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Trace Determination of Heptachlor in Soil Samples by Toner@$CuFe_2O_4$ Nanocomposites based Microextraction-Gas Chromatography-Mass Spectrometry

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Abstract

In this paper, a green, sensitive, and accurate analytical method was described for the determination of heptachlor at low levels in the GC-MS system. In this context, the preconcentration of heptachlor was achieved by applying the dispersive solid-phase microextraction (DSPME) method prior to the separation and quantification in the GC-MS system. Toner@$CuFe_2O_4$ nanocomposites were synthesized by the hydrothermal synthesis method and used as the sorbent for the first time in literature. Under the optimal conditions determined by the univariate optimization approach, the limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.61 µg kg^{-1} and 2,0 µg kg^{-1}, respectively, and the sensitivity of the GC-MS system was enhanced by 68.5-fold. The applicability of the Toner@$CuFe_2O_4$-DSPME-GC-MS system was assessed by spiking tests applied to soil samples. The recovery results in the range of 93.2% and 105.7% obtained by applying the

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matrix matching calibration strategy proved the feasibility of the method. The Eco-scale and BAGI tools developed for green and analytical applicability assessment gave scores of 85 and 65, respectively, confirming that the method is environmentally friendly and analytically applicable.

Keywords: Heptachlor, pesticide, microextraction, nanocomposite, gas chromatography

1. Introduction

In agricultural and environmental activities, synthetic pesticides have been employed for decades to protect plants and crops from harmful pests and to control the growth of undesirable organisms caused infestations [1]. Since World War II, organochlorine pesticides (OCPs), belong to persistent organic pollutants (POPs), produced industrially, have been widely used in agriculture to date, particularly due to their proven effectiveness against insects and other pests. However, the biological accumulation, persistence in the environment, and toxicity of OCPs have increased the importance of the protection the human health and the ecosystem [2]. Heptachlor, one of the OCPs, is a chlorinated dicyclopentadiene compound that was widely employed to control pests such as termites and disease-carrying insects. However, it was banned in the United States and other developed countries in the late 1970s due to harmful effects on living metabolism [3]. Heptachlor and its metabolites have the potential to persist for long periods in various environments, particularly in soil, around the world. Moreover, the presence

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of chlorine heteroatoms, low solubility in water, and a tendency to preferentially separate into the lipophilic phase render these compounds highly toxic. Due to these toxic effects, heptachlor has been reported as a carcinogenic hydrocarbon to have disruptive effects on the central nervous system, immune system, and reproductive system in humans [4]. Accordingly, the critical limit for heptachlor exposure that poses a risk to vital functions or health has been reported as 35 mg m^{-3} by the National Institute for Occupational Safety and Health. On the other hand, the permissible exposure limit for heptachlor established by the Occupational Safety and Health Administration is 0.50 mg m^{-3} for an 8.0-hour time-weighted average [1]. Consequently, the accurate and sensitive determination of heptachlor at low levels in various samples where humans are likely to be exposed is critically important. For this goal, researchers have been focused to achieve the determination of heptachlor with high accuracy using different analytical techniques.

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Chromatography is a frequently used approach for the effective separation and identification of heptachlor. For this purpose, gas chromatography-electron capture detector (GC-ECD) [5,6], gas chromatography-mass spectrometry (GC-MS) [5,7], liquid chromatography-mass spectrometry (LC-MS) [8] and high-performance liquid chromatography - diode array detector (HPLC-DAD) [9] have been previously reported for the determination of heptachlor. GC–MS is a powerful tool used for the separation and detection of volatile and semi-volatile chemicals. Additionally, the mass spectrum

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obtained from the fragmentation of chemicals in MS systems enables the high-accuracy identification of chemicals. Unlike the LC-MS system, GC-MS has better peak capacity, high chromatographic resolution, and a single mobile phase system such as helium gas [10]. On the other hand, the lack of these advanced analytical tools to eliminate interference caused by complex sample matrices reveals the necessity of sample preparation procedures for the determination of trace levels of organic analytes. The application of sample preparation methods is an important step to minimize interference effects prior to analytical measurements and increase the accuracy of results. Among these, dispersive liquid-liquid microextraction (DLLME) [11], single-drop microextraction (SDME) [12], hollow-fiber liquid phase microextraction (HF-LPME) [13], and dispersive solid phase microextraction (DSPME) [14] have frequently reported for the preconcentration of organic analytes. Among them, DSPME is utilized as a versatile method, particularly in environmental studies, for the preconcentration of analytes with different polarities. The fact that DSPME significantly reduces solvent dependency enhances its environmentally friendly properties. Futhermore, the use of different materials as sorbents in the DSPME method has increased the interest in analytical chemistry, especially in the preconcentration/separation of environmental pollutants such as volatile organic compounds, persistent organic pollutants, and pesticides from various environmental matrices [15]. In few decades, a variety of sorbent material have been introduced for different purpose. Among them, nanomaterials (NPs) are innovative materials

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that contribute significantly to the development of sensitive methods for the detection of trace levels of pesticides, thanks to their prominent characteristics such as large surface area, numerous active sites, and different surface functions [16]. Furthermore, as scientific research increasingly focuses on innovative materials, the development of new structures with superior features that reduce costs and labor is becoming increasingly important. In parallel, the recyclability of waste materials has become a topic of growing interest for the production of materials through simple synthesis procedures and at low cost. These waste materials contain plenty of toner particles in ink cartridges, which are separated as electronic waste after duplication and printing processes. Considering the scale of copying and printing activities worldwide, the fact that toner powder is separated as waste on a wide amount means that reprocessing these materials will support economic and scientific development on a global scale [17]. The composition of the toner particles in question generally consists of iron, carbon, silicon, and certain binding polymers, and the toner content varies according to the research and development formulations of printer manufacturers [18]. Thanks to their magnetic properties, toner particles can be used individually in preconcentration and treatment processes, as well as in combination with different materials to form composites, thereby serving as sorbent materials with superior properties. On the other hand, metal ferrites are gaining significant attention due to their outstanding physical and chemical properties, reduced costs, and simplified synthesis steps.

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Depending on the crystal lattice type, garnet, hexagonal, and spinel structures have been reported in the literature [19]. In addition, the tendency of metal ferrites to form composite structures is a promising area of research for the development of new types of materials using toner particles. Moreover, In light of this, the motivation for our study was to introduce a new sorbent that not only exhibits an upward trend but also allows for the utilization of waste materials, thereby offering a new perspective on DSPME-based approaches for the preconcentration/separation of organic and inorganic contaminants.

This study aimed to develop an innovative analytical method for the determination of trace levels of heptachlor belonging to the insecticide class in soil samples by GC-MS after the preconcentration using a toner-based $CuFe_2O_4$ nanocomposite-supported DSPME method. The toner@$CuFe_2O_4$ nanocomposite structures synthesized by the hydrothermal method were used as sorbent material for the first time for the preconcentration of an organic analyte in the literature. This study, which has high economic and environmental contribution values by converting waste materials into useful materials, is expected to be a good research topic for various scientific studies.

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2. Materials and Method

2.1. Chemicals and Reagents

Analytical grade chemicals were used throughout the study to develop the extraction procedure. Heptachlor standard (CAS:76-44-8, >98.0%) was

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obtained from Sigma-Aldrich (Darmstadt, Germany). Acetonitrile (ACN, ≥ 99.9%) were purchased from Merck (Darmstadt, Germany) to prepare the stock solutions at necessary concentrations by gravimetrically and used as the extraction solvent. Methanol (≥ 99.9%) and ethanol (≥ 99.8%) were obtained from Merck (Darmstadt, Germany) for the optimization the extraction solvent type. Ultra-pure water having 18.2 Ω-cm as resistance from the Elga Flex 3 Water Purification System was employed for preparation and dilution of samples, and cleaning of experimental equipment. The toner used in the nanoparticle synthesis stage was supplied from waste printer cartridges available in our laboratory. Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$, ≥ 99%, Merck, Darmstadt, Germany) and iron (II) ammonium sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2.6H_2O$, Carlo Erba, Cornaredo, Italy). Buffer solutions were prepared using potassium hydrogen phthalate, tris, and sodium tetraborate decahydrate salts obtained from Merck (Darmstadt, Germany), at concentrations of 0.40 M, 0.90 M, and 0.12 M, respectively, and hydrochloric acid (37%) and sodium hydroxide (NaOH) were utilized to adjust the H_3O^+ concentration of the solutions.

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2.2. Instrumentation

An Agilent HP6890 gas chromatograph consisting of a 5% phenyl-methylpolysiloxane-based HP-5MS column with dimensions of 30 m x 250 µm x 0.25 µm (length x inner diameter x film thickness) and an integrated HP5973 mass spectrometer were utilized for the chromatographic separation and qualitative/quantitative determination of heptachlor, respectively. High-

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purity of helium (99.995%) bought from a local supplier (İstanbul, Türkiye) was used as the carrier gas in the GC-MS system with an operating flow rate of 1.2 mL/min and pressure at 14.94 psi. Sample injections were performed in splitless mode, and the injection volume was set to 1.0 µL. The inlet temperature was fixed at 290 °C. The characteristic ions were set the m/z ratios of 100, 272, and 274 for the qualitative/quantitative determination of heptachlor. A suitable temperature program was applied to ensure the effective separation of heptachlor including the initial temperature of 100 °C, 25 °C min^{-1} to 250 °C, 10 °C min^{-1} to 280 °C, holding at 280 °C for 1.0 minute and holding at 300 °C for 1.0 minute, respectively. The acquisition was performed for selective ion monitoring (SIM) mode. The retention time of the heptachlor was determined to be 6.05 minutes. The chromatograms for heptachlor (10.2, 21.1 and 51 mg kg^{-1} in 100% ACN) are illustrated in Figure 1.

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An Isolab-M1010002 model vortex (Eschau, Germany) and Biocomma SDC-4000 model multitube vortex (Guangdong, China) were employed to mix the standard/sample solutions during the experiments. In synthesis, extraction and recovery stages, all samples were centrifuged to effectively separate the phases by using Biobase BKC- TL5II model centrifuge (Zhangqiu, China). An Heraeus and a Nuve FN120 model oven and (Ankara, Türkiye) were used for the removal the moisture and carrying out the hydrothermal synthesis of toner@$CuFe_2O_4$ nanocomposites, respectively. A four-digit Shimadzu (Japan)

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ATX224R precision balance was utilized for the preparation of standard/sample solutions by gravimetrically and for weighing solid samples.

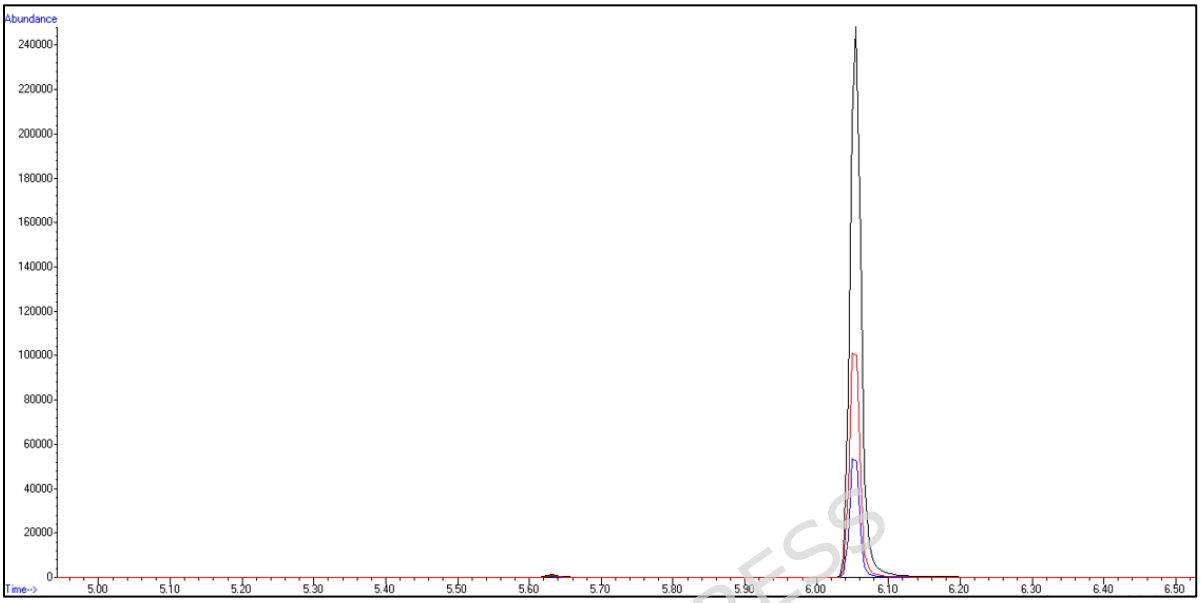


Figure 1. Chromatograms of heptachlor under optimal GC-MS conditions

2.3. Synthesis procedure for toner@$CuFe_2O_4$ nanocomposites

Toner@$CuFe_2O_4$ nanocomposites were synthesized by adopting a synthesis procedure in literature using the hydrothermal method [20]. For this purpose, 100 mg of toner was added into 30 mL of pure water and kept under ultrasonication for 60 min to enhance the dispersive characteristic. Then, 2.5 g of $CuSO_4 \cdot 5H_2O$ and 7.84 g $(NH_4)_2 \cdot Fe(SO_4)_2.6H_2O$ were added into the solution. The pH value of the resulting solution was adjusted to the range of 10.0 – 10.5 by adding 5.0 M of NaOH dropwise to adjust the pH between 10 and 10.5. After pH adjustment, the final mixture was transferred to a teflon-lined stainless steel autoclave and reacted under hydrothermal conditions at 180 °C for 24 hours. After the reaction was completed, the mixture was

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cooled to room temperature. After phase separation, nanoparticles were washed three times with ethanol and ultrapure water to remove impurities and then were dried in an oven at 50 °C for 24 hours. To improve the crystal structure of the nanoparticles, the calcination process was performed at 600 °C for 4.0 hours.

2.4. Toner@$CuFe_2O_4$ DSPE-GC–MS procedure

Initially, 25 mg of nanoparticle was weighed into a 50 mL centrifuge tube. Next, 32 mL of sample/standard solution in 1.0% ACN was added to the tube containing the nanoparticles. The pH of the sample was adjusted with 1.5 mL of pH 6.0 buffer solution. The resulting mixture was then vortexed for 40 s to ensure homogenization and then centrifuged at 3000 rpm for 3 minutes to achieve the phase separation. After centrifugation, the aqueous phase was carefully decanted and 70 µL of acetonitrile was added to elute the analytes from the surface of sorbent. Then, separated extraction phase was transferred to a suitable vial and sent to the GC-MS system for analysis.

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2.5. Samples

The feasibility of developed method was evaluated using soil samples collected from the Horseshoe Island in Antarctica. Two soil samples were left in an oven at 50 °C for one day to remove the possible moisture. The dried soil samples were then ground in a mortar to obtain a larger surface area and 1.0 g of soil was gravimetrically diluted to 20 g with ACN. The mixture was left on a mechanical stirrer for 30 minutes to ensure effective extraction.

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After the centrifugation, resulting extract phase was also filtered through a 0.45 µm PTFE filter to remove the possible particles. The filtered extracts were sent directly to the GC-MS for blank analysis under the specified system operating conditions, and no analytical signal was detected. Then, heptachlor standards at different concentrations in the range of 27 and 209 µg kg^{-1}. were added to the sample solution to perform the spiking experiments under optimum DSPME-GC-MS conditions.

3. Results and Discussion

Important extraction parameters affecting the increase in detection power of the GC-MS system including pH, buffer volume, sample volume, sorbent amount, mixing type and duration, eluent type and volume were optimized by a single-variable optimization approach. The mean peak areas and related standard deviation values were used to evaluate the optimal conditions of method.

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3.1. The characterization studies of toner@$CuFe_2O_4$

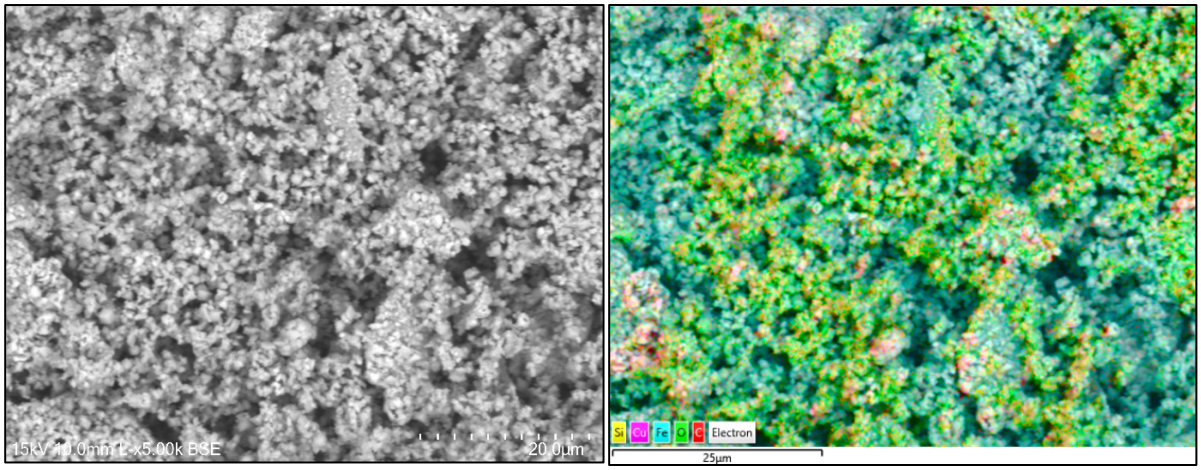
The characterization studies of toner@$CuFe_2O_4$ nanocomposites were performed for morphological investigation, identify crystalline properties, elemental mapping, evaluation of functional groups and surface charge by scanning electron microscope (SEM), x-ray diffraction (XRD) techniques, energy dispersive x-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and zeta potential, respectively. Figure 2a showed the surface of sorbent via SEM image. In Figure 2b, the EDS layered image was presented to illustrate the physical elemental distribution in structure. XRD

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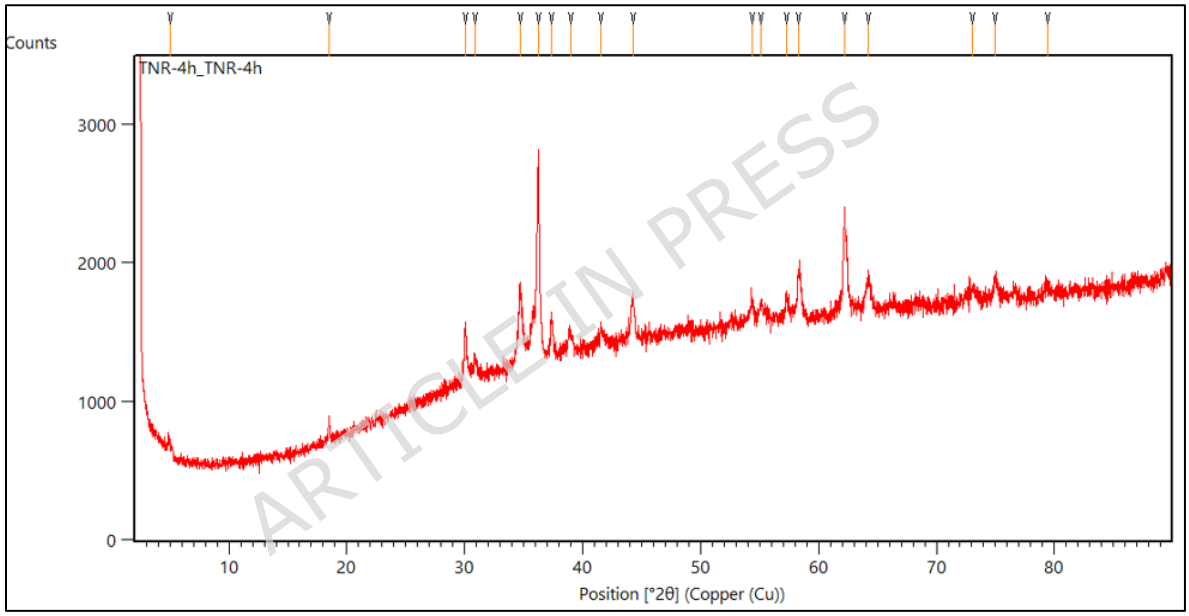
analyses were carried out at 40 mA and 45 kV generator settings, with a step size of 0.013° in the 2θ angular range of 2.0–90°. The 2θ angles obtained with Cu-Kα radiation with a wavelength of 1.5406 Å are shown in Figure 2c. The dominant peaks were observed at 18.3 (111), 30.0 (220), 36.2 (311), 44.3 (400), 58.3 (511), 62.2 (440) and 75.0 (533) was in accordance with the literature findings and presented the cubic phase of $CuFe_2O_4$ (JCPDS No. 06-0545) [21–23]. In the EDS elemental mapping shown in Figure 2d, the weight percentages of Fe, C, O, Cu, and Si were found to be 55.2%, 4.0%, 16.1%, 24.5%, and 0.2%, respectively. In FT-IR spectrum given in Figure 2j, C-O bond was observed near 1140 cm^{-1} as the stretching peak resulting of toner, while Fe-O and Cu-O bonds were recorded as spinel structure near 430 and 530 cm^{-1}, respectively [24,25]. Moreover, zeta potential of sorbent was found to be +8.6 mV with a mean count rate of 215.9 kpcs and indicates a moderately positive surface charge. These results confirm the successful formation of the toner@$CuFe_2O_4$ nanocomposite structure. Accordingly, the distribution of these elements in Figure 1b was shown individually in Figures 2e-i, confirming that they were found within the structure.

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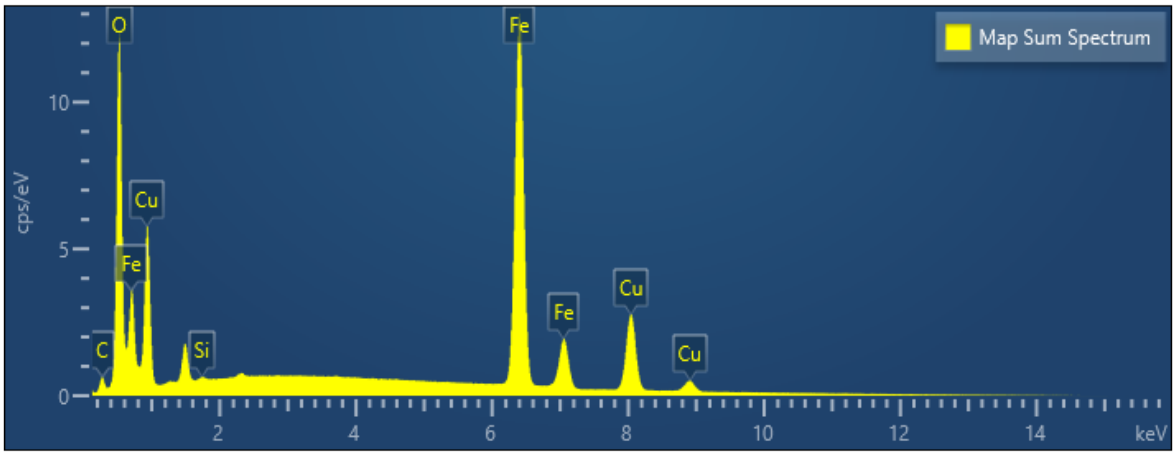
(a) (b)



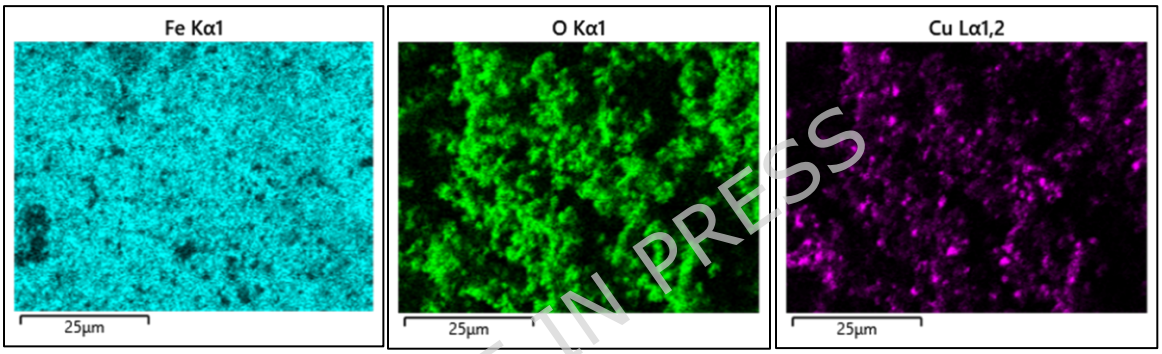
(c)

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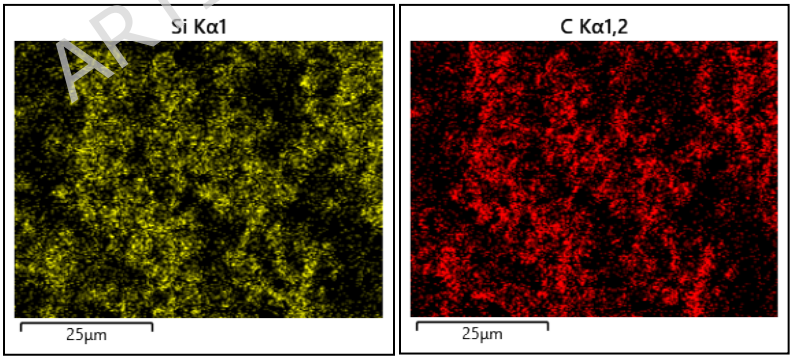
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(d)



(e) (f) (g)



(h) (i)

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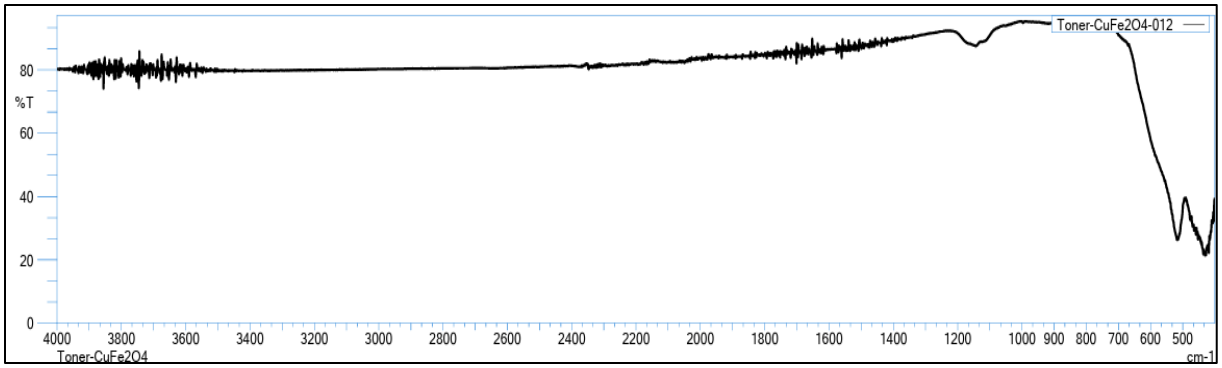


Figure 2. (a) SEM image, **(b)** EDS layered image, **(c)** XRD image**, (d)** EDS spectrum mapping, **(e-f-g-h-i)** distribution of Fe, O, Cu, Si and C in structure, **(j)** FT-IR spectrum**,** respectively.

3.2. Optimization of pH and Volume of Buffer Solution

The acidity of the medium in which the analyte is present is one of the key factors controlling the adsorption behavior of the analyte. The pH of the solution should be at an appropriate value to ensure maximum interaction between the analyte and the adsorbent and to achieve high recovery values [26]. Accordingly, the acidity level of the sample medium needs to be set based on the characteristics of the analyte and sorbent. Moreover, the stability and presence of different molecules at a specific pH level are also important for the formation of molecular interactions between the analyte and the sorbent [27]. In highly acidic aqueous environments, iron-containing nanoparticles tend to dissolve in the solution. This dissolution results in a decrease in the interaction between the analyte and the adsorbent. Additionally, at low pH levels, hydronium ions in the solution tend to interact with the nanoparticle surface rather than analyte ion(s), reducing the extraction efficiency of target analyte(s) [28]. Within this scope, five different buffer solutions in the range of pH 4.0-8.0 were tested for the evaluation the

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extraction efficiency. As seen in the results given in Figure 3, the mean peak areas increased from pH 4.0 to pH 5.0 and decreased from pH 5.0 to pH 6.0. Since repeatability of pH 5.0 lower than pH 6.0, pH 6.0 was selected as the optimal condition. Then, it was determined by additional experiments that 1.5 mL of buffer solution was sufficient for buffering the solution, and 1.5 mL of pH 6.0 was kept constant throughout the study.

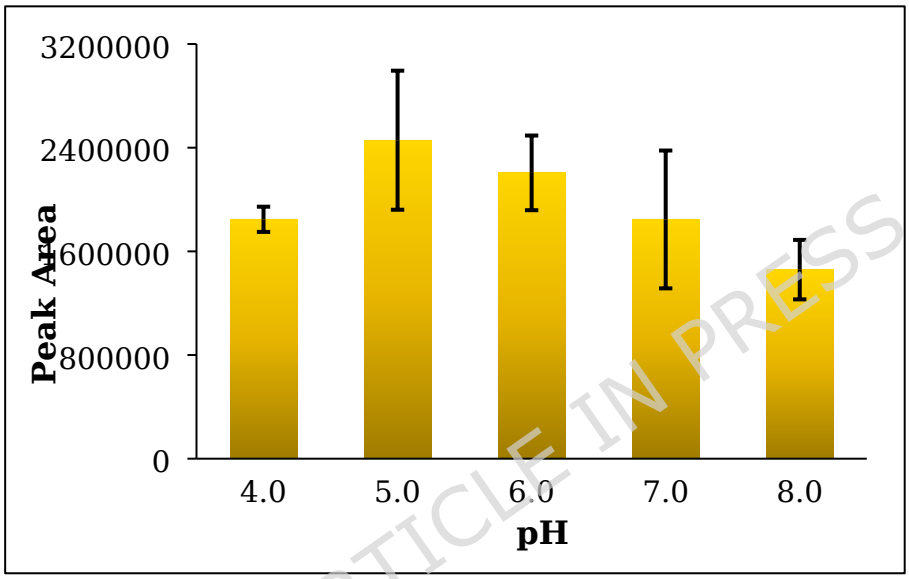


Figure 3. The impact of pH on the extraction efficiency of heptachlor (*Experimental conditions: 8.0 mL of 1.0 mg kg^{-1} heptachlor standard solution in 1.0% of ACN; 15 mg toner@$CuFe_2O_4$ nanocomposites; 30 s vortex, 75 µL of ACN for elution*) (n=3 represents the standard deviation).

3.3. The Effect of the Initial Sample Volume

Sample volume is a key factor to evaluate the adsorption capacity of sorbent, increase the preconcentration factor, and enhance the detection power [29]. However, since the use of excessive sample volumes will also increase the amount of analyte transferred to the active regions of the adsorbent, over-saturation may occur, and extraction efficiency may be negatively affected. Hence, the determination of the suitable sample volume is a crucial step in

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extraction methods [30]. In this context, extraction efficiency was evaluated under equal conditions for sample volumes of 8.0, 16, 24, 32, and 40 mL including 1.0 mg kg^{-1} heptachlor standard solution in 1.0% of ACN. As given in Figure 4, the mean peak areas showed a linear increase from 8.0 mL to 40 mL. The lowest average peak area was observed at a sample volume of 8.0 mL, while the average peak area for a 40 mL sample volume was approximately 20% higher than the value observed at 32 mL. However, considering the low reproducibility recorded for 40 mL and the fact that high sample volume usage is not compatible with an environmentally friendly approach, the optimal initial volume was selected as 32 mL.

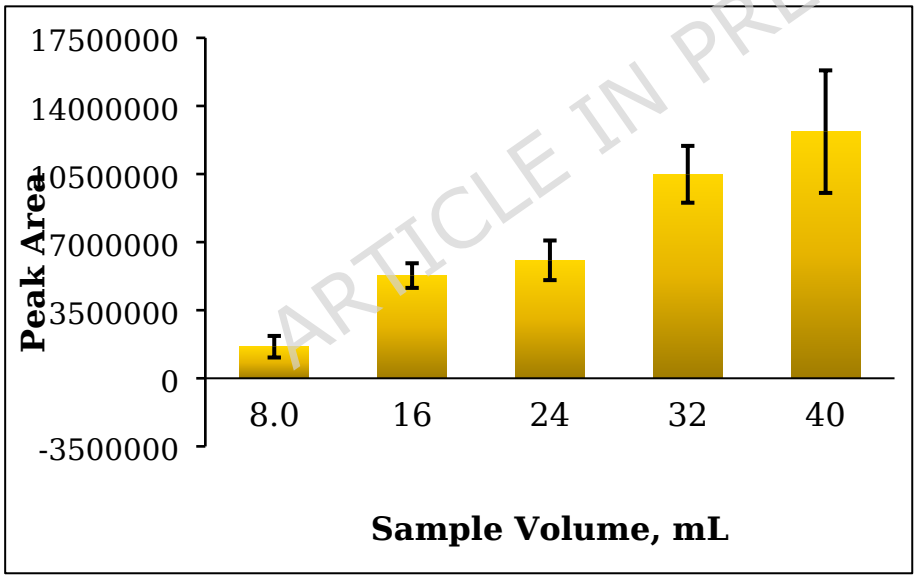


Figure 4. The impact of sample volume on the extraction efficiency of heptachlor (*Experimental conditions: different volumes of 1.0 mg kg^{-1} heptachlor standard solution in 1.0% of ACN, 1.5 mL of pH 6.0 buffer solution; 15 mg toner@$CuFe_2O_4$ nanocomposites; 30 s vortex; 75 µL of ACN for elution* (n=3 represents the standard deviation).

3.4. The Effect of Sorbent Mass

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The amount of sorbent employed is one of the critical parameters that directly affects the extraction efficiency. To elaborate, insufficient sorbent for a certain sample volume leads to low extraction efficiency due to insufficient surface area [31]. On the other hand, excessive use of sorbents increases chemical consumption, thereby increasing both process costs and sorbent consumption, which goes against the principles of green chemistry. Consequently, using the lowest possible amount of adsorbent helps reduce the volume of the elution solvent during the elution stage. As a result of this, the method becomes more environmentally friendly and sustainable [31,32]. Through this approach, extraction outputs were examined for five different sorbent masses ranging from 7.5, 15, 20, 25, and 30 mg under the same conditions, as well as for a sorbent-free solution. Figure 5 showed that the mean peak areas increased from 0 mg to 25 mg, reached the highest value at 25 mg, and decreased by approximately 20% at 30 mg. It was predicted that the desorption solution would be insufficient to elute the analytes from the total surface area for 30 mg. As a result, considering the enrichment factor and high repeatability, 25 mg was selected as the optimal sorbent amount.

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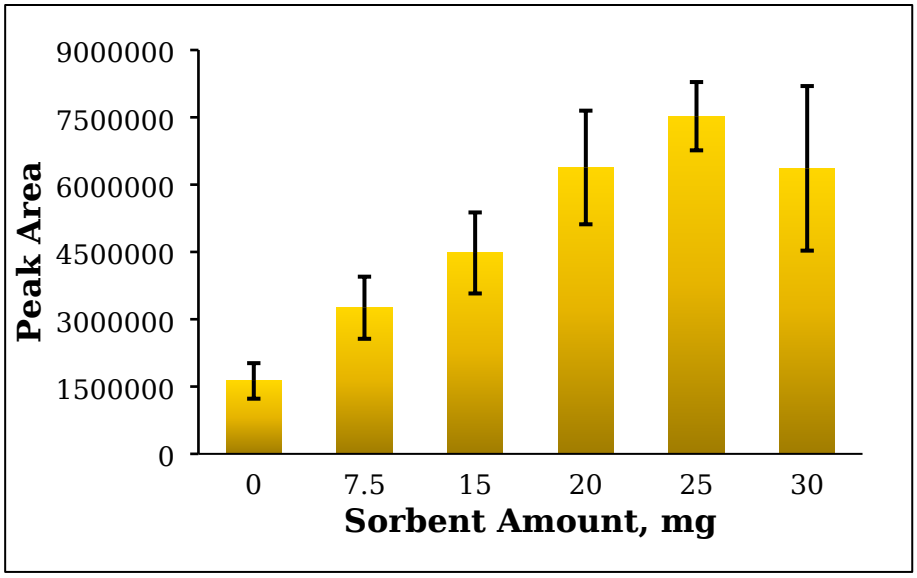


Figure 5. The impact of sorbent amount on the extraction efficiency of heptachlor (*Experimental conditions: 32 mL of 1.0 mg kg^{-1} heptachlor solution in 1.0 of ACN%; 1.5 mL of pH 6.0 buffer solution; 30 s vortex; 75 µL of ACN for elution)* (n=3 represents the standard deviation).

3.5. The Effect of the Mixing Type and Mixing Period

The interaction force between the sorbent and the analyte directly affects extraction efficiency, and various agitation methods have been used to increase the interaction between the two phase [33]. Moreover, prolonged interaction of the sorbent with the analyte solution may cause the release of analyte ions from the sorbent surface. Therefore, optimization of the agitation method and period makes an extraction protocol more efficient [34]. In this context, three different mixing types including ultrasonication, vortex and mechanical shaker were applied at first step to investigate the interactions between toner@$CuFe_2O_4$ nanocomposites and heptachlor. Here, acoustic cavitation plays a significant role as the primary driving force behind the effects of ultrasound-assisted extraction. The expansion and compression cycles caused by periodically repeated ultrasonic energy generate a

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vibration, thereby accelerating the interaction between the analytes in the medium and the sorbent material [35,36]. The vortex mixer generates strong vibrational effects and creates a turbulent vortex flow that enhances agitation efficiency, while mechanical shaker ensures continuous mixing by increasing contact between the analyte and the sorbent phase [37]. The recorded results showed in Figure 6 that the best sorbent and analyte interaction was observed by vortex agitation based on mean peak areas compared to the other methods. Consequently, vortex was selected as the optimal mixing type. Then, six different mixing period ranging from 10 to 50 s, and 0 s (no-mixing) were examined by vortex under equal conditions at a constant stirring rate of 3000 rpm. It was observed that the mean peak areas increased from 0 to 40 s and close results were recorded between 40 s and 50 s. Therefore, 40 s was selected as the optimal mixing period.

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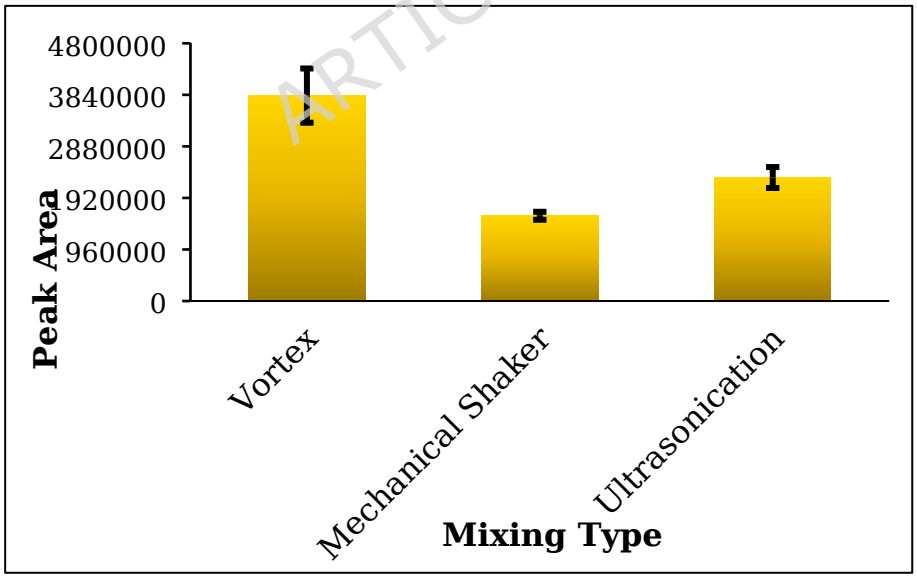


Figure 6. The impact of mixing type on the extraction efficiency of heptachlor (*Experimental conditions: 32 mL of 1.0 mg kg^{-1} heptachlor solution in 1.0 of ACN%; 1.5 mL of pH 6.0 buffer solution; 25 mg*

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toner@$CuFe_2O_4$; 75 µL of ACN for elution) (n=3 represents the standard deviation).

3.6. Effect of the Desorption Solvent Type and Volume

The desorption process of the analyte(s) and sorbent is primarily dependent on the type of eluent used throughout the preconcentration protocol. At this point, the eluent helps break the interaction between the sorbent and analyte(s). For an extraction procedure, major eluent criteria include compatibility with the analyte and sorbent, the ease of separation of the analyte(s) from the sorbent, and the ability to form complexes [38]. Three different types of organic eluents acetonitrile, ethanol, and methanol were evaluated to investigate the effective desorption of the heptachlor from the toner@$CuFe_2O_4$ nanocomposites surface. No significant difference in desorption ability was observed between the mean peak areas obtained from the three tested eluent types. Therefore, acetonitrile was selected as the desorption solvent due to high repeatability.

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Moreover, it is important to keep the eluent volume at low levels provides an increase in the enrichment factor considering the signal to noise ratio [39]. Therefore, different acetonitrile volumes ranging from 50 to 150 µL were added for the desorption of heptachlor analytes. As shown in Figure 7, the mean peak areas obtained for heptachlor gradually decreased as the eluent volume increased due to the dilution of the analyte. Additionally, the highest two mean peak areas were recorded for 50 µL and 70 µL. Although the highest mean peak area was recorded at an eluent volume of 50 µL as a

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numerical output, considering the phase collection difficulties for 50 µL during the operation and the possibility of reduced desorption capability, especially in complex samples, the optimum acetonitrile volume was determined to be 70 µL, where high reproducibility was achieved.

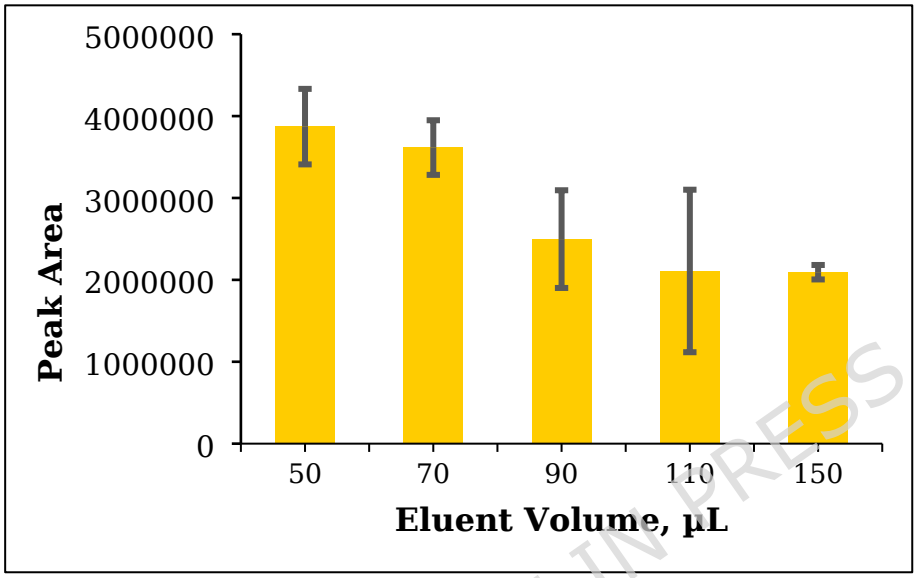


Figure 7. The impact of eluent volume on the extraction efficiency of heptachlor (*Experimental conditions: 32 mL of 1.0 mg kg^{-1} heptachlor solution in 1.0 of ACN%; 1.5 mL of pH 6.0 buffer solution; 25 mg toner@$CuFe_2O_4$; 40 s vortex*) (n=3 represents the standard deviation).

3.7. Assessment of the system analytical performance

Analytical parameters such as limit of detection (LOD), limit of quantification (LOQ), determination coefficient (R^2), linear operating range, and % relative standard deviation (%RSD) are crucial for the analytical evaluation of the developed systems. All standard solutions were prepared gravimetrically using a sensitive balance. The calibration plot was established with six different concentrations ranging from 10.8 to 517.5 µg kg^{-1}. For all concentrations except 10.8 µg kg^{-1}, the mean peak areas were calculated from three replicate measurements. Signal to noise (S/N) ratio was defined

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as the ratio of the peak height of the heptachlor to the baseline noise. LOD and LOQ calculations were performed by multiplying the standard deviation of the lowest concentration (S/N≥3) at least 7 replicates on the linear calibration plot by three and ten, respectively, and dividing by the slope of each plot equation. Accordingly, under optimal experimental conditions *(32 mL of sample containing 1.0% ACN, 1.5 mL of pH 6.0 buffer solution, 25 mg toner@$CuFe_2O_4$ nanocomposite, 40 s vortex, 70 µL of ACN*), LOD and LOQ were found to be 6.2 and 20.6 µg kg^{-1} for GC-MS and 0.61 and 2.03 µg kg^{-1} for toner@$CuFe_2O_4$ based DSPME-GC-MS, respectively. The increase in the sensitivity of the GC-MS system was determined to be 68.5 by comparing the slopes of the calibration plot equations with the unit of µg/kg for the improved GC-MS (y=7077.5x+360.05) and GC-MS (y=103.39x-44279) systems. %RSD was 10.7% for the lowest concentration in calibration plot. The recorded analytical numbers for each system were summarized in Table 1.

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Table 1. Analytical performance of the GC-MS and toner@$CuFe_2O_4$ based DSPME-GC-MS

Method	LOD, µg kg^{-1}	LOQ, µg kg^{-1}	R^2	Linear Equation (µg kg^{-1})	Enhancement in sensitivity
GC-MS	6.2	20.6	0.9997	y = 103.39x - 44279	-
Toner@$CuFe_2O_4$-DSPME-GC-MS	0.61	2.03	0.9989	y = 7077.5x + 360.05	68.5

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3.8. Assessment of Literature Outputs for the Heptachlor Determination

The analytical performance of the developed method was assessed with similar extraction methods using DSPE, as reported in the literature for the detection of heptachlor and other organochlorine pesticides. The relevant results are shown in the Table 2.

Table 2. A literature brief for the evaluation of analytical performance of other methods

Analytical Method	LOD	Linear Range	R^2	EF*	Reference
IL-µSPE-GC-MS[1]	0.36 µg L^{-1}	1.0 – 100 µg L^{-1}	0.9974	35.9	[40]
AuNPs-SPME-GC-ECD[2]	0.13 µg L^{-1}	1.4 – 7.0 µg L^{-1}	0.9880	-	[41]
TF-SPME-GC-MS/MS[3]	1.6 µg L^{-1}	100-900 µg L^{-1}	≈0.93	-	[42]
SF-SPME-GC-ECD[4]	0.17 µg L^{-1}	1.0 - 1000 µg L^{-1}	0.9926	-	[43]
Toner@$CuFe_2O_4$-DSPME-GC-MS	0.61 µg kg^{-1}	10.8 to 517.5 µg kg^{-1}	0.9989	68.5	This study

[1] *Ionic liquid micro-solid-phase extraction-gas chromatography-mass spectrometry*

[2] *Gold nanoparticles-solid-phase microextraction-gas chromatography-electron capture detection*

[3] *Thin film-solid-phase microextraction-gas chromatography-tandem mass spectrometry*

[4] *Multiwalled carbon nanotubes/polypyrrole composite coated on steel fiber based solid-phase microextraction-gas chromatography-electron capture detection*

**Enhancement factor*

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In 2021, Hassan et al. synthesized two ionic liquids based on 4-methylbenzenamine tetrachloroferrate (III) and 1-naphthylammonium tetrachloroferrate (III) for the preconcentration of heptachlor in environmental water samples. They achieved a LOD of 0.36 μg L^{-1} and an enrichment factor of 35.9 in the GC-MS system using the ionic liquids, which are solid at room temperature, as sorbents [40]. In 2017, Gutiérrez-Serpa et al. synthesized Au nanoparticles as a sorbent for the determination of heptachlor at low levels and recorded an LOD of 0.13 μg L^{-1} in a GC-electron capture detection (ECD) system with a narrow working range [41]. Most recently, Poojary and Ghosh introduced a carbon fiber-based thin film-supported SPME method for the determination of heptachlor in the GC-MS/MS system. The developed method had an LOD of 1.6 μg L^{-1} while the linear working range included very high concentrations of 100-900 μg L^{-1} [42]. Asadollahzadeh and Noroozian synthesized the multiwalled carbon nanotubes/polypyrrole composite to achieve the extraction of heptachlor and a LOD of 0.17 μg L^{-1} was reported in GC-ECD system [43]. As seen, the toner@$CuFe_2O_4$-based DSPME-GC-MS method developed within the scope of this study is comparable to the expensive and complex systems mentioned in other studies, and even offers an alternative for the high-accuracy determination of heptachlor at different concentrations. On the other hand, enhancement factor of many studies was not reported in related manuscripts. Despite of them, the toner@$CuFe_2O_4$-based DSPME-GC-MS method presented an enhancement in sensitivity as 68.5-fold. Additionally, the

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process of recycling toner waste contributes to the creation of high additional value.

3.9. Recovery Studies

The reliability of an analytical method is evaluated not only by accuracy and precision but also by recovery test results. Recovery studies are a critical stage in investigating the measurement efficiency of the analyte after extraction in the real sample. The low recovery percentages obtained may indicate systematic errors such as losses during the adsorption process, matrix-related interference effects, or insufficient extraction efficiency. Hence, recovery tests are one of the key parameters in method validation, especially for trace levels of analyte(s), demonstrating the applicability of the method to real samples and the reliability of quantitative results. The real samples were specified in the “Samples” section of the preparation stage. Accordingly, the soil samples were extracted with ACN and extracts were spiked at four different concentrations in the range of 27 and 209 μg kg^{-1} containing the 1.0% of ACN following blank analyses. The peak areas obtained from measurements performed after the extraction procedure under optimal conditions were evaluated using the external calibration equation. Recovery results of around 130% for all samples indicated the presence of positive interference. Hence, the matrix matching calibration plot equations were generated based on the measurement results against the concentration of each sample. The percentage recovery results for one soil sample were determined using the calibration plot derived from the other soil

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sample, and vice versa. As presented in Table 3, the percentage recoveries for heptachlor were between 93.2% and 105.7 and these results showed the applicability of developed method with high accuracy.

Table 3. Recovery calculations of soil samples employing external and matrix matching calibration strategy (n=4).

	Spike Concentration, µg kg^{-1}	**External Calibration Recovery ± SD, %**	**Matrix Matching Calibration Recovery ± SD, %**
SOIL 1	62.5	118.1 ± 16.5	94.4 ± 12.3
	118.4	128.1 ± 9.0	98.7 ± 6.7
	207.4	139.4 ± 6.9	105.7 ± 5.1
SOIL 2	62.9	127.3 ± 9.0	93.2 ± 6.6
	118.0	128.4 ± 27.1	94.3 ± 20
	209.5	132.3 ± 4.0	97.1 ± 2.4

**SD: Standard Deviation*

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3.10. Assessment of greenness of the developed DSPME-GC-MS protocol

Today, many scientists adopt the principle of “green chemistry compatibility” in the methodologies they develop/present. In addition to the analytical goals of the study, environmental sensitivity and practical applicability are also considered. The green chemistry concept, which includes twelve fundamental principles, was introduced to the scientific community by Anastas and Warner and has gained worldwide acceptance [44]. Consequently, sustainability has

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been considered in scientific studies for the protection of human health and the environment, and various tools such as BAGI [45], Eco-Scale [46], AGREEprep [47], AMGS [48], ComplexGAPI [49], and GAPI [50] have been developed to ensure objective green assessments. Among them, The blue applicability grade index (BAGI) is an important tool utilized as a complement to green chemistry and combines the analytical, ecological, and practical targets of an analytical method based on the red-green-blue (RGB) model with the blue category, which encompasses time efficiency, cost efficiency, requirements, and practicality properties [45]. In the “Eco-Scale” tool, penalty points determined based on the type and amount of chemicals and reagents employed in the procedure, the instruments utilized, and the amount of waste generated are deducted from a total of 100 points, and the environmental friendliness of the experimental procedures is evaluated based on the final score [46]. In this study, BAGI score was found to be 65 based on the criteria list of tool and Eco-scale score was calculated as 85 considering the penalty points. These results demonstrated that the proposed method has excellent green and practical properties.

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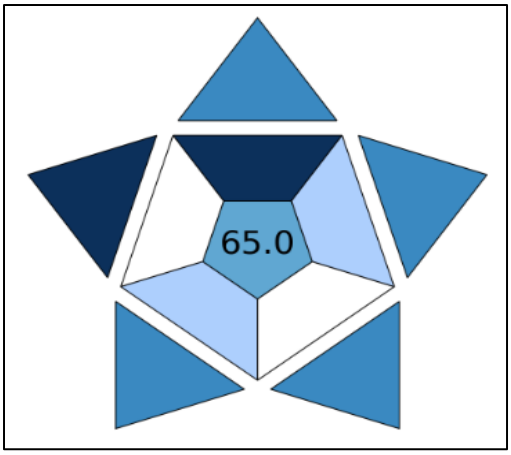


Figure 8. BAGI pictogram of developed method

4. Conclusion

Organochlorine pesticides are still widely used. It is important to monitor these chemicals, which cause serious health problems for humans and other living organisms, not only in products intended for consumption but also in natural environments such as soil and water that come into close contact with these products. In this study, an easy-to-apply, environmentally friendly, and innovative analytical method was developed for the determination of heptachlor. Under the optimal conditions determined by a univariate optimization approach, LOD was calculated as 0.61 μg kg^{-1} and the sensitivity of the GC-MS system was improved by 68.5-fold. The feasibility of the developed method was investigated through recovery studies performed on soil samples, and the recovery results obtained at nearly 100% by the matrix matching calibration strategy demonstrated the analytical suitability of the method. The assessment of the green and analytical applicability of the method was carried out using the Eco-scale and BAGI tools, and the recorded

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scores of 85 and 65, respectively, indicated that the method is environmentally friendly and analytically applicable. It is expected that the developed toner@$CuFe_2O_4$ based DSPME method will contribute to the approach of developing economically valuable methods by converting waste into useful tools, as well as offering ease of application and high extraction efficiency. On the other hand, it is anticipated that the DSPME method developed with a nanocomposite synthesized through an innovative perspective will contribute to the limited number of studies reported in the literature on the determination of heptachlor.

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None

Conflict of Interest

The authors declare that they have no conflicts of interest.

Data Availability

Data will be made available with reasonable request.

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Author Contributions

Esra Sultan Doru: Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. Büşra Ali: Formal analysis, Methodology, Validation, Writing – original draft. Hakan Serbest: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. Sezgin Bakirdere: Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – review & editing.

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