

*Original Research Article***REMOVAL OF  $\alpha$ - AND  $\beta$ -ENDOSULFAN FROM SOILS BY USING NATURAL AND SYNTHETIC SURFACTANTS**

**Aims:** The aim of this work was studying a process of surfactant-assisted soil washing for the remediation of a soil spiked with  $\alpha$ - and  $\beta$ -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 with surface tension and critical micellar concentration (CMC) of every surfactant.

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

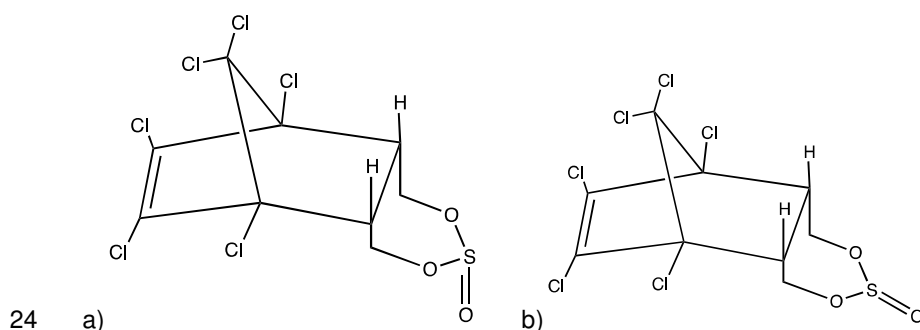
**Conclusion:** Natural surfactants did not show CMC in the range of concentration tested. Guar gum did not show a reduction of surface tension, even when concentration increases up to 1200 mg/L. In the case of mesquite seed gum, the surface tension slightly decreases from 73 to around 65dyn/cm. Tween 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 were of 160, 250 and 900 mg/L, respectively. Considering all surfactants, the extraction obtained of  $\alpha$ -endosulfan is in the range of 65 to 94% with a mean of 79%, while extraction of  $\beta$ -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  $\alpha$ -endosulfan was 94% obtained with canarcel 20 ( $C^*$  of 11.6) while for  $\beta$ -endosulfan best extraction efficiency was 80% obtained using canarcel 20 ( $C^*$  of 11.6) and guar gum (383 mg/L).

**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 environmental is 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, presence of high concentration of could be also associated to 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 use 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,  $\alpha$  and  $\beta$ , 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].



25 **Figure 1.** Molecular structure of a)  $\alpha$ -endosulfan and b)  $\beta$ -endosulfan .

26 Surfactants can be added to pesticide-contaminated soils to enhance the treatment efficiency of soil  
 27 washing. The ability of surfactants to enhance the water solubility of hydrophobic organic compounds  
 28 (HOCs) provides a potential mean of improving the treatment efficiency of *ex situ* soil washing  
 29 systems for remediating pesticide-contaminated soils [6-7]. This treatment has been used for  
 30 cleaning-up polyaromatic compounds, diesel and crude oil [8-10]. Pesticides also have being studied,  
 31 Villa et al. [10] who carried out a washing process with a soil spiked with DDT; and Wang and Keller [6,  
 32 11] reported that atrazine and diuron using an anionic surfactant and a washing process with an  
 33 anionic surfactant.

34 Surfactants form aggregated structures called micelles above a certain aqueous surfactant  
 35 concentration, that concentration is called Critical Micellar Concentration (CMC) and is defined as the  
 36 concentration at which the surface tension of surfactant solution reaches a limiting constant value  
 37 [12]. In aqueous solution, surface tension decrease with addition of surfactant and CMC is the point  
 38 where reaches constant surface tension [13]. CMC is a variable that is used as reference; this value  
 39 was determined by diluting surfactant in distilled water, but this variable change in presence of a  
 40 solid [14].

41 Natural surfactants are surface-active compounds synthesized by a variety of microorganisms or  
 42 contained in seeds, which has being studied as an alternative to remove organic and inorganic  
 43 contaminants [15-17]. Additionally removal of pollutants by washing surfactant solution has been  
 44 demonstrated by pilot-scale [18-19]. More recently, in our previous works we reported the soil  
 45 washing of a soil contaminated with 2,4-D using different surfactants in a turbine-agitated acrylic tank  
 46 and the elimination between 63 and 98% of the initial concentrations of methyl parathion by  
 47 surfactant-enhanced soil washing and treatment of the produced wastewaters in an aerobic-  
 48 submerged biofilter [20-21].

49 The aim of this work was to evaluate the surfactant-enhanced soil washing of soils spiked with  $\alpha$  and  
 50  $\beta$ -endosulfan as a remediation process.

## 52 2. MATERIAL AND METHODS

### 54 2.1 Soil contamination

55 Soil employed along this work was collected from a farm, which produced chili. The site is localized in  
 56 the Estate of Hidalgo, México at 20°10'14.19"N and 99°18'40.77"W, where endosulfan has been  
 57 used. Soil was collected following NOM-021-SEMARNAT-2000, [22] it was collected superficial soil (0-  
 58 5 cm), the sample was placed in a plastic bag and transported at laboratory where was stored at 4 °C.  
 59 The soil was screened through mesh 10 (<2 mm).

60 Soil was spiked with a commercial pesticide (Thiodan, BAYER, Mexico containing 33 % w/w of  $\alpha$ -  
 61 and  $\beta$ -endosulfan) and allowed to rest at 4°C in a dark environment. Soil was mixed one time by  
 62 week during one month. At the end of the impregnation process, soils were sampled and the amount  
 63 of pesticide was measured accordingly to the method explained later in this section. Real  
 64 concentration was obtained by analytical method. Pesticide extraction percent was calculated by  
 65 difference between background concentration, spiked concentration and residual concentration.

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## 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 (Drogueria Cosmopolita, 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 (*Prosopis sp*) that grows in arid zones in Mexico. [25] Mesquite seed gum is extensively used in a variety of industrial applications due to their emulsifying, microencapsulation, thickening and stabilizing properties, among others [26]. Guar gum is obtained from the seed of the legume *Cyamopsis tetragonolobus* (Leguminosae), this polysaccharide that has high molecular weight and high viscosity [27-28].

## 2.3 Surface tension measurements

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 [29] 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 by 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.

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

| Commercial brand<br>[CAS number]       | Chemical nature                              | HLB | CMC<br>mg/L                                    | mM <sup>a</sup>          |
|----------------------------------------|----------------------------------------------|-----|------------------------------------------------|--------------------------|
| <b>Nonionic:</b>                       |                                              |     |                                                |                          |
| Tween 80<br>[9005-65-6]                | Polyoxyethylene sorbitan monooleate (POE 20) | 15  | 25 <sup>b</sup> ;<br>(13-65.4)[13,18,21,23,24] | 0.02 <sup>b</sup> - 0.05 |
| Canarcel 20<br>[9005-64-5]             | Sorbitan monolaureate (POE 20)               | 8.6 | 60 <sup>b</sup>                                | NR                       |
| Eumulgin W-400<br>[9016-45-9]          | Ethoxylated nonylphenol (POE 6)              | NR  | 10 <sup>b</sup>                                | 0.03 <sup>b</sup>        |
| Mesquite                               | Galactomannan                                | NR  | NR                                             | NR                       |
| Guar gum                               | Galactomannan                                | NR  | NR                                             | NR                       |
| <b>Ionic:</b>                          |                                              |     |                                                |                          |
| Surfacpol A                            | NR                                           | NR  | 250 <sup>b</sup>                               | NR                       |
| Texapon KD<br>[68585-34-2]<br>Cationic | Sodium lauryl ether sulphates                | NR  | 160 <sup>b</sup> ; 1,458 [24]                  | 0.42 <sup>b</sup>        |

|                                                    |                                          |      |                              |                    |
|----------------------------------------------------|------------------------------------------|------|------------------------------|--------------------|
| Dehyquart A<br>[112-02-07]<br><b>Zwitterionic:</b> | Cetyl trimetyl ammonium<br>chloride      | 21.4 | 900 <sup>b</sup> ; 5500 [24] | 0.281 <sup>b</sup> |
| Polafix LO<br>[3332-27-2]                          | Myristyl dimethylamine<br>oxide          | NR   | 180 <sup>b</sup>             | 0.53 <sup>b</sup>  |
| Dehyton KB<br>[4292-10-8]                          | Propyl Cocoamidopropyl<br>betaine (CAPB) | NR   | 180 <sup>b</sup>             | 0.70 <sup>b</sup>  |

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

## 2.5 Pesticide extraction and quantification

Endosulfan was extracted by sonication (US-EPA Method 3550C) <sup>[30]</sup> using XX 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) [31] 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 final temperature of 240°C, at a rate of 5 °C/min. Nitrogen was used as carrier gas.

## 3. RESULTS AND DISCUSSION

### 3.1 Surfactants critical micellar concentration

#### 3.1.1 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 [16]. 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. These values are comparable to those reported by Torres et al. <sup>[24]</sup> where 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 as much 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 identity as one of their advantages over synthetic surfactants in enhancing biodegradation processes [32].

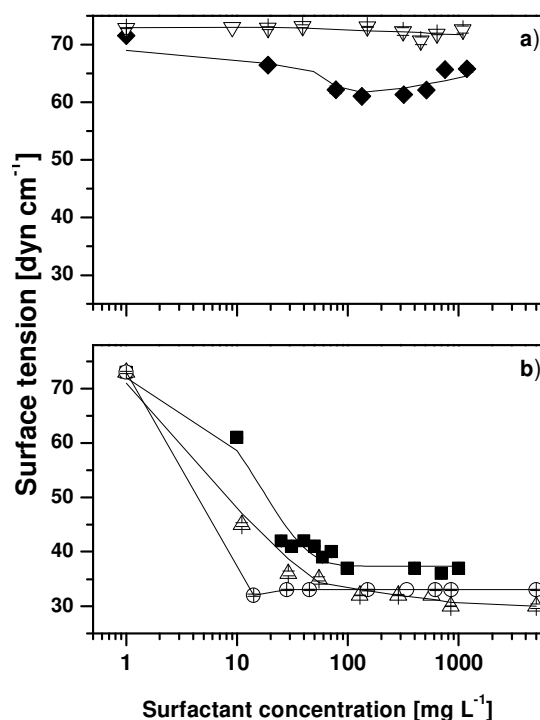


**Figure 2.** Surface tension as a function of nonionic surfactants concentration a) ◆ mesquite; ▽ guar gum. b) ■ tween 80; △ canarcel 20; ○ eumulgin W-400. Bars mean standard deviation with n=4.

In the 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 with 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.

### 3.1.2 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 Torres, et al. <sup>[24]</sup> Of course reported CMC values depends on the specific product purity, the method employed for measurement, etc.

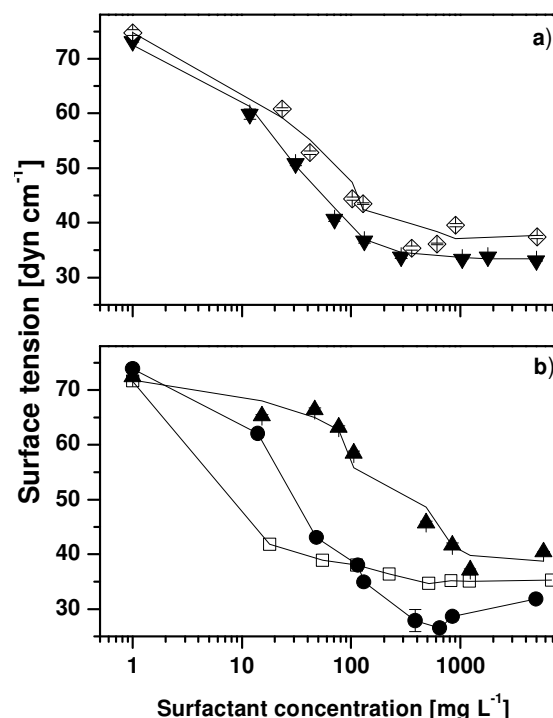


**Figure 3.** Surface tension as a function of ionic surfactants concentration a)  $\diamond$  dehyton KB;  $\blacktriangledown$  polafix LO. b)  $\square$  surfacpol A;  $\blacktriangle$  dehyquart A;  $\bullet$  texapon KD. Bars mean standard deviation with  $n=4$ .

### 3.2 Extraction of endosulfan

The initial concentration of  $\alpha$ -endosulfan and  $\beta$ -endosulfan determinate in no-washing sample was 0.640 and 0.135 mg/kg, respectively ( $\alpha$ -endosulfan:  $\beta$ -endosulfan ratio  $\sim 5:1$ ). Controls without surfactant using only distilled water were performed obtaining an average reduction in concentration of 60.5% and 39.14% for  $\alpha$ - and  $\beta$ -endosulfan. Kumar and Philip [33] found that distilled water desorbed around 40% of  $\alpha$ -endosulfan, however in a sandy soil desorption was around 85%, indicating that adsorption of  $\alpha$ -endosulfan towards soil particles was influenced by the composition of the soil.

Considering all surfactants, the extraction obtained of  $\alpha$ -endosulfan was in the range of 65 to 94% with a mean of 79%, while extraction of  $\beta$ -endosulfan was in the range of 41 to 80%, with a mean of 61%, each cases are discussed in the following sections. The lower extraction efficiency of  $\beta$ -endosulfan could be related to its higher bioavailability and consequently its higher biodegradation but this could be also related to physical processes of adsorption. However, Kumar and Philip [33] determined that  $\alpha$ -endosulfan had better adsorption capacity than  $\beta$ -endosulfan in four types of Indian soils.

#### 3.2.1 Nonionic surfactants

The extraction efficiency of  $\alpha$ - and  $\beta$ -endosulfan with the two natural nonionic surfactants tested is shown in the Figure 4. Extraction of  $\beta$ -endosulfan was lower than  $\alpha$ -endosulfan in all cases but it was not observed a correlation between surfactant concentrations and extraction of both isomers. The highest extraction of  $\alpha$ - and  $\beta$ -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  $\alpha$ - and  $\beta$ -endosulfan were obtained using 683 mg/L reaching around 80% and 70%, respectively. These maximum extraction values of  $\alpha$ - and  $\beta$ -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.

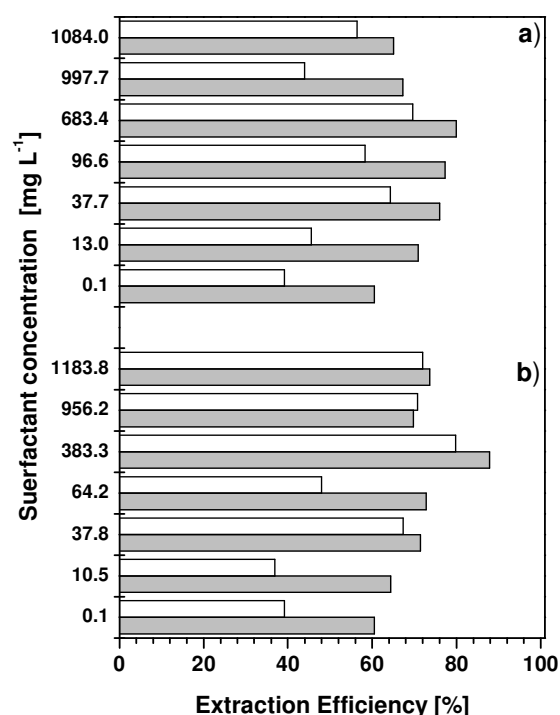


**Figure 4.** Extraction efficiency of (■) α-endosulfan and (□) β-endosulfan with nonionic surfactants: a) guar gum; b) mesquite.

The 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). In the case of tween 80 extraction 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 were 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. On the contrary, for canarcel 20 and emulgin W-400 there were observed a range of concentration of surfactant that favors the extraction of endosulfan and above and over that range there was not effect observed or even low extraction was observed. Reduction in solubility at higher concentrations can be explained due surfactant may be absorbed onto soil and reduce adsorption from organic compounds [34-35]. Jayashree et al. [36] found that concentration of tween above CMC (0.5, 1 and 2 g/L) enhanced the release of α-endosulfan, reporting extraction recoveries of 60% and 90% with 100 mg/L in 24 h and 2000 mg/L in 48 h, respectively. In this work at 1046 mg/L and 28 h, 79% of initial α-endosulfan was extracted.

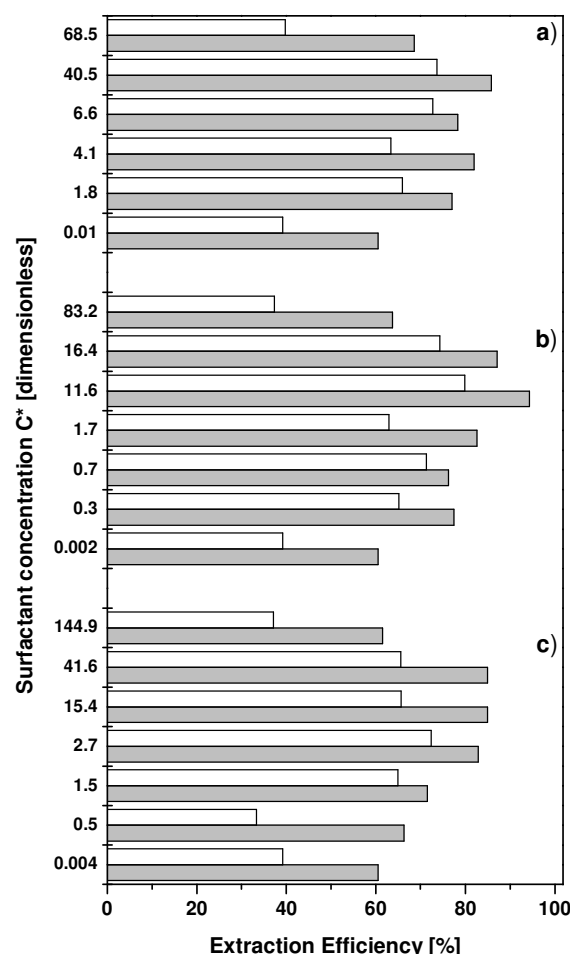


**Figure 5.** Extraction efficiency of (■)  $\alpha$ -endosulfan and (□)  $\beta$ -endosulfan with nonionic surfactants a) tween 80; b) canarcel 20; c) eumulgin W-400. C\*= Surfactant concentration/CMC.

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. Under that CMC value, the predominant mechanism is the micellization of pesticide, though the phenomena of increment in solubilization.

Jayashree et al. [36] reported the surfactant washing of soils contaminated with a mixture of  $\alpha$ - and  $\beta$ -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  $\alpha$ - and  $\beta$ -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 surfactin tween80 and triton X100, respectively. However, values of removal with controls (using only water) were not reported.

On the other hand, Torres et al. [21] 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, anioninc 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 mezquite seed gums in a concentration of 100 mg/L.

### 3.2.2 Ionic surfactants

The extraction efficiency obtained with ionic surfactants is showed in Figure 6, values ranging from 72-85% and 54-79% for  $\alpha$ -endosulfan and  $\beta$ -endosulfan were observed. Worst results, in terms of lower extraction efficiency and 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. [21] 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.

#### 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 65dyn/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 were of 160, 250 and 900 mg/L, respectively. Considering all surfactants, the extraction obtained of  $\alpha$ -endosulfan is in the range of 65 to 94% with a mean of 79%, while extraction of  $\beta$ -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  $\alpha$ -endosulfan was 94% obtained with canarcel 20 ( $C^*$  of 11.6) while for  $\beta$ -endosulfan best extraction efficiency was 80% obtained using canarcel 20 ( $C^*$  of 11.6) and guar gum (383 mg/L).

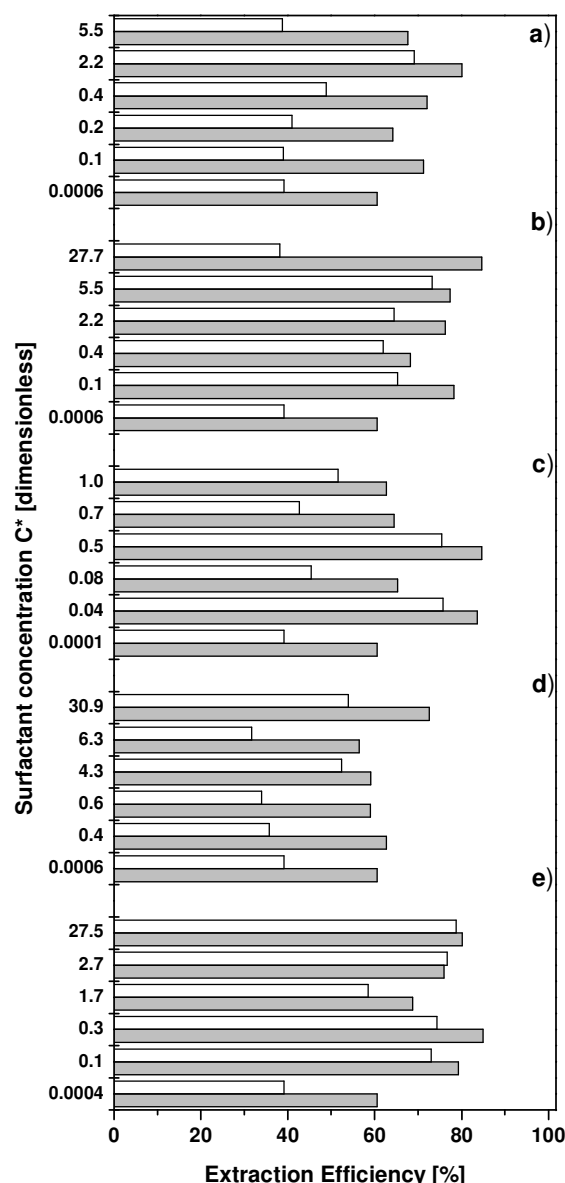


**Figure 6.** Extraction efficiency of (■)  $\alpha$ -endosulfan and (□)  $\beta$ -endosulfan with ionic surfactants a) dehyton KB; b) polafix LO; c) dehyquart; d) texapon KD; e) surfacpol A. C\* = Surfactant concentration/CMC.

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