Extraction of neonicotinoid pesticides from aquatic environmental matrices with sustainable terpenoids and eutectic solvents

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ABSTRACT

The potential environmental impact and adverse effects of the occurrence of pesticides in the aquatic environment have raised great social and political concern, leading to their control by means of several regulations, such as the European Directive 98/83/EC. In this regard, the three neonicotinoid pesticides analyzed in this work (acetamiprid, imidacloprid, and thiamethoxam) have been included in the surface water European Watch Lists under the Water Framework Directive. This research proposes the use of terpenoid-based solvents for the extraction of the three emerging contaminants previously mentioned. An initial screening of the extraction solvents was carried out through the COSMO-RS methodology, selecting the most favourable pure terpenes, eutectic terpenoid-based and conventional solvents. Furthermore, relevant issues were experimentally analyzed, such as extraction in more realistic multicomponent mixtures together with key parametric studies covering operating temperature and matrix influence. Carvacrol, a pure terpenoid not applied before as an extraction solvent of pesticides, has been revealed as an effective and sustainable substitute for conventional solvents for the first time to the best of our knowledge. Specifically, carvacrol exhibited overall extraction yields of around 97.5 % from a river water matrix at a volumetric S/F ratio of 0.1 and 303.2 K. High extraction yields from river water matrices regardless of temperature pointed to the potential of this solvent for a wide range of industrial application.

1. Introduction

In recent decades, plant protection products have played a key role in sustainable food production and in the elimination of insect-borne diseases. Consequently, the pesticide industry has experienced exceptional growth since the 1980 s and has increased the presence of these pollutants in both surface water and groundwater [1]. According to the literature, the concentration of pesticides in wastewaters ranges from 0.1 to 107 mg/L [2].

The pesticide market has evolved significantly since the first inorganic, botanical or simple aliphatic compounds, reducing crop losses from 42 to 9 %. Despite these benefits, their massive use has led to a major impact on the environment, ranking as one of the main emerging pollutants [1,3,4]. Thus, great efforts have been made over the last few years to develop new plant protection compounds presenting lower application rates, persistence and toxicity to non-target species. In this context, the so-called neonicotinoid or pyrethroid pesticides, whose application rates (0.01 and 0.1 kg/ha) are considerably lower than those of organochlorine compounds (3 kg/ha), have been introduced more recently [5,6]. Their success can also be attributed to their low toxicity to vertebrates, their high toxicity to insects, their flexibility in application methods and their systemic activity [4,7].

The growing social concern about the occurrence of these pollutants, for which information is still scarce, is leading to the development of new regulations. For instance, under Directive 2000/60/EC, contaminants for which limited information is available but suspected to pose a significant risk have been included in the named European Watch Lists. The increasing relevance of neonicotinoid pesticides and their presence on the European Watch Lists have turned the spotlight on them [8].

Neonicotinoid pesticides are a new type of neurotoxic compound whose mode of action is similar to that of nicotine. Based on the pharmacophore of their chemical structure, they are classified into

nitroenamines, *N*-nitroguanidines, and *N*-cyanoamidines. In addition, they are either cyclic or open-chain compounds. Imidacloprid and thiamethoxam, both presenting cyclic structures, belong to the group of *N*-nitroguanidines. Acetamiprid, presenting an open-chain structure, is in the *N*-cyanoamidine group [9,10].

Conventional methods for wastewater treatment are generally ineffective for removing some micropollutants, such as pesticides. However, their potential adverse health effects, even at very low concentrations, impose interest in developing ad hoc water treatments for these compounds. A wide variety of physical, chemical and biological techniques have been proposed in the literature for the removal of pesticides in aqueous solution: advanced oxidation processes, chlorination, membrane bioreactors, adsorption, membrane filtration or extraction processes [2,11–19].

Liquid-liquid extraction is effective for the separation of pesticides in an aqueous solution. However, it presents some drawbacks, such as the use of large doses of solvents, which may cause a severe impact on the environment when they are partially soluble in water [20–23]. For this reason, the search for natural and eco-friendly solvents is essential for the sustainable application of this technique. In this context, the present article proposes the application of terpenes, terpenoids, and their eutectic mixtures, as alternative extraction solvents.

Terpenes and terpenoids are natural products that have a recurrent isoprene skeleton. The difference between both groups of compounds lies in the presence or not of oxygen atoms in their chemical structure. That is, while terpenoids are simple hydrocarbons, terpenoids are their oxygenated derivatives. However, both terms are generally used indistinctly. Terpenoids may be classified according to the number of carbon atoms into hemiterpenoids (C5), monoterpenoids (C10), sesquiterpenoids (C15), diterpenoids (C20), sesterterpenoids (C25), triterpenoids (C30), sesquarterpenoids (C35), tetraterpenoids (C40) and polyterpenoids (C > 40) [24,25].

Terpenes and terpenoids can be considered renewable due to their biomass origin, also presenting a lower hazard and environmental impact. For instance, carvacrol has been used in ships' ballast water management systems, proving its natural degradation and minimising its environmental impact. This terpenoid has also been proposed as a functional agent for a wide range of health benefits, such as food preservative due to its antimicrobial and antioxidant properties. The use of terpenes and terpenoids as solvents in extraction processes is relatively recent, with only 46 articles published in the literature in 2020. Furthermore, although there is a wide variety of terpenes and terpenoids, only a few have been studied in the literature [26–29].

In this research, the experimental application of pure terpenoids, such as carvacrol and thymol, for the extraction of three neonicotinoid pesticides, acetamiprid, imidacloprid, and thiamethoxam, is proposed after their selection by molecular simulation screenings using COSMO-RS. The utilization of pure terpenoids has not been previously reported in the literature for the removal of these types of emerging contaminants. Terpenoid-based eutectic solvents, i.e., mixtures whose melting temperature is lower than that of the pure components, have also been tested experimentally [30–32].

2. Experimental section

2.1. Solvent screening with the COSMO-RS method.

Several solvents were screened using the Conductor-like Screening Model for Real Solvents (COSMO-RS) approach. Turbomole 7.4 software was used to optimize the molecules of the pesticides and terpenoids, selecting COSMO continuum solvation method with a BP86/TZVP computational level using solvent effect by a single point calculation. The full information of the optimized molecule is stored in a *.cosmo file, which makes them available in COSMOtherm software, version 19.0.4, for predicting purposes [33]. The affinity of each extractant was evaluated by calculating the activity coefficients and excess enthalpies

by contributions, namely hydrogen bonding, Van der Waals and electrostatic misfit, of acetamiprid, imidacloprid, and thiamethoxam at infinite dilution and 323,15 K in a wide list of terpenoids, hydrophobic eutectic solvents and conventional solvents. The mole fraction of the pesticide in each solvent was 5·10-5 for the simulations, which ensured the infinite dilution region [34]. As previously reported by other authors, the eutectic solvents were simulated as a mixture of two different compounds at the eutectic composition [35–39]. According to the pKa values shown in Table S1 of the Supplementary Material, the pesticides considered are in their neutral form in most of the pH range [40–44]. Therefore, the simulations were carried out considering this fact.

2.2. Chemicals

The compounds selected as suitable extractants with the COSMO-RS approach were two terpenoids (thymol and carvacrol), three eutectic solvents (thymol + octanoic acid, thymol + decanoic acid, and thymol + dodecanoic acid), and two conventional solvents (ethyl acetate and methyl isobutyl ketone). These solvents and the three neonicotinoid pesticides considered (acetamiprid, imidacloprid, and thiamethoxam) are detailed in Table S2 of the Supplementary Material. This includes suppliers, chemical structures, purities, and melting temperatures (Tm).

The aqueous solutions were prepared with both ultrapure water from PURELAB® Flex Water Purification System (Veolia) and a river water sample collected in the Manzanares river (Madrid, Spain). The characterization of the latter, which could be considered an environmentally-relevant aqueous matrix, is summarized in Table 1. The total organic carbon, total carbon and total nitrogen content were measured by a Shimadzu TOC-V CPH analyzer. The conductivity and pH were determined with a Mettler Toledo conductivity meter and a 2002 Crison pH meter. These values are within the range published in the literature for this kind of surface water [45–47].

2.3. Preparation of eutectic solvents and pesticides aqueous solutions.

The three eutectic solvents were prepared at the eutectic composition. For the mixtures thymol + octanoic acid, thymol + decanoic acid, and thymol + dodecanoic acid, the thymol mole fractions are 0.33, 0.44, and 0.56, respectively [39]. These solvents were stirred in a thermostatic bath at 323.2 ± 0.1 K until a homogeneous liquid appeared.

Monocomponent aqueous solutions of acetamiprid, imidacloprid, and thiamethoxam at 50 mg/L were prepared with ultrapure water. Additionally, two multicomponent solutions were prepared at 50 mg/L of each pesticide by using both ultrapure water and river water. The pH value of the pesticide aqueous solutions were around 5.5 and 7.0 for ultrapure water and river water, respectively.

2.4. Liquid-liquid extraction of neonicotinoid pesticides from aqueous solutions.

The liquid–liquid extractions were performed by contacting the aqueous pesticide solutions previously described with the organic solvents selected. The volumetric Solvent/Feed ratios (S/F) were as follows: 0.10, 0.25, 0.50, 1.00, and 2.00. Both phases were stirred for 12 h in glass vials, maintaining the temperature constant by using a C-MAG

Table 1
Macroscopic characterization of a river water sample.

Parameters	Value
pH	7.33
Chemical Oxygen Demand (mg/L)	<15
Total Organic Carbon (mg/L)	3.17
Total Carbon (mg/L)	7.42
Total Nitrogen (mg/L)	0.61
Total Dissolved Solids (mg/L)	64
Conductivity at 20 °C (μS/cm)	38.21

HS 7 dry bath (IKA). To observe the effect of this parameter in the extraction process, two temperatures were considered, 323.2 ± 0.1 K and 303.2 ± 0.1 K. After mixing, the two phases were left to settle for 4 h, and a sample of each was taken for further analyze. The raffinate, aqueous phase, was tested by using an analytical High Performance Liquid Chromatograph VARIAN ProStar with Diode Array Detector, and a Teknokroma chromatographic column (25 × 0,46 cm; 5 µm). The HPLC method developed consisted of a mixture (70 % acetonitrile + 30 % aqueous acetic acid solution 75 mM) as a mobile phase, a volumetric flow rate of 0.85 mL/min, an oven temperature of 303.2 K, an injection volume of 20 µL, and wavelengths of 223 nm and 275 nm. The retention times were 6.8 min, 10.1 min, and 11.6 min for thiamethoxam, imidacloprid and acetamiprid, respectively. The limits of detection were 0.1 mg/L for thiamethoxam and acetamiprid, while for imidacloprid it was 0.05 mg/L.

Finally, the influence of the feed pH value on the extraction process was analyzed. The pH value of the multicomponent aqueous solution with the river water matrix was modified by adding HCl and NaOH and the same procedure for the extraction process was repeated as above. The modified feed pH values were 1.0; 3.0; 5.0; 7.0; and 9.0.

3. Results and discussion

3.1. Solvent screening with the COSMO-RS method.

One of the methods reported in the literature for solvent screening is based on activity coefficients, which might be estimated by using the COSMO-RS method [33,48–51]. In this regard, a lower infinite dilution activity coefficient of the solute would indicate a higher affinity for the extraction solvent. Figs. 1-2 show the infinite dilution activity coefficients of acetamiprid, imidacloprid, and thiamethoxam in a wide range of terpenoids, hydrophobic eutectic solvents and conventional solvents at 323.2 K.

As shown in Fig. 1, thymol and carvacrol exhibit the lowest activity coefficient values in the group of terpenes and terpenoids. In this study, eleven solvents containing no heteroatoms in their hydrocarbon skeleton, i.e. terpenes, have been considered: myrcene, ocimene, sabinene, limonene, phellandrene, terpinene-alfa, 3-carene, pinene-beta,
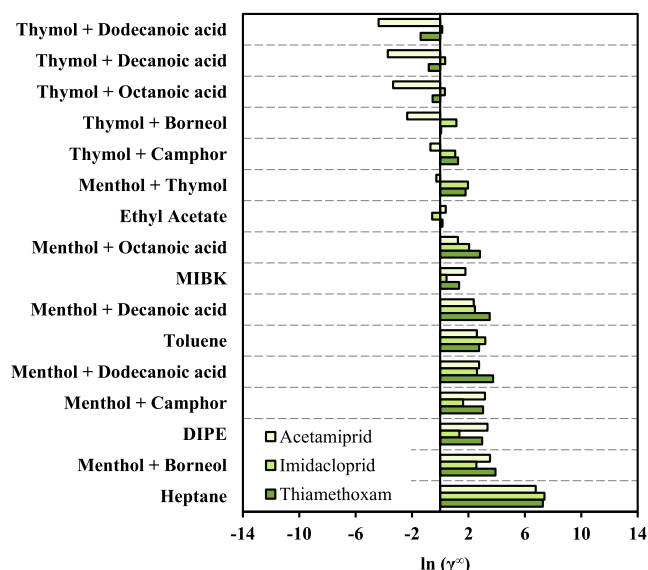
camphene, pinene-alfa and pinane. In general, these compounds seem to have a lower affinity for the three neonicotinoid pesticides, excluding eucalyptol, which has a lower activity coefficient for acetamiprid than myrcene and ocimene. As shown through the excess enthalpy contributions by hydrogen bonding, Van der Waals, and electrostatic interactions, shown in Figures S1-S3 of the Supplementary Material, the lesser influence of hydrogen bonding and dipole–dipole interactions could explain this behaviour for terpenes compared to terpenoids [52–54]. Since the entropic contribution is not governing these mixtures, promoting hydrogen bonding interactions has been concluded as the better strategy to promote low activity coefficients.

Eutectic solvents consisting of two terpenoids exhibit activity coefficients between those of pure terpenoids, as shown in Fig. 2. However,
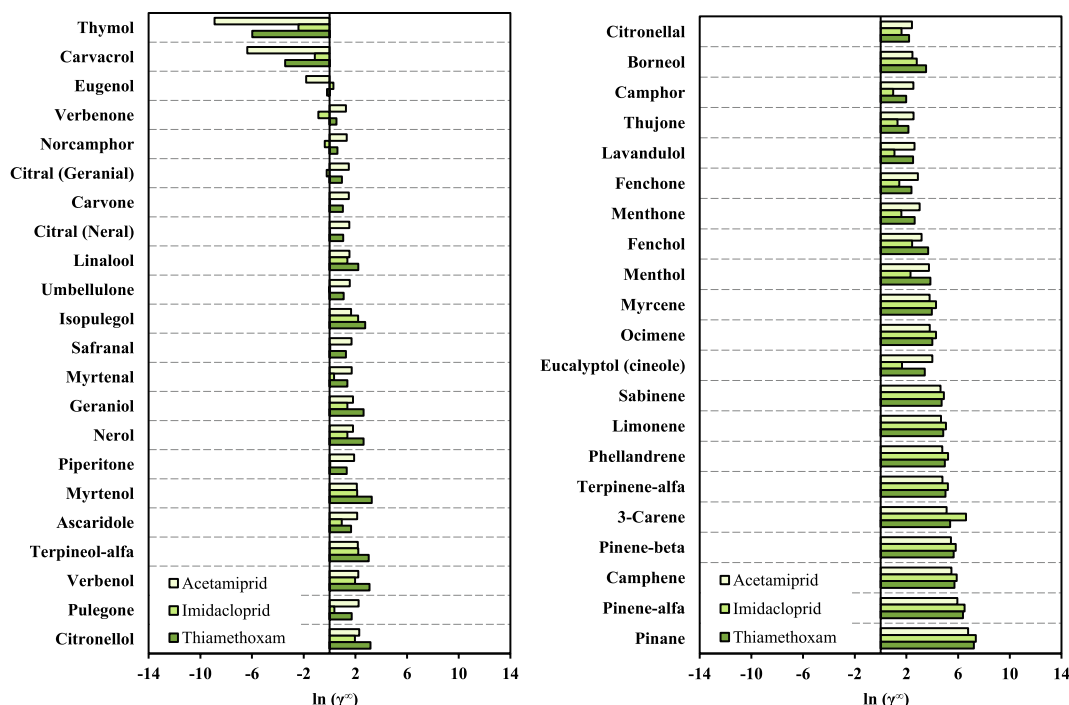
Fig. 2. Infinite dilution activity coefficients of acetamiprid, imidacloprid, and thiamethoxam in several hydrophobic eutectic solvents and conventional solvents at 323.2 K.

Fig. 1. Infinite dilution activity coefficients of acetamiprid, imidacloprid, and thiamethoxam in several terpenoids at 323.2 K.

it has been reported in the literature that they can show improved experimental results compared to those predicted by molecular simulation [35,37]. The eutectic mixtures with the lowest activity coefficients were those composed of thymol and carboxylic acids: thymol + octanoic acid, thymol + decanoic acid, and thymol + dodecanoic acid.

Among conventional solvents, those with the highest affinity for the three pesticides are ethyl acetate and methyl isobutyl ketone. In both cases, a lower compromise situation is reached compared to terpenes and eutectic solvents.

From the infinite dilution activity coefficients estimated by molecular simulation with COSMO-RS, seven extractants for the removal of neonicotinoid pesticides have been selected: two terpenoids (carvacrol and thymol), three eutectic mixtures (thymol + octanoic acid, thymol + decanoic acid, and thymol + dodecanoic acid) and two conventional solvents (ethyl acetate and methyl isobutyl ketone).

3.2. Extraction of single components from ultrapure water at 323.2 K.

The seven solvents selected in the molecular simulation stage were tested to extract each of the three pesticides from single-component aqueous solutions. The temperature was 323.2 K in order to ensure that all of the solvents remained in the liquid state and to be able to compare them under the same operating conditions. The extraction of each pesticide was determined from its concentration in the aqueous phase, in mg/L, before ($C_{i,0}^{aq}$) and after the extraction ($C_{i,f}^{aq}$), as shown in equation (1).

$$Yld_i\,(\%) = \frac{C_{i,0}^{aq} - C_{i,f}^{aq}}{C_{i,0}^{aq}} \bullet 100 \tag{1}$$

Figs. 3-5 show the extraction yields of imidacloprid, acetamiprid and thiamethoxam, respectively, at 323.3 K and different volumetric S/F ratios.

Experimental results revealed that the extraction yields of the three neonicotinoid pesticides are very similar for the two terpenoids. The high extraction yields with thymol and carvacrol could be due to the presence of the hydroxyl group in their molecular structures, which would enhance hydrogen bonding type molecular interactions. The delocalization of electrons as a consequence of resonance in the aromatic ring would increase the acidity of the hydrogen present in this group, favoring, even more, its capacity as hydrogen bond donors. This fact, together with their capacity to behave also as hydrogen-bond acceptors, could explain the high affinity of these two terpenoids for the three pesticides tested.

As predicted by COSMO-RS, pure terpenoids exhibited higher yields than their eutectic mixtures. In addition, an expectable and slight increase in extraction yield was observed as the alkyl chain length increased: (thymol + octanoic acid) < (thymol + decanoic acid) <
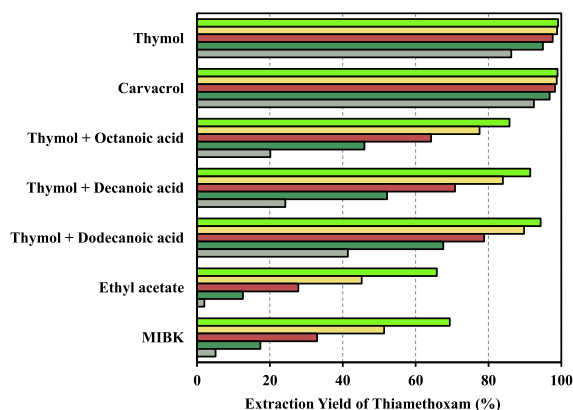

Fig. 3. Extraction yields of thiamethoxam from ultrapure water at 323.2 K and several volumetric S/F ratios.
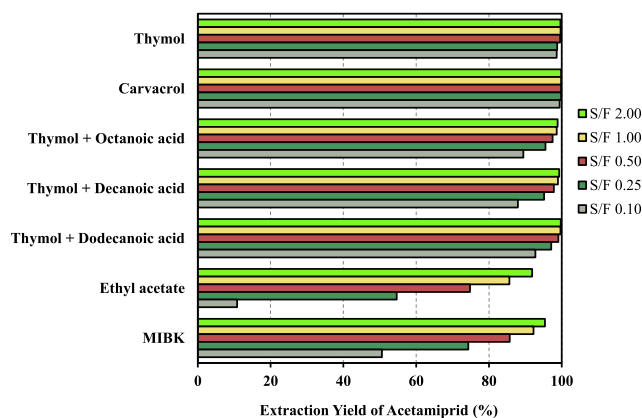

Fig. 4. Extraction yields of acetamiprid from ultrapure water at 323.2 K and several volumetric S/F ratios.
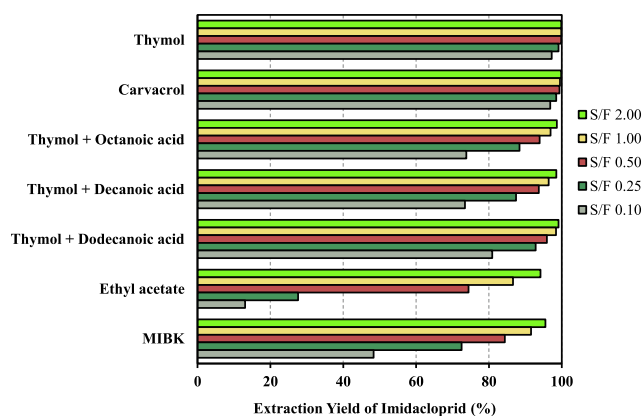

Fig. 5. Extraction yields of imidacloprid from ultrapure water at 323.2 K and several volumetric S/F ratios.

(thymol + dodecanoic acid). Specifically, thiamethoxam is the pesticide with the most pronounced variation.

In the literature, only a limited number of terpenes and terpenoids, in the form of eutectic mixtures, have been reported to be used to extract pesticides. However, applying these extraction solvents as pure agents has not been studied so far [29,55–57]. The relatively recent use of these compounds in extraction processes, together with the novel character of neonicotinoid pesticides, highlights the relevance of research in this field.

Florindo et al. (2017) proposed the use of hydrophobic eutectic solvents formed by natural organic acids (octanoic, decanoic and dodecanoic acids) and the terpenoid DL-menthol. In that study, the eutectic solvents that presented the highest extraction yields allowed the removal of 75 %, 70 % and 40 % for acetamiprid, imidacloprid, and thiamethoxam, respectively, using an S/F ratio of 1.00 [57]. However, under the same operating conditions, the eutectic solvents suggested in the present investigation (thymol + carboxylic acids) allow to achieve yields of 98.6–99.6 %, 96.4–98.4 %, and 77.5–89.7 % for acetamiprid, imidacloprid, and thiamethoxam, respectively. Therefore, thymol appears to formulate eutectic solvents capable of extracting a greater amount of pesticide from an aqueous solution. Although the eutectic solvents described in this study achieve higher yields than those reported in the literature so far, the use of pure terpenoids exhibited even more favorable results and avoided the use of a binary solvent. That is, both thymol and carvacrol exhibited extraction yields higher than 99.6 %, 99.4 and 97.6 % for acetamiprid, imidacloprid, and thiamethoxam, respectively.

Conventional solvents seem to be the most unsuitable compounds for

the extraction of neonicotinoid pesticides, as evidenced by their low yields even at high S/F ratios. This could be due to the fact that, unlike terpenoids, MIBK and ethyl acetate are characterized by behaving only as hydrogen-bond acceptors, i. e. they do not possess acidic hydrogens attached to an element of high electronegativity. As shown in the chemical structures of Table S2, all three pesticides act as hydrogen bond acceptors, and only imidacloprid has a hydrogen atom bonded to an element electronegative enough to act as a hydrogen bond donor. This would imply less impact on the intermolecular interactions between these solvents and the neonicotinoid pesticides. Thus, the extraction capacity of conventional solvents would not be due to hydrogen bond formation so much as to other types of intermolecular interactions, such as Van der Waals and electrostatic interactions.

In addition, the influence of the S/F ratio increases in the following order: terpenes < eutectic solvents < conventional solvents. In this regard, pure terpenes seem to present lower solvent requirements compared to their eutectic mixtures to achieve similar yields. This difference is considerably greater for conventional solvents. Although the prices of the terpenoids (carvacrol 10–25 \$/kg [58] and thymol 9–11 \$/kg [59]) may be higher than those of conventional solvents (MIBK 1.0–1.5 \$/kg [37] and ethyl acetate 1.3 \$/kg [60]), the very low S/F ratio required to achieve extraction yields above 90 %, coupled with their low toxicity and solvent losses, places them in a more favorable status for the application in terms of both holdup costs and operating costs, respectively.

In fact, the losses of the extraction solvent in the aqueous phase were considerably higher for conventional solvents, reaching values around 1.52 wt% and 10.18 wt% for MIBK and ethyl acetate, respectively. Concerning the pure terpenes, carvacrol showed a solubility in the raffinate of 0.17 wt%, while thymol 0.25 wt%. As reported in the literature, the eutectic solvents comprising thymol + carboxylic acid presented lower thymol losses in water than the pure terpene, obtaining values lower than 0.10 wt% [61].

As previously discussed, both terpenes and eutectic solvents are more suitable than conventional ones. In particular, carvacrol seems to exhibit the most favourable conditions, not only because of its high extraction yields and low losses to water but also because it has a melting temperature that allows extraction at room temperature, see Table S2. The latter would avoid the energy costs associated with heating. Therefore, carvacrol has been selected to be assessed in a multicomponent extraction process, also analyzing the effect of the matrix and the influence of temperature.

3.3. Multicomponent extraction: Matrix effect and temperature influence.

The results from individual extractions led to the study of new issues, which are closely related to the implementation of the process on an industrial scale. One of them is the proof of the extraction efficiency from multicomponent aqueous solutions since more than one type of neonicotinoid pesticide is likely to be present in the real matrices. This was accomplished by calculating the extraction yields of each pesticide according to equation (1), and also the overall extraction yields according to equation (2):

$$Yld_{Overall}\,(\%) = \frac{\sum_{i=1}^{3}\left(C_{i,0}^{aq} - C_{i,f}^{aq}\right)}{\sum_{i=1}^{3} C_{i,0}^{aq}} \bullet 100 \qquad (2)$$

where $C_{i,0}^{aq}$ and $C_{i,f}^{aq}$ are the concentrations of each pesticide in the aqueous phase, in mg/L, before and after the extraction.

In addition, it is worth studying the effect of the matrix on the extraction process, comparing the feasibility of this technology in aqueous solutions prepared with ultrapure water and with an environmentally relevant resource such as river water, where this type of emerging pollutants can be found. On the other hand, the high extraction yields obtained in extractions of single components at 323.2 K using

the carvacrol as solvent highlight the importance of evaluating the extraction process at 303.2 K (a more representative room temperature), which would avoid the possible energy costs associated to heating conditioning.

The multicomponent extraction yields from ultrapure water and from a river water matrix by using carvacrol and MIBK at S/F 0.10 and two temperatures, 323.2 K and 303.2 K are shown in Fig. 6. The results obtained for the S/F ratios 0.25, 0.50, 1.00 and 2.00 are given in Figures S4- S7 in the Supplementary Material.

Concerning the influence of temperature, a slight increase in individual and overall extraction yields was observed with decreasing temperature for both carvacrol and MIBK. This would favor the multicomponent extraction process at a more representative room temperature, i.e., around 303.2 K. This would also avoid the energy requirement associated with heating conditioning and minimize operating costs if the process developed in this article were scaled up.

Moreover, the effect of the matrix showed different trends depending on the pesticide. For imidacloprid and thiamethoxam, the yields in the river water matrix were lower than those obtained for ultrapure water. Therefore, the solutes present in the river water matrix seem to favor the solvation of the two neonicotinoid pesticides in the aqueous phase, decreasing their mass transfer to the organic solvent. On the contrary, the extraction yields of acetamiprid were higher with the river water matrix, indicating that the solutes present in the river water matrix favor their transfer to the organic phase due to a salting-out effect. The behavior previously analyzed for each of the three pesticides is the same for the two solvents analyzed, MIBK and carvacrol. However, the matrix effect seems to be considerably lower for the terpene. In general, the differences associated with the matrix effect appear to decrease with increasing S/F ratio, as evidenced in Figures S4-S7 of the Supplementary Material. It should be noted that the most suitable S/F ratio for carvacrol is 0.10, as it allows to reach overall extraction yields close to 98 %. A higher solvent dosage would not justify the slight rise in the extraction yield, which would increase operating and investment and costs.

Finally, comparing single versus multicomponent extraction from ultrapure water at 323.2 K, see Figs. 3-6, scarcely any differences were observed for carvacrol. However, MIBK achieved higher extraction yields of each of the three pesticides in the multicomponent process compared to single extraction. Specifically, thiamethoxam was the neonicotinoid pesticide that showed the most significant variation when using MIBK.

The feed pH is a further process variable that could lead to a variation in the extraction yield results. Therefore, a thorough study has been carried out using five different feed pH values: 1.0; 3.0; 5.0; 7.0; and 9.0. Carvacrol was selected as the extraction solvent, as it is the most suitable for its potential to be applied on an industrial scale. Fig. 7 shows the influence of feed pH on multicomponent extraction yields from river
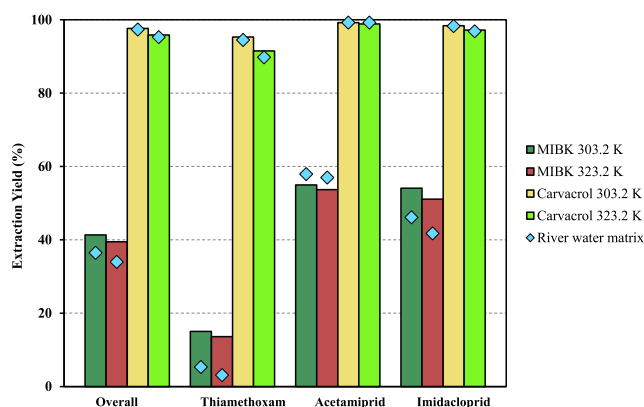

Fig. 6. Multicomponent extraction yields of pesticides from ultrapure water and river water matrix by using carvacrol and MIBK at S/F 0.10 and two temperatures, 323.2 K and 303.2 K.
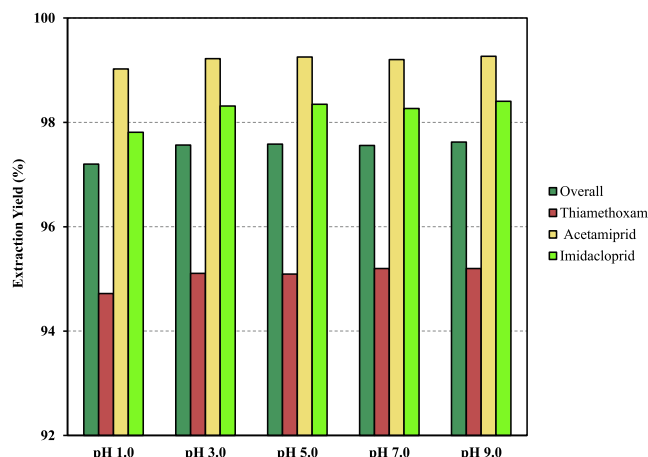
Fig. 7. Feed pH influence on multicomponent extraction yields of pesticides from river water matrix by using carvacrol at S/F 0.10 and 303.2 K.

water matrix at S/F 0.10 and 303.2 K.

The results of this study revealed that the feed pH value has a negligible effect on extraction yields, making carvacrol even more versatile for its industrial-scale application in the extraction of neonicotinoid pesticides, avoiding the need to modify the feed pH to ensure high extraction yields. Moreover, according to the pKa values of the nenonicotinoid pesticides, shown in Table S1, the pesticides are in their neutral form in most of the pH range. However, at pH values around 1, the protonated (cationic) form of the three compounds increases. As reported in the literature, charged solutes generally exhibit a stronger interaction with water, favoring partitioning into the aqueous phase [62–64]. Due to this fact, the extraction yields are slightly lower at feed pH of 1. Despite the latter, carvacrol seems to stabilize both the neutral and cationic forms without almost any variation in the extraction yields. Finally, it should be noted that in the natural feed solution, i.e., without pH modification, the pesticides are in their neutral form. This fact applies to the feed solution with both ultrapure water (natural feed pH $\approx$ 5.5) and river water matrix (natural feed pH $\approx$ 7.0).

4. Conclusions

The growth of the pesticide industry has favoured the presence of these emerging pollutants in the aquatic environment, which also present a potential environmental impact. This study focuses on removing neonicotinoid pesticides in an aqueous solution by using ecological and environmentally friendly solvents, such as terpenoid-based solvents. For this purpose, an initial screening was performed by molecular simulation with the COSMO-RS methodology, selecting two pure terpenes and three eutectic solvents as alternatives to conventional solvents.

Experimental extraction tests showed promising results. The pure terpenes achieved considerably higher extraction yields than the conventional ones, whereas this difference was slightly smaller for the eutectic solvents analyzed. Specifically, carvacrol exhibited extraction yields around 95 % for thiamethoxam and above 98 % and 99 % for imidacloprid and acetamiprid, respectively, at a volumetric S/F ratio of 0.1, 303.2 K and ultrapure water. In addition, the matrix, feed pH and temperature effect were practically negligible for the selected terpene, not limiting its competitive S/F ratio for the three pesticides. Carvacrol has not been proposed so far in the literature for the removal of pesticides in wastewater, opening this work a wide range of possibilities regarding the potential of this solvent to extract neonicotinoid pesticides from aqueous streams in an industrial context.

CRediT authorship contribution statement

Pablo Gutiérrez-Sánchez: Investigation, Formal Analysis, Software,

Methodology, Writing - original draft, Writing - review & editing. **Pablo Navarro:** Software, Writing - review & editing. **Silvia Álvarez-Torrellas:** Conceptualization, Writing - review & editing. **Juan García:** Conceptualization, Funding acquisition, Project administration, Writing - review & editing. **Marcos Larriba:** Conceptualization, Funding acquisition, Methodology, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.122148.

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