

RESEARCH ARTICLE

Comparison of Solid Phase Extraction Based on MIP and DLLME for Separation of Fenpyroximate Pesticide from Aqueous solution

ANAHITA MORADIDOUST¹, ALI MAZLOOMIFAR^{2*}, ALI AKBAR SAFEKORDI³, MOHAMMAD YOUSEFI², KAMBIZ LARIJANI¹

¹Department of Chemistry, Science & Research Branch, Islamic Azad University, Tehran, Iran, Email: mazloomifar@iausr.ir

²Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran

³Department of Chemistry Engineering, Sharif University of Technology, Tehran, Iran.

*Corresponding Author

ABSTRACT

In this paper, we evaluate the performance of molecular-imprinted polymer (MIP) and dispersive liquid-liquid microextraction (DLLME) methods for extraction and separation of Fenpyroximate (Fen) pesticide from aqueous samples. The effective parameters for pesticide microextraction such as adsorbent dose, pH, contact time, stirring rate, to achieve high removal percentage were studied using the response surface method. The effect of influencing factors on microextraction, such as type and volume ratio of dispersive and extractive solvents, salt concentration, pH, and extraction time were investigated and optimized. The maximum recovery (94 %) of the pesticide was obtained using 0.55 wt. % MIP as an adsorbent in pesticide solution with pH 5.9 at 512 rpm on 58 minutes. However, the recovery efficiency (93%) was achieved by DLLME with an extraction solvent-to-dispersive volume ratio of 25 /75, the salt concentration of 3.5 wt. %, and pH 6.0, during 72 seconds of extraction time. This high separation efficiency is achieved in a very short time. The reason is the structure of this method, because in DLLME the transfer level of aqueous and organic phases reaches its maximum value, and as a result, the largest extraction will be achieved. The results showed that both extraction methods have high potential to effectively reduce pesticides from aqueous solutions, but, DLLME method is suggested to have higher priority due to the very short separation time.

KEYWORDS:

Molecularly Imprinted Polymer, Dispersive Liquid Liquid Microextraction, Fenpyroximate, Pesticide Removal, Statistical Modeling.

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INTRODUCTION

The growth of the population has led to the uncontrolled entry of chemical fertilizers, pesticides, hormone products, and other environmental hazards into the agricultural sector, so that it can respond to the growing demand for food [1]. But this increase in production has been accompanied by numerous environmental problems such as pollution of water resources as

well as problems for humans. In modern agriculture, pesticides are chemical toxins widely used to develop crops and control plant pests [2]. Fenpyroximate pesticide, ortus brand (Ortus SC5%) is a miticide from Phenoxypyrazol chemical group with very high contact and infiltration ability to control quadrupeds and octopuses'pests, used as a suspension (SC5%) [3]. This pesticide is stable in weakly acidic and alkaline solutions and is also resistant to sunlight (UV) and rainfall. This compound has

high gastrointestinal toxicity but poor skin toxicity on humans and homothermic animals [4]. Since water pollution is one of the major challenges of the present century, it is therefore imperative to research the treatment and removal of hazardous substances from both the land and the aquatic environment [5]. Depending on the conditions, the toxic pollutants from the environment can be removed by physical, chemical, biological, or hybrid processes, including membrane filtration, photocatalytic ozonation, coagulation, advanced oxidation, ion exchange, and microextraction. Micro-extraction methods are a new approach to sample preparation, which has grown tremendously in the last decade. The molecular-imprinted polymer (MIP) method is a suitable alternative in separation studies, due to its simplicity, low cost, high sensitivity, and the possibility of automating the extraction. This extraction method is either solvent-free or requires a small amount of solvent so it is a green and environmentally friendly method in extraction processes. Also, solid-phase microextraction is possible, using a small sample volume (a few milliliters or less) [6]. Besides, the dispersive liquid-liquid microextraction (DLLME) method is also a fast and easy extraction method based on the contact surface between the two liquid phases. In this method, the centrifuging step, which is a time-consuming step in the extraction, is eliminated, and it also allows the use of lower-density solvents as the extraction solvent on the DLLME. Thus, it expands the applicability of a larger range of extractive solvents [7]. Response surface modeling was also used to optimize the fenpyroximate (Fen) removal conditions. Response surface modeling (RSM) is a statistical technique by which a limited number of experiments are systematically performed in addition to obtaining information on the effect of experimental variables on the response, it can also predict optimal operating conditions [8]. So far, RSM techniques have been used to optimize the removal conditions of some pesticides by adsorption. This method significantly reduces the number of tests required to achieve optimal conditions.

The central composite design (CCD) method was used to investigate the extraction rate in RSM. This method is examined at five levels for each agent and allows for careful investigation of response variations by factors. For this purpose, the experimental design of the CCD, which is one of the most practical of response surface designs, were conducted [9].

EXPERIMENTAL

Chemicals and Devices

Fenpyroximate pesticide (97%) was obtained from Dr. Ehrenstorfer Chemicals (Augsburg, Germany). Molecular Imprinted Polymer (MIP) particles were prepared from Ethylene Glycol Dimethacrylate (EGDMA, purity: 98%) as a crosslinking agent and methacrylic acid (MAA, 98%) as a functional monomer, both purchased from Merck, Germany. Also, 2, 2-

azobis(2-methyl propionitrile (AIPN, 98 %, from Sigma-Aldrich Co) was used as an initiator. Phosphoric acid (65%, Merck, German) and sodium hydroxide (99%, Merck, German) was used to prepare phosphate buffer solutions as a carrier electrolyte. In this study organic solvents were used for various applications; for example, as mobile phase in high performance liquid chromatography or dispersing solvent and extraction solvent such as carbon tetrachloride, dichloromethane, chloroform, benzyl chloride, acetonitrile, methanol, ethanol, and acetone. All solvents were obtained from German Merck. The high Performance Liquid Chromatography (HPLC), model Agilent 1290 Infinity II with four-solvent equipped with EX 1600 UV detector was used. This device contains a constant injection volume of 10 μ L. The C- 18 non-polar columns, with a diameter of 4.6 mm and a length of 250 mm, gives us the best separation with the machine conditions. The 827 metrohm pH meter was used to measure the pH of the solutions. The apparent structure of the MIP particles was studied using Mira 3-XMU field emission scanning electron microscope (FESEM). The presence of functional groups of synthesized MIP particles and the interaction between MIP particles and pesticides were investigated using the infrared spectroscopy method on Bruker-tensor 27.

Synthesis of MIP

Molecularly Imprinted Polymer particles for Fen pesticide (Fen-MIP) were synthesized through copolymerization of MAA and EGDMA. To this end, 0.3 mL MAA as a monomer, 35.0 mL of dry chloroform as a solvent, and 0.2 g of Fen as a molecular template were combined and placed in a 100.0 mL round-bottomed flask, and the mixture was kept isolated for 15 min. Then, 20.0 mL of EGDMA as a crosslinker and 0.22 g of AIBN as initiator were added to the mixture, the flask was then sealed, and the mixture was purged with N₂ gas for 15 min. The copolymerization was completed in a water bath at 65.0 °C within 24 h. For removal of pesticide molecules from polymer structure, the resulting copolymer was dried and ground, and then washed at 10.0 %v/v acetic acid in methanol for 24 h. Therefore, no Fen was detected in the solvent from the washing polymer by HPLC. In the next step, the synthesized polymers were washed three times with deionized water to remove the washing solution. The synthesized polymer particles were then dried in an oven at 55 °C. Non-imprinted polymer (NIP) particles were also synthesized by a similar procedure, except that the MAA polymerization was performed in the absence of Fen molecules.

Removal of Fen by MIP

To obtain the highest rate of pesticide removal from aqueous solution by MIP based SPME, independent variables such as solution pH (2.0-10.0), MIP dose (0.1 -1.0 g), the contact time of polymer particles with the solution (10 - 75 min) and stirring

rate of solution (400 - 800 rpm) were chosen and their effects on the removal of pesticide from the solution were investigated. Using MIP particles, the pesticide extraction conditions were optimized based on the response surface statistical method, and a mathematical model was developed to predict pesticide removal from the solution. Indeed, with the help of this statistical method and with the least number of experiments, the simultaneous effect of all four independent

variables and their interactive impact on pesticide removal was studied comprehensively. The design of experiments, statistical analysis of the obtained data, and mathematical modeling was performed using Design of Expert V.11 software package. By introducing the variables and their studied levels into the software (Table 1), 30 tests were proposed to optimize the conditions.

Table 1: Experimental Range and Levels of the Independent Variables

Parameters	Unit	Symbol	Levels				
			- α	-1	0	1	α
pH	-	A	2	4	6	8	10
MIP	g	B	0.1	0.33	0.55	0.75	1
Time	Min	C	10	26.25	42.50	58.75	75
Stirr S	rpm	D	400	500	600	700	800

The microextraction of fenpyroximate pesticide by MIP-SPME was performed in optimum conditions as follows: 590 mg of MIP particles was added to 100 mL of 0.1 M phosphate buffer at pH 5.9 (as adsorption solution) containing 100 ppm pesticide and stirred for 58 minutes at 512 rpm on a magnetic stirrer (Falcon 100) until a balance was created between the polymer and the pesticide solution. The resulting mixture was then centrifuged for 10 minutes at 5000 rpm (centrifuge device, Eppendorf, MiniSpin, Germany). The supernatant was prepared by the passage of the solution in a 0.22 μm syringe filter for HPLC analysis. The concentration of residual pesticide in solution was obtained by HPLC equipped with a UV-100 detector. Each solution was prepared and tested in three replications. The pesticide removal was calculated based on extraction recovery (ER %) using the following equation (1) :

$$ER (\%) = \frac{C_0 - C_f}{C_0} \quad (1)$$

Here, C_0 and C_f are the initial concentration and residual concentration of the Fen in the solution. In addition, the adsorption capacity of NIP and MIP particles for removal of Fen from aqueous was compared. In these tests, both polymers (NIP or MIP) were added to solutions containing pesticides and the separation process was carried out under optimum conditions. The polymer was then mixed with 3 mL of desorption solution (acetic acid/methanol) and stirred for 1 one hour in the shaker

at a speed of 200 rpm. The mixture was then centrifuged at 10,000 rpm for 10 minutes. The concentration of the pesticide in the supernatant solution (C_{ads}), which was the same as the amount absorbed by the polymer particles, was detected by HPLC. The adsorption capacity of polymer particles (Q) (mg/g of polymer) was calculated using the following equation.

$$Q = \frac{C_{ads}V}{m} \quad (2)$$

Where V is the volume of the solution (mL) and m is the amount of used polymer particles (g).

Removal of Fen by DLLME

To obtain the best conditions for the removal of pesticides from the solution by using DLLME, with the highest removal efficiency, four operational factors including extraction solvent to dispersant solvent ratio (chloroform ratio to acetonitrile - 10 - 90 % v/v, namely; Sol ratio), extraction time (20 - 160 s), solution pH (3-11) and salt concentration (0.1 - 15.0 wt.%) were selected as independent variables affecting pesticide removal efficiency. Optimization of pesticide removal conditions was performed using response surface methodology and the design of experiment package software (V. 11). The studied variables and their range of studies are listed in (Table 2). This software designs 30 tests based on the CCD method.

Table 2: Experimental Range and Levels of the Independent Variables of Dispersive Liquid-Liquid Microextraction

Parameters	Unit	Symbol	Levels				
			- α	-1	0	1	α
Sol Ratio	v/v	A	10	30	50	70	90
Salt	%wt	B	0.1	3.825	7.55	11.275	15
pH	-	C	3	5	7	9	11
Time	s	D	20	55	90	125	160

The extraction process was performed in the optimal conditions as follows: 0.1 mL of 100 ppm pesticide solution was added to 100 mL distilled water to reduce the standard sample concentration to 1 ppm. Then, 5.0 mL Fen pesticide (1 ppm) was transferred into the test conical tube, and 0.12 g of salt was added to it, and then the tube was shaken well until the mixture was completely dissolved. 300 μ L mixture of extraction-dispersive solution (25/75) was injected to the solution containing Fen, and the pH of the solution was adjusted to 6.0 with hydrochloric acid and ammonia. (The buffer solution cannot adjust the pH, as it may interfere with the ionic content in the solution and change the solution nature). The tube sealed and the solution was shaken for 72 seconds (extraction time) to form a cloudy solution. The tube was then centrifuged at 2000 rpm for five minutes. The solution was transformed into two phases. In the lower phase, which is the organic phase, the solution was placed at the bottom of the tube, because of its heavy weight. The upper solution was separated by a syringe and injected directly into HPLC to determine the amount of pesticide. The efficiency of the DLLME method is characterized by an enrichment factor (EF) and extraction recovery (ER). Enrichment factor (EF) is calculated as shown in (3), where C_0 represents the initial concentration of the analyte in the sample, and C_{sed} represents the concentration of the analyte in the sedimented extraction solvent. The ER is also calculated

according to (2).

$$EF = \frac{C_{sed}}{C_0} \quad (3)$$

RESULTS AND DISCUSSION

Determination of Fen by HPLC

Detection of pesticide (Fen) in samples was performed using HPLC. In order to draw the calibration curve, standard solutions of pesticides were made in the concentration range of 10 - 500 ppm; then these solutions were injected on the machine. The amount of Fen was identified with a UV detector at the wavelength of 285 nm as an area under the plotted curve. The calibration curve of the pesticide was obtained by plotting a linear diagram of the area under a curve in terms of pesticide concentration (Figure 1). To measure the concentration of pesticide in the unknown sample, 1.0 μ L of the solution was inserted into the HPLC apparatus with a syringe and then its chromatogram was recorded. The concentration of the unknown sample was calculated by applying the area under the chromatogram curve obtained at each stage of the microextraction process in the equation on the calibration curve ($y = 161.74x + 6573.1$). In the measurements, pure acetonitrile was selected as the mobile phase with a solvent elution flow of 1 mL/min at 285 nm.

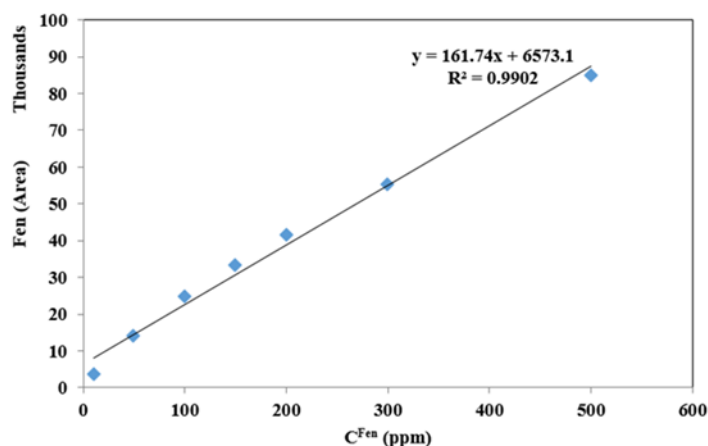


Figure 1: Calibration Curve of Fen Pesticide at 10 - 500 ppm.

Absorption Capacity of MIP and NIP

To evaluate the adsorption capacity of the synthesized polymer particles in pesticide removal, a series of solutions with a certain concentration of pesticide (25 - 150 ppm, mg/L) were prepared. Then, 590 mg of MIP (or NIP) was added to 0.5 mL of pesticide solution with pH = 5.9 and stirred on a magnetic stirrer for 58 minutes at 512 rpm. The polymer particles were separated from the solution by centrifuging and were placed in a desorption solution (1.0 % v.v acetic acid in methanol) for one hour. The mixture was then centrifuged at 10,000 rpm for 10

minutes. The concentration of pesticide in the supernatant solution was obtained by HPLC. Figure 2 shows the amounts of pesticide extracted from MIP and NIP particles versus different concentrations of Fen. It is apparent in this figure that the amount of pesticide extracted in both polymers increases with increasing the initial pesticide concentration to 100 ppm and then reaches a constant value. It can also be seen that the extraction capacity of MIP and NIP is 13.89 and 2.0 mg/g, respectively. These indicate high adsorption capacity and high affinity of MIP particles to Fen pesticide compared to NIP particles. MIPs have a higher extraction rate due to the

presence of molecularly imprinted sites compared to NIPs. This result showed that the synthesis of MIP was performed well and

that these polymers have the capability of selectively extracting the pesticide molecules.

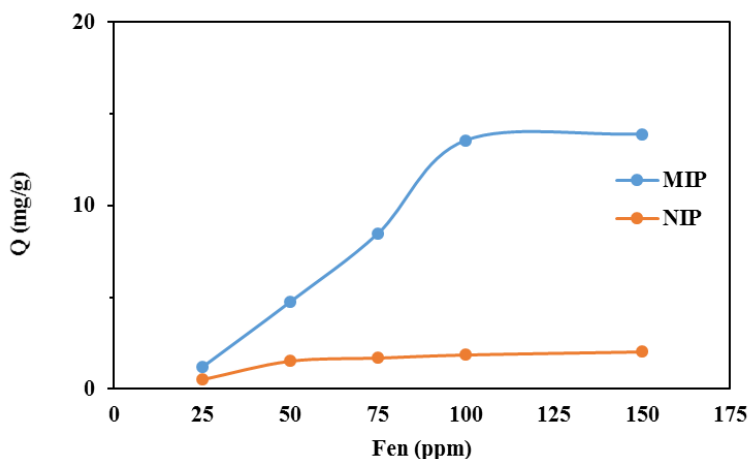


Figure 2: Comparison of the Adsorption Capacity of MIP and NIP for Removal of Fen Pesticide

Optimization of Microextraction Conditions

Response Surface Methodology (RSM) is a set of statistical techniques used to optimize the processes in which the response is influenced by several variables. The graphical representation of the mathematical model defines the term of response surface method. The number of experiments is reduced with the help of this statistical design, and all the coefficients of the quadratic regression model and the interactions of the factors can be estimated [10]. In this study, RSM was used for both extraction methods for the separation and removal of Fen pesticide. In SPE, the effects of pH, contact time, amount of MIP particles, and stirring rate as independent variables were investigated at five levels on extraction recovery. In DLLME, the effects of the ratio of the dispersive solution to extraction solution, salt concentration, pH, and extraction time as independent variables were evaluated in five levels. Besides, the type of extraction solvent and the type of dispersive solvent were also investigated by the single-factor method.

MIP

For the extraction of Fen pesticide under optimum conditions, four influencing factors including pH, time, amount of MIP particles, and solution stirring rate were investigated. As previously mentioned, the central composite design (CCD) was used to design the RSM. The design of the experiment led to drawing the response surface curve and reaching the optimum point for SPME. In the CCD, the number of factors studied was four and the number of tests required was $4 + 26$. Sixteen experiments were performed at axial points (24), eight tests at star points, and six at center points. The corresponding 3D

curves are plotted based on the polynomial function model to analyze the effect of operational parameters on extraction recovery. Surface response curves (3D) can be useful in understanding the effects of selected independent variables. These diagrams can be considered as a method to predict extraction recovery for different amounts of tested variables.

Figure 3 shows the surface response diagram for the interaction between pH and the amount of MIP particle on extraction recovery, when the extraction time and stirring speed were 49 min and 551 rpm, respectively. The extraction recovery increased linearly with increasing pH in the range of 2.0 to 6.0 and decreased in alkaline conditions, namely, 6.0 to 10.0, respectively. In general, the relationship between extraction efficiency and pH can be related to the surface conditions and surface charge of MIP particles and pesticide molecules. In the molecular imprinting process, reversible bonds are formed between the functional monomers (herein methacrylic acid) and the template molecule (Fen), which usually includes reversible covalent bonds, electrostatic interactions, coordination with metal core or hydrophobic or van der Waals [12]. In this work, non-covalent bonds based on the hydrogen bonds between the template molecule (Fen) and the functional monomers of MAA and EGDMA could easily be formed between the -OH groups and the C=O, OH- and O- groups in the synthesis process of the MIP. Given that the PKA of the MAA monomer is 4.65, it can be expected that the functional groups of R-COOH in MAA will be deprotonated in mildly alkaline and acidic medium (>4.65) and converted to R-COO-. However, Fen functional groups have positive partial charges or at least neutral ones. It is therefore proposed that hydrogen bonds be formed between COO- and H bonded to O on Fen or COO- on Fen and -OH on MAA, thereby Fen being adsorbed on specific sites

and accumulating on the surface of the MIP particles. It is also seen that increasing the amount of MIP particles to the optimum amount has a positive effect on extraction recovery. In this regard, it can be stated that the higher the MIP particles

in the SPME, the higher the number of active and specific sites for the adsorption of pesticide molecules. As a result, more pesticide molecules are adsorbed onto the MIP particles and removed from the solution during the extraction process.

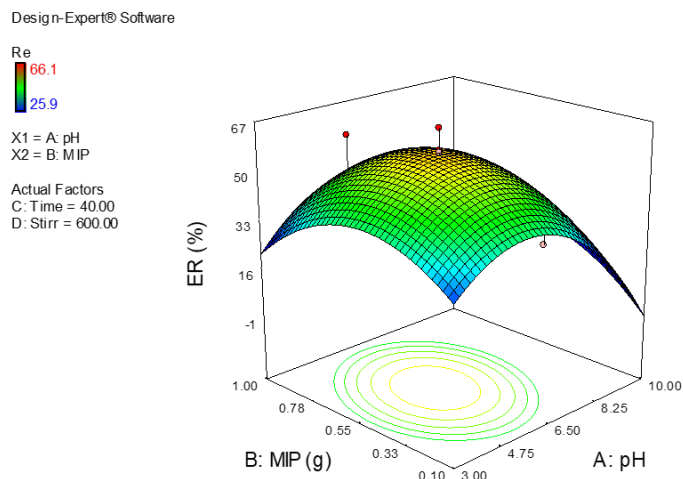


Figure 3: Three-dimensional Representation of Interaction Effect of MIP - pH on Fen Extraction Recovery.

Figure 4 shows a 3D surface curve of the interaction between the time and the stirring rate of the solution on the extraction recovery, when the pH and the amount of MIP particles were 5.35 and 0.28 % wt, respectively. As can be seen from the figure, extraction recovery increased with increasing the contact time from 10 to 58 minutes and then reached a constant value. Contact time is one of the most important parameters in the adsorption and surface diffusion process [13].

Through studying the effect of contact time of MIP particles in the solution containing Fen, it can be stated that in 58 minutes, the pesticide molecules have sufficient time to be placed and permeate into the polymer matrix and occupy specific pores and saturate of polymer particles. As a result, the passage of time after the optimal time does not affect the higher accumulation of pesticide molecules on MIP. On the other hand, it was observed that stirring speed in the range of 400 to 600 rpm has a positive effect on Fen extraction.

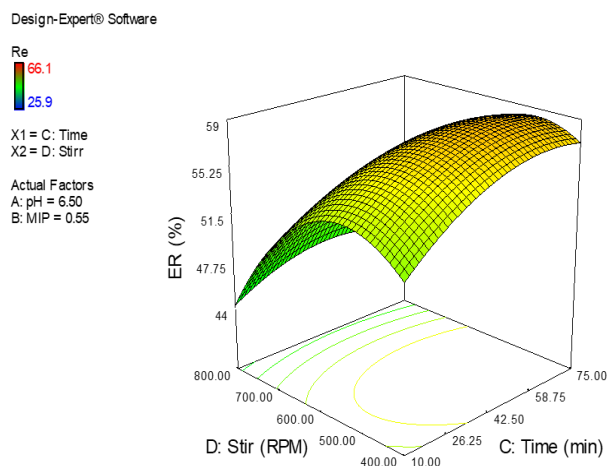


Figure 4: 3D Graph of Response Surface for Simultaneous Effect of Stirring Rate and Extraction Process Time on Fen Extraction.

One of the important goals of this study was to find the optimal operational parameters to increase the extraction recovery of pesticides, using a mathematical model. The operating parameters were optimized based on a five-level CCD. To improve the process, a multiresponse method called "the

optimal function", which finds the operating conditions that have the best response was used for this purpose. Table 3 shows the numerical optimization results for pesticide extraction.

Table 3: Optimal Values Obtained from Operational Variables and Response

pH	MIP (%wt)	Time (s)	Stir (RPM)	ER (%)
5.9	0.59	58	512	94.46

Optimization of DLLME

The application of statistics in the design of experiments to investigate the various factors influencing responses reduces the number of experiments required to achieve optimal conditions and thus, reduces time and cost [16]. For this purpose, the central composite design was used to optimize the effective parameters in the microextraction of the pesticide from aqueous solutions. Factors influencing this process include pH, extraction/dispersant solvent ratio, extraction time, and salt concentration. The five levels for each operational factor are presented in Table 2. As mentioned, one of the capabilities of RSM and DOE software is to show the simultaneous influence of the variables studied and their trace in the 3D curve, which is a good tool for expressing the response variations in the studied ranges of the independent variables. In this section, the three-dimensional curves of the simultaneous effects of the independent variables, the extraction solvent ratio to dispersive solvent (10-90%), salt concentration (0.1 - 15 % wt), pH of the solution (3-11) and microextraction time (20-160 seconds) on the dependent variable, ie pesticide extraction efficiency, is shown in Figures 5 and 6.

The changes of the Fen extraction by DLLME as a function of the extraction solvent ratio to dispersive solvent and salt concentration are shown in Figure 5, at the extraction time and pH constant of 70 s and 8.0, respectively. As the graph shows, increasing the ratio of the extraction solvent to dispersive

solvent from 10 to 30% v/v had a positive effect on extraction efficiency, and excessive solvent ratio hurt pesticide extraction. It was also stated above that the dispersive solvent will act as a bridge between the extraction solvent and the water, thereby causing the extraction solvent to be dispersed or converted into tiny droplets. on the other hand, higher amounts of dispersive solvent cause the dominating volume of dispersive solvent to volume of extraction solvent and the lower analytes to enter the organic phase and consequently, decrease the extraction efficiency. It is also seen that salt concentration has a significant effect on extraction efficiency. Similar research has reported that the amount of ions in the aqueous sample has a great effect on phase separation and extraction rate. Since, some of the extraction solvents are dissolved in water, if the ions in the solution are high and the solution is made more polarized by adding ions, these ions can expel the extraction solvent, thus dissolving a small amount of the extraction solvent in water. Therefore, the remaining time of extraction solvent is reduced in the aqueous solution, and as a result, the extraction efficiency will be lower. Hence, the ionic strength of the solution should be such that the retention time of the solvent in the water is high, but the solution easily converts into two phases. Here, it was observed that the highest removal efficiency is obtained in a salt concentration of 3.5 wt. %. This means that the salt in the range creates such an environment that the extraction solvent is present for a long time in the vicinity of the pesticide molecules.

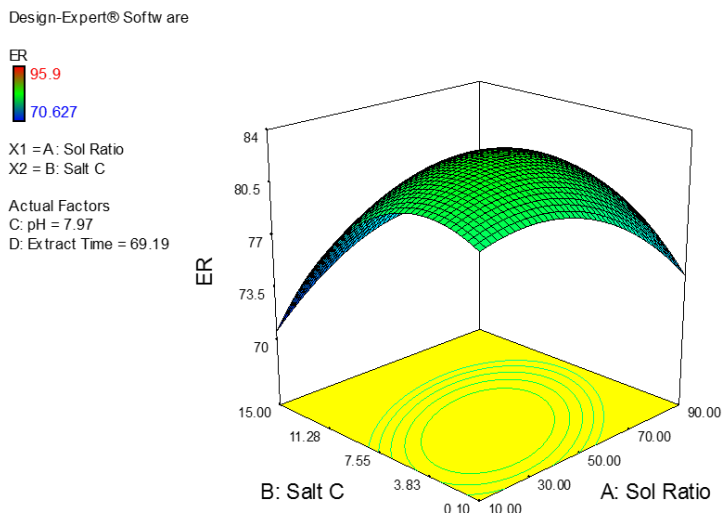


Figure 5: Changes in the Extraction Efficiency of Fen Pesticide under the Influence of Extraction Solvent to Dispersive Ratio and Salt Concentration at Extraction time (70 s) and pH (8.0).

Figure 6 shows the dependence of changes in pesticide extraction by DLLME, under the influence of extraction time and pH at constant extraction solvent- dispersive ratio (35% vol.) and salt concentration (6.5 wt.%). It can be seen that the highest pesticide extraction was obtained under neutral conditions and the extraction efficiency decreased in mildly acidic and mild alkaline conditions. The pesticide molecules have several functional groups, turns into an acidic molecule

because of its weak acidic strength in aqueous solutions. Thus, solution conditions must be such that the pesticide molecules are neutralized in the environment, so they dissolve more easily in organic solvents. In the neutral medium, the pesticide molecule does not have an acidic or alkaline agent, the so-called neutral molecule, so it is more easily dissolved in the extraction solvent and inserted in the organic phase and separated from the aqueous solution [16].

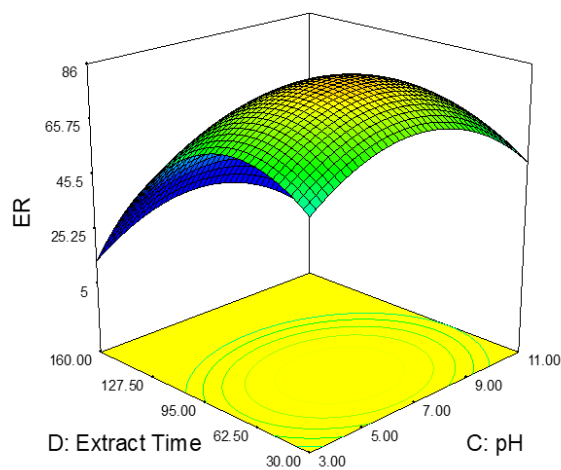


Figure 6: 3D Surface Curve of the Interaction of pH and Extraction Time on Extraction Recovery at Constant Extraction Solvent Ratio (35 % v.v) and Salt Concentration (6.5 wt%).

The desirability function consisting of maximum pesticide separation efficiency by DLLME from aqueous was defined based on five level CCD plane. The developed model by CCD suggested

the following conditions for the effective reduction of the pesticide from solution in table 4.

Table 4: Optimal Conditions of Operational Variables of DLLME for Pesticide Extraction.

Sol Ratio	Salt C (%wt)	pH	Extract Time (s)	ER
75/25	3.5	6.04	72	93.01

Selection of Extraction Solvent & Dispersive Solvent

The extraction solvent has great importance in DLLME. In general, solvents can be selected as extraction solvents that are denser than water, so that in the extraction process they are easily separated from the aqueous phase and deposited. The amount of toxin solubility in these solvents should be higher than water so that the organic phase transfer is facilitated and extraction has a higher efficiency [14]. The

lower solubility of these solvents in water leads to higher separation efficiency because the phase separation occurs easily. In this study, the effects of four organic solvents, namely carbon tetrachloride, dichloromethane, chloroform, and benzyl chloride on pesticide separation efficiency were compared for the selection of the best solvent. Among these solvents, benzyl chloride cannot be used for toxin detection, because it has absorption at 285 nm and its peak overlaps with the pesticide peak. The results of pesticide extraction recovery using selective solvents are shown in Figure 7.

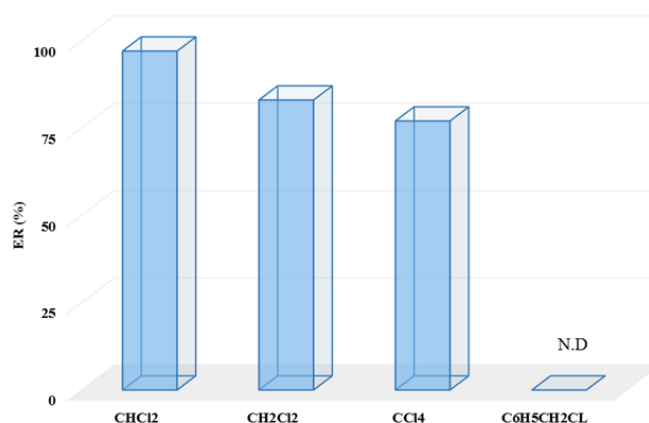


Figure 7: Choice of the Type of Extraction Solvent. 5.0 mL of 0.1 M Phosphorus Solution at pH 6.0 Containing 100 ppm Fen Pesticide, Extraction time 72 seconds, and Acetonitrile as Dispersive Solvent (75% ratio)

The dispersive solvent also plays a key role in the DLLME and it acts as a bridge between the extraction solvent and water [14]. Here, the four organic solvents of acetonitrile, methanol, ethanol, and acetone were selected as dispersive solvents, and their effect on pesticide extraction efficiency was investigated, the results of which are shown in Figure 8. As shown, the

acetonitrile solvent performs better than other solvents and has the highest efficiency. Acetonitrile has a better advantage as a dispersive solvent, because of its use in the mobile phase in HPLC, which will eliminate the potential interference with other solvents. Acetone is not capable as a solvent for detecting the peak because it absorbs at 285 nm.

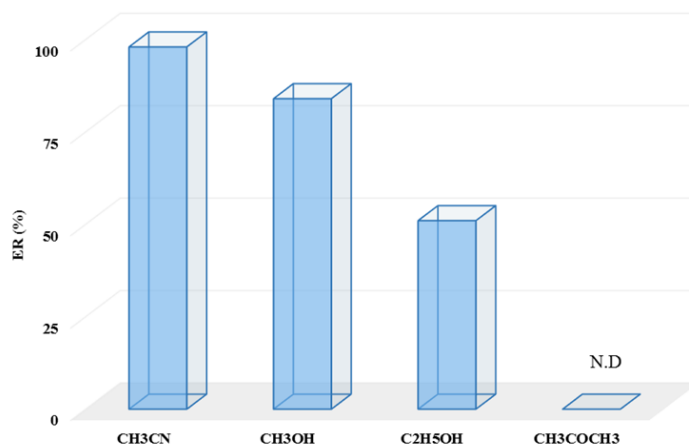


Figure 8: Influence Type of Dispersive Solvent on Recovery of Fen. 5.0 mL of 0.1 M Phosphorus Solution at pH 6.0 Containing 100 ppm Fen Pesticide, Extraction Time 72 Seconds, and Chloroform as Extraction Solvent (25% ratio).

CONCLUSION

The results indicated that both methods of the (MIP) and (DLLME) have high selectivity in pesticide extraction from aqueous solutions. The MIP particles as the extraction phase have specific sites for the separation of the pesticide from aqueous solutions. The separation is, of course, effective at low pesticide concentrations and seems to remain constant at high pesticide concentrations after the sites are occupied by Fen molecules and the polymer surface is saturated. Unlike the solid phase method, in the DLLME method, since the structure of the method is different, the separation process will be different, because in this method the transfer rate of aqueous and organic phases reaches its maximum value, so the highest extraction is achieved. Using this method, the removal process is done only once, and high efficiency is attained. Also, the time taken to prepare the sample without the deleterious effect on the sensitivity of the method is minimal. Also, this method avoids excessive consumption of toxic organic solvents such as chlorine organic solvents. Consequently, dispersive liquid-liquid microextraction is recommended for pesticide removal, because of its rapidity, cheapness as well as low environmental damage.

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