International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869 (O) 2454-4698 (P), Volume-11, Issue-6, June 2021

Implementation of ultrasonic assisted dispersive liquid-liquid extraction (UA-DLLE) coupled with HPLC-UV for the determination of pesticides in water sample

Rajib Jarder

Abstract- **Determination of hazardous substance like pesticide analyte in water at trace levels is a challenging task for the determination and separation depends on recovery of analyte in each of the multistep extraction analysis. Direct measurement of trace components even through sophisticated instruments is rare and often requires a preliminary step for sample clean up, analyte isolation and enrichment. Extraction of analyte from bulk is quite popular as it is encompasses ultrasonic assisted dispersive liquid-liquid extraction (UA-DLLE) coupled with HPLC-UV. Different classes of pesticides like chloronicotinyle-insecticide, triazole-fungicides and s-triazine-herbicides group of pesticide were simultaneously evaluated by this work. The influencing parameters in the extraction, the type and volume of the extraction solvents (ES), ultrasonication time, centrifugation time and its speed, pH and increase of ionic strength. Good linearity was observed in a range of 0.1 - 200 μg.L^{-1} with the correlation coefficient $r^2 >$ 0.997. The recoveries for pesticides ranged between 80.66% to 93.75%.The corresponding preconcentration factors were 546.02, 422.37 and 558.00 for imidacloprid, flusilazole and atrazine. The relative standard deviations (RSD) range 2.1% to 3.6% and limit of detection (LOD) ranges 0.27 to 0.37μg.L^{-1}.**

Index Terms- **Water, Pesticides, UA-DLLE, HPLC-UV.**

I. INTRODUCTION

The use of pesticides in agricultural cultivation causes serious danger, not only to the environment, but also to human health. Pesticides, used to protect crops, need special attention and checking for their persistence and effects on crop products and on such environments as soil, air, and water. Now a day, some of the banned pesticides, however have been illegally used by cultivators owing to poor awareness of the possible consequences and a desire for profit. We choose three different classes of pesticide; one insecticide, fungicide and other herbicide for their different mode of activity and function in protection of crops. To control pests or insects such as plant bugs, white flies, aphids, plant hoppers, thrips, and other harmful pest species, we use a systemic insecticide name imidacloprid, 1-(6-chloro-3-pyridinylmethyl)-*N*-nitroimidazolidin-2-ylideneamine [1]. Owing to its very high insecticidal effectiveness and low mammalian toxicity, imidacloprid has been used worldwide for vegetable, soil and foliar application and seed treatment etc. Flusilazole, 1-{[bis (4-fluorophenyl) methylsilyl] methyl}-1H-1, 2, 4-triazole, a fungicide, which has a broad spectrum application against diseases caused by fungi and almost any class of pathogens. This fungicide has been applied worldwide to several fruits, as well as cereals, vegetables, and nuts [2]. Atrazine, 1-Chloro-3-ethylamino-5-isopropylamino-2, 4, 6-triazine is the triazine class of herbicide. It is used to protect and prevent pre-emergence broad leaf weeds in crops such as sugarcane, maize and on turf, such as residential lawns and golf courses. Migration of pesticides into ground water through soil layers has serious significance on the ecological balance [3-6].

The extraction, identification and trace level determination of pesticide and residue becomes an effortful task for the analytical chemists. A few extraction methods and its wide range of application and instrumental technique illustrated. The chromatographic analysis with the instruments like HPLC-UV [7-9], GC [10-12] were applied for the determination of pesticides from different sample such as water, soil, food and vegetables etc. Some well known preconcentration and recovery techniques liquid-liquid extraction (LLE) observed it was very expensive and loss of high amoun of solvent. Rezaee, M. et al. in 2006, suggest an extraction methd DLLME [13] which is very useful. In 2007, the application of ultrasonic radiation in liquid-liquid extraction methods was first reported by de Castro and Priego-Capote [14] where a new approach that is modification of LLE. After one year Regueiro et al. in 2008

[15], developed an extraction method which applied a miniaturized approach to UA-DLLE by using a micro volume of organic phase to provide the advantage over the DLLE. Fontana et al. [16] also applied this method. Zhou et al. used an ionic liquid in ultrasonic radiation to determine some aromatic amines in real water samples [17]. Ultrasonication helps the extraction and determination of chlorinated phenoxyacetic acids [18], PAH [19, 20], phenolic preservatives [21], trichloroanisole [22], chloramphenicol [23], diethofencarb and pyrimethanil fungicides [24], polychlorinated biphenyls (PCBs), triclosan [25], nitroaromatic explosives [26], geosmin and antidepressant drugs [27], 2-methylisoborneol [28], PEs [29], OPPs [30], pyrethroids [31], copper [32], mercury [33], gold [34], siloxanes [35] and dye [36] etc. in different sample matrices. The new implementation of ultrasonication assisted work for the extraction and determination of trace imidacloprid, flusilazole and atrazine in water sample. Ultrasonic frequencies (≥20 kHz) i.e. sound energy agitate particles to accelerate the formation of the fine cloudy solution in absence of disperser solvents, which markedly increased the extraction efficiency and reduced the equilibrium time.

II. EXPERIMENTAL

A. Principle and mechanism

The basic principle for solute extraction is same as the liquid-liquid extraction where the solute distributes between two solvents according to the solubility difference in two solvents. Here, phase separation is assisted by ultrasound.

B. Instrumentation and conditions

The chromatographic analysis of pesticides were performed on Cecil (CE 4201) HPLC coupled with UV-Vis recording spectrophotometer and 20 µL injection loop manual injector of design: hyper-clon 5µ ODS (C_{18}) 120A: size 150 x 4.60 m 5 micron fitted with quaternary pump, acetonitrile:water [(80:20, v/v)] used as mobile phase with flow rate of 1.0 $ml.min^{-1}$. UV-VIS: Shimadzu model UV-2401 PC spectrophotometer also used in this experiment. Blank solution used in reference cell for performance in the spectral measurements. The column temperature was 30°C. The detector wavelength (λ_{max}) set at 270 nm. The injection volume was 20 µL. A Rotofix centrifuge was used for phase separation. Systronics, India: model no 335 digital pH meter used for measurements the pH of the solution. A 52Hz and 230 V.A.C. single ultrasonic water bath (model-o-compact, Sl. no.-642, Mumbai, India) was used for dispersion of analyte to the sediment phases.

C. Reagents, materials

Imidacloprid (ICP), flusilazole (FLU) and atrazine (ATZ) were obtained from Sigma Aldrich. tetrachloroethane ($C_2H_2Cl_4$), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), carbontetrachloride (CCl_4), acetonitrile (CH_3CN), were of HPLC grade (Merck, India). Q-Millipore water is used. HCl of 0.01(N) and NaOH of 0.01(N) solution are used for maintained the pH of the experimental solution. Different salt like NaCl, KCl, Na_2SO_4, K_2SO_4 were used for increase the ionic strength.

D. Preparation of stock solution

Quantitatively measure the appropriate amount of pesticides and it dissolved in minimum volume of CH_3CN. This stock solutions diluted with Q-Millipore water for working standard solutions in a different concentrations range of 0.1 – 200 μgL^{-1}. The filed water samples collected from river were passed through a 0.45 µm pore size membrane filter which was ready for proposed extraction method. All samples were collected free of air bubbles in amber glass containers and carried to the laboratory.

III. ANALYTICAL METHODS

A. UA-DLLE method

5.0 mL filtered aqueous sample placed in 15.0 mL centrifuge tube with conical bottom and then 0.6 mL of for imidacloprid and 0.8 ml for flusilazole and 1.0 ml for atrazine of $C_2H_2Cl_4$ separately used in each for experiment, injected by 2.5 ml dispovan syringe rapidly in it. The fine droplets of $C_2H_2Cl_4$ disperse entirely in the aqueous phase, cloudy state appeared after ultrasonication, two phase separated by centrifugation. The upper lighter phase of tube was withdrawn with a syringe, and the denser phase at bottom was used for chromatographic analysis with the minimum time lag.

B. Mathematical representation of Enrichment Factor (E_F) and Recovery Factor (R_F)

$E_F = C_{sed} / C_o$ (i)

Recovery factor (in percentage) as, $R_F = (W_{sed} / W_o) \times 100 = (C_{sed} V_{sed} / C_o V_o) \times 100$ (ii)

Where, $C_{sed}, V_{sed}, W_{sed}$ are concentration, volume, amount of solute in sediment phase, C_o, V_o, W_o are concentration, volume, amount of solute in aqueous phase respectively.

E_F and R_F can be related as, $R_F = E_F \times (V_{sed} / V_o) \times 100$ (iii).

IV.RESULTS AND DISCUSSION

Many principal roles of parameters optimized the performance of this method such as ES selection, ES volume, ultrasonication time, centrifugation time, pH, ionic strength observed which were illustrated below.

A. Extraction solvent selection

The choice of extraction solvent is a key step in this technique. Physicochemical properties of ES govern the emulsification phenomenon and improve the recovery of analyte from aqueous solutin. The analyte has to have high interested for the ES. This solvent has to be water immiscible with aqueous phase and easily separated from the aqueous bulk. The water solubility (25°C) and density values of the selected organic solvents are 2.9 $gm.L^{-1}$and 1.60 $g.mL^{-1}$ ($C_2H_2Cl_4$), 17.5 $gm.L^{-1}$and 1.33 $g.mL^{-1}$ (CH_2Cl_2), 17.5$gm.L^{-1}$ and 1.48 $g.mL^{-1}$ ($CHCl_3$), 0.81 $gm.L^{-1}$ and 1.59 $g.mL^{-1}$ (CCl_4) which leads to a biphasic system after centrifuging. A typical experiment took place using 0.70 mL of ES, in 5.0 ml aqueous sample for each ES in several extractions. Here used ultrasonication time 10.0 min and centrifugation time 3.0 min with speed 3000 rpm for each and every case. Among these solvents $C_2H_2Cl_4$ showed better performance than that rest ES which presented in Fig. 1. Therefore $C_2H_2Cl_4$ selected as the best ES and it used for next step.

B. Extraction solvent volume

In order to study the effect of ES volume on extraction efficiency, a series of volume (0.1–1.2 mL) of $C_2H_2Cl_4$ were examined. However, the volume of denser phases also decreased with reducing the volume of ES. When the volume of ES was very small, it was difficult to separate the sediment phase transfer. On the other hand, with the increase of ES, the concentration of analyte in the sediment phase was reducing due to the dilution effect. It is observed that when $C_2H_2Cl_4$ volume 0.60 mL for imidacloprid, 0.80 ml for flusilazole and 1.0 ml for atrazine give better result in this extraction. The results (Fig. 2.) imply that the enrichment factors increased with the decrease of extraction solvent volume in the tested range. Here sample containing dissolved CH_3CN acts as disperser solvent indirectly.

C. Ultrasonication time

Ultrasonication time is one of the principal factors in UA-DLLE. It affects both mass transfer and emulsification process, and thus the extraction recovery of the analytes was very fast, probably due to large contact area between the extraction solvent and aqueous phase. The effects of the sonication time were studied over 0.0 to 18 min (Fig. 3). The higher ultrasonic frequency ($\geq$ 25 kHz) gives better efficiency.The recovery factors gradually increased from 0.0 - 9.0 min for ICP, 0.0 - 12.0 min for FLU and 0.0 - 15.0 min for ATZ and then decreases when further increasing the ultrasonic time. Therefore ultrasonic time, 9.0 min for imidacloprid, 12.0 min for flusilazole and 15.0 min for atrazine were used in subsequent experiments and after that, remained almost constant or gradually decreased. At the time of ultrasonication, temperature increases from 25 to 40°C was also investigated. This increasing temperature had very small effect on the extraction efficiency.

D. Centrifugation time

Centrifugation leading to break down the emulsion and accelerate the phase-separation process of biphasic system. Different centrifugation times were presented ranging from 1.0 to 15min at 3000 rpm. The highest recovery was observed with use $C_2H_2Cl_4$ as an extraction solvent for each and every case. Time more than 3.0 min, the percent of recovery were almost remain same. The selected Centrifugation time was 3min for each type of extraction.

E. Role of pH

The pH of the sample solution is another important factor that influences on the extraction. It determines the ionic state or neutral forms of the analytes in solution. The effect of sample pH in the range of 2.0–12.0 on the extraction was investigated which is shown in Fig. 4. At a lower pH probably existed in their neutral forms where higher pH values the analytes were ionized. Extraction efficiency was optimal at pH 6.0 for imidacloprid, 10.0 for flusilazole and 5.0 for atrazine respectively which was beneficial for their distribution into the organic phase.

F. Addition of salt

Salt promotes the transfer of the analytes towards the organic phase and decrease solubility of analytes in the aqueous phase. Salt could also increase the viscosity of the solution. Addition of different types of salt (NaCl, KCl, Na_2SO_4, K_2SO_4) with different amounts ranges 0.0 – 15.0% (w/v) into water samples were investigated while the other conditions were kept constant. Efficiency of emulsion formation could be drastically reduced with addition of NaCl and KCl was observed and the extraction efficiency decreased. K_2SO_4 shows better result than other Na_2SO_4. Fig. 5 indicates that there is significant recovery increase with the addition of K_2SO_4 salt. The optimum K_2SO_4 salt concentrations are 7.5% (w/v), 5.0% (w/v), and 2.5% (w/v), for imidacloprid, flusilazole and atrazine respectively.

G. Evaluation of the method

Proposed UA-DLLE method was characterized by the linearity, accuracy, precision, repeatability, recovery and preconcentration, limit of detection and limit of limit of quantitation (LOQ). For the establishment of the calibration curve, the water samples, which were free of the analytes, were spiked with each of ICP, FLU, ATZ concentration levels of 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 50.0, 100.0 and 200.0$\mu g.L^{-1}$ respectively. For each level, five replicate extractions were performed. Here Linearity was observed in the range from 0.1 to 200.0 $\mu g.L^{-1}$ with the correlation coefficients (r) ranging from 0.9977 to 0.9989. The recovery calculated from three spiking levels in the range of the calibration curves. The repeatability study was evaluated in terms of intraday and interday precisions. For running this reverse phase HPLC, $CH_3CN:H_2O$ [(80:20, v/v)] used as mobile phase passed at flow rate of 1.0 ml.min^{-1}and run time is 10 min. The detector set at λ_{max} of the solute is 270 nm, injection volume: 20μL, standard solute solution showed sharp peak at retention time near about 1:21.9, 1:30.1, 1:44.1, 2:48.2 [mm:ss] for acetonitrile, imidacloprid, atrzine and flusilazole respectively. Starting time of peaks is 1:19.3, 1:24.5, 1:38.7, 2:37.7 [mm:ss] and end time, 1:24.5, 1:30.5, 1:47.0, 3:48.5 [mm:ss]. Peak area of solvent with three pesticides are as 10.8, 19.5, 54.0, 72.2 mAs and peak height, 6.5, 7.2, 10.0, 6.9 mA for imidacloprid, atrazine and flusilazole respectively. Before and after extraction of three pesticides are shown in Chromatograms (Fig. 6) at optimum condition. Characteristics features are presented in Table 1. Method validity judged from recovery study for field samples which is shown in Table 2.

V. CONCLUSION

This method offers a good developed alternative for routine analysis due to its high selective, sensitive, easy operation, low cost and consumption of organic solvents and at the same time reliability, excellent enrichment, over a wide range of applications and determination of pesticides in laboratory or filed aqueous sample. The extra advantage of this method is that it does not require disperser solvent, only ultasonication is applied.

ACKNOWLEDGEMENT

We are highly obliged to the Kalyani University and Jangipur College for unavoidable support.We also grateful to Prof. Dr Mitali Sarkar, for his strong valuable controversy and suggestion on the various extraction methods.

REFERECES

1. Elber, A, Overbeck, H., Iwaya, K., Tsuboi, S., Imidacloprid, a novel systemic nitromethylene analogue insecticide for crop protection. Brighton Crop Prot. Conf. Pests Dis., 2, 21-28 (1990)
2. Gupta, S. K., Shyam, K. R., Post-infection activity of ergosterol biosynthesis inhibiting fungicides against pea rust, J Mycol Plant Pathol., 30, 414–415,(2000)

3. Pang, G. F., Fan, C. L., Liu, Y. M.,Cao, Y. Z, Zhang, J. J., Fu, B. L., Li, X. M., Li, Z.Y, and Wu, Y. P., Multi-residue method for the determination of 450 pesticide residues in honey, fruit juice and wine by double-cartridge solid-phase extraction/gas chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry. Food Addit. Contam., 23, 777–810, (2006)

4. Lehotay, S. J., De Kok, A., Hiemstra, M., and Van Bodegraven, P.,Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. J. AOAC Int., 88, 595–614 (2005)

5. Anagnostopoulos, C., Bourmpopoulou, A, and Miliadis, G., Development and validation of a dispersive solid phase extraction liquid chromatography mass spectrometry method with electrospray ionization for the determination of multiclass pesticides and metabolites in meat and milk. Anal. Lett., 46, 2526–2541(2013)

6. Liu, H., Song, J., Zhang, S., Qu, L., Zhao, Y., Wu, Y., and Liu, H., Analysis of residues of imidacloprid in tobacco by high-performance liquid chromatography with liquid–liquid partition cleanup., Pest Manag. Sci., 61, 511-514 (2005)

7. Al-Rimawi, F., Development and validation of an analytical method for metformin hydrochloride and its related compound (1-cyanoguanidine) in tablet formulations by HPLC-UV. Talanta, 79, 1368-1371, (2009)

8. Kumar, P., Singh, S. P., Shrikant, K., and Madhukar, D., Analysis of buffalo liver samples for the presence of chlorpyrifos residues by using high performance liquid chromatography,. Turk. J. Vet. Anim. Sci., 35, 219-226, (2011)

9. Kukusamude, C., Santalad, A., Boonchiangma, S., Burakham, R., Srijaranai, S., and Chailapakul, O. Mixed micelle-cloud point extraction for the analysis of penicillin residues in bovine milk by high performance liquid chromatography. Talanta., 81, 486–492(2010)

10. Zang, X., Wang, J., Wang, O., Wang, M., Ma, J., Xi, G. and Wang, Z. Analysis of captan, folpet, and captafol in apples by dispersive liquid–liquid microextraction combined with gas chromatography, Anal. Bioanal. Chem., 392, 749–754, (2008)

11. Amvrazi, E. G., and Tsiropoulos, N. G. Application of single-drop microextraction coupled with gas chromatography for the determination of multiclass pesticides in vegetables with nitrogen phosphorus and electron capture detection, J. Chromatogr. A, 1216, 2789–279 (2009)

12. Faria, A. M., Dardengo, R. P., Lima, C. F., Neves, A. A., and Queiroz, M. E. L. R. Determination of disulfoton in surface water samples by cloud-point extraction and gas chromatography. Inter. J. Environ. Anal. Chem., 87, 249–258, (2007)

13. Rezaee, M., Assadi, Y., Milani Hosseini, M. R., Aghaee, E., Ahmadi, F., and Berijani, S. Determination of organic compounds in water using dispersive liquid–liquid microextraction. J. Chromatogr. A, 1116, 1–9, (2006)

14. De Castro, M. L., and Priego-Capote, F. Ultrasound-assisted preparation of liquid samples. Talanta, 72, 321-334 (2007)

15. Regueiro, J., Llompart, M., Garcia-Jares, C., Garcia-Monteagudo, J. C., and Cela, R. Ultrasound-assisted emulsification–microextraction of emergent contaminants and pesticides in environmental waters. J. Chromatogr. A. 1190, 27-38 (2008)

16. Fontana, A. R., Wuilloud, R. G., Martínez, L. D., and Altamirano, J. C. Simple approach based on ultrasound-assisted emulsification-microextraction for determination of polibrominated flame retardants in water samples by gas chromatography–mass spectrometry. J. Chromatogr. A. 1216, 147-153 (2009)

17. Zhou, Q., Zhang, X., and Xiao, J. Ultrasound-assisted ionic liquid dispersive liquid-phase micro-extraction: A novel approach for the sensitive determination of aromatic amines in water samples. J. Chromatogr. A.1216, 4361-4365 (2009)

18. Lin, S. L., and Fuh, M. R. Orthogonal array optimization of ultrasound-assisted emulsification–microextraction for the determination of chlorinated phenoxyacetic acids in river water. J. Chromatogr. A. 1217, 3467-3472 (2010)

19. Cheng, J., Matsadiq, G.; Liu, L., Zhou, Y. W., and Chen, G. Development of a novel ultrasound-assisted surfactant-enhanced emulsification microextraction method and its application to the analysis of eleven polycyclic aromatic hydrocarbons at trace levels in water. J. Chromatogr. A. 1218, 2476-2482 (2011)

20. Ozcan, S., Tor, A., and Aydin, M. E. Determination of polycyclic aromatic hydrocarbons in waters by ultrasound-assisted emulsification-microextraction and gas chromatography–mass spectrometry. Anal. Chim. Acta. 665, 193-199 (2010)

21. Regueiro, J., Llompart, M., Psillakis, E., Garcia-Monteagudo, J. C. Ultrasound-assisted emulsification–microextraction of phenolic preservatives in water. Talanta. 79, 1387-1397(2009)

22. Fontana, A. R.; and Altamirano, J. C. Sensitive determination of 2, 4, 6-trichloroanisole in water samples by ultrasound assisted emulsification microextraction prior to gas chromatography–tandem mass spectrometry analysis.Talanta. 81, 1536-1541(2010)

23. Campone, L., Celano, R., Piccinelli, A. L., Pagano, I., Cicero, N., Di Sanzo, R., ... and Rastrelli, L. Ultrasound assisted dispersive liquid-liquid microextraction for fast and accurate analysis of chloramphenicol in honey. Food Res. Int. 115, 572-579 (2019)

24. Cheng, J., Xia, Y., Zhou, Y., Guo, F., and Chen, G. Application of an ultrasound-assisted surfactant-enhanced emulsification microextraction method for the analysis of diethofencarb and pyrimethanil fungicides in water and fruit juice samples. Anal. Chim. Acta. 701, 86-91(2011)

25. Cabaleiro, N., Pena-Pereira, F., de la Calle, I., Bendicho, C., and Lavilla, I. Determination of triclosan by cuvetteless UV–vis micro-spectrophotometry following simultaneous ultrasound assisted emulsification–microextraction with derivatization: Use of a micellar-ionic liquid as extractant. Microchem. J. 99, 246-251(2011)

26. Cortada, C., Vidal, L., and Canals, Determination of nitroaromatic explosives in water samples by direct ultrasound-assisted dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry. Talanta. 85, 2546-2552 (2011)

27. Ebrahimzadeh, H., Saharkhiz, Z., Tavassoli, M., Kamarei, F., and Asgharinezhad, A. A. Ultrasound-assisted emulsification microextraction based on solidification of floating organic droplet combined with HPLC-UV for the analysis of antidepressant drugs in biological samples. J. Sep. Sci. 34, 1275-1282 (2011)

28. Cortada, C., Vidal, L., and Canals, A. Determination of geosmin and 2-methylisoborneol in water and wine samples by ultrasound-assisted dispersive liquid–liquid microextraction coupled to gas chromatography–mass spectrometry. J. Chromatogr. A. 1218, 17-22 (2011)

29. Kamarei, F., Ebrahimzadeh, H., and Yamini, Y. Optimization of ultrasound-assisted emulsification microextraction with solidification of floating organic droplet followed by high performance liquid chromatography for the analysis of phthalate esters in cosmetic and environmental water samples. Microchem. J. 99, 26-33 (2011)

30. Fontana, A. R., Camargo, A. B., and Altamirano, J. C. Coacervative microextraction ultrasound-assisted back-extraction technique for determination of organophosphates pesticides in honey samples by gas chromatography–mass spectrometry. J. Chromatogr. A. 1217, 6334-6341 (2010)

31. Feo, M. L., Eljarrat, E., and Barceló, D. A rapid and sensitive analytical method for the determination of 14 pyrethroids in water samples. J. Chromatogr. A**. 2010**, 1217, 2248-2253.

32. Liao, X., Liang, B.; Li, Z., and LiL, Y. A simple, rapid and sensitive ultraviolet-visible spectrophotometric technique for the determination of ultra-trace copper based on injection-ultrasound-assisted dispersive liquid–liquid microextraction. Analyst. 136, 4580-4586 (2011)

33. Ragheb, E.; Shamsipur, M.; Jalali, F.; Sadeghi, M.; Babajani, N.; and Mafakheri, N. Microchem. J. **2021**. 166, 106209.

Ragheb, E., Shamsipur, M., Jalali, F., Sadeghi, M., Babajani, N., & Mafakheri, N. (2021). Magnetic solid-phase extraction using metal–

organic framework-based biosorbent followed by ligandless deep-eutectic solvent-ultrasounds-assisted dispersive liquid–liquid microextraction (DES-USA-DLLME) for preconcentration of mercury (II). Microchemical Journal, 166, 106209.

34. Tajik, S., and Taher, M. A. New method for microextraction of ultra trace quantities of gold in real samples using ultrasound-assisted emulsification of solidified floating organic drops. Microchim. Acta. 173, 249-257(2011)

35. Cortada, C., dos Reis, L. C., Vidal, L., Llorca, J., and Canals, A. Determination of cyclic and linear siloxanes in wastewater samples by ultrasound-assisted dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry. Talanta. 120, 191-197(2014)

36. Dil, E. A., Ghaedi, M., Asfaram, A., Zare, F., Mehrabi, F., and Sadeghfar, F. Comparison between dispersive solid-phase and dispersive liquid–liquid microextraction combined with spectrophotometric determination of malachite green in water samples based on ultrasound-assisted and preconcentration under multi-variable experimental design optimization. Ultrason Sonochem. 39, 374-383 (2017)

RAJIB JARDER*

Department of Chemistry, Jangipur College, Jangipur-742 223, Murshidabad, (W.B.), India.

List of figure and table:

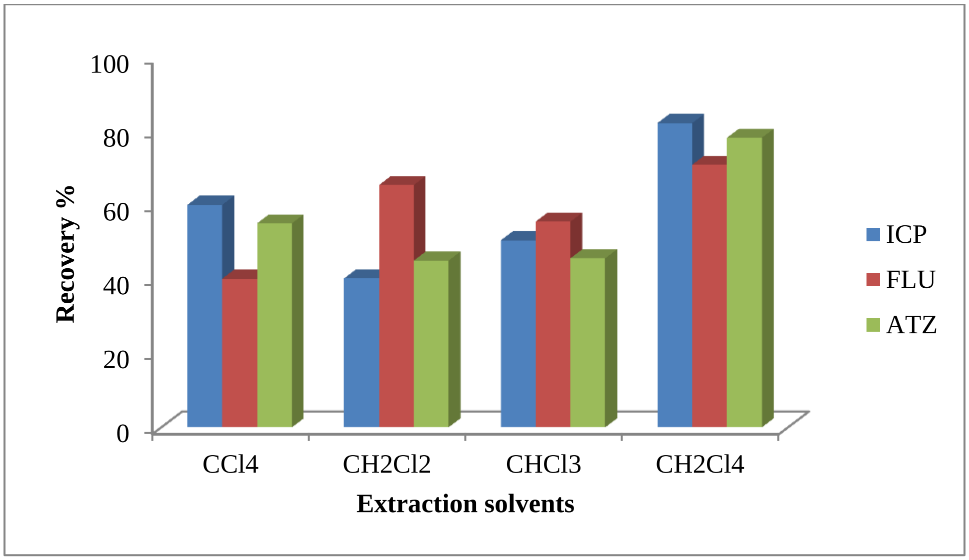

Fig. 1: Extraction solvent selection.

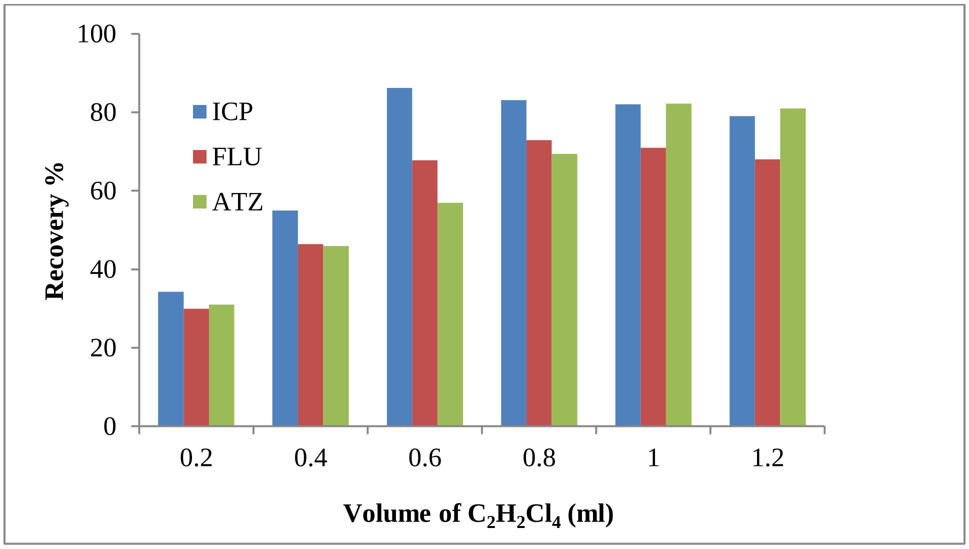

Fig. 2: Role of $C_2H_2Cl_4$ volume on recovery.

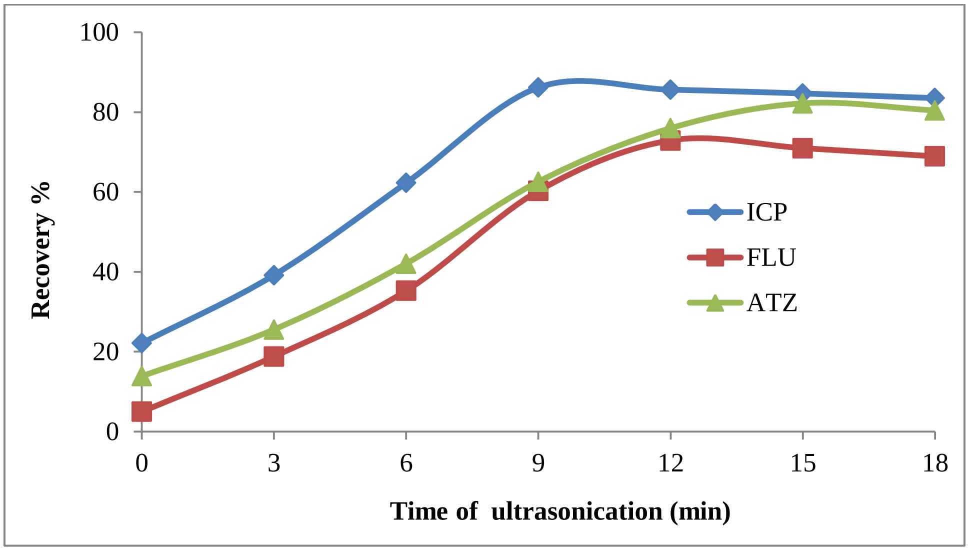

Fig. 3. Role of ultasonication time on recovery when $C_2H_2Cl_4$ acts as ES.

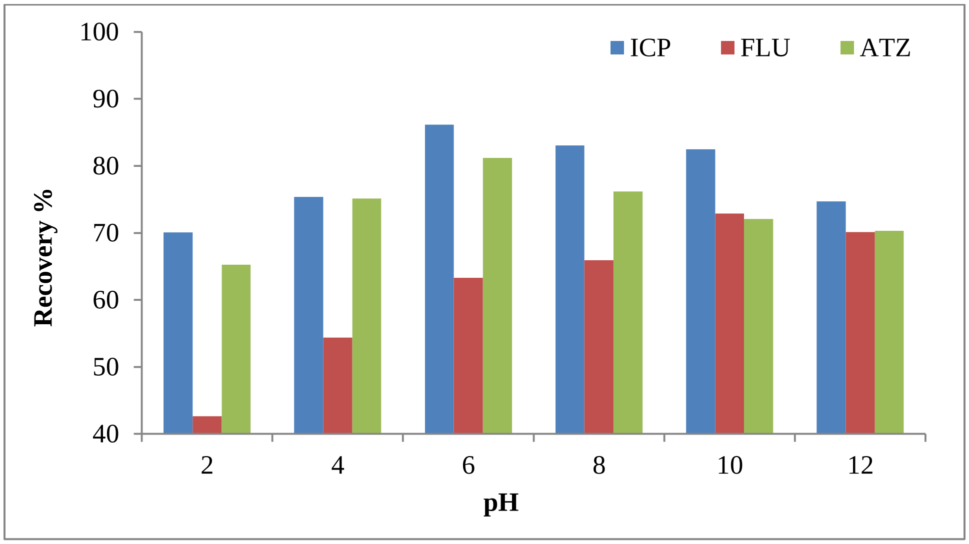

Fig. 4: Role of pH on recovery.

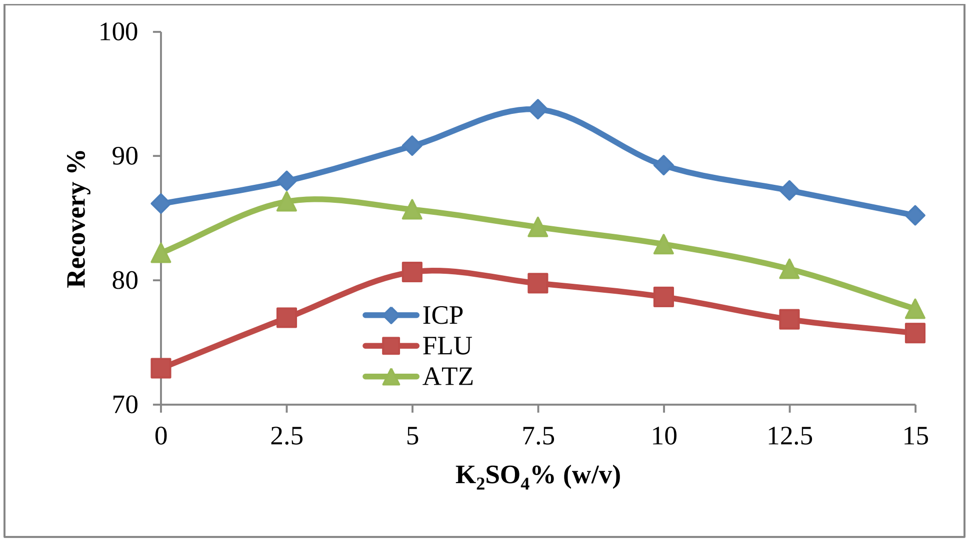

Fig. 5: Role of K_2SO_4 salt addition on recovery.

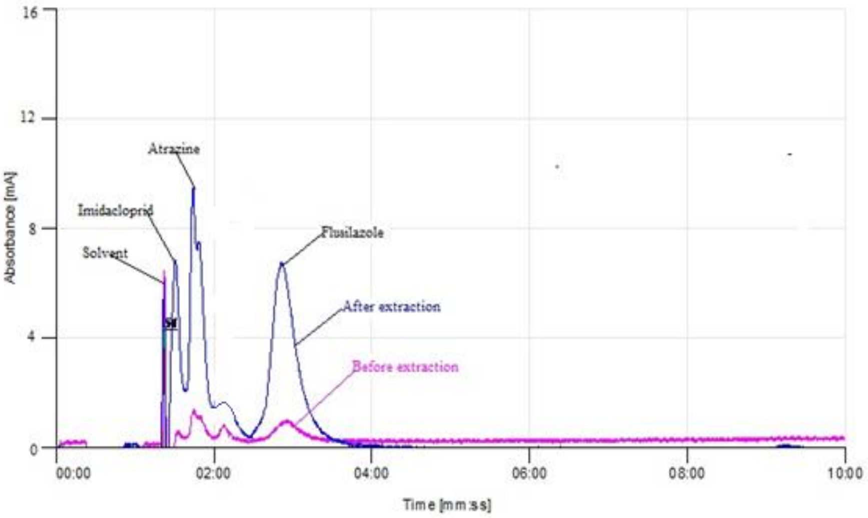

Fig. 6: HPLC-UV Chromatograms of three pesticides before and after extraction at optimum condition.

Table 1: Analytical features of the UA-DLLE.

Parameter	***Solute***		
	Imidacloprid	***Flusilazole***	***Atrazine***
LOD (µg.L^{-1})	0.27	0.37	0.35
LOQ (µg.L^{-1})	0.85	1.13	1.1
Linear range (µg.L^{-1})	0.1-200	0.1-200	0.1-200
Correlation coefficients (r)	0.9977	0.9989	0.9979
Intraday precision, RSD (%)	3.2	3.6	3.3
Inter day precision, RSD (%)	2.4	2.1	2.8
Preconcentration factor	546.02	422.37	558.00

Table 2: Determination of pesticides in spiked field water sample.

Solute	***Matrix#* *(Water)***	***Amount* (µg.L^{-1}) *(repeatability, n=5)***		***Standard deviation***	***Recovery (%)***
		Added	***Found***		
Imidacloprid	**W$_1$**	10	9.37	1.20	93.75
	W$_2$	20	18.5	1.12	92.55
	W$_3$	50	46.55	0.072	93.21
Flusilazole	**W$_1$**	10	7.95	0.642	80.66
	W$_2$	20	16.25	0.049	81.25
	W$_3$	50	40.39	0.35	80.79
Atrazine	**W$_1$**	10	8.61	0.059	86.66
	W$_2$	20	17.56	1.52	87.89
	W$_3$	50	43.52	0.26	87.51

[#] Source (field water sample collected from Jalangi river at Jalangi, Murshidabad, Tehatta, Nadia, & Mayapur, Nadia,W.B., India.)