and reach human beings through the food chain, causing negative effects on the health of exposed humans (WHO, 2011; Mason *et al.*, 2014; Hailegnaw *et al.*, 2015; Abbas *et al.*, 2016).

Several lead removal methods have been developed, the method selection depends on some

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basic parameters such as the pH or the metal initial concentration (Azimi *et al.*, 2017). Among the numerous removal methods are the adsorption with carbon nanotubes, electrochemical methods, the use of porous material such as calcium hydroxyapatite, or blast furnace granular slag packed columns (Bazrafshan *et al.*, 2015; Mousa *et al.*, 2016; Saleh, 2016).

Spherical agglomeration technique (SAT), which has been used for the manufacture of high-value products, is attracting increasing attention in the bioprocessing area (Pitt *et al.*, 2018). The SAT has proven to be an efficient method for the removal of heavy metals; it consists of four stages (Figs. 1-5 in Online Resource 1): 1) heavy metal precipitation performed by a controlled NaOH dosage in an specific pH range; 2) hydrophobization step, to change the hydrophilic nature of the surface of the metal hydroxide using an industrial or natural surfactant; 3) wetting with n-heptane in order to unify the hydrophobic chains of the surfactant; and 4) the agglomeration step, where initiator ( $\text{Ca}^{2+}$ ) is used to change and redistribute the agglomerates charge, thus allowing the free ions to react in the surfactant solution (Figs. 4 and 5 in Online Resource 1). SAT is performed under controlled physical-chemical parameters such as temperature, pH magnitude and stirring speed (Gonzalez-Valdez *et al.*, 2013; Alcázar-Medina *et al.*, 2014).

Industrial surfactants, used in second stages of SAT, can have a serious impact on human health and the aquatic environment due to their high toxicity and almost no biodegradability (Li *et al.*, 2013). On the other hand, natural surfactants (biosurfactants) such as saponins, have advantages over their industrial counterparts in biodegradability, low toxicity, ecological acceptability and efficacy in extreme conditions (Liu *et al.*, 2017). Natural surfactants have been used in the past for lead removal processes. Manawi *et al.* (2018) studied the effect of Acacia Gum (AG) as chelating polymer on the removal of lead from contaminated water; AG is an approved food additive and used as surfactant, emulsifier and stabilizer.

Saponins are plant secondary metabolites found mainly as glycosides, which consist of sugars linked to a steroid or triterpenoid structure and represent a diverse group of compounds widely distributed in the plant kingdom, characterized by their physico-chemical properties (Netala *et al.*, 2015). Agaves have been widely studied for different uses (Lara-Hidalgo *et al.*, 2017; Solís-García *et al.*, 2017;

Acosta-Domínguez *et al.*, 2018). In the Agavaceae family, diverse saponins have been identified, where *Agave lechuguilla* Torr. (lechuguilla) represents a prospective biomass source (Nava-Cruz *et al.*, 2015). The lechuguilla is an endemic plant from the Chihuahua desert, grows in the 200,000 km<sup>2</sup> of the arid and semiarid lands of northern Mexico, where its leaf material is widely exploited by farmers to obtain fibers used in the manufacture of various products (Ortiz-Mendez *et al.*, 2017). Lechuguilla leaves have a saponin content of about 15-25 mg/g in dry weight, these saponins have been widely identified and reported (Juarez *et al.*, 2014; Sidana *et al.*, 2016). Juarez *et al.* (2014) made an indirect quantification of saponin in the extract of lechuguilla leaves; Alcázar-Medina *et al.* (2014) reported the presence of saponins in lechuguilla extract by HPLC-DAD analysis: UV spectra from extract coincided in wavelengths and retention times (34.4; 36.9; 38.6 min), with the ones from commercial saponin standard. On the other hand, Romero-González *et al.* (2005) reported in their work the presence of yuccagenin and ruizgenin; Sidana *et al.* (2016) reported in their review the main presence of hecogenin and manogenin.

Although there is a wide variety of techniques and processes for the removal of heavy metals in water, it is necessary to deepen in an economic and environmentally friendly process. Lechuguilla leaves represent a residue of lechuguilla exploitation in northern Mexico, whose inadequate disposal could become a problem if not addressed properly. This study focuses on the application of SAT in the removal of lead from modeled water samples while using lechuguilla extract with high saponin content as biosurfactant.

## 2 Methodology

### 2.1 Reagents and equipment

The lead removal experiments in aqueous solution were carried out using a lead nitrate standard of 1000 mg/L (CENAM, DMR- 63e, México), NaOH (J.T. Baker, B13C54), n-heptane (SIGMA CHEMICAL) and  $\text{CaCl}_2$  (J.T. Baker, X12591). Distilled water was used (HYCEL, Mexico) for the different lead concentration preparations in aqueous solution. A Perkin-Elmer atomic absorption spectrophotometer (AAS) (model 700 AAnalyst; Massachusetts, USA) was used for the determination of residual lead,

calcium and sodium. Particle size of the formed lead hydroxide was determined by a scanning electron microscope (SEM) (JEOL 5800LV, Japan). A rotary evaporator (Buchi, R-114, Germany) was used to concentrate the lechuguilla extracts.

## 2.2 A. lechuguilla extracts preparation

The lechuguilla leaf material was collected from several wild plants located at coordinates 25° 02' 23.8" N, 103° 46' 50.9" W, in the state of Durango, Mexico. The extracts were obtained by means of the maceration of 100 g of dry leaf with ethanol (70% v/v), as in the method described by González-Valdez *et al.* (2013). Extract aqueous solution (8.43 g/L) was prepared using distilled water.

## 2.3 Lead hydroxide formation and particle size determination

In order to determinate the size of lead hydroxide precipitates at pH 9, a controlled precipitation was first performed. Precipitates formation was achieved by adding NaOH (1M solution) to the lead aqueous solution (10 mg/L), at room temperature (22 °C) and keeping constant agitation ( $\omega = 600$  rpm) until reaching pH 9. The lead hydroxide precipitates samples were carefully deposited with glass pipettes in metal slides preheated to 90 °C to promote solvent evaporation. Particle size was determined by SEM under an electron beam of 20 kV and magnification ranging from 1500 to 12000X.

## 2.4 Application of SAT

All SAT experiments were performed in flat bottom baffled ball flasks containing 1 L lead aqueous solution (1, 5 and 10 mg/L), and providing constant agitation of 600 rpm with stainless steel propellers (3.5 cm x 2.5 cm of surface) at room temperature (22 °C), for the complete duration of the experiment (155 min). Duration and conditions for each SAT step have been previously studied and optimized (Gonzalez-Valdez *et al.*, 2013; Alcázar-Medina *et al.*, 2014). For the SAT first stage (precipitation, 15 min), the pH was adjusted to 9 with a 1M NaOH aqueous solution in order to obtain lead precipitates (Alcázar-Medina *et al.*, 2014). In the second stage (hydrophobization, 30min), the lechuguilla extract was added in different doses (0.1, 0.3, 0.5, 1 and 2 g of extract/g of lead in the sample). In the third stage (wetting, 20 min), the conditioning substance, n-heptane (C<sub>7</sub>H<sub>16</sub>), was added in a ratio of

6.3 mL/g of lead in the sample in order to coat the hydrophobic solids formed in the second stage of SAT, with a thin film of similar hydrophobic affinity (Proal *et al.*, 1997; Wu *et al.*, 2015). In the fourth and last step (agglomeration, 90 min), a 1 M aqueous solution of CaCl<sub>2</sub> was added at a ratio of 10:1 and 20:1 of calcium (parts of Ca<sup>2+</sup> by part of contaminant) respectively, with respect to the stoichiometric proportion of the contaminant (lead), in order to achieve the crystalline nuclei growth. At the end of the technique, the formed agglomerates were separated from the aqueous solution using Whatman #40 filter paper and lead, calcium and sodium residual concentration in the sample were determined by the method established by AAS as established by the water quality standard in Mexico NMX-AA-051-SCFI-2001 (Secretaría de Economía, 2001).

## 2.5 Experimental design and statistical analysis for lead removal in aqueous models

A 5x3 factorial random block design for lead removal was used in aqueous models with five dose levels of lechuguilla extract (0.1, 0.3, 0.5, 1 and 2 g of extract/g of lead) and three levels of initial lead concentration (1, 5 and 10 mg/L). The experimental design relates the effect of the factor dose of lechuguilla extract, the concentration of the metal in the sample and their interaction. Also, the calcium dosage levels were studied separately in each design. Every experiment was done by triplicate according to the methodology proposed by Alcázar-Medina *et al.* (2014). The analysis of variance (three way ANOVA) and multiple analyses of variance (MANOVA) were made using the general linear model (GLM) for the experimental design, with the verification of the variance assumptions of normality, independence and homogeneity. The Pearson determination coefficient ( $R^2$ ) was estimated to verify the goodness of fit of the model by Statistica, v7 for Windows (stat Soft Inc., 2004). Then, the means comparison was performed with Fisher's Least Significant Difference Test (LSD), to determine the effects of the initial lead concentration, the dose of extract, the calcium dose applied and the effect of the interactions between factors, using as dependent variables the percentage of lead removal, residual lead concentration and residual calcium concentration. Finally, a quadratic fit response surface was obtained from the experimental data.

### 3 Results and discussion

#### 3.1 Average particle size of precipitate

Fig. 1 shows a micrograph of the lead precipitates in hydroxide form obtained at a temperature of 22 °C, a pH 9 and constant angular velocity during the stirring of 600 rpm. The precipitates from this research go accordingly with other reports, which confirm that the maximum lead precipitates in the form of hydroxides are obtained for a  $\text{pH} \geq 9$  (Cechinel and de Souza, 2014). It also coincides with the work done by Huang *et al.* (2017), where in the range of 8-10, the concentration of  $\text{Pb}(\text{OH})^+$  reduces, mainly due to  $\text{Pb}(\text{OH})_2$  precipitation. The scale on the micrograph shows a colloidal size (1-10  $\mu\text{m}$ ) for the precipitate. This fulfills theoretical basis of SAT for high dispersion systems.

In order to agglomerate, flocculants can be added to destabilize particles and form larger ones with the assistance of stirring (Carolin *et al.*, 2017). Because of this, it is essential to maintain the system under constant agitation during the precipitation stage. Furthermore, in order to ensure the change of hydrophilic solute towards a hydrophobic nature, the continuity of the SAT stages is required, directed towards a suitable coating of the hydrophilic precipitate with specialized particles (biosurfactant) of a hydrophobic nature (Yang *et al.*, 2015).

#### 3.2 Lead removal by SAT

Chemical coagulation requires addition of chemical reagents to change the state of dissolved and suspended solids and cause its precipitation; such addition increases dissolved constituents in wastewater (Verma *et al.*, 2012). SAT works under a similar effect, achieving total charge neutralization (stopping electromagnetic repulsion) and hydrophobicity by the end of its application, thus avoiding redissolution of contaminants. In SAT, as in coagulation, pH and concentration of ions are greatly important.

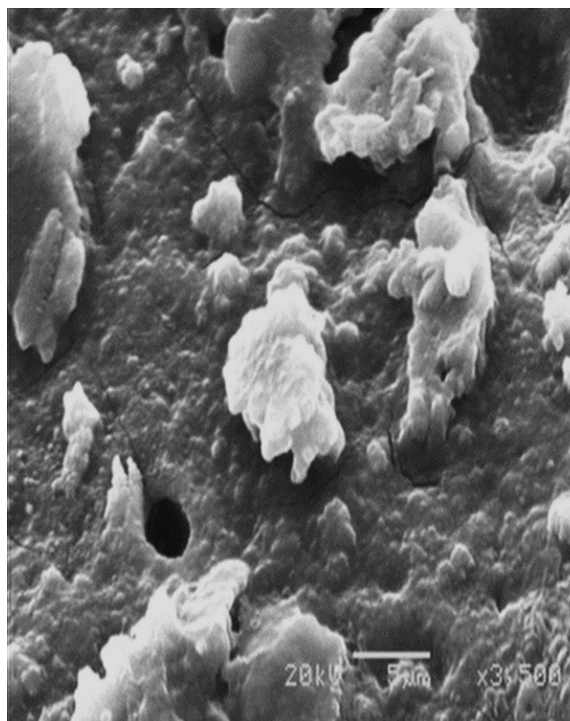


Fig. 1 SEM micrograph of  $\text{Pb}(\text{OH})_2$  precipitates obtained at 22 °C,  $\text{pH} = 9$  and constant stirring  $\omega = 600$  rpm, with a magnification of 3500X.

Results, obtained in previous studies using different processes and reagents, indicate that one of the most important parameters in lead removal is pH (Verma *et al.*, 2012; Mukhopadhyay *et al.*, 2016; Mukherjee *et al.*, 2018). In alkaline conditions, formation of  $\text{Pb}(\text{OH})_2$  contributes to good Pb removal but when pH is higher than 10, a decrease in removal is to be expected due to the increase on lead hydroxide solubility (Manawi *et al.*, 2018). For this reason, this work focused on pH under 10.

Al Omar *et al.* (2016) tested an adsorption process with carbon nanotubes functionalized by choline chloride based deep eutectic solvents and obtained a removal efficiency of 91.1% at pH 5; for Rahimi *et al.* (2015), the maximum efficiency removal happened at pH 5.2 using Iron oxide/hydroxide nanoparticles and Kamaraj *et al.* (2015) obtained a maximum removal efficiency of 99.3%, using an electrocoagulation process at pH 7.

According to consulted literature, point of zero charge for  $\text{Pb}(\text{OH})_2$  is reached at a pH of around 11 (Kosmulski, 2009; Kosmulski, 2011). At a pH solution under such magnitude, metallic hydroxide surface should be positively charged, attracting negative ions, which would form the compact layer of the colloid.

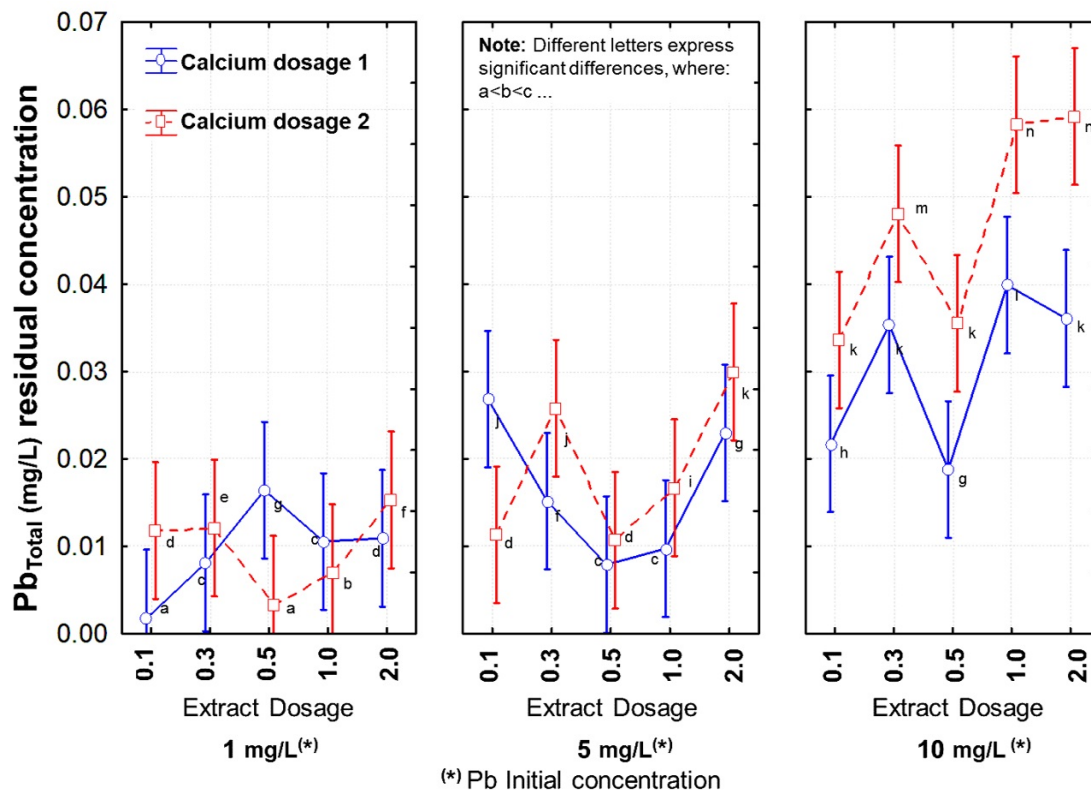


Fig. 2. Comparison of means (Fisher LSD) for the residual concentration of Pb<sub>Total</sub> in aqueous models by spherical agglomeration for the 5x3 factorial design, plus two calcium dosage levels (10:1 and 20:1 ratios). Superscript letters represent statistically different results.

In this study, at first stage of SAT (colloid formation and precipitation), such negative ions should be  $(\text{NO}_3)^-$  from the dissociation of the lead nitrate standard, and  $\text{OH}^-$  from NaOH and remaining from  $\text{Pb}(\text{OH})_2$  formation. Thus, diffuse layer is constituted mainly by  $\text{Na}^+$  and in the second stage of SAT, hydrophobization by Na-saponin complexes is formed (Fig. 2 in Online Resource 1) (Hong *et al.*, 2002).

As stated before, for the second stage of SAT, lechuguilla extracts (biosurfactants), were added. The heavy metal removal, according to Sarubbo *et al.* (2015), is possible because of the biosurfactants physicochemical properties based on its capacity to form complexes with metals.

Manawi *et al.* (2018) reported a direct relationship between Pb removal and dose of Acacia gum (AG) used as chelating agent. In their study, 0.6% removal increased was found when the AG dose was changed from 2,000 to 40,000 mg/L in starting Pb concentration of 250  $\mu\text{g/L}$ . In the present research, not such relationship was found for the smallest Pb initial

concentration tested (Table 1). Also, as can be seen in Table 1, in none of the initial lead concentrations tested, better results were obtained from highest extract dose.

In previous studies using the spherical agglomeration technique, removal levels of above 95% indicate that the SAT is effective for heavy metal removal (González-Valdez *et al.*, 2013; Alcázar-Medina *et al.*, 2014). Table 1 presents the data obtained under the experimental design 5x3 for each calcium dosage in the SAT experiments. Results demonstrate that the lead in aqueous media is removed by SAT, through the hydrophobization of lead hydroxide colloidal systems using lechuguilla extracts in aqueous solution as biosurfactants. Results (Table 1) show that biosurfactant effectiveness is similar than chemically synthesized surfactants like sodium dodecyl benzenesulfonate reported by Corpuz *et al.* (2018) for lead removal in aqueous solutions via flotation and most importantly comply with the standards in the Mexican normativity (SSA, 2000;

Table 1. Pb<sub>Total</sub> removal by SAT at pH = 9, under a factorial design 5x3 plus two levels of calcium dosage (10:1 and 20:1), using extracts of *A. lechuguilla*.

Initial Pb concn. (mg/L)	Extract dose (g/g Pb)	Ca dose ratio	Residual Pb concn. (mg/L)	Residual Ca concn. (mg/L)	Residual Na concn. (mg/L)	Final pH	% Pb removal
10	2	10:1	0.036 <sup>k</sup> ± 0.007	51.150 <sup>h</sup> ± 3.61	144.5	7.43	99.639 <sup>d</sup> ± 0.07
10	1	10:1	0.040 <sup>l</sup> ± 0.005	52.050 <sup>h</sup> ± 0.21	101.5	7.31	99.601 <sup>d</sup> ± 0.05
10	0.5	10:1	0.019 <sup>g</sup> ± 0.012	49.65 <sup>g</sup> ± 1.63	103.5	7.40	99.812 <sup>d</sup> ± 0.12
10	0.3	10:1	0.035 <sup>k</sup> ± 0.001	51.80 <sup>h</sup> ± 1.27	105	7.29	99.647 <sup>d</sup> ± 0.01
10	0.1	10:1	0.022 <sup>h</sup> ± 0.007	51.15 <sup>h</sup> ± 2.19	58.1	7.48	99.783 <sup>d</sup> ± 0.07
5	2	10:1	0.023 <sup>i</sup> ± 0.008	32.55 <sup>f</sup> ± 0.07	55.8	7.10	99.541 <sup>d</sup> ± 0.16
5	1	10:1	0.010 <sup>c</sup> ± 0.000	35.85 <sup>f</sup> ± 1.91	57.65	7.06	99.805 <sup>d</sup> ± 0.01
5	0.5	10:1	0.008 <sup>c</sup> ± 0.001	34.50 <sup>f</sup> ± 3.68	34.5	7.16	99.842 <sup>d</sup> ± 0.03
5	0.3	10:1	0.015 <sup>f</sup> ± 0.001	21.60 <sup>e</sup> ± 0.14	35.25	6.63	99.697 <sup>d</sup> ± 0.01
5	0.1	10:1	0.027 <sup>j</sup> ± 0.002	20.10 <sup>e</sup> ± 2.83	24	7.03	99.463 <sup>d</sup> ± 0.05
1	2	10:1	0.011 <sup>d</sup> ± 0.002	10.90 <sup>c</sup> ± 2.55	20.1	6.99	98.909 <sup>b</sup> ± 0.15
1	1	10:1	0.011 <sup>c</sup> ± 0.003	8.51 <sup>c</sup> ± 0.74	15.6	6.54	98.945 <sup>c</sup> ± 0.31
1	0.5	10:1	0.016 <sup>g</sup> ± 0.003	5.24 <sup>b</sup> ± 1.03	18.8	7.27	98.359 <sup>d</sup> ± 0.26
1	0.3	10:1	0.008 <sup>c</sup> ± 0.002	7.38 <sup>c</sup> ± 0.84	20.95	7.14	99.190 <sup>d</sup> ± 0.25
1	0.1	10:1	0.002 <sup>a</sup> ± 0.001	4.23 <sup>a</sup> ± 0.29	25.45	7.77	99.823 <sup>d</sup> ± 0.00
10	2	20:1	0.059 <sup>n</sup> ± 0.001	88.46 <sup>l</sup> ± 3.79	95.45	6.91	99.408 <sup>d</sup> ± 0.01
10	1	20:1	0.058 <sup>n</sup> ± 0.003	78.33 <sup>k</sup> ± 1.31	121.00	7.53	99.418 <sup>d</sup> ± 0.03
10	0.5	20:1	0.036 <sup>k</sup> ± 0.002	66.40 <sup>j</sup> ± 0.00	96.90	6.54	99.645 <sup>d</sup> ± 0.02
10	0.3	20:1	0.048 ± 0.003	64.44 <sup>j</sup> ± 0.51	102.00	6.54	99.520 <sup>d</sup> ± 0.03
10	0.1	20:1	0.034 <sup>k</sup> ± 0.004	59.27 <sup>i</sup> ± 1.84	115.50	6.62	99.664 <sup>d</sup> ± 0.04
5	2	20:1	0.030 <sup>k</sup> ± 0.001	52.56 <sup>h</sup> ± 0.53	46.45	6.85	99.401 <sup>d</sup> ± 0.03
5	1	20:1	0.017 <sup>g</sup> ± 0.001	51.28 <sup>h</sup> ± 2.04	45.50	6.64	99.666 <sup>d</sup> ± 0.02
5	0.5	20:1	0.011 <sup>d</sup> ± 0.008	52.52 <sup>h</sup> ± 3.11	47.25	5.94	99.786 <sup>d</sup> ± 0.15
5	0.3	20:1	0.026 <sup>j</sup> ± 0.008	54.75 <sup>h</sup> ± 2.87	45.50	6.25	99.484 <sup>d</sup> ± 0.15
5	0.1	20:1	0.011 <sup>d</sup> ± 0.008	53.29 <sup>h</sup> ± 0.65	46.20	5.76	99.774 <sup>d</sup> ± 0.15
1	2	20:1	0.015 <sup>f</sup> ± 0.011	15.81 <sup>d</sup> ± 2.15	16.70	5.81	98.471 <sup>d</sup> ± 1.08
1	1	20:1	0.007 <sup>b</sup> ± 0.007	10.63 <sup>c</sup> ± 0.04	17.00	6.28	99.302 <sup>d</sup> ± 0.69
1	0.5	20:1	0.003 <sup>a</sup> ± 0.003	9.67 <sup>c</sup> ± 0.54	18.85	6.25	99.662 <sup>d</sup> ± 0.33
1	0.3	20:1	0.012 <sup>e</sup> ± 0.006	9.67 <sup>c</sup> ± 0.54	17.50	6.18	98.791 <sup>d</sup> ± 0.62
1	0.1	20:1	0.012 <sup>d</sup> ± 0.009	10.70 <sup>c</sup> ± 1.90	19.90	6.34	98.821 <sup>a</sup> ± 0.86
Drinking water			0.01 mg/L <sup>1-2</sup>	500 mg/L <sup>1</sup>	200 mg/L <sup>1-2</sup>	6.5-8.5 <sup>1</sup>	
Waste-water			0.2 mg/L <sup>2</sup>	-	-	5.0-10 <sup>2</sup>	

<sup>1</sup>World Health Organization guidelines for drinking water quality  
<sup>2</sup>Drinking Water quality standard in the Mexican normativity: NOM-127-SSA1-1994  
<sup>3</sup>Wastewater quality Standard in the Mexican normativity: NOM-001-ECOL-1996  
a, b, c, d ..... i superscript: Represent differences from the Fisher LSD Test

SEMARNAT, 1997).

The results of Table 1 allow us to confirm that the change in affinity of the lead precipitates, from a hydrophilic to a hydrophobic nature, is due to the

action of lechuguilla extracts, for all doses of extract used (0.1, 0.3, 0.5, 1.0 and 2.0 g of extract/g of metal) which shows that the effect of *Agave lechuguilla* Torr. is similar than that of *Yucca decipiens* (Bailon-

Salas *et al.*, 2018) for lead removal. Furthermore, the use of SAT in the removal of lead in aqueous solution satisfies the permissible limits for this metal. In all cases of initial experimental concentration of Pb present in the models (1, 5 and 10 mg/L), the residual concentration of this element is well below the permissible limit (Total Residual Pb < 0.2 mg/L), according to the normativity mentioned for wastewater discharges into national water bodies (SEMARNAT, 1997). For lower initial lead concentration treatments, was even possible to reach residual concentration as low as the ones established by drinking water regulations (SSA, 2000; WHO, 2011), where the lowest residual lead concentration were reached under an extract dose below 1 g/g Pb, this fact might be caused due to the extract saturation of the system when doses higher of 1 g/g Pb are used.

Lechuguilla extract is capable of adequately covering the lead precipitates particles, thus inducing fully hydrophobic affinity to the system. Then the proper wetting effect from the wetting agent (n-heptane), added under constant and controlled agitation ( $\omega=600$  rpm), generates adequate conditions of kinetic shocks between the particles and the consequent growth of the formed nuclei (SAT stage 3). This observation is in agreement with the mechanism of spherical agglomeration proposed in literature where, in the wetting step, droplets of the bridging liquids capture, in this case, the hydrophobized particle and form the agglomerate nuclei (Orlewski *et al.*, 2018).

Complete charge neutralization is of great importance in this kind of processes as allows particle destabilization and agglomeration (Carolin *et al.*, 2017). Thus, the addition of CaCl<sub>2</sub> in agglomeration step of SAT is required. Once dissociated, Ca<sup>2+</sup> would bridge with hydroxyl groups present in the surfactant tail, bringing two saponin particles together (Fig. 4 in Online Resource 1), similar to mechanism suggested by Verma *et al.* (2012) for bridging of dye molecules. It can be observed (Table 1) that the residual concentrations of both lead and calcium were lower, on average, when using Calcium Dose 1 with respect to Dose 2.

Additionally, Table 1 shows the final pH values, where all values are in accordance with what is established by the aforementioned Mexican regulations, indicating the adequate hydrophobization of the lead precipitates for the different doses of calcium applied to the system, in ratios of 10:1 and 20:1 (Dose 1 and Dose 2 of calcium) respectively.

Average residual lead concentration is lower when the agglomeration step is done under the addition of the CaCl<sub>2</sub> aqueous solution in the ratio 10:1 (Dose 1), compared with a ratio 20:1 (Dose 2), respectively, for most of the experimented biosurfactant dose (g of extract/g of metal) (Fig. 2). This suggests that at lower doses of Ca<sup>2+</sup>, a more rapid and uniform charge distribution is generated in the hydrophobic system, generating stable agglomerates. Therefore, adding the agglomeration agent (1M CaCl<sub>2</sub>) in the last step, stabilized charge agglomerates that reach 1 mm in diameter and contain the contaminant are formed, which agree with other reports (Peña and Nagy, 2015).

A visual analysis of the sample at the end of every experiment showed that the later stages of the technique (wetting and agglomeration) were carried out correctly, since no residues of the reaction were observed, neither at the bottom and walls of the flask, nor in the propellers used for the agitation. All this indicates a suitable hydrophobic liquid-solid interaction that, in the case of lead removal, can be observed under a wide dose range of aqueous solution of lechuguilla extract (0.1, 0.3, 0.5, 1.0 and 2.0 g of extract/g of metal). These results agree with Alcázar-Medina *et al.* (2014), who achieved high Cu(II) removal (99% removal), by using extracts of *A. lechuguilla* by SAT application.

From the addition of the 1M solution of CaCl<sub>2</sub>, used to generate a correct balance of charges in the hydrophobic system, the residual concentration of calcium ([Ca<sup>2+</sup>] < 100 mg/L) meets the permissible limits established for the normativity (NOM-001-ECOL-1996), for all the experiments carried out. This indicates that both applied doses of the agglomeration agent are adequate (CaCl<sub>2</sub>), with a lower residual calcium concentration when applying Dose 1 (10:1 calcium ratio), noting also lower residual calcium results when using lower doses of lechuguilla extract (0.1-0.5 g of extract/g of metal) in the hydrophobization step.

In the case of the residual sodium concentration (Table 1), it always complies clearly with the Mexican normativity permissible limits for all experiments (NOM-127-SSA1-1994). It can also be observed, for 5 and 10 mg/L lead initial concentrations, that at lower extract dose, the residual sodium is lower at the end of the SAT and for extract dose of 1 mg/L of lead initial concentration, the smallest residual sodium concentration (15.6 mg/L) is reached.

These results are important when considering costs from the use of chemical reagents in the SAT taking

Table 2. Results on the two ANOVAs for both residual concentration of  $Pb_{Total}$  and  $Ca^{2+}$  taken as dependent variables, in aqueous models for the 5x3 factorial design. The ANOVA tests the effect of factors and its interactions on the dependent variable.

Effect	Degrees of Freedom (DF)	PbTotal Analysis		Ca <sup>+2</sup> Analysis	
		F	p	F	p
<b>Intercept</b>	1	993.2899	<0.001	23111.89	<0.001
<b>PbTotal Initial concn.</b>	2	152.163	<0.001	3832.59	<0.001
<b>Calcium dosage</b>	1	21.1616	<0.001	1082.02	<0.001
<b>Extract dosage</b>	4	12.0169	<0.001	41.56	0
<b>Initial concn. PbTotal * Calcium dosage</b>	2	13.315	<0.001	156.32	0
<b>PbTotal Initial * Extract Dosage</b>	8	5.0761	<0.001	8.67	<0.001
<b>Calcium Dosage* Extract Dosage</b>	4	1.7988	<0.001	6.91	<0.001
<b>PbTotal Initial Concn. * Calcium Dosage* Extract Dosage</b>	8	2.6525	<0.001	26.27	<0.001

the lower residual sodium concentration as a reference. Best parameters to remove the lead in aqueous solution ( $Pb < 10$  mg/L) are: biosurfactant (1 g/g Pb) and 1M of the agglomeration agent  $CaCl_2$  (Dose 1). These results match the presented in previous works for  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  removal in aqueous solutions by SAT and flotation techniques, using sodium oleate as surfactant in the hydrophobization step (Proal *et al.*, 1997; Deliyanni *et al.*, 2017).

### 3.3 Statistical analysis

The residual analysis of the linear factorial 5x3 random block model fulfilled the assumptions of normality, independence and homogeneity of variance. The determination coefficient for both experimental series ( $R^2$ ) was higher than 0.90. This value is an indication that the experimental design is trustworthy ( $p < 0.05$ ). Also, it shows that the spherical agglomeration technique is effective given that high percentages of lead removal were achieved (>97%) and final concentrations of lead, calcium and sodium comply with the water quality normativity established for wastewater in Mexico (SEMARNAT, 1997).

Taking the residual lead as dependent variable, a three way ANOVA (Table 2) was performed. The ANOVA tests the effect of factors and its interactions on the dependent variable. Same analysis was performed taking the residual calcium as dependent variable. Analyses showed as statistically significant the effects of Initial lead concentration, calcium and

extract dosage, and all the interactions between factors for both residual lead and residual calcium (Table 2).

A MANOVA was performed to determine the effect of the factors and their interactions when taking two dependent variables (residual lead and calcium). MANOVA showed the existence of significant differences in all the factors tested, as well as their interaction over the residual lead (Table 3). This suggests that the parameters by themselves, as well as the interaction among them, are determinant factors in the Pb removal efficiency by the SAT in aqueous media, by using an extract of *A. lechuguilla* as biosurfactant.

The Fisher LSD (Fig. 2), for the calcium Dose 1 case (10:1 parts of calcium with respect to the stoichiometric proportion of the contaminant), showed significant differences between the lead initial concentrations of 1 and 5 mg/L. Nevertheless, no differences were found between the lead initial concentrations of 5 and 10 mg/L. The best metal removal percentage (99.8%) was reached with the lead initial concentration of 1 mg/L. Regarding the lechuguilla extract dose, significant differences were observed when using a dose of 0.1 g of extract/g of metal, with respect of the others extract concentrations used (2, 1, 0.5 and 0.3 g of extract/g of metal), obtaining for this biosurfactant dose the best average results.

For a calcium ratio 20:1 (Dose 2), the LSD (Table 1, fig. 2) showed significant differences between the lead initial concentrations in aqueous solution of 5 and



Table 3. MANOVA for the residuals of  $Pb_{Total}$  in aqueous models, after application of the spherical agglomeration technique for the 5x3 factorial design. A MANOVA tests the effects of factors when more than one dependent variable is tested.

Effect	Value	Degrees of Freedom (DF)	F	p
<b>Intercept</b>	0.001292	2	11204.17	<0.001
<b>Initial Conc. PbTotal</b>	0.001615	4	346.34	<0.001
<b>Calcium Dosage</b>	0.026973	2	523.07	<0.001
<b>Extract dosage</b>	0.083182	8	17.89	<0.001
<b>Initial Conc. Pb<sub>Total</sub> * Calcium Dosage</b>	0.050592	4	49.97	<0.001
<b>Initial Conc. Pb<sub>Total</sub> * Dosage Extract</b>	0.13078	16	6.4	<0.001
<b>Calcium Dosage* Extract Dosage</b>	0.45858	8	3.46	0.002
<b>Initial Conc. Pb<sub>Total</sub> * Dosage Extract * Extract Dosage</b>	0.071482	16	9.93	<0.001

10 mg/L. However, between the lead initial concentrations of 1 and 5 mg/L in aqueous solution no significant differences were found. The highest removing average was obtained in the level of 10 mg/L of lead initial concentration in aqueous solution. With respect to the lechuguilla extract dose, no significant differences were found between the levels 0.1, 0.3 and 1 g of extract/g of metal. However, it was observed significant differences with the 2 g of extract/g of metal dose, in relation to the other concentrations.

Finally, for this case (calcium Dose 2) and for all the other lead initial concentrations in aqueous solution (1, 5 and 10 mg/L), the best lead removal result was obtained with an extract dose of 0.5 g of extract/g of metal. Although the lead removal percentage ranges from 97.89 to 99.84, in the quadratic fit response surface plots (Figs. 3 and 4), differences were observed between treatments with Dose 1 and Dose 2 of calcium for each one of the lechuguilla extract dosage levels and each level of lead initial concentration. This suggests a clear interaction among the extract dose applied (0.1, 0.3, 0.5, 1.0 and 2.0 g of extract/g of metal) and the lead initial concentration (1, 5 and 10 mg/L).

Quadratic fit response surface graph for the residual Pb, for a 10:1 Ca relation (Dose 1 of calcium), is represented by equation:

$$Pb_{Res} = 0.0086 - 0.0007 * Pb_0 - 0.00002 * ED + 0.0001 * Pb_0^2 + 0.00503 * Pb_0 * ED + 2.01 \times 10^{-5} * ED^2 \quad (1)$$

where  $Pb_0$  represents the initial concentration of Pb and ED, the extract dose used. In the corresponding graph (Fig. 3), it is possible to appreciate, taking as

reference the axis that represents the extract dose, that the residual lead concentration decreases as the dose of extract becomes greater than 0.1 g of extract/g of metal. The lead residual concentration reaches a minimum point when a dose of 1 g of extract/g of metal is used, for a lead initial concentration of 1 mg/L. From this point on, when the dose extract increases, the lead residual concentration increases proportionally. This results match previous reports, where guar gum was used for Pb removal from wastewater: in samples with initial Pb concentration of 15 mg/L, gradual increase of gum dose resulted in Pb removal increase till the best results of 83% removal, further gum dose increase resulted in lower Pb removal (Mukherjee et al., 2018).

Likewise, quadratic fit response surface graph corresponding to a ratio of 20:1 (Dose 2 of calcium, fig. 4) is represented by the next equation:

$$Pb_{Res} = 0.0097 - 0.0009 * Pb_0 - 0.00003 * ED + 0.0004 * Pb_0^2 + 0.0001 * Pb_0 * ED + 2.01 \times 10^{-5} * ED^2 \quad (2)$$

In this case, a similar behavior to that obtained with a calcium ratio of 10:1 (Dose 1) is observed; however, it has a higher lead residual concentration. In the lead removal experiments, performed with this calcium dose (20:1), the lowest point of residual lead concentration is at a dosage of 0.6 g extract/g of metal, for a lead initial concentration of 1 mg/L, showing that with a higher calcium dosage to the system, the  $Ca^{2+}$  ions present a greater interaction with the biosurfactant, thus completing the balance of charges within the hydrophobic system and consequently promoting faster growth of the agglomerates.

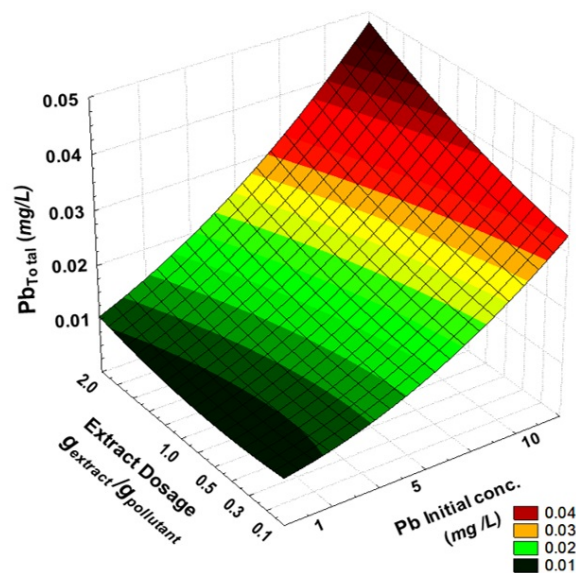


Fig. 3 Response surface for the residual concentration of Pb<sub>Total</sub> (mg / L), for a Calcium dose 10:1 ratio in aqueous models.

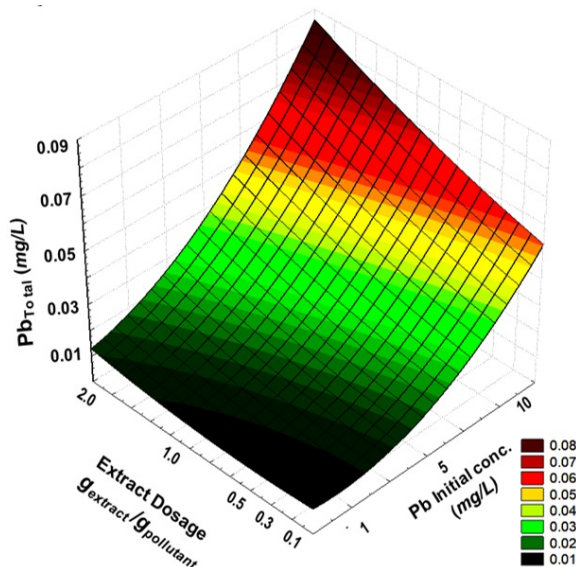


Fig. 4 Response surface for the residual concentration of Pb<sub>Total</sub> (mg / L), for a Calcium dose 20:1 ratio in aqueous models.

In fact, a higher presence of Ca<sup>2+</sup> ions in the aqueous solution, the greater the demand for biosurfactant in order to be able to incorporate this metal into the final product of the agglomeration (Figs. 6 and 7 in Online Resource 1).

In regard to lead initial concentration (1, 5 and 10 mg/L), it is observed in both graphs (Fig. 3 and

4) an increase tendency in the amount of residual lead as the initial concentration of the same increases. These results are similar to those reported by Manawi *et al.* (2018), who found lead removal dependent on initial lead concentration. They found a decrease of about 60% on Pb removal when initial concentration increased from 250 μg/L to 35 mg/L; they stated that lead concentration decreased as initial lead concentration increased, blaming the effect on the saturation of chelating sites in AG.

In this research, similar effect is observed, as authors suggest that the excess Pb species present in solution required higher surfactant dose and ions to agglomerate. However, this does not affect the success of the application of the SAT, since high lead removal percentages were reached and the residual concentration of lead and calcium, in all experimental cases carried out, correctly comply with the permissible limits established for wastewater quality.

## Conclusions

The particle size of the lead precipitate is colloidal (1-10 μm), complying with the bases of the spherical agglomeration theory for high dispersion systems.

The lechuguilla extract is capable of adequately covering the particles of the lead precipitates, thus conferring a fully hydrophobic affinity to the system.

Dose of the wetting agent (n-heptane) in the hydrophobic particles was adequate under constant and controlled agitation of 600 rpm, generating adequate kinetic shocks between the particles and the consequent growth of the agglomerates formed.

The agglomeration agent (1M of CaCl<sub>2</sub>), added in the last step, facilitates the formation of agglomerates with the contaminant in aqueous solution (lead), reaching a diameter of 0.5-1mm. Likewise lead removal was better under the 10:1 ratio than the 20:1 ratio Calcium dose.

The ANOVA indicated that parameters metal initial concentration, extract and calcium doses and the interactions between them, have a significant effect ( $p < 0.05$ ) on residual levels of lead and calcium.

The MANOVA, applied to both series of experimental tests and determined for the Pb and Ca residual concentrations together, showed the existence of significant effect from the initial concentration of the metals, the lechuguilla extract dose, the interaction extract dose - Ca dose, in the interaction extract

dose - initial Pb concentration, as well as the general interaction: initial Pb concentration - extract dose - Ca dose.

Lead removal was demonstrated in aqueous models by SAT, applying extracts of lechuguilla in aqueous solution (8.43 g/L), highest lead removal efficiency was achieved when applying the lower CaCl<sub>2</sub> dose and lechuguilla extract below 1 g extract/g of pollutant. Lead removal reached 99.8% and residual lead complies with the standards in the Mexican regulations, established for discharges of waste water into national waters.

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### Nomenclature

AAS	Atomic absorption spectrophotometer
AG	Acacia Gum
ANOVA	Analysis of variance
ED	Extract dose
GLM	General linear model
HPLC-DAD	High-Performance Liquid Chromatography with Diode-Array Detection
LSD	Least Significant Difference Test
MANOVA	Multiple analyses of variance
Pb <sub>0</sub>	Initial concentration of Pb
Pb <sub>Res</sub>	Residual Pb
Pb <sub>total</sub>	Total Pb
R <sup>2</sup>	Pearson determination coefficient
SAT	Spherical Agglomeration Technique
SEM	Scanning electron microscope
TAE	Técnica de Aglomeración Esférica
UV	Ultraviolet radiation
v/v	volume/volume

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