Article Subject (see Index Terms below and write one here) _____

Hydrophobically Functionalised Magnetic Nanocomposite as a New Adsorbent for Pre-concentration of Organochlorine Pesticides in Water Solution

T.S. Hubetska[1], I. Krivtsov[1], N.G. Kobylinska[2], J.R. García[1]

[1]Department of Organic and Inorganic Chemistry, University of Oviedo-CINN, Oviedo, 33006, Spain
[2]Department of Analytical Chemistry, Taras Shevchenko National University of Kyiv, Kyiv, 01601, Ukraine

Abstract— Magnetite (Fe_3O_4) nanoparticles modified by a non-ionic surfactant Triton X-100 have been applied for magnetic solid phase extraction of organochlorine pesticides (OCPs) from water medium. The magnetic core-shell nanoparticles decorated with layers of silica and Triton X-100 have been prepared through step-by-step technique. The synthesised materials have been thoroughly characterised using transmission electron microscopy, powder X-ray diffraction analysis, nitrogen physisorption, elemental analysis, and vibrating sample magnetometry. The synthesised solids have been tested for the pre-concentration of OCPs present in water for their subsequent analysis by gas chromatography coupled with mass spectrometry. The effect of type and volume of the eluent and extraction solvent, breakthrough volume and extraction time on the adsorbent performance has been established. The proposed method has demonstrated a good linearity ($R^2 > 0.9915$) in the range of 1–10000 ng kg^{-1}, with the detection limit of 0.5-1.0 ng kg^{-1} at S/N = 3, and a precision of % RSD of ≤11.7 %. The pre-concentration factors obtained under the optimal conditions have been in the range of 2362–10593 for 100 mL of sample solution.

Index Terms— magnetite; adsorption; magnetic solid-phase extraction; GC-MS; organochlorine pesticide.

I. INTRODUCTION

The separation and determination of pesticides residues in conventional water resources have important applications in the control of chemical pesticides use, thus protecting environment and human health. Organochlorine pesticides (OCPs) cause adverse effects on aquatic biota, wildlife and human health as they are persistent and capable of bioaccumulation [Duodu 2016, Liu 2017].

Chromatography methods equipped with various detection systems are normally applied for controlling the pesticides presence [Gauglitz 2018]. The sample preparation process is indispensable, since pesticides are found in complex matrices requiring the separation of the analyte at rather low concentration levels [Deme 2014, Tan 2011]. Commonly used pesticide sample preparation technologies include solid-phase extraction (SPE) [Yang 2011], solid phase microextraction (SPME) [Filho 2010], matrix solid-phase dispersion, magnetic solid-phase extraction (MSPE), etc. [Yonghua 2018]. The MSPE is a relatively new approach for SPE, which is based on the use of magnetic adsorbents. Magnetic materials with trapped analytes can be easily separated from the sample matrix by an external magnetic field [Ravikumar 2011, Wierucka 2014]. Therefore, it is necessary to explore and establish the optimal approach for shortening the pre-treatment time and improving the efficiency of pesticides separation in water samples [Tan 2011, Farajzadeh 2017].

A wide range of application of magnetite (Fe_3O_4) nanoparticles is due to the relative simplicity of the synthesis and their unique properties being the consequence of quantum effects. The typical features of magnetic nanoparticles (MNPs) are high coercivity, large surface area, supermagnetism and low toxicity. The properties of Fe_3O_4 are size and morphology dependant [Sheng-Nan 2014]. The synthetic methods of Fe_3O_4, such as solvothermal synthesis [Liang 2013, Chen 2014, Kim 2015], thermolysis of organometallic compounds in high-boiling solvents are reported. However, the most convenient of all is the co-precipitation. MNPs of magnetite are prone to aggregation, due to their high surface energy inherent of finely dispersed structures, and they are also non-selective as adsorbing material. This problem can be solved by the covering the Fe_3O_4 surface using core-shell technique with organic (surfactants, fatty acids, polymers) or inorganic (SiO_2, C, TiO_2, Al_2O_3, and ZrO_2) substances. Although the shell itself is not selective for OCPs, it allows easily anchor certain functional groups of interest onto the material surface [Wierucka 2014].

Hydrophobic functionalization is the best choice for developing of the materials with high pesticides uptake [Fidalgo-Used 2003] such as the case of commercial SPE (C18) widely used for removing polar compounds from various matrices [Chen 2016, Li 2014]. Triton X-100 has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group. The hydrophobic group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl, which can selectively bind pesticides. It is a key issue to combine the characteristics and advantages of both the hydrophobic functional groups of non-ionic surfactant and MNPs, as to achieve the separation and determination of trace level OCPs in water samples.

In order to make possible the application of MNPs in acidic media, avoid particles aggregation and introduce surface functional groups, the magnetic particles need to be coated with a protective sol-gel silica layer. Hydrophilic polyethylene oxide groups of non-ionic

_____

surfactant can then be covalently bonded to the surface of MNPs bearing epoxy groups. In this way, one can easily prepare chemically stable Triton X-100 modified material.

Although many research works have been conducted on the application of MNPs for OCPs removal from water solutions, the optimal conditions providing the best materials' performance are yet to be found. The present work is focused on the preparation of non-ionic surfactant modified magnetite-silica nanocomposites (Fe_3O_4/Triton), and it also reports the evaluation of feasibility of its use as magnetic solid phase extragent for simultaneous extraction and pre-concentration of some OCPs from water medium prior to GC–MS analysis.

II. EXPERIMENTAL PART

A. Materials

All applied chemicals were of analytical grade and used as received without further purification. Ultra-pure water was obtained with a Milli-Q apparatus.

The standard solution of the pesticides was purchased from Aldrich (Heptachlor, Aldrin, Dieldrin, Lindane, 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (p,p'-DDE) and 1,1'-(2,2,2-trichloroethane-1,1-diyl) bis(4-chlorobenzene) (p,p'-DDT) were purchased from Sigma-Aldrich. The working solution of pesticides and the I.S. were prepared in methanol (1.0 g mL^{-1}) and stored at 4°C in a refrigerator in dark.

B. Synthesis

The MNPs were prepared by the modified co-precipitation method in ammonia medium at 60 °C [Kobylinskaya 2017].

Preparation of epoxy-derived samples (Fe_3O_4/GTMO): The magnetic Fe_3O_4/GTMO nanocomposites were prepared by a one-pot hydrolysis of tetraethoxysilane (TEOS) and 3-glycidyloxypropyl silane (GTMS). First, the suspension of the MNPs in ethanol solution (near 1.8 g of Fe_3O_4 was mixed with 400 mL of ethanol) was added to 10 mL of ultra-pure water and sonicated for 15 min, then 2.0 mL of ammonium hydroxide (25%) was introduced. Subsequently, the mixture of 5.0 mL of TEOS and 3.0 mL of GTMS in 10.0 ml of EtOH was added to it in portions (36 times by 0.5 mL every 10 min). The suspension was then mechanically stirred at 50 °C in an oil bath. After approximately 1 h, the flask was removed from the bath and allowed to cool down to room temperature following by 5 h of mechanical stirring. The resultant product was washed water for 5 times, and dried to powder overnight.

Preparation of the Triton X-100 grafted nanocomposites (Fe_3O_4/Triton): A 1.8 g of Fe_3O_4/GTMO was suspended in 250 mL of ACN and stirred at room temperature in 500 mL three-neck round bottom flask equipped with a reflux condenser. Then, 10 mL of ACN containing 0.25 g of Triton X-100 was added to the reaction mixture and the reaction was carried out under N_2 atmosphere and mechanical stirring for 30 min. The reaction continued overnight at a constant temperature while stirred. The resulted solids were collected by magnetic filtration, washed with ACN and ethanol, and then dried in air overnight.

C. Characterization methods.

The crystalline phase composition of the prepared materials has been determined using powder X-ray diffraction (PXRD). PXRD data were obtained at room temperature using a PAN Analytical X'Pert Pro high resolution diffractometer operating at a Ni-filtered CuKα (1.5406 Å) radiation. The crystallite sizes of the Fe_3O_4 powders were calculated by applying the Scherrer equation [Scherrer 1918] to the (311) peak. Fourier transform infrared (FTIR) spectra were recorded from the samples pressed in pellets with KBr using a Varian 620-IR spectrometer. The size and morphology of the MNPs were determined by transmission electron microscopy (TEM) with help of a JEOL 2100F operating at 200 kV. Carbon and hydrogen content in the nanocomposites was determined by a Vario Macro CNHS/O Analyser. Nitrogen adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2020 instrument. Before the measurement the samples were outgassed at 120 °C. Magnetic properties of the samples were measured by vibrating sample magnetometer (EV9 VSM with PPMS-14T system) at room temperature using 100 Oe/sec magnetic field in a driving mode with Nb_3Sn magnet between +22 to -22 kOe longitudes at 300 K with the sensitivity of 10^{-5} emu and 0.5% precision.

D. Sample preparation and determination of OCPs.

Typically, for each extraction procedure, 50 mg of Fe_3O_4/Triton was added to 100 mL of a sample solution. The mixture was vortexed for 5 min for the extraction, and the MNPs were isolated from the suspension by a NdFeB magnet. The pre-concentrated analytes were desorbed with 2 mL of ACN by vortexing for 5 min. The desorption solution was transferred into a centrifuge tube and evaporated to near dryness under nitrogen stream. The solid residue was re-dissolved in 0.05 mL of hexane and analysed by GC-MS. The total time of the whole process was about 20 min. The analysis was performed on Isq LT single quadrupole GC-MS (Thermo Fisher Scientific). The extracted compounds were separated on an HP-Ultra-1MS capillary column (60 mm x 0.25 mm x 0.25 mm).

III. RESULTS AND DISCUSSION

A. Material Synthesis and Characterization

The Fe_3O_4/Triton was synthesized using two-steps method. In this way, surfactant motives were covalently bonded onto the surface of MNPs via reaction salinization. The step-by-step reaction procedures to synthesize Triton grafted nanocomposites were controlled by various instrumental methods.

The PXRD patterns indicate that the obtained samples are in the form of spinel type iron oxide, Fe_3O_4 (250540-ICSD) (Fig. 1). A broad diffraction maximum near 23° appearing on the PXRD pattern of the Fe_3O_4/GTMO composite is undoubtedly attributed to the amorphous SiO_2 (Fig. 1). The Fe_3O_4 and Fe_3O_4/GTMO samples show the same set of the diffraction maxima, except for the broad peak at 23°, implying that the crystal structure of the Fe_3O_4 nanoparticles embedded in SiO_2 remains unchanged. The average crystallite sizes calculated using the Scherrer equation for the (311) reflection is 12.2 nm, 17.9 nm and 19.6 nm for Fe_3O_4, Fe_3O_4/GTMO and Fe_3O_4/Triton, respectively. The particle size of the Fe_3O_4/Triton nanocomposite suggests that the further agglomeration in the

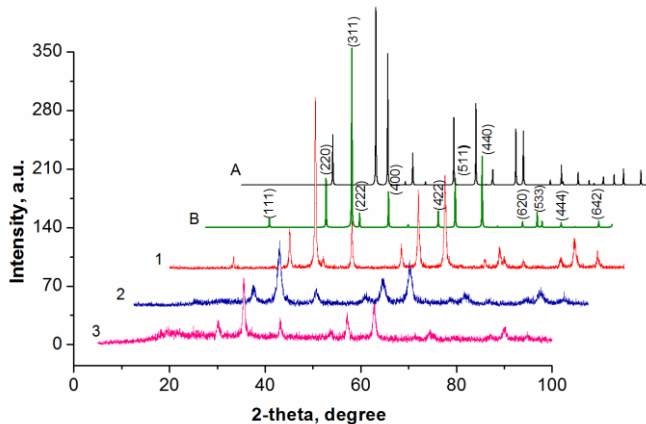silanization reaction containing magnetite powders in ACN medium does not occur.

Fig. 1. PXRD patterns of Fe$_3$O$_4$ (1), Fe$_3$O$_4$/GTMO (2), Fe$_3$O$_4$/Triton (3) and the standard hematite (A) and magnetite (B).
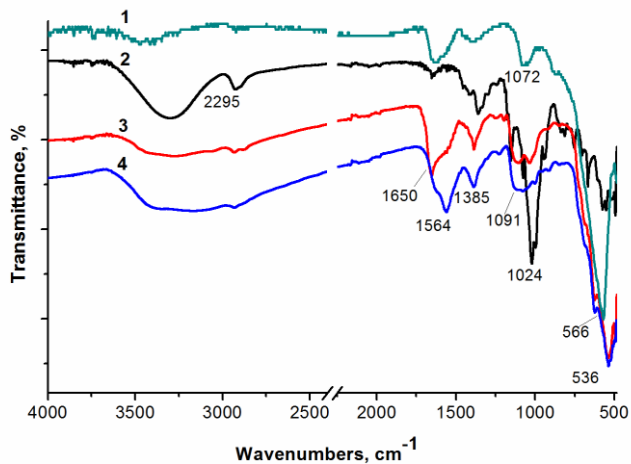
Fig. 2. FTIR spectra *in situ* of bare Fe$_3$O$_4$ (1), Triton X-100 (2) Fe$_3$O$_4$/GTMO (3) and Fe$_3$O$_4$/Triton (4).

FTIR spectra of the multifunctional magnetic nanocomposites show all the bands characteristic of the individual substances constituting the composite (Fig. 2). The absorbance in the range of 566 cm^{-1} corresponds to the Fe-O vibration of the magnetite core of the core-shell particle. The strong broad absorbance at about 1090 cm^{-1} is typical for the ν_{as}(Si-O-Si) vibrations, thus indicating that SiO$_2$ has successfully been deposited on the surface of the Fe$_3$O$_4$ core (Fig. 2 c,d). Additionally, the CH$_3$- and CH$_2$ peaks around 2950 to 3050 cm^{-1} are manifested for pure non-ionic surfactant and the prepared nanocomposite Fe$_3$O$_4$/Triton. FTIR spectroscopy reveals the decreased absorption intensity at 3350-3450 cm^{-1} on the spectrum of the Fe$_3$O$_4$/Triton sample with respect to that of bare Triton X-100, thus indicating that OH groups of the hydrophilic-chain non-ionic surfactant interact with the epoxy groups of the functionalised silica-shell. In Figure 2c there is a new peak at 1720 cm^{-1} that is characteristic of carboxyl group ν(C=O) produced in the result of the epoxy-groups oxidation on the surface of Fe$_3$O$_4$/GTMO while treating with Triton X-100. The absorbance peak at 1460 cm^{-1} and some other weak maxima at 750, 2960 and 3050 cm^{-1} are

assigned to the ν(C-H) and ν(C-H) vibrations of phenyl rings of Triton X-100. The ν(C=C) of aromatic ring stretching at 1460 cm^{-1} overlaps with the ν_s(C-H) of CH$_2$–groups (1455 cm^{-1}) scissoring band. It confirms that the modification of the Fe$_3$O$_4$ nanoparticles by Triton X-100 has been achieved.

The N$_2$ adsorption-desorption isotherms of the as-prepared magnetite and the fictionalized nanocomposites have II-type shape according to the IUPAC classification [Thommes 2015] without hysteresis loop, typical for non-porous material. The BET specific surface area of the functionalised materials calculated from the adsorption isotherm is higher than that of the corresponding pristine magnetite (see Table 1).

Table 1. Specific surface area (S$_{BET}$), data of elemental (C,H) analysis and concentrations of grafted groups (C$_L$) of the bare MNPs and the obtained nanocomposites

Sample	C, %	H, %	C$_L$, mmol g^{-1}	S$_{BET}$, m^2 g^{-1}
Fe$_3$O$_4$(pristine)	-	-	-	43
Fe$_3$O$_4$/GTMO	6.0	1.1	0.84	155
Fe$_3$O$_4$/Triton	14.6	24.0	0.42	150

The concentrations of the grafted glycidyloxypropyl groups and non-ionic moieties on the surface of the nanocomposites calculated on the basis of elemental analysis are 0.84 and 0.42 mmol g^{-1}, respectively (Table 1). It can be concluded that not all epoxy groups on the surface of Fe$_3$O$_4$/GTMO become bonded to the hydroxyl groups of Triton X-100 because this reaction is stoichiometric. This observation signifies that in fact, the surface of the Fe$_3$O$_4$/Triton solid is bifunctional. Hereby, it provides a further evidence for the successful immobilization of non-ionic moieties onto the magnetic nanocomposite surface.
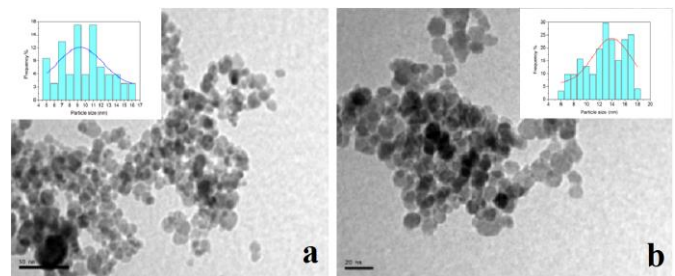

Fig. 3. TEM images and size distribution histograms of bare Fe$_3$O$_4$ (a) and Fe$_3$O$_4$/Triton (b).

According to TEM data the pristine MNPs and the obtained nanocomposites have a spherical shape (Fig. 4). TEM image of the Fe$_3$O$_4$ nanoparticles reveals a narrow particle size distribution centred at 10±2 nm. According to previous results [Liu 2016], magnetite particles exhibit superparamagnetic properties if their size is below 25 nm, which is a critical size of magnetite. Having such dimensions each particle has only one magnetic domain, and when a magnetization curve is plotted, the curve will intersect the zero point and has no reminisce and coercively. Hence, by definition the produced MNPs are superparamagnetic. The modification of the MNPs by non-ionic moieties does not lead to the changes of particle sizes. Although, it is clear that the particle size distribution is more uniform for the Fe$_3$O$_4$/Triton sample (Fig. 3 inset).

_____

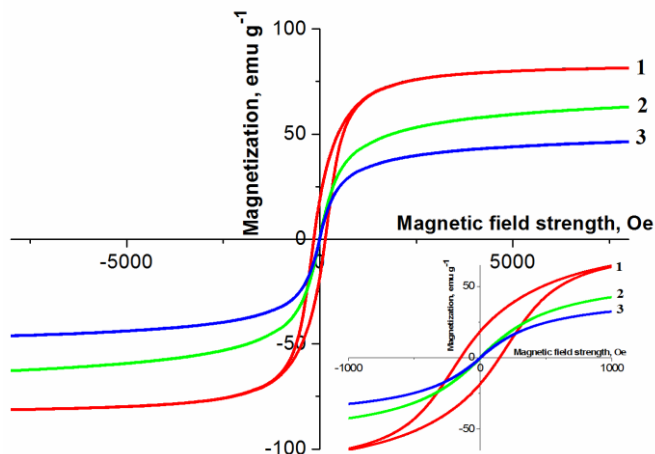Fig. 4. Magnetic hysteresis loops of pristine Fe_3O_4 (1), Fe_3O_4/GTMO (2) and Fe_3O_4/Triton (3).

When the applied magnetic field is removed, MNPs should exhibit no coercively or reminisce. The two most important properties of MNPs for their application in MSPE are the superparamagnetism and the high saturation magnetisation value.

The hysteresis loop that is characteristic of superparamagnetic behaviour can be clearly observed for pristine Fe_3O_4 and Fe_3O_4/Triton. The synthesised magnetic nanoparticles have almost zero coercivity and reminisce (Fig. 4), thus proving their superparamagnetic properties. According to the definition of superparamagnetism, the particles themselves do not have permanent magnetic moments but can respond to an external magnetic field [Chunming 2016].

The saturation magnetisation of pristine Fe_3O_4 is 80.5 emu g^{-1}, which is lower than that of the bulk magnetite, 92 emu g^{-1} [Zaitsev 1999]. On the other hand, the saturation magnetisation of Fe_3O_4/Triton is 62 emu to 1 g of particles, which is below the value obtained for pristine MNPs. This might be due to the bonding of the nonmagnetic materials (silica and non-ionic surfactant) to the nanoparticles surface, hence quenching their magnetic moment. In addition, the disordered surface region of the prepared magnetic nanoparticles increases the surface spin disorientation. It might lead to the reduction of the effective magnetic moment. However, the decrease of the magnetisation value for Fe_3O_4/Triton comparing with the pristine Fe_3O_4 or bulk material is observed, it still can be used even under a relatively low external magnetic field.

The prepared MNPs can be separated quickly and efficiently under the magnetic field in just 1 min and re-dispersed immediately once the external magnetic field is off. Although the magnetisation of Fe_3O_4/Triton decreases as a cause of functionalization, the magnetic response of Fe_3O_4/Triton is sufficiently high for the application in MSPE.

The prepared MNPs can be separated quickly and efficiently under the magnetic field in just 1 min and re-dispersed immediately once the external magnetic field is off. Although the magnetisation of Fe_3O_4/Triton decreases as a cause of functionalization, the magnetic response of Fe_3O_4/Triton is sufficiently high for the application in MSPE.

B. Chromatographic Analysis

The effect of the amount of Fe_3O_4/Triton is investigated by varying its loading in the range of 20–60 mg. The extraction capacities remain unchanged, when the amount of adsorbent exceeds 50 mg indicating the complete saturation of the Fe_3O_4/Triton active centres. The study of the effect of the sample volume for only one of the OCPs, lindane, showed that the optimal value of this parameter cannot exceed 250 mL. In order to reach the equilibrium of magnetic separation procedure, extraction time was investigated in the range of 1 to 10 min. Exactly, 5 min was selected as the optimum extraction time.

The desorption of the analyte from the surface of Fe_3O_4/Triton has been studied using as eluents hexane, acetonitrile, dichloromethane. The order of elution efficiency is the following: acetonitrile > dichloromethane > hexane. This dependency can be attributed to the fact in hexane and dichloromethane the adsorbent particles aggregation occurs, reducing their efficiency. The optimum volume of acetonitrile is 2.0 mL after 5 min of stripping time. After evaporation of the eluate of the sample, a solvent for a chromatographic study is to be added. The comparison of dichloromethane, isooctane and hexane as solvents for GC-MS has allowed establishing the order of their elution efficiency: hexane > isooctane > dichloromethane. This could be explained by the higher solubility of the OCPs in hexane, which we consider the optimal choice for this analytical procedure.

Principal analytical parameters including linearity, correlation coefficient (R^2), limit of detection (LOD) and limit of quantification (LOQ), relative standard deviation (RSD) have been determined as to validate the technique applying the MSPE probe preparation. The calibration curves built on the basis of the measurement of a series of standard solutions containing individual OCPs are linear in the range from 1 to 1000 ng kg^{-1} with the high R^2 value of 0.9915. The LOD and LOQ value calculated 0.0044 and 0.0147 ng kg^{-1}, respectively. In addition, the precision of the MSPE by Fe_3O_4/Triton combined with the GC-MS technique, expressed as RSD and assessed by three parallel extractions of analytes resulting to have a value not exceeding 11.77 % for each sample. The pre-concentration factors obtained under the optimal conditions have been in the range of 2362–10593 for 100 mL of sample water solution. The results have demonstrated that this methodology can be applicable to the pesticides analysis in aqueous media.

IV. CONCLUSION

In this study, novel hydrophobically functionalised magnetic nanocomposite has been prepared and applied as a magnetic solid phase extraction agent for the GC–MS analysis of OCPs. The obtained results have illustrated the successful synthesis of the Fe_3O_4/Triton nanoparticles. Rapid adsorption and efficient uptake of OCPs is observed for the prepared composite, which is due to the high concentration of hydrophobic functional groups on the MNPs surface. Hence, OCPs can be efficiently concentrated from water solution by the developed solids even at their trace concentrations. The results suggest that the obtained nanocomposites have a potential application in the determination of trace OCPs in water solution with good accuracy and precision.

ACKNOWLEDGMENT

REFERENCES

Y Chen, S Cao, L Zhang, C Xi, X Li, Z Chen, G Wang, "Preparation of size-controlled magnetite nanoparticles with agraphene and polymeric ionic liquid coating for the quick, easy, cheap, effective, rugged and safe extraction of preservatives from vegetables", Journal of Chromatography A, 2016, v. 1448, pp. 9-19.

F Chen, R Liu, S Xiao, "One-step solvothermal synthesis of epichlorohydrin-modified magnetic Fe_3O_4 microspheres in ethylene glycol", Materials Letters, 2014, v. 130, pp. 101-103.

S Chunming, "Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature", Journal of Hazardous Materials, 2016, v. 322, pp. 48-84.

P Deme, T Azmeera, P Devi, P. R. Jonnalagadda, R Prasad, V Sarathi, "An improved dispersive solid-phase extraction clean-up method for the gas chromatography negative chemical ionisation tandem mass spectrometric determination of multiclass pesticide residues in edible oils", Food Chemistry, 2014, v. 142, pp. 144–151.

G. O. Duodu, A. Goonetilleke, G. A. Ayoko, "Optimization of in-cell accelerated solvent extraction technique for the determination of organochlorine pesticides in river sediments", Talanta, 2016, v. 150, pp. 278-285.

A. Y. Farajzadeh, L. Khoshmaram, "Combination of dispersive solid phase extraction and dispersive liquid– liquid microextraction for extraction of some aryloxy pesticides prior to their determination by gas chromatography", Microchemical Journal, v. 131, pp. 182–191.

N. Fidalgo-Used, G. Centineo, E. Blanco-González, A. Sanz-Medel, "Solid-phase microextraction as a clean-up and preconcentration procedure for organochlorine pestisides determination in fish tissue by gas chromatography with electron capture detection", Journal of Chromatography A, v. 1017, pp 35-44.

A. M. Filho, F. N Santos, P. A. P. Pereira, "Development, validation and applica- tion of a methodology based on solid-phase micro extraction followed by gas chromatography coupled to mass spectrometry (SPME/GC–MS) for the deter- mination of pesticide residues in mangoes", Talanta, 2010, v. 81, pp. 346–354.

G. Gauglitz, B. Wimmer, T. Melzer, C. Huhn, "Glyphosate analysis using sensors and electromigration separation techniques as alternatives to gas or liquid chromatography", Analytical and Bioanalytical Chemistry, 2018, v. 410, #. 3, pp. 725-746.

S. Kim, K-I. Katsumata, K. Okada, "Highly dispersed iron oxide nanoparticles synthesized by solvothermal method adding electrostatic stabilizers", IEEE Transactions on Magnetics, 2015, v. 51, #. 7, pp. 425-431.

N. G. Kobylinskaya, E. A. Khainakova, M. E. Díaz-García, V. N. Zaitsev, "Nanocomposites based on magnetite modified by chelate groups for a solid-phase concentration of heavy-metal ions from aqueous solutions", Protection of Metals and Physical Chemistry of Surfaces, 2017, v. 53, pp. 675-684.

Y. Li, L. Qiao, F. Li, Y. Ding, Z. Yang, M. Wang, "Determination of multiple pesticides in fruits and vegetables using a modified quick, easy, cheap, effective, rugged and safe method with magnetic nanoparticles and gas chromatography tandem mass spectrometry", Journal of Chromatography A, 2014, v. 1361, pp. 77-87.

J. Liang, L. Li, H. Kang, "Solvothermal synthesis, growth mechanism, and magnetic property of self-assembled 3D multileaf α-Fe_2O_3 superstructures", Powder Technology, 2013, v. 235, pp. 475-478.

Y. Liu, Z. Gao, R. Wu, Z. Wang, T. W. Xianghen, D. Chan, "Magnetic porous carbon derived from a bimetallic metal –organic framework for magnetic solid –phase extraction of organochlorine pesticides from drinking and environmental water samples", Journal of Chromatography A, 2017, v. 1479, pp 55-61..

I. Lui, M. D. Kaminski, Y. Guan, H. Chen, H. Liu, A. J. Rosengart, "Preparation and characterization of hydrophobic superparamagnetic magnetite gel", Journal of Magnetism and Magnetic Materials, 2006, v. 306, #. 2, pp. 248–253.

C. Ravikumar, R. Bandyopadhyaya, "Mechanistic study on magnetite nanoparticle formation by thermal decomposition and coprecipitation routes", The Journal of Physical Chemistry C, 2011, v. 115, pp. 1380–1387.

P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen", Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, 1918, v. 26, pp 98-100.

S. Sheng-Nan, W. Chao, Z. Zan-Zan, H. Yang-Long, S. S. Venkatraman, X. Zhi-Chuan, "Magnetic iron oxide nanoparticles: Synthesis and surface coating techniques for biomedical applications", Chinese Physics B, 2014, v. 23, #. 3, 037503.

G. H. Tan, M. K. Chai, "Sample Preparation in the Analysis of Pesticides Residue in Food by Chromatographic Techniques", Pesticides - Strategies for Pesticides Analysis, 2011, pp. 27-58.

M. Wierucka, M. Biziuk, "Application of magnetic nanoparticles for magnetic solid-phase extraction in preparing biological, environmental and food samples", Trends in Analytical Chemistry, 2014, v. 59, pp. 50-58.

M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K.S.W. Sing, "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)", Pure and Applied Chemistry, 2015, v. 87, pp. 1051-1069.

X. Yang, H. Zhang, Y. Liu, J. Wang, Y. C. Zhang, A. J. Dong, H. T. Zhao, C. H. Sun, J. Cui, "Multiresidue method for determination of 88 pesticides in berry fruits using solid-phase extraction and gas chromatography–mass spectrometry: determi- nation of 88 pesticides in berries using SPE and GC–MS", Food Chemistry, 2011, v. 127, pp. 855–865.

W. Yonghua, R. Min, L. Guanghua, "Recent applications of metal-organic frameworks in sample pretreatment", Journal of Separation Science, 2018, v. 41, #. 1, pp. 180-194.

V. S. Zaitsev, D. S. Filimonov, I. A. Presnyakov, R. J. Gambino, B. Chu, "Physical and chemical properties of magnetite and magnetite-polymer nanoparticles and their colloidal dispersions", Journal of Colloid and Interface Science., 1999, v. 212, pp. 49-57.