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Implementation of Cloud Point Extraction Using Surfactants in the Recovery of Polyphenols from Apricot Cannery Waste

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Abstract: The objective of this study was to investigate the feasibility of using Cloud Point Extraction (CPE) to isolate natural antioxidants (polyphenols) from apricot cannery waste (ACW). Four different food-grade surfactants (Genapol X-080, PEG 8000, Tween 80, and Lecithin) were tested at varying concentrations to evaluate the effectiveness of the technique. It was observed that low concentrations of surfactants in one-step CPE resulted in less than 65% polyphenol recovery, which necessitated further extraction steps. However, high concentrations of surfactants were found to significantly improve polyphenol extraction from ACW for all surfactants tested. Among the four surfactants, PEG 8000 was found to be the most effective in most circumstances; specifically, adding only 2% of the surfactant per step in a two-step CPE was enough to effectively extract polyphenols with recovery rates better than 99%. When 10% *w*/*v* of PEG 8000 was used, recoveries greater than 92% were obtained. Since PEG 8000 is a reagent with low toxicity and the CPE method is simple, rapid, cheap, sensitive, and selective, the extracted organic compounds from ACW can be used as natural antioxidants in food technology. This has important implications for the development of natural and sustainable food additives.

Keywords: cloud point extraction; polyphenols; surfactants; apricot cannery waste; food industry

Citation: Giovanoudis, I.; Athanasiadis, V.; Chatzimitakos, T.; Kalompatsios, D.; Bozinou, E.; Gortzi, O.; Nanos, G.D.; Lalas, S.I. Implementation of Cloud Point Extraction Using Surfactants in the Recovery of Polyphenols from Apricot Cannery Waste. *Eng* **2023**, *4*, 1225–1235. https://doi.org/10.3390/eng4020072

Academic Editor: Antonio Gil Bravo

Received: 1 April 2023
Revised: 18 April 2023
Accepted: 19 April 2023
Published: 21 April 2023

1. Introduction

Free radical chemistry has been a subject that has attracted a lot of attention recently owing to the potential negative impact of reactive oxygen species (ROS) on both food systems and human health. Antioxidants are crucial in reducing oxidative processes and mitigating the consequences of ROS [1]. In food and pharmaceutical processing and storage, lipid peroxidation is a major cause of product degradation, but antioxidants can scavenge free radicals and extend shelf life by slowing this process [2]. In the human body, antioxidants are also beneficial, as they can help slow the progression of many chronic illnesses [3]. As a safer alternative to synthetic antioxidant compounds such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), natural antioxidants have gained increasing attention [4]. There has been an extensive awareness in studying natural additives, particularly fruit and vegetable residues, which are abundant in beneficial chemicals. The valorization of these byproducts can not only provide a sustainable solution to waste management but also produce natural antioxidants that may be included into food technology to improve the health and well-being of consumers [5].

Apricot (*Prunus armeniaca* L.) is a highly sought-after fruit in the market due to its vibrant color, unique flavor, and impressive nutritional profile. This fruit is rich in carotenoids, which are responsible for its distinctive yellow and orange peel color, making it visually appealing to consumers [6]. While the apricot originated in China, it found its way to

Europe through Armenia, leading to its scientific name [7]. Additionally, apricots are an abundant source of phenolic compounds, which are mainly found in the fruit's skin and pulp [8]. Rutin, catechin, epicatechin, and chlorogenic acid are among the dominant phenolic substances present in apricot cultivars, and their levels vary among different varieties [9]. Polyphenols derived from fruit waste are widely used as natural additives to food and preservatives due to their unique biological properties [10]. While solid/liquid (S/L) extraction is commonly used in the industry to recover polyphenols, this method has several drawbacks, including the extensive use of organic solvents, high manufacturing costs, and time-consuming processes [11,12]. Similarly, other methods such as microwave-assisted extraction, membrane processes, or supercritical fluid extraction are not suitable for bulk operations due to their high energy needs or expensive equipment [13,14]. Furthermore, conventional solvents are unable to extract both polar and non-polar bioactive compounds at the same time, making it challenging to extract all chemical constituents of the plant. Therefore, a major demand arises for a low-priced, high-throughput method to analyze apricot-derived bioactive compounds.

Novel liquid–liquid extraction (LLE) methods, such as two-phase (or multi-phase) separation, are gaining popularity for the extraction and concentration of active chemicals from natural materials. Aqueous two-phase extraction, dispersive liquid–liquid extraction, micellar extraction, and cloud-point extraction (CPE) are some of the novel approaches that have emerged [15,16]. Among them, CPE is regarded to be both an ecologically benign and biocompatible approach for extracting and concentrating active chemicals from plant-based resources, with possible applications in the food and pharmaceutical industries. Nonetheless, several drawbacks include the formation of emulsions, the requirement of hazardous organic solvents, and hence the production of vast amounts of pollutants make liquid–liquid extraction techniques laborious, costly, and ecologically unfriendly. In addition, aqueous two-phase extraction uses are restricted to laboratory environments and remain in pilot-size operations, as seen by the abundance of the literature reviews [17,18]. On the other hand, CPE is a simple and inexpensive technique for extracting bioactive chemicals from liquid matrices that employ surfactants [19]. It also gives the opportunity to use food-grade surfactants so that food industries can directly insert the extracted compounds into their products [20]. Above a certain micellar concentration, these molecules can form spontaneous aggregates (micelles) in aqueous solutions [21]. These formed structures can bind with either hydrophobic or hydrophilic compounds via dipole–dipole interactions and hydrogen bonding to be deployed for separation [22]. The micellar system characteristics and CPE factors that influence the extraction of high nutritional value compounds were investigated by Carabias-Martinez et al. [23]. The essential characteristics of a sample handled by CPE are the pH level and ionic strength, along with its temperature and the amount of surfactant used [24]. Most ionic surfactants are non-volatile and considered to be either relatively non-toxic or harmless chemicals, with the least toxicological or dermatological concerns [25]. Several surfactants, including Triton X-114, Triton X-100, and Brij 30, have been successfully employed to isolate bioactive plant components [26]. Several surfactants that might be employed in the CPE approach are found in nature. Lecithin is a natural surfactant that is widely used in the food sector. It is an inexpensive and low-toxicity compound [27]. El-Abbassi et al. [28] established an efficient and quick CPE process for extracting polyphenols from olive mill effluent utilizing Triton X-100 as the solvent for the extraction process. After one step of CPE, the recovery was 66.5%.

To the best of our knowledge, there is a scarcity of studies concerning the extraction of polyphenols from apricot cannery waste using CPE. To address the current gap in knowledge, this study aims to explore the potential of CPE using low biological hazard surfactants for polyphenol extraction from apricot cannery waste. This study investigated the efficiency of different food-grade surfactants, including Genapol X-080, PEG 8000, Tween 80, and natural surfactant Lecithin, at varying concentrations for polyphenol extraction from apricot waste. The effectiveness of CPE extraction cycles, as well as the antiradical activity of the extracted polyphenols, were evaluated for each surfactant. By conducting

these experiments, the study sought to identify the optimal surfactant concentration for the efficient extraction of polyphenols from apricot waste using CPE and to determine the most effective surfactant for this purpose.

2. Materials and Methods

2.1. Chemicals, Reagents, and Materials

Methanol, 1,1-diphenyl-2-picrylhydrazyl (DPPH), and Genapol X-080 were all obtained from Sigma-Aldrich (Steinheim, Germany). Gallic acid, anhydrous sodium carbonate, and Folin–Ciocalteu reagent were purchased from Penta (Prague, Czech Republic). PEG 8000 was obtained from Alfa Aesar (Karlsruhe, Germany). Citric acid anhydrous was purchased from Merck (Darmstadt, Germany). Tween 80 was purchased from Panreac (Barcelona, Spain). Sodium chloride and soya lecithin (>97%) were purchased from Carlo Erba (Milano, Italy). To produce the deionized water used in the experiments, a deionizing column was employed.

Apricot (*Prunus armeniaca* 'Bebeco' variety) cannery wastewater (ACW) was obtained from the stream resulting from the peeling step (for the reason of being the main contributor to the total waste stream) from ELBAK S.A. (Falani, Larissa, Greece).

2.2. CPE Procedure

The CPE method was carried out with slight modification from Chatzilazarou et al. [29]. Selection of the experimental parameters (i.e., pH, temperature, etc.) was carried out based on preliminary experiments. A Remi Neya 16R (Remi Elektrotechnik Ltd., Palghar, India) was used to centrifuge 70 g ACW for 20 min at 4500 rpm, so as to remove the solids. Prior to CPE, solid-free ACW samples were adjusted to a pH value of 3.5 with 2 N citric acid [30]. To accelerate the phase separation process by increasing the bulk density of the aqueous phase, 3% w/v sodium chloride was added to the sample. Sodium chloride also decreases the cloud point temperature [31]. The concentration of surfactants tested were 2, 5, and 10% w/w. A magnetic stirrer Heidolph MR Hei-Standard was used to equilibrate the temperature and stir the samples during CPE. The samples were stirred at 800 rpm and equilibrated at 65 °C for 20 min. After centrifuging the mixture for 5 min at 3500 rpm at 30 °C (first extraction stage), the phases were separated by decanting. The surfactant-rich phase had high viscosity. The volumes of both surfactant and aqueous phases were measured after centrifugation. The unextracted polyphenols in the aqueous phase were then decanted and either extracted once (second CPE step) or twice using the same method (third CPE step). Since each CPE experiment was repeated three times under identical conditions, the recovery findings represent the means of three extraction trials.

2.3. Polyphenol Recovery by CPE

The % polyphenol recovery was measured using a polyphenol mass balance. The surfactant recovery was estimated in accordance with previous descriptions [29,32].

$$\text{Recovery } (\%) = \frac{Cs \cdot Vs}{Co \cdot Vo} \times 100 = Co \cdot Vo - \frac{Cw \cdot Vw}{Co \cdot Vo} \times 100 \quad (1)$$

where Co is the concentration of polyphenols in the initial sample volume Vo (10 mL), Cw is the concentration of polyphenols in the water phase volume Vw, and Cs is the concentration of polyphenols in the surfactant phase volume Vs.

2.4. Total Polyphenol Content

Total polyphenols were measured photometrically using a modified Folin–Ciocalteu method by Katsoyannos et al. [33]. An amount of 100 μL of the sample was mixed with 100 μL of the Folin–Ciocalteu reagent, and after 2 min, 800 μL (5% w/v) of sodium carbonate solution was added. Finally, a Shimadzu spectrophotometer (UV-1700, Shimadzu Europa GmbH, Duisburg, Germany) was utilized to measure the absorbance of the solution at 750 nm after 20 min incubating at 40 °C in the absence of light.

2.5. Determination of Antioxidant Activity

The DPPH technique established by Tsaknis and Lalas [34] was employed to calculate the antioxidant activity of both extracted polyphenols in the surfactant phase and polyphenols that remained in the sample after CPE treatment. Briefly, 4 mL of sample was combined with 1 mL of 0.1 mM DPPH solution in methanol. The mixture was thoroughly mixed and allowed to remain in the dark for 30 min at room temperature. The absorbance was determined at 517 nm. The following equation was used to calculate the % scavenging:

$$\% \text{ Scavenging} = A_{\text{control}} - \frac{A_{\text{sample}}}{A_{\text{control}}} \times 100 \quad (2)$$

where A_{control} and A_{sample} represent the corresponding absorbances.

2.6. Statistical Analysis

All analyses were carried out in triplicate. The results were reported as the standard deviation of the three replicate mean values. After assessing the data with the Kolmogorov–Smirnov test, statistically significant differences were investigated using the Kruskal–Wallis test. Statistically significant differences were assessed for $p < 0.05$.

3. Results and Discussion

The objective of this work was to evaluate the potential of using CPE with low biological hazard surfactants to extract polyphenols from ACW. Four different food-grade surfactants (Genapol X-080, PEG 8000, Tween 80, and Lecithin) were tested, and the recovery of polyphenol extraction was measured. Considering the findings from other studies (vide infra), we opted to increase polyphenol extraction. To ensure consistency, the CPE method was conducted at 65 °C, with a sodium chloride concentration of 3% w/v, and at a pH level of 3.5. Previous research by Kiai et al. [35] suggested that the optimum temperature for CPE is between 50 and 70 °C when using surfactants such as Genapol X-080, Tween 80, and Triton-X. Additionally, Shi et al. [36] suggested that concentrations below 20% w/v of sodium chloride would not result in effective phase separation. However, in our case, a much lower sodium chloride concentration (3% w/v) proved to be adequate for the completion of separation, possibly due to the different material used (apricot peeling waste in our case) and procedure. Furthermore, the optimum pH level was set to 3.5 because polyphenols are protonated at low pH values, and thus, they interact extensively with micellar clusters of non-ionic surfactants, making them quite soluble in the micelle [28]. In contrast, polyphenols are deprotonated at high pH values, which reduces their solubility in hydrophobic micelles [37]. The recovery of polyphenols was tested in three different concentrations (2, 5, and 10% w/w) and with three extraction steps. According to Santana et al. [30], higher polyphenol extraction yields require high concentrations of surfactants. In the first step of extraction, each surfactant at a 10% concentration had a statistically significant ($p < 0.05$) higher extraction recovery than any other concentration used. However, this pattern did not apply to the other extraction cycles. Therefore, it is important to compare the extraction yields in different steps between the surfactants. Finally, the method employed herein was a modified (based on preliminary experiments) version of the method discussed by Chatzilazarou et al. [29], who investigated the usage of surfactant Genapol X-080 in order to isolate lycopene and total carotenoids from red-fleshed orange. Authors used a 0.5–15% v/v concentration of surfactant. The optimum CPE conditions were 30 min extraction at 55 °C, 35% sodium chloride, and pH level at 2.53. The recorded recoveries in carotenoids and lycopene were both slightly above 90% after three CPE steps.

3.1. Effect of Surfactant Concentration via CPE with Genapol X-080

Genapol X-080 belongs to the class of alkylpolyethylene glycol ethers, and is a non-ionic surfactant. The chemical structure of Genapol X-080 consists of a hydrophilic polyethylene glycol (PEG) chain attached to a lipophilic alkyl chain. It is commonly used in various

sectors, including the food, cosmetic, and pharmaceutical industries, as an emulsifier, solubilizer, and wetting agent [38]. Figure 1 depicts the results of Genapol X-080, which demonstrate a clear association between the amount of surfactant employed and the recovery of polyphenols. It was observed that the use of higher concentrations of Genapol X-080 led to higher polyphenol recoveries, as expected. However, the recovery rate remained below 60% in samples with low surfactant content, indicating the importance of additional CPE steps.

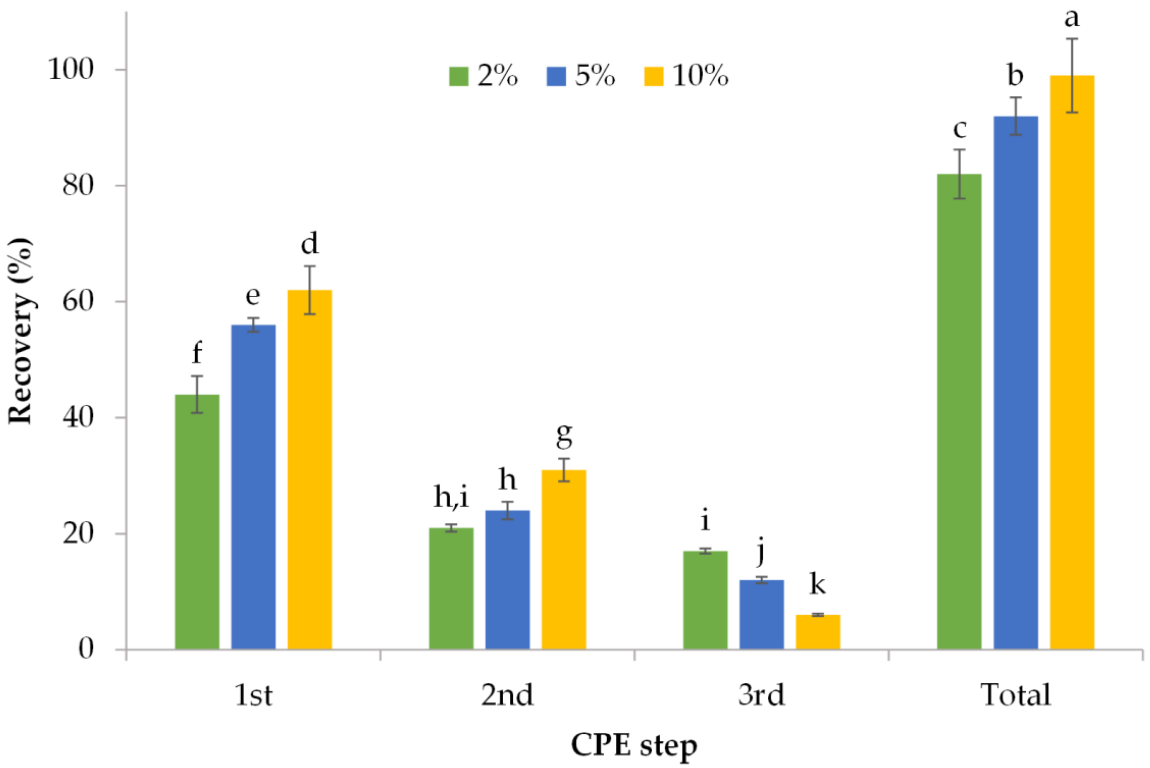

Figure 1. Percentage of polyphenol recovery with Genapol X-080 in different concentrations and extraction steps; standard deviation is shown with error bars; different letters (i.e., a–k) indicate samples that differ significantly (statistical difference for $p < 0.05$) using Student's *t*-test.

The first step of extraction using 2, 5, and 10% *w*/*v* Genapol X-080 resulted in extraction yields of 44, 56, and 62%, respectively. Statistically significant ($p < 0.05$) differences were found in every extraction step. The most efficient way to recover 82% of the total polyphenols was by using 2% Genapol X-080 thrice, whereas the most cost-effective approach was to use 5% Genapol X-080 twice, resulting in 92% polyphenol recovery. Our findings are similar to Kiai et al. [35], who investigated the extraction of table olive processing wastewater polyphenols with the use of the surfactant Genapol X-080 and CPE. At 70 °C equilibrium time and 4.0 pH level for 30 min CPE, they reached an approximate 60% recovery while using a 10% concentration of the surfactant. These results highlight the importance of carefully selecting the concentration of the surfactant and the extraction steps needed to optimize the recovery of polyphenols.

3.2. Effect of Surfactant Concentration via CPE with PEG 8000

PEG 8000 is a polyether, water-soluble, waxy solid that is commonly used as a thickening agent, lubricant, solvent, and surfactant in a wide range of usages, including pharmaceuticals, cosmetics, and food products. PEG 8000 has low toxicity and is considered safe for human use [39]. The results of polyphenols extracted via CPE from ACW samples using three different concentrations of PEG 8000 are presented in Figure 2. As seen in the figure, the recovery of polyphenols is highly dependent on the concentration of the surfactant

used. Specifically, increasing the concentration of PEG 8000 led to a higher recovery of polyphenols. However, when using low concentrations of PEG 8000, the recovery rate remained below 60%, indicating the importance of additional CPE steps. The extraction yields of 2, 5, and 10% w/v PEG 8000 in the first step of extraction were 55, 70, and 92%, respectively. Statistically significant differences ($p < 0.05$) were noted in most cases. It is worth noting that the second step of extraction using 2% PEG 8000 provided a high recovery rate of 44%. Interestingly, the recovery of polyphenols in the first two steps of extraction using 2 and 10% PEG 8000 was almost the same (~99%). Thus, a satisfactory recovery rate of polyphenols could be obtained by conducting a two-step extraction by using 2% of the surfactant in each step, which was as effective as the extraction using 10% PEG 8000. Our results are consistent with those of Chatzilazarou et al. [32], who also used the CPE method at 65 °C and obtained a recovery rate of 55.2% using 5% w/v PEG 8000 for one step of extraction from wine sludge. These findings suggest that using 2% PEG 8000 in ACW can be a cost-effective method for extracting a significant number of polyphenols. A wide variety of food industries could use the CPE technique because it is compatible with most food matrices. For instance, an apricot cannery industry could use this method with PEG 8000 in a two-step extraction with 2% w/v surfactant in each step. It would need around 20 Kg of PEG 8000 for each CPE step with 2% w/v concentration. Given that PEG 8000 costs around EUR 100/Kg, it would cost approximately EUR 4000 for a two-step CPE per ton of ACW. Other methodology reported by De Marco et al. [40] requires LLE with mixing the same volumes of olive mill wastewater with solvents such as hexane or ethyl acetate. Despite the encouraging results, it has a considerably higher cost and it could not be used directly in food.

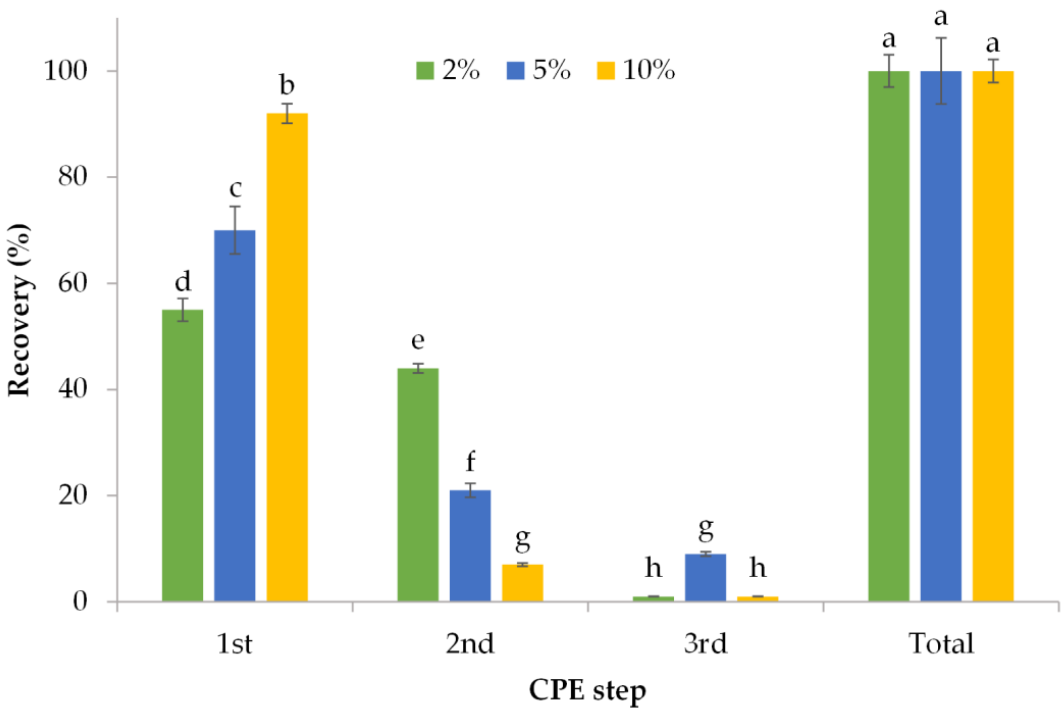

Figure 2. Percentage of polyphenol recovery with PEG 8000 in different concentrations and extraction steps; standard deviation is shown with error bars; different letters (i.e., a–h) indicate samples that differ significantly (statistical difference for $p < 0.05$) using Student's *t*-test.

3.3. Effect of Surfactant Concentration via CPE with Tween 80

Tween 80, frequently referred as Polysorbate 80, acts as a non-ionic surfactant of the polysorbate family. It is a water-soluble liquid that is widely utilized as a stabilizer, an emulsifier, and solubilizer in various sectors, including food, pharmaceuticals, and personal care. It stems from natural sources such as sorbitol, ethylene oxide, and oleic

acid. Tween 80 is known for its ability to increase both the bioavailability and the solubility of insoluble medicines, as well as for its emulsifying properties in food products. It is generally regarded as safe by regulatory agencies such as the FDA and has a wide range of applications due to its versatile properties [41]. Figure 3 shows the findings of the polyphenol CPE in ACW samples using three distinct concentrations of Tween 80. The results revealed that polyphenol recovery was related to the concentration of Tween 80 utilized. Statistically significant differences ($p < 0.05$) were recorded among the various tested concentration for the two first steps of the extraction. The first extraction step yielded 66, 75, and 88% of polyphenols with 2, 5, and 10% w/v Tween 80, respectively. Among the 5 and 10% w/v Tween 80 concentrations, the first two extraction steps yielded high recovery rates of approximately 97 and 100%, respectively. An economically feasible method for extracting polyphenols from ACW is to use 5% Tween 80 twice. Stamatopoulos et al. [42] conducted a study on the isolation and CPE of polyphenols from olive leaf extract with some modifications. They employed 35% w/v sodium sulfate as salt, pH 2.6, and 4% w/v Tween 80, achieving excellent extraction yields in a single extraction step (>90%).

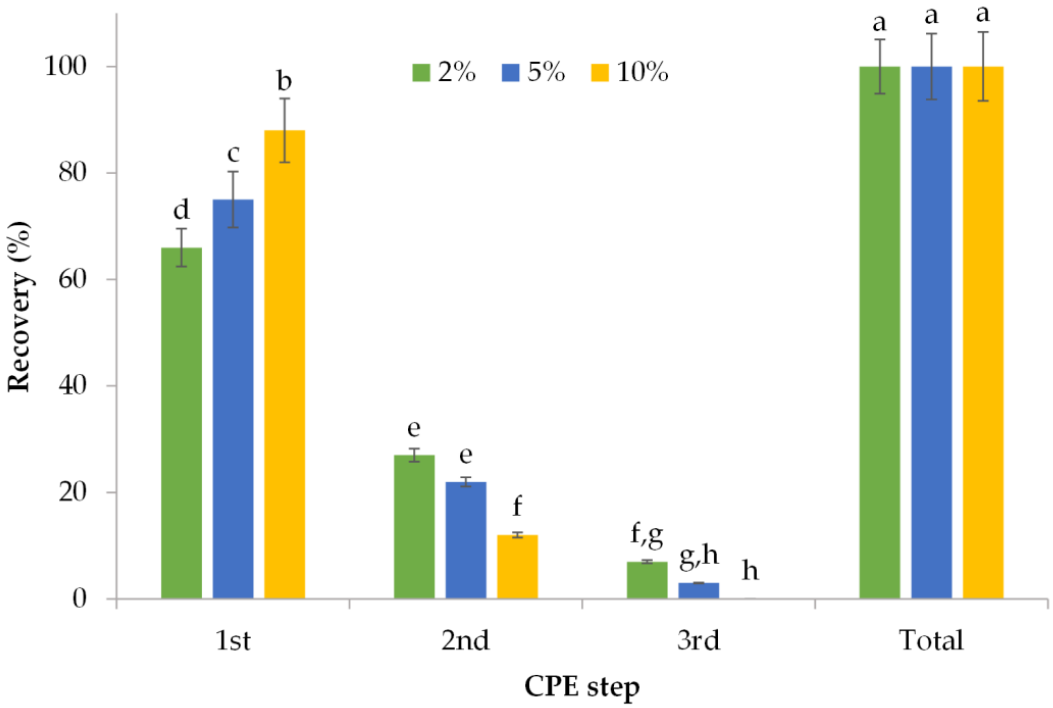

Figure 3. Percentage of polyphenol recovery with Tween 80 in different concentrations and extraction steps; standard deviation is shown with error bars; different letters (i.e., a–h) indicate samples that differ significantly (statistical difference for $p < 0.05$) using Student's *t*-test.

3.4. Effect of the Surfactant Concentration via CPE with Lecithin

Lecithins are naturally extracted amphiphilic molecules composed of phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylinositol (PI), and phosphatidic acid (PA). They are often used as common emulsifiers in the food industry and have no maximum level restrictions. Lecithins are quite a preferable alternative to synthetic components, which is attributed to both regulatory demands and also to the health benefits of phospholipids [43]. The results of polyphenol CPE in ACW samples using three different concentrations of lecithin are illustrated in Figure 4. The recoveries of polyphenols with 2, 5, and 10% w/v lecithin were relatively low, at 40, 56, and 73%, respectively. Statistically significant differences ($p < 0.05$) were recorded in most cases. Although the extraction yield in each step was not as high as with other surfactants, lecithin is a cheap, natural, edible, and non-toxic surfactant compared to other options [27]. Our results were similar to those of Alibade et al. [44], who investigated the usage of lecithin in the CPE technique

for extracting antioxidant compounds from winery sludges. They conducted experiments to optimize the CPE parameters and found that after three steps of extraction with 5% *w*/*v* lecithin, the recovery ranged from approximately 65 to 87%. Additionally, Karadag et al. [45] used lecithin to extract polyphenols from olive mill effluent and achieved a yield of approximately 50% by employing 12.5% *w*/*v* lecithin.

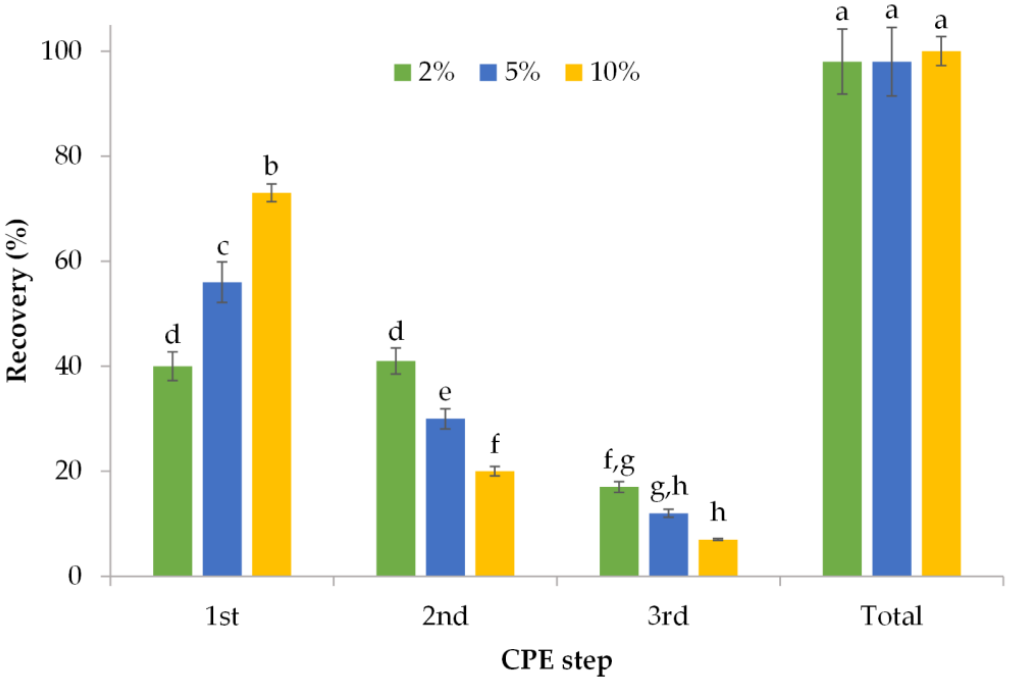

Figure 4. Percentage of polyphenols recovery with Lecithin in different concentrations and extraction steps; standard deviation is shown with error bars; different letters (i.e., a–h) indicate samples that differ significantly (statistical difference for $p < 0.05$) using Student's *t*-test.

3.5. Antioxidant Activity of the Recovered Polyphenols

Compound extraction from a sample might be desirable provided that the isolated compounds preserve their characteristics. Consequently, it was essential to determine if the extracted polyphenols maintain their antioxidant activity or if it was impacted by CPE extraction. Total polyphenol content (TPC) was measured as mg of gallic acid equivalents per liter (mg GAE/L) using the Folin–Ciocalteu technique, and the DPPH test was used to evaluate the antiradical activity. No statistically significant differences ($p > 0.05$) were observed in both tests for the polyphenols prior to and after the CPE step. We identified 2% PEG 8000 as the most efficient and cost-effective surfactant to examine polyphenol recovery and scavenging activity. As such, a two-step CPE was applied, and Table 1 illustrates the results of these two methods. TPC of initial ACW was measured at 55.2 mg GAE/L and 54.6 mg GAE/L after the CPE method, where high recovery yields were achieved. Our findings are similar to Hong et al. [46], who measured 0.65 mg GAE/g from apricot waste but defined as waste whole fruit samples that are typically discarded by the clients owing to their poor quality. As for the DPPH test, the percentage of scavenging activity of the initial ACW was fairly low. However, the CPE method caused the percentage of scavenging activity to be close to the initial ACW sample. Due to the scarcity of other studies on recovering polyphenols in ACW via CPE, we could only compare our results with Cheaib et al. [47], who investigated the isolations of polyphenols from apricot pomace waste via solid–liquid extraction. While exploring the optimal conditions for solid–liquid extraction (temperature, extraction solvent), they achieved an approximate 4% scavenging activity in 90 min extraction with water as the solvent at 25 °C.

Table 1. Total polyphenolic content (TPC) and antioxidant activity in ACW.

Phase	TPC (mg GAE/L)	Percentage of Scavenging
Initial ACW sample	55.2 ± 1.7 [a,*]	6.3 ± 0.5 [a]
CPE extract from ACW	54.6 ± 1.5 [a]	5.9 ± 0.3 [a]

* Data represent mean values ± standard deviation of three replicates; no statistically significant differences ($p > 0.05$) were found between the samples (e.g., [a]).

4. Conclusions

The feasibility of using the CPE procedure to separate natural antioxidants (polyphenols) from ACW was studied. The efficiency of the method was tested using a range of food-grade surfactants at various concentrations. Owing to its efficiency, minimum cost and duration, and the utilization of harmless extraction solvent, the CPE method is an appealing alternative to the liquid–liquid or liquid–solid solvent extraction of polyphenols. Further CPE steps might be employed to improve the acquired polyphenol recoveries. However, the optimization of CPE conditions (equilibration time, salt addition, pH value) may result in an even simpler polyphenol isolation technique, even avoiding the need for the second extraction step. PEG 8000 was found to be the most cost-effective surfactant to attain a high polyphenol yield. Just 2% *w*/*v* PEG 8000 when added twice in a two-step extraction was enough to acquire ~99% recovery. The natural surfactant lecithin did not provide statistically significant differences in polyphenol recovery when compared to the other surfactants. Furthermore, many low-toxicity and specifically greener surfactants should be investigated to see whether they are more effective than the previous examples.

Author Contributions: Conceptualization, I.G. and S.I.L.; methodology, V.A. and T.C.; software, V.A. and E.B.; validation, I.G. and V.A.; formal analysis, I.G., V.A., and T.C.; investigation, I.G. and V.A.; resources, S.I.L.; data curation, I.G. and V.A.; writing—original draft preparation, I.G., V.A., T.C., and D.K.; writing—review and editing, I.G., V.A., T.C., D.K., E.B., O.G., G.D.N., and S.I.L.; visualization, V.A.; supervision, O.G., G.D.N., and S.I.L.; project administration, S.I.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank ELBAK S.A. fruit canning factory, Falani, Larissa, Greece, for donating the apricot cannery wastewater (ACW).

Conflicts of Interest: The authors declare no conflict of interest.

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