

REMOVAL OF α - AND β -ENDOSULFAN FROM SOILS BY USING NATURAL AND SYNTHETIC SURFACTANTS

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Aims: The aim of this work was studying a process of surfactant-assisted soil washing for the remediation of a soil spiked with α - and β -endosulfan (6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide).

Place and Duration of Study: The work was carried out at UPIBI-IPN during 2016.

Methodology: An agricultural soil was collected and spiked with a commercial pesticide. Ten surfactants (nonionic, ionic, cationic, zwitterionic and natural) were selected for washing the soil using concentrations ranging between 0.001 to 0.2 % w/w for each surfactant. Residual endosulfan concentrations were evaluated before and after washing soil process. Moreover, the extraction efficiency was related to surface tension and critical micellar concentration (CMC) of every surfactant.

Results: Better extraction efficiency was observed for α -endosulfan, its average extraction efficiency was around 73% and 55% for β -endosulfan. These values were significantly higher (up to 40%) than those observed in control experiments (water without surfactant). The maximum extraction of α -endosulfan was 90% and it was obtained using canarcel 20 at 10 times CMC. On the other hand, the maximum extraction of β -endosulfan was around 80% when surfactant polafix LO was used at a concentration of 700 times CMC, indicating that the surfactant-assisted soil washing process was suitable for extraction of pesticides from polluted soil. However, the wastewater produced should be treated in a subsequent process.

Conclusion: Natural surfactants did not show CMC in the range of concentration tested. Guar gum did not show a reduction of surface tension, even when concentration increases up to 1200 mg/L. In the case of mesquite seed gum, the surface tension slightly decreases from 73 to around 65 dyn/cm. Tween 80, canarcel 20 and emulgin W-400 showed a CMC of 65, 60 and 10 mg/L. CMC of dehyquart A, surfacpol A and texapon KD was of 160, 250 and 900 mg/L, respectively. Considering all surfactants, the extraction obtained of α -endosulfan is in the range of 65 to 94% with a mean of 79%, while extraction of β -endosulfan was in the range of 41 to 80%, with a mean of 61%. Accordingly to the nature of surfactants, best extraction efficiencies were obtained as follows nonionic > nonionic natural > ionic. Best extraction efficiency of α -endosulfan was 94% obtained with canarcel 20 (C^* of 11.6) while for β -endosulfan the best extraction efficiency was 80% obtained using canarcel 20 (C^* of 11.6) and guar gum (383 mg/L). This information is highly valuable for designing a soil washing process for treatment of pesticide-polluted soil using natural compounds as surfactants.

Keywords: endosulfan, soils, surfactants, soil washing, critical micellar concentration

1. INTRODUCTION

Pesticides have been used from early last century for controlling pests. The major source of pesticides in the environment is a consequence of agricultural activities. Particularly, higher levels of pesticides in soils can be the result of spills and accidents involving pesticide handling that take place on farms, pesticide formulating and manufacturing plants [1]. Furthermore, the presence of high concentration of could be also associated with the indiscriminate use of pesticides, overtaking the natural capacity of soil microorganisms to eliminate them.

Among the organochlorine pesticides, endosulfan was one of the most widely used until its inclusion in the Annex A of the Stockholm Convention in 2011. This indicates that parties must take measures to eliminate its production and use with specific exemptions [2]. Commercial endosulfan contains two stereoisomers, α and β , known also as endosulfan I and II in a 7:3 ratio (Figure 1). Endosulfan and its transformation product, endosulfan sulfate are between the main pesticides detected in air and soil in Mexico [3-5].

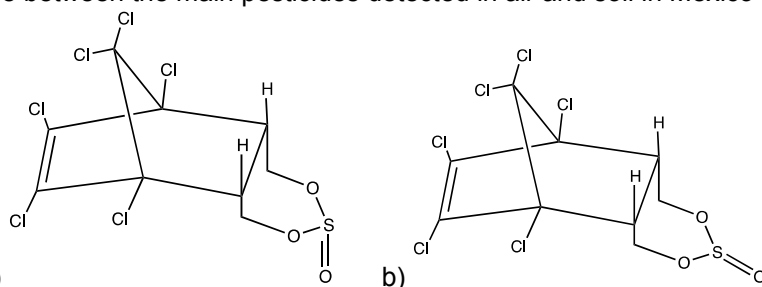


Figure 1. The molecular structure of a) α -endosulfan and b) β -endosulfan.

Surfactants can be added to pesticide-contaminated soils to enhance the treatment efficiency of soil washing. The ability of surfactants to enhance the water solubility of hydrophobic organic compounds (HOCs) provides a potential mean of improving the treatment efficiency of *ex-situ* soil washing systems for remediating pesticide-contaminated soils [6-7]. This treatment has been used for cleaning-up polyaromatic compounds, diesel and crude oil contaminated soils [8-10]. The removal of DDT (an organochlorine pesticide) also has been studied, in a washing process with a spiked soil, in a bioremediation system with biosurfactant-producing microorganism and in a remediation process using foam flushing [10-13]; while Wang and Keller [6, 11] reported the treatment of atrazine and diuron contaminated soils using an anionic surfactant. Mixed systems of bacterial population with biosurfactant have been also studied for degradation of organophosphate pesticides [14].

It is well known that surfactants form aggregated structures called micelles above a certain aqueous surfactant concentration, called Critical Micellar Concentration (CMC) which is defined as the concentration where the surface tension of surfactant solution reaches a limiting constant value [15]. In aqueous solutions, surface tension decrease with the addition of surfactant and CMC is the point where reaches constant surface tension [16]. CMC is a variable that is used as a reference. This value is determined by diluting surfactant in distilled water, but this variable can change in presence of solids such as soil particles [17].

Natural surfactants are surface-active compounds synthesized by a variety of microorganisms or contained in seeds, which has been studied as an alternative to removing organic and inorganic contaminants [18-20]. Additionally, removal of pollutants by washing surfactant solution has been demonstrated by pilot-scale [21-22]. More recently, in our previous works, we reported the soil washing of a soil contaminated with 2,4-D using different surfactants in a turbine-agitated acrylic tank and the elimination between 63 and 98% of the initial concentrations of methyl parathion by surfactant-enhanced soil washing and treatment of the produced wastewaters in an aerobic-submerged biofilter [23-24].

The aim of this work was to evaluate the surfactant-enhanced soil washing of soils spiked with α and β -endosulfan as a remediation process.

2. MATERIAL AND METHODS

2.1 Soil characterization and contamination

Soil employed along this work was collected from a farm, which produced chili. The site is localized in the Estate of Hidalgo, México at 20°10'14.19"N and 99°18'40.77"W, where endosulfan has been used. The soil was collected following NOM-021-SEMARNAT-2000, [25] it was collected superficial soil (0-5 cm), the sample was placed in a plastic bag and transported and stored at 4°C. The soil was screened through mesh 10 (<2 mm). Some characteristics of the soil sample were carried out, such as texture, pH, water capacity, bulk density and total heterotroph's count, all determinations in accord with Torres et al [24]. The soil was spiked with a commercial pesticide (Thiodan, BAYER, Mexico containing 33 % w/w of α - and β -endosulfan) and allowed to rest at 4°C in a dark environment. The soil was mixed one time by week during one month. At the end of the impregnation process, soils were sampled and the amount of pesticide was measured accordingly to the method explained later in this section. Real concentration was obtained by the analytical method. Pesticide extraction percent was calculated by the difference between background concentration, spiked concentration and residual concentration.

2.2 Surfactants

Different surfactants were employed for enhanced soil washing including, nonionic, ionic and zwitterionic surfactants, their characteristics are summarized in Table 1. Nonionic surfactants included tween 80 (DrogueríaCosmopolita, Mexico); canarcel 20 (Canamex, Mexico); emulgin W-400 (Conjunto Lar, Mexico) and two natural surfactants, mesquite seed and guar gums. Two ionic and one cationic surfactants were also tested, surfacpol A and texapon KD and dehyquart A, respectively, all obtained from Conjunto Lar, Mexico. The two zwitterionic surfactants, polafix LO and dehyton KB were obtained from Polaquimia, Mexico. Mesquite seed gum is obtained from a native tree (*Prosopissp*) that grows in arid zones in Mexico[28]. Mesquite seed gum is extensively used in a variety of industrial applications due to their emulsifying, microencapsulation, thickening and stabilizing properties, among others [29]. Guar gum is obtained from the seed of the legume *Cyamopsistetragonolobus*(Leguminosae), this polysaccharide that has high molecular weight and high viscosity [30-31].

Table 1. Surfactants employed in this work and some of its physicochemical properties

Commercial brand [CAS number]	Chemical nature	HLB	CMC mg/L	mM ^a
Nonionic:				
Tween 80 [9005-65-6]	Polyoxyethylenesorbitanmonooleate (POE 20)	15	25 ^b ; (13-65.4)[16,21,24,26,27]	0.02 ^b - 0.05
Canarcel 20 [9005-64-5]	Sorbitanmonolaureate (POE 20)	8.6	60 ^b	NR

Eumulgin W-400 [9016-45-9]	Ethoxylatednonylphenol (POE 6)	NR	10 ^b	0.03 ^b
Mesquite	Galactomannan	NR	NR	NR
Guar gum	Galactomannan	NR	NR	NR
Ionic:				
Surfacpol A	NR	NR	250 ^b	NR
Texapon KD [68585-34-2] Cationic	Sodium lauryl ether sulphates	NR	160 ^b ; 1,458 [27]	0.42 ^b
Dehyquart A [112-02-07] Zwitterionic:	Cetyltrimetyl ammonium chloride	21.4	900 ^b ; 5500 [27]	0.281 ^b
Polafix LO [3332-27-2]	Myristyl dimethylamine oxide	NR	180 ^b	0.53 ^b
Dehyton KB [4292-10-8]	Propyl Cocoamidopropyl betaine (CAPB)	NR	180 ^b	0.70 ^b

HLB- hydrophile-lipophile balance. CMC- critical micelle concentration. ^a This value depends of the molar mass. ^b This work. POE- Nonionic polyoxyethylene. NR- Not reported.

2.3 Surface tension measurements

The surface tension of all solutions including the stock was determinate using a tensiometer (Model 14814, Fisher Scientific). Calibration was made using distilled water and hexane. A stock solution was prepared to provide a concentration of 0.5 % (w/w) of all surfactants except for natural surfactants, which was prepared at 0.1 % (w/w). From stock solution, seven solutions were obtained in the range of 0.001 to 0.2 % w/w. This procedure has been previously described by Hagenhoff et al. [32]. The values were calculated from the average of four replications. CMC was calculated by the interception of two lines drawing in a chart of concentration vs surface tension of surfactants solutions.

2.4 Soil washing

The soil washing procedure was as follows, 10 g of contaminated soil were put inside 80 mL flask with 40 mL of surfactant solution prepared with distilled water and shaken during 23 hours at 28°C. Flasks were closed with plastic caps and covered with aluminum foil to prevent light exposure. Soils were dried at environmental temperature. Pesticide concentration was assessed in the spiked soil and the washed samples, following the methodology described below.

2.5 Pesticide extraction and quantification

Endosulfan was extracted by sonication (US-EPA Method 3550C) [33] using 10 g of soil, the pesticides extraction recovery from soil is above 96% with this methodology. The quantification was performed by gas chromatography (US-EPA Method 8081B) [34] with an electron capture detector (Varian 3400, USA) equipped with a J&W Scientific DB-5 column (Agilent, USA). The temperatures of the detector and injector were 300°C and 250°C, respectively, while oven initial temperature was 160°C and increased up to the final temperature of 240°C, at a rate of 5 °C/min. Nitrogen was used as carrier gas.

3. RESULTS AND DISCUSSION

3.1 Soil characterization

Some characteristics evaluated for this soil are presented in Table 2. As observed, it is mainly a clayed-loamy soil with a pH slightly lower than 7, bulk density is about 2 g/cm³, water capacity is above 8% and the total heterotrophs count is in the range of reported values for a bioremediation process (1x10⁶ FCU/g).

Table 2. Soil characterization

Parameter	
Texture	Sand 20.80% Loam 44% Clay 35.20%
pH	6.46
Humidity	13.60%
Bulk density	2.08 g/cm ³
Water capacity	8.05%
Heterotroph's count	1.1x10 ⁶ FCU/G

3.2 Surfactants critical micellar concentration

3.2.1 Nonionic surfactants

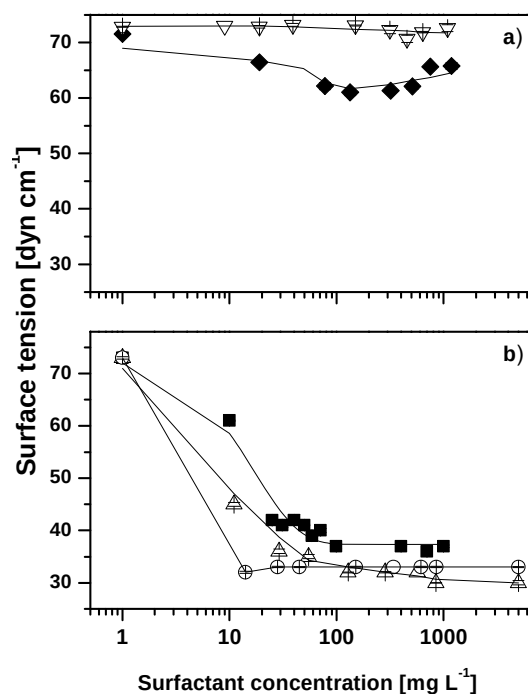
In the case of natural surfactants, they did not show CMC in the range of the concentrations tested (Figure 2a) this has been also reported by other authors [19]. Guar gum did not show a reduction of surface tension, even when concentration increases up to 1200 mg/L. The natural molecules maybe do not lower the surface tension of water, but they form stable emulsions and helps in the contaminated soil washing process [27]. In the case of mesquite seed gum, the surface tension slightly decreases from 73 to around 65 dyn/cm. These values are comparable to those reported by Torres et al. [27] where the surface tension of natural surfactants, i.e., locust bean gum (LBG), guar gum and a rhamnolipid produced by *Pseudomonas sp* were compared. They observed that while the rhamnolipid reduced the water surface tension to values up to 29 dyn/cm (at concentrations around 0.04%), LBG and guar gum reached values of 58 and 59 dyn/cm, respectively (at concentrations of 0.5 and 0.03%). This lack of true micellar formation of biosurfactants has been identified as one of their advantages over synthetic surfactants in enhancing biodegradation processes [35].

At Figure 2b is compared the CMC of tween 80, canarcel 20 and emulgin W-400. These three surfactants showed a CMC of 65, 60 and 10 mg/L. These values can be related to the molecular weight of these compounds since tween 80 is a heavy molecule (1309.68 g/mol) while emulgin W-400 has a mass molar of 308.46 g/mol.

3.2.2 Ionic surfactants

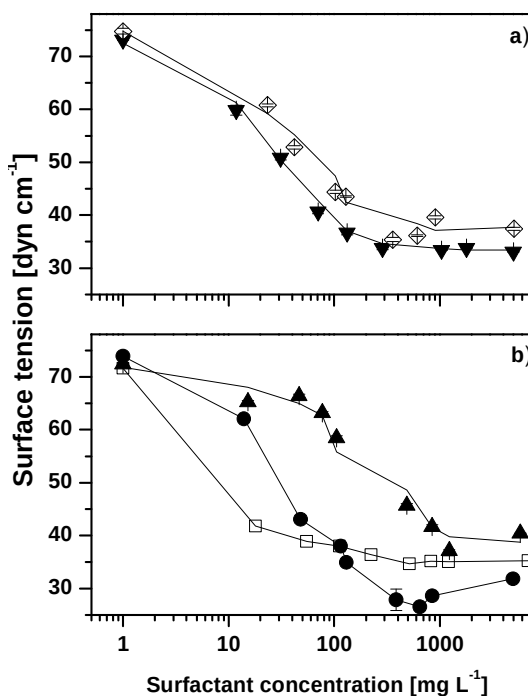
The commercial products, dehyton KB and polafix LO, has the same active substance according to the suppliers in consequence, the CMC was similar for this two surfactants, ~180 mg/L (Figure 3a). In Figure 3b is shown the comparison of CMC of dehyquart A, surfacpol A and texapon KD (160, 250 and 900 mg/L, respectively). CMC values obtained in this work for texapon and dehyquart are one order of magnitude lower than that reported by

178 Torres, et al. [27]. Nevertheless, reported CMC values depends on the specific product
 179 purity, the method employed for measurement, etc.



180

181 **Figure 2.** Surface tension as a function of nonionic surfactants concentration a) $\blacklozenge$
 182 mesquite; ∇ guar gum. b) $\blacksquare$ tween 80; $\triangle$ canarcel 20; $\circ$ eumulgin W-400. Bars mean
 183 standard deviation with $n=4$.



184

Figure 3. Same as in Figure 2. a) $\diamond$ dehyton KB; $\blacktriangledown$ polafix LO. b) $\square$ surfacpol A; $\blacktriangle$ dehyquart A; $\bullet$ texapon KD. Bars mean standard deviation with n=4.

3.3 Extraction of endosulfan

The initial concentration of α -endosulfan and β -endosulfan determinate in the no-washing sample was 0.640 and 0.135 mg/kg, respectively (α -endosulfan: β -endosulfan ratio ~5:1). Controls without surfactant using only distilled water were performed obtaining an average reduction in the concentration of 60.5% and 39.14% for α - and β -endosulfan. Kumar and Philip [36] found that distilled water desorbed around 40% of α -endosulfan, however in a sandy soil desorption was around 85%, indicating that adsorption of α -endosulfan towards soil particles was influenced by the composition of the soil. Considering all surfactants, the extraction obtained of α -endosulfan was in the range of 65 to 94% with a mean of 79%, while extraction of β -endosulfan was in the range of 41 to 80%, with a mean of 61%, each case is discussed in the following sections. The lower extraction efficiency of β -endosulfan could be related to physical processes of adsorption into soil. However, Kumar and Philip [36] determined that α -endosulfan had higher adsorption capacity than β -endosulfan in four types of Indian soils.

3.3.1 Nonionic surfactants

The extraction efficiency of α - and β -endosulfan with the two natural nonionic surfactants tested is shown in Figure 4.

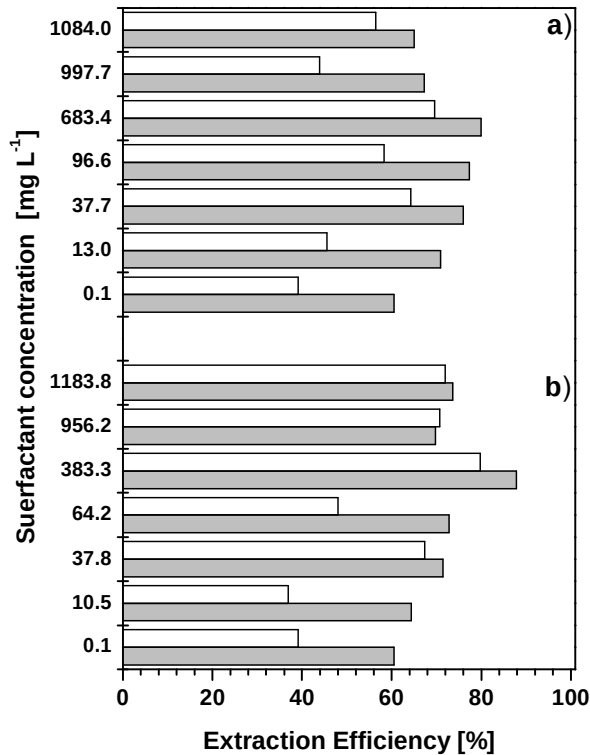
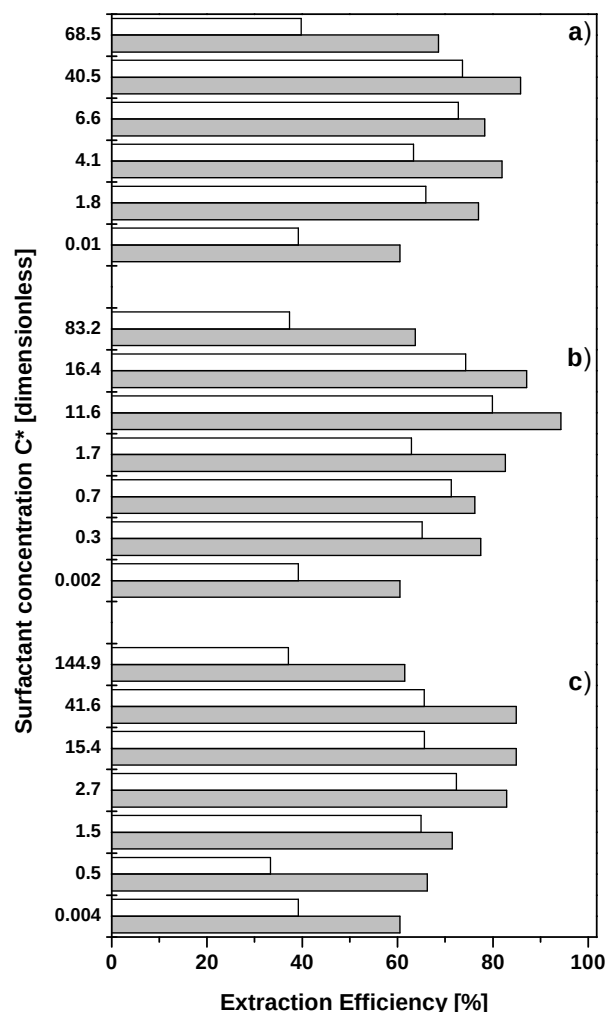


Figure 4. Extraction efficiency of ($\blacksquare$) α -endosulfan and ($\square$) β -endosulfan with nonionic surfactants: a) guar gum; b) mesquite.

Extraction of β -endosulfan was lower than α -endosulfan in all cases but it was not observed a correlation between surfactant concentrations and extraction of both isomers. The highest extraction of α - and β -endosulfan was around 90% and 80%, respectively and they were obtained using 383 mg/L of mesquite seed gum. In the case of gum guar, the maximum extraction of α - and β -endosulfan was obtained using 683 mg/L reaching around 80% and 70%, respectively. These maximum extraction values of α - and β -endosulfan were significantly higher than those values found in controls without surfactant, 60 and 40%, respectively. On the contrary, in the two lowest concentrations tested the extraction efficiencies observed were similar to those of the controls. Furthermore, at concentrations above of 683 and 383 mg/L of mesquite seed and guar gums, it seems that the effect in the extraction was similar or lower to the maximum obtained.

Figure 5 shows the extraction efficiency of the other nonionic surfactants used, in this case, it was plotted the surfactant concentration C^* , calculated as surfactant concentration divided by CMC. Surfactants concentrations under and above CMC were studied ($C^* < 1$ and $C^* > 1$, respectively).



225

226 **Figure 5.** Extraction efficiency of (■) α -endosulfan and (□) β -endosulfan with
 227 nonionic surfactants a) tween 80; b) canarcel 20; c) eumulgin W-400. C^* = Surfactant
 228 concentration/CMC.
 229

In the case of tween 80 extractions of 86% and 73% for α - and β - isomers, respectively were obtained at a C^* of 40.5 and comparable extraction efficiencies were found using eumulgin W-400 at a C^* of 15.4. On the other hand, the higher extraction efficiency of both isomers was obtained using canarcel 20 (94 and 80% for α - and β - isomers, respectively) at a C^* of 11.6. In the case of tween 80, the extraction efficiency was not related to the surfactant concentration.

It has been previously discussed that under the CMC value of surfactants, the predominant phenomenon is the lowering of the solution surface tension and hence, an increase in the solubilization of the pesticide[1,17]. Under that CMC value, the predominant mechanism is the micellization of pesticide, though the phenomena of increment in the solubilization.

Jayashree et al. [37] reported the surfactant washing of soils contaminated with a mixture of α - and β -endosulfan. They employed a natural surfactant (surfactin) and two nonionic synthetic surfactants (tween 80 and triton X-100). The soil was spiked with 10-80 mg/kg of a mixture of α - and β -endosulfan. Surfactant concentrations were in the range of 500-2,000 mg/L, for desorption times between 6 and 48 hours. Maximum endosulfan removals were about 91, 85 and 70% for surfactant tween80 and triton X100, respectively. However, values of removal with controls (using only water) were not reported.

On the other hand, Torres et al. [24] reported the washing of a garden soil intentionally contaminated with methyl-parathion in concentrations of 0.413 and 12.9 mg/kg. Surfactant-enhanced washing was carried out using nonionic, anionic and natural surfactants yielding methyl-parathion removal between 75 and 97% (for the higher methyl-parathion concentration). For the lower methyl-parathion soil concentration, removals between 63 and 87% were achieved. Best methyl-parathion removal was observed with locust bean, guar and mesquite seed gums in a concentration of 100 mg/L.

3.3.2 Ionic surfactants

The extraction efficiency obtained with ionic surfactants is shown in Figure 6, values ranging from 72-85% and 54-79% for α -endosulfan and β -endosulfan was observed. Worst results, in terms of the lower extraction efficiency and the higher concentration of surfactant added, were found with texapon KD while with dehyquart best results were observed. However, these values are lower compared with the extraction with natural nonionic surfactants. Torres et al. [24] reported that texapon 40 at a concentration of 100 mg/L was able to remove 85% and 69% of methyl-parathion from a soil spiked with initial concentrations of 0.413 and 12.9 mg/kg.

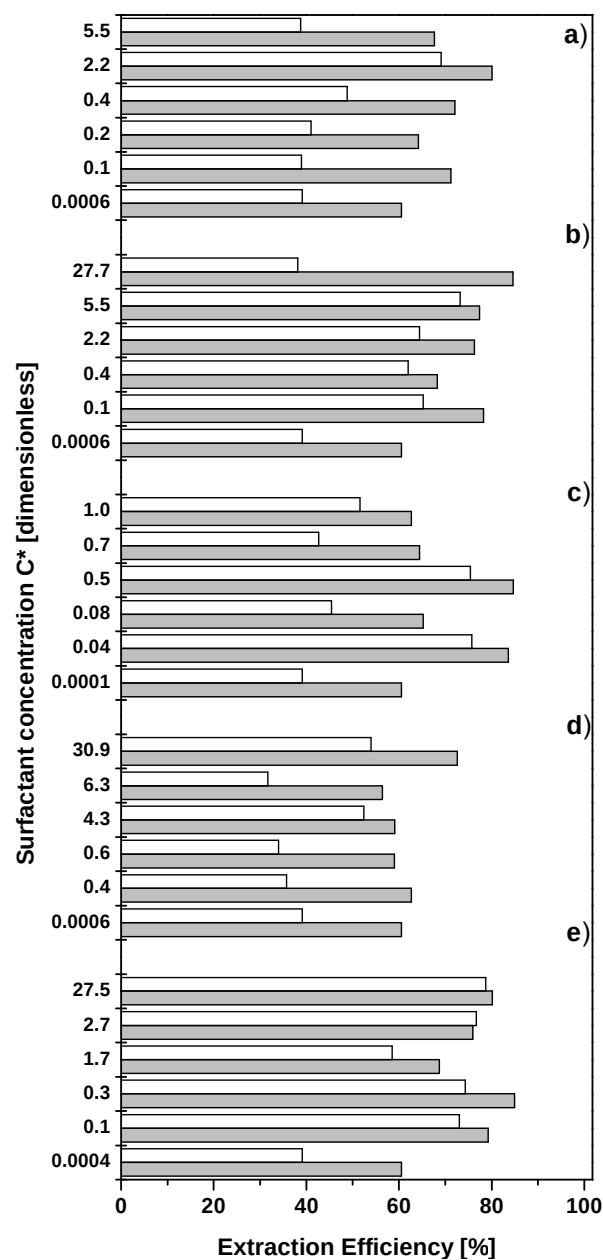


Figure 6. Extraction efficiency of (α -endosulfan and (β -endosulfan with ionic surfactants a) dehyton KB; b) polafix LO; c) dehyquart; d) texapon KD; e) surfacpol A. C^* = Surfactant concentration/CMC.

4. CONCLUSION

Natural surfactants did not show CMC in the range of concentration tested. Guar gum did not show a reduction of surface tension, even when concentration increases up to 1200 mg/L. In the case of mesquite seed gum, the surface tension slightly decreases from 73 to around 65 dyn/cm. Tween 80, canarcel 20 and emulgin W-400 showed a CMC of 65, 60 and

10 mg/L. CMC of dehyquart A, surfacpol A and texapon KD was of 160, 250 and 900 mg/L, respectively. Considering all surfactants, the extraction obtained of α -endosulfan is in the range of 65 to 94% with a mean of 79%, while extraction of β -endosulfan was in the range of 41 to 80%, with a mean of 61%. Accordingly to the nature of surfactants, the best extraction efficiencies were obtained as follows nonionic > nonionic natural > ionic. Best extraction efficiency of α -endosulfan was 94% obtained with canarcel 20 (C* of 11.6) while for β -endosulfan best extraction efficiency was 80% obtained using canarcel 20 (C* of 11.6) and guar gum (383 mg/L). This information is highly valuable for designing a soil washing process for treatment of pesticide-polluted soil using natural compounds as surfactants.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

AUTHORS' CONTRIBUTIONS

I Ortiz carried out the endosulfan analysis and wrote the first manuscript version. MA Avila developed the experimental study. L Torres coordinated the whole work and participated in the correction of the paper. All authors read and approved the final manuscript.

REFERENCES

- [1] Mata-Sandoval, J.C.; Karns, J.; Torrents, A. Influence of Rhamnolipids and Triton X-100 on the desorption of pesticide from soil. *Environ. Sci. Technol.* 2002, 36, 4669-4675.
- [2] United Nations Environmental Program (UNEP). Adoption Of An Amendment To Annex A of The Stockholm Convention on Persistent Organic Pollutants. Decision SC-5/3. 2011. Available at: <http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx> (accessed April 28, 2014).
- [3] Goswami, S.; Vig, K.; Singh, D.K. Biodegradation of α and β endosulfan by *Aspergillus sydoni*. *Chemosphere*. 2009, 75, 883-888
- [4] Wong, F.; Alegria H.A.; Bidleman T.F. Organochlorine pesticides in soils of Mexico and the potential for soil-air exchange. *Environ. Poll.* 2010, 158, 749-755
- [5] Becker, L.; Scheringer, M.; Schenker, U.; Hungerbühler, K. Assessment of the environmental persistence and long-range transport of endosulfan. *Environ. Poll.* 2011, 159, 1737-1743.
- [6] Wang, P.; Keller, A.A. Partitioning of hydrophobic pesticides within a soil-water-anionic surfactant system. *Water Res.* 2009, 43, 706-714
- [7] Mulligan, C.N.; Yong, R.N.; Gibbs, B.F. Surfactant-enhanced remediation of contaminated soil: a review. *Eng. Geol.* 2001, 60, 371-380.
- [8] Zhou, W.; Zhu, L. Enhanced soil flushing of phenathrene by anionic-nonionic mixed surfactant. *Water Res.* 2008, 42, 101-108.

323 [9] Han, M.; Ji, G.; Ni, J. Washing of field weathered crude oil contaminated soil with an
 324 environmentally compatible surfactant, alkyl polyglucoside. *Chemosphere*. 2009, 76, 579–
 325 586.

326 [10] Villa, R.D.; Trovó, A.G.; Nogueira, R.F.P. Soil remediation using a coupled process: soil
 327 washing with surfactant followed by photo-Fenton oxidation. *J. Haz. Mat.* 2010, 174, 770–
 328 775.

329 [11] Wang, P.; Keller, A.A. Sorption and desorption of atrazine and diuron onto water
 330 dispersible soil primary size fractions. *Water Res.* 2009, 43, 1448-1456.

331 [12] Wang, B.B.; Wang, C.L.; Liu, W.X.; Liu, X.Y.; Hou, J.Y.; Teng, Y.; Luo, Y.M.; Christie,
 332 P. Biosurfactant-producing microorganism *Pseudomonas* sp SB assists the phytoremediation
 333 of DDT-contaminated soil by two grass species. *Chemosphere*. 2017, 182, 137-142.

334 [13] Lv, C.; Chen, J.; Wang, X. Evaluation of surfactant performance in *in situ* foam flushing
 335 for remediation of dichlorodiphenyltrichloroethane-contaminated soil. *Int. J. Environ. Sci.*
 336 *Technol.* 2017, 14, 631-638.

337 [14] Singh, P.; Saini, H.S.; Raj, M. Rhamnolipid mediated enhanced degradation of
 338 chlorpyrifos by bacterial consortium in soil-water system. *Ecotoxicol. and Environ. Safety*.
 339 2016, 134, 156-162.

340 [15] Hoang, T.K.H.; La, V.B.; Deriemaeker, L.; Finsy, R. Ostwald Ripening of alkane
 341 emulsions stabilized by Polyethylene Glycol Monolaurate. *Langmuir*, 2001, 17, 5166-5168.

342 [16] Patist, A.; Bhagwat, S.S.; Penfield, K.W.; Aikens, P; Shah, D.O. On the measurement
 343 of critical Micellar Concentration of Pure and Technical-grade Nonionic surfactants. *J surfact.*
 344 *Deterg.* 2000, 3, 53-58.

345 [17] Beigel, C.; Barruio, E.; Carvet, R. Sorption of Low Levels of Nonionic and Anionic
 346 Surfactants on Soil: Effects on Sorption of Triconazole Fungicide. *Pestic. Manage. Sci.* 1998,
 347 54, 52-60.

348 [18] Miller, R.M. Biosurfactant-facilitated remediation of metal-contaminated soil. *Environ.*
 349 *Health Perspect.* 1995, 103, 59-62.

350 [19] Mulligan, C.N. Environmental applications for biosurfactants. *Environ. Poll.* 2005, 133,
 351 183-198.

352 [20] Cameotra, S.S.; Makkar, R.S. Biosurfactant-enhanced bioremediation of hydrophobic
 353 pollutants. *Pure Appl. Chem.* 2010, 82, 97-116.

354 [21] Lee, M.; Kang, H.; Do, W. Application of nonionic surfactant-enhanced in situ flushing to
 355 a diesel contaminated site. *Water Res.* 2005, 39, 139–146.

356 [22] Svab, M.; Kubal, M.; Müllerova, M.; Raschman, R. Soil flushing by surfactant solution:
 357 Pilot-scale demonstration of complete technology. *J. Haz. Mat.* 2009, 163, 410–417.

358 [23] Bandala, E.R.; Aguilar, F.; Torres, L.G. Surfactant-enhanced soil washing for the
 359 remediation of sites contaminated with pesticides. *Land Contam. Reclam.* 2010, 18, 151–
 360 159.

361 [24] Torres, L.G.; Ramos, F.; Ávila-Chávez, M.A.; Ortiz, I. Removal of methyl parathion by
 362 surfactant-assisted soil washing and subsequent wastewater biological treatment. *J. Pestic.*
 363 *Sci.* 2012, 37, 240-246.

364 [25] Diario Oficial de la Federación (DOF). NORMA Oficial Mexicana, que establece las
 365 especificaciones de fertilidad, salinidad y clasificación de suelos. NOM-021-SEMARNAT-
 366 2000 Estudios, muestreo y análisis. 31 de diciembre de 2002. Available at:
 367 <http://www.profepa.gob.mx/innovaportal/file/3335/1/nom-021-semarnat-2000.pdf>
 368 (accessed April 28, 2014).

369 [26] Chou, D.K.; Krishnamurthy, R; Randolph, T.W.; Carpenter J.F.; Manning, M.C. Effects
 370 of Tween 20 and Tween 80 on the stability of Albutropin during agitation. *J. Pharm. Sci.*
 371 2005, 94, 1368-81.

372 [27] Torres, L.G.; Moctezuma, A.; Avendaño, J.R.; Muñoz, A.; Gracida, J. Comparison of
 373 bio- and synthetic surfactants for EOR. *J. Petrol. Sci. Eng.* 2011, 76, 6-11.

374 [28] López-Franco, Y.L.; Goycoolea, F.M.; Valdez, M.A; Calderón de la Barca, A.M. Goma
 375 de Mezquite: una alternativa de uso industrial. *Interciencia*. 2006, 31, 183-189.

376 [29] Orozco-Villafuerte, J.; Cruz-Sosa, F.; Ponce-Alquicira, E.; Vernon-Carter, E.J. Mesquite
 377 gum: fractionation and characterization of the gum exuded from *Prosopis laevigata* obtained
 378 from plant tissue culture and from wild trees. Carbohydr. polym. 2003, 54, 327-333.

379 [30] Fijan, R.; Sostar-Turk, S.; Lapasin, R. Rheological study of interactions between non-
 380 ionic surfactants and polysaccharide thickeners used in textile printing. Carbohydr. Polym.
 381 2007, 68, 708–717.

382 [31] Wang, W.; Wang, A. Preparation, characterization and properties of superabsorbent
 383 nanocomposites based on natural guar gum and modified rectorite. Carbohydr. Polym. 2009,
 384 77, 891–897.

385 [32] Hagenhoff, K.; Dong, J.; Chowdhry, B.Z.; Leharde, S.A. Aqueous solution of anionic
 386 surfactants mixed with soils show a synergistic reduction in surface tension. Water Air soil
 387 Pollut. 2010, 209, 3-13.

388 [33] US Environmental Protection Agency (US- EPA). Ultrasonic Extraction, Method 3550C.
 389 Washington, DC, Feb, 2007. Available at <https://www.epa.gov/sites/production/files/2015-12/documents/3550c.pdf> (accessed 26 Feb, 2018).

390 [34] US Environmental Protection Agency (US EPA). Organochlorine Pesticides by Gas
 391 Chromatography, Method 8081B, Washington, DC, Feb, 2007. Available at
 392 <https://www.epa.gov/sites/production/files/2015-12/documents/8081b.pdf> (accessed 26 Feb,
 393 2018).

394 [35] Makkar, R.S.; Rockne, K.J. Comparison of synthetic and biosurfactants in enhancing
 395 biodegradation of polycyclic aromatic hydrocarbons. Environ. Toxicol. Chem. 2003, 22,
 396 2280-2292.

397 [36] Kumar, M.; Philip, L. Adsorption and desorption characteristics of hydrophobic pesticide
 398 endosulfan in four Indian soils. Chemosphere. 2006, 62, 1064-1077.

399 [37] Jayashree, R.; Vasudevan, N.; Chandrasekaran, S. Surfactant enhanced recovery of
 400 endosulfan from contaminated soils. Int. J. Environ. Sci. Tech. 2006, 3, 251-259.

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