MULTIWALL CARBON NANOTUBE-G-(AGAROSE-G-POLYMETHYL METHACRYLATE) AND (AGAROSE-G-POLYMETHYL METHACRYLATE) SORBENTS FOR EXTRACTION OF PESTICIDES AND HEAVY METAL IONS FROM AQUEOUS MATRICES

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In the name of Allah, Most Gracious, Most Merciful

To my beloved husband Mohammad Reza Isvandzibaei, who are provided me hope with support, help and encouragement that greatly contributed to the successful completion of my studies,

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ABSTRACT

Rapid developments in agriculture and industrial sectors have increased the levels of toxic heavy metals and pesticide residues in the environment. Many sample pretreatment methods utilized in the determination of heavy metals and pesticide residues are often time consuming, labor intensive and require substantial amounts of organic solvents. Thus, new approaches in miniaturized sample preparation are imperative. In this study, new modified agarose sorbents were prepared, characterized and applied to the extraction and pre-concentration of pesticides and heavy metal ions from aqueous matrices. Poly(methyl methacrylate)-grafted-agarose (Agarose-g-PMMA) was successfully synthesized using microwave radiation and ceric ammonium nitrate (CAN) as the radical initiator. The optimum condition for graft copolymerization was found to be at 9 g monomer, 0.4 g CAN, 60 s microwave irradiation time under 700W microwave radiation for 1 g of agarose. The graft copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy, CHN analysis, field emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC) analysis, thermal gravimetric analysis (TGA) and gel permeation chromatography (GPC). A micro-solid phase extraction (μ-SPE) utilizing Agarose-g-PMMA as sorbent combined with gas chromatography-microelectron capture detection was developed for the determination of selected pesticides, namely diazenon, chlorpyrifos, hexaconazole and azaconazole in water samples. Under optimized conditions, low limits of detection (LODs) (0.004 - 0.024 ng mL^{-1}) were obtained with good recoveries (82.23 - 103.58%). Agarose-g-PMMA was also employed as sorbent in dispersive micro-solid phase extraction (D-μ-SPE) combined with inductively coupled plasma-mass spectrometry for the analysis of heavy metals namely cadmium, nickel, copper and zinc in vegetables and natural water samples. Under the optimum conditions, the developed method showed excellent LODs (0.6 - 1.8 ng L^{-1}) and good relative recoveries (92.0 - 103.0%) for the analytes. The Agarose-g-PMMA was covalently-modified with multi-walled carbon nanotubes (MWCNTs) and the composite formed (MWCNTs-g-Agarose-g-PMMA) was characterized by FTIR, TGA and transmission electron microscopy (TEM). A SPE method incorporating MWCNTs-g-Agarose-g-PMMA as sorbent was developed and combined with flame atomic absorption spectrometry for the determination of lead ions in natural water samples. The method provided fast analysis and showed good sensitivity and excellent precision and suitable for extraction and pre-concentration of pesticide residues and trace metal ions in water and vegetable samples.

ABSTRAK

Pembangunan pesat dalam sektor pertanian dan perindustrian telah meningkatkan tahap logam berat toksik dan sisa racun perosak dalam persekitaran. Banyak kaedah pra-rawatan sampel yang digunakan dalam penentuan logam berat dan sisa racun perosak biasanya memakan masa yang panjang, intensif buruh dan memerlukan sejumlah pelarut organik yang banyak. Justeru, pendekatan baru dalam penyediaan sampel bersaiz kecil adalah sangat penting. Dalam kajian ini, bahan pengerap agarosa terubahsuai baru telah disediakan, dicirikan dan digunakan bagi pengekstrakan dan pra-pemekatan racun perosak dan ion logam berat di dalam matriks akueus. Poli(metil metakrilat)-cangkuk-agarosa (Agarose-g-PMMA) telah berjaya disintesis menggunakan sinaran gelombang mikro dan serik ammonium nitrat (CAN) sebagai pemula radikal. Keadaan optimum bagi ko-pempolimeran cangkuk telah didapati sebagai 9 g monomer, 0.4 g CAN, 60 s masa penyinaran gelombang mikro di bawah sinaran gelombang mikro 700 W bagi 1 g agarosa. Polimer cangkuk telah dicirikan dengan spektroskopi inframerah transformasi Fourier (FTIR), analisis CHN, mikroskopi elektron imbasan pancaran medan (FESEM), analisis kalorimetri pengimbasan pembezaan (DSC), analisis gravimetri terma (TGA) dan kromatografi penelapan gel (GPC). Pengekstrakan fasa pepejal mikro menggunakan Agarose-g-PMMA sebagai bahan pengerap digabungkan dengan kromatografi gas-pengesan penangkapan mikroelektron telah dibangunkan bagi penentuan racun perosak terpilih, iaitu diazenon, klorpirifos, heksakonazola dan azakonazola di dalam sampel air. Di bawah keadaan yang optimum, had pengesanan (LOD) yang rendah (0.004 - 0.024 ng mL^{-1}) telah diperoleh dengan perolehan balik yang baik (82.23 - 103.58%). Agarose-g-PMMA juga telah digunakan sebagai bahan pengerap dalam pengekstrakan fasa pepejal mikro (D-μ-SPE) digabungkan dengan spektrometri jisim-plasma ganding aruhan bagi analisis logam berat iaitu kadmium, nikel, kuprum dan zink di dalam sampel sayur-sayuran dan air semula jadi. Di bawah keadaan optimum, kaedah yang dibangunkan itu menunjukkan LOD yang cemerlang (0.6 - 1.8 ng L^{-1}) dan perolehan balik relatif yang baik (92.0 - 103.0%) bagi analit tersebut. Agarose-g-PMMA telah diubahsuai secara kovalen dengan nanotiub karbon dinding berbilang (MWCNT) dan komposit yang terbentuk (MWCNTs-g-Agarose-g-PMMA) telah dicirikan dengan FTIR, TGA dan mikroskopi elektron penghantaran (TEM). Kaedah SPE yang mengandungi MWCNTs-g-Agarose-g-PMMA sebagai bahan pengerap telah dibangunkan dan digabungkan dengan spektrometri penyerapan atom nyala bagi penentuan ion plumbum di dalam sampel air semula jadi. Kaedah tersebut memberikan analisis yang cepat, menunjukkan kepekaan yang baik dan kepersisan yang cemerlang, serta sesuai bagi pengekstrakan dan pra-pemekatan sisa racun perosak dan ion logam surih di dalam sampel air dan sayur-sayuran.

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LIST OF ABBREVIATIONS

AA	-	Acrylic acid
APS	-	Ammonium peroxydisulfate
ATRP	-	Atom Transfer Radical Polymerization
CAN	-	Ceric ammonium nitrate
CHN	-	Carbon hydrogen and nitrogen analysis
CNTs	-	Carbon nanotubes
DMF	-	Dimethyl formamide
DSC	-	Differential scanning calorimetry
D-μ-SPE	-	Dispersive micro-solid phase extraction
EF	-	Enrichment factor
FESEM	-	Field emission scanning electron microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
G (%)	-	Percentage grafting
GC	-	Gas chromatography
GPC	-	Gel permeation chromatography
HPLC	-	High performance liquid chromatography
KPS	-	Potassium persulfate
LLE	-	Liquid-liquid extraction
LOD	-	Limit of detection
LOQ	-	Limit of quantification
MMA	-	Methyl methacrylate
M_n	-	Number average molecular weight
M_w	-	Mass avearge molecular weight
MWCNTs	-	Multiwall carbon nanotubes
PANI	-	Polyaniline
PBMA	-	Poly(butyl methacrylate)

PDI	-	Polydispersity index
PDMS	-	Polydimethylsiloxane
PEMA	-	Poly(ethyl methacrylate)
PHMA	-	Poly(hexyl methacrylate)
PMMA	-	Poly (methyl methacrylate)
PNVI	-	Poly(N-vinyl imidazole)
PS	-	Polystyrene
PVP	-	Polyvinylpyrrolidone
r.p.m	-	Rotation per minute
R^2	-	Coefficients of determination
RR	-	Relative recovery
RSD	-	Relative standard deviation
SBSE	-	Stir bar sorptive extraction
SPE	-	Solid phase extraction
SPME	-	Solid phase microextraction
T*g*	-	Glass transition temperature
UV	-	Ultraviolet
μ-SPE	-	Micro solid phase extraction

LIST OF SYMBOLS

%	-	Percent
°C	-	Degree celcius
cm	-	Centimeter
g	-	Gram
g/mol	-	Gram per mol
kg	-	Kilogram
$K_{o/w}$	-	Octanol-water distribution coefficient
L	-	Liter
M	-	Molarity
mg	-	Milligram
min	-	Minutes
mL	-	Milliliter
mL/min	-	Milliliter per minute
mm	-	Millimeter
ng	-	Nanogram
nm	-	Nanometer
ppb	-	Part per billion
ppb	-	Part per billion
s	-	Second
v/v	-	Volume per volume
µg	-	Microgram
µg/L	-	Microgram per liter
µg/mL	-	Microgram per mililiter
µL	-	Microliter

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Rapid development of industrial and agriculture are resulting in incrementing levels of heavy metals and pesticide residues in biological and environmental samples, and this pollutants have toxic effects on human health and growth of plant. These toxic heavy metals and pesticide residues can gradually pile up in the human being through the food chain. When the amounts are very high, the metals can be hazardous to human health. Biological and environmental sample matrices are complex and often contain interfering elements and organic compounds that can mask or interfere with the compounds of interest, thus, direct analysis may not be possible. The sample preparation step before chromatographic analysis is considerable intricate, and expensive.

Many routine pretreatment methods utilized in the determination of heavy metal are often time period consuming, labor intensive and substantial amount of organic solvent wasting. Sample preparations are very commonly carried out using conventional extraction methods such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) to isolate, extract and concentrate target analytes. However, LLE are time consuming, labour-intensive and multi-stage operations. SPE has significant improvement over LLE by minimizing the consumption of chemicals and disposal cost of organic wastes.

Researchers have been devoted to the development of miniaturized sample preparation which resulted in significant solvent and sample savings. Apparently, the introduction and development of new materials/sorbents for microextraction have promising alternative to overcome some problems that occurred in analytical chemistry field. This microextraction is called sorbent/material-based microextraction. These relatively new techniques include such as solid phase microextraction (SPME) (Cavaliere *et al.,* 2012), stir bar sorptive extraction (SBSE) (Maggi *et al.,* 2008), dispersive solid phase extraction (DSPE) (Guan *et al.,* 2013) and micro solid phase extraction (μ-SPE). Microextraction is one of the solventless microextraction techniques that dramatically simplifies the sample preparation procedures by combining the integration of sampling, isolation and enrichment in one step (Pawliszyn, 1997).

Carbon nanotubes (CNTs) have attracted special interest in multidisciplinary study and have shown potential applications in many research areas since their discovery by Iijima in 1991 (Iijima, 1991). Their nanometer size, high aspect ratios, and more importantly their excellent mechanical, electrical and conducting properties make them highly suitable in the preconcentration of metal ions and organic pollutants in the treatment of polluted biological and environmental samples.

CNTs are generally insoluble and astringently aggregate due to Van der Waals magnetization among the nanotubes, engendering a quandary when homogenous dispersion is desirable. To surmount this barrier, sundry physical and chemical approaches have been explored including direct suspension of CNTs in polymer solution via sonication, in situ polymerization in the presence of CNTs, and the chemical modification of CNTs to enhance solubilization. Overall, the grafting of CNTs to polymer through covalent functionalization appears to be one of the most attractive and efficacious ways to achieve homogenous dispersion of CNTs in polymer matrices in order to make high quality nanocomposites. This technique has been used to make nanocomposites of CNT-polymers, mostly utilizing synthetic based polymers. However, information on the utilization of natural biopolymer grafted to carbon nanotube is currently scarce and thus of interest in this study.

Generally, chemical modification is the inter-conversion or replacement of functional groups or atoms (including hydrogen) already present on the main chain (backbone) (Ebdon, 1991). This can also be described as the alteration of chemical structure of group of atoms or molecules by introducing another group of atoms or molecules via chemical means which can provide hybrid materials with improved chemical and physical properties. Chemical modification of polymer is a process which polymers/monomers are transformed into distinct copolymers via chemical means, having improved chemical and physical properties. Chemical modification of high polymers is an important aspect of polymer science which continues to receive considerable attention. One of the important aspects in the chemical modification is in the reaction of polymers leading to block and graft copolymers. An example of the formation of graft and block copolymers from synthetic polymers has been reported (Stevens, 1999). Recently, more research works have been introduced to prepare graft copolymers from natural polymers. For example, cellulose has been grafted with several monomers to improve its properties. These include homogenous graft copolymerization of styrene onto cellulose in sulphur dioxide-diethylamine-dimethyl sulphoxide solvent (Tsuzuki *et al*., 1980), acrylonitrile and methyl methacrylate monomers grafted onto cellulose in dimethyl sulphoxide-paraformaldehyde solvent (Nishioka & Kosai, 1981), methyl acrylate onto cellulose (Nishioka *et al*., 1983), hydroxyethyl methacrylate graft copolymerization onto cellulose (Nishioka *et al*., 1986), grafting of styrene monomer onto starch (Kaewtatip and Tanrattanakul, 2008).

Graft copolymerization is one of the interesting and promising techniques used to prepare a well-defined copolymer with novel architecture, composition and functionalities. As a result, graft copolymers have a variety of potential applications in many fields including textile industries, medical, pharmaceuticals and chromatography column (separation) technology. A graft copolymer is a macromolecular chain with one or more sort of block connected to the main chemical chain as side chain(s). Thus, grafted polymer has the general structure of polymer backbone or trunk polymer with different points along its size. An external factor is utilized to create free radical sites on this preformed polymer (polysaccharide in case of grafted polysaccharides) for starting graft copolymerization.

Graft-modification of polysaccharides is widely research in recent years to obtain macromolecular materials greater to the source polysaccharides, exhibiting more preponderant resistance to heat or abrasion, more preponderant oil/water repellant qualities, or medicament activity and higher mechanical vigor. In their native form polysaccharides are fairly resistant to degradation under shear and perform as subsidiary flocculants (Singh *et al*., 2000), but have poor shelf life because of their susceptibility to biodegradation. On the other hand synthetic polymers can be facilely modified, but poor shear resistant is their properties. Natural polysaccharides grafted to synthetic polymers can be changed into highly customizable matrices with hybrid properties opportune for different applications (Gref *et al*., 2002, Ohya, 2001).

1.2 Problem Statement

In the last two decades, efficient and sensitive analytical instrumentation have been introduced for various applications. However, sample preparation today remains considered as the most crucial step in the whole analytical process. Numerous sample preparation techniques have been developed with the following main goals: to improve the selectivity in extraction, to minimize the initial sample sizes, to facilitate the automation and to reduce or eliminate the volume of organic solvent involved in the extraction (Curylo *et al*., 2007; Smith, 2003).

Based on the aims of sample preparation techniques, traditional LLE method does not fulfill current requirements and it has been displaced by new extraction techniques such as SPE, D-µ-SPE, µ-SPE, magnetic solid phase extraction (MSPE) and solid phase membrane tip extraction (SPMTE). Several comprehensive reviews on the current advances in sample preparation field and emphasizing the importance of sample preparation in the analytical process have been published (Turiel and Martín-Esteban, 2010; Augusto *et al*., 2010).

In recent years, adsorption of toxic compounds by polysaccharides and modified polysaccharides is increasing because these sorbents are low-cost (Górecki *et al.*, 1999). Polysaccharides have poor shelf life and bad resistant in their natural forms but they can be changed into hybrid properties under grafting for various applications. To the best of our knowledge, there has been no report on agarose (as polysaccharide) grafted with methyl methacrylate copolymer using ceric ammonium nitrate (CAN) as redox initiator with microwave assisted method were synthesized and characterized.

Raw multiwall carbon nanotube (MWCNTs) are suitable for adsorption of toxic compounds but they are generally insoluble and severely aggregated, due to Van der Waals attraction among the nanotubes, creating a problem when homogenous dispersion is desirable, thus modification of MWCNTs is important. Modifications of MWCNTs by special functional groups or polymers have been proven to be more selective than raw or oxidized MWCNTs because of their excellent properties. Thus in this study, agarose was used as new natural polymer for the modification of MWCNTs and subsequent separation of lead as heavy metal.

1.3 Objectives of the Study

This study embarks on the following objectives:

1. To prepare graft polymer based on agarose grafted with methyl methacrylate using microwave-assisted method and to characterize the properties of agarose and graft copolymer.
2. To graft the Agarose-g-PMMA with MWCNTs and to characterize the physical properties of the products obtained using FTIR, FESEM and TGA.

3. To develop Agarose-g-PMMA micro-solid phase extraction combined with gas-chromatography with micro-electron capture detector for the analysis of selected pesticides in environmental water samples.
4. To develop and apply Agarose-g-PMMA dispersive micro-solid phase extraction combined with inductively plasma-mass spectrometry for the extraction and determination of selected heavy metals in vegetables and natural waters.
5. To develop and apply MWCNTs-g-Agarose-g-PMMA-SPE combined with flame atomic absorption spectrometric detection to the determination of lead ions in vegetables and natural waters.

1.4 Scope of the Study

This study was designed to prepare agarose-g-PMMA using microwave-assisted method. Characterization of agarose-g-PMMA was by using Fourier transformed infrared (FTIR) analysis to ascertain the presence of methyl methacrylate on the agarose backbone. Glass transition temperatures were studied by means of differential scanning calorimetry (DSC), which measures endothermic and exothermic heat flow of the copolymer (in relation to their chemical structure and molecular weight) as a function of temperature/time. Thermal stability of the selected graft copolymer was studied by thermogravimetric analysis (TGA), which is based on the continuous measurement of change in weight of sample as a function of temperature. Molecular weight and molecular weight distribution of the hydrolyzed grafted poly methyl methacrylate (PMMA) were also evaluated using gel permeation chromatography (GPC). CHN analysis was also carried out to determine the percentage elemental composition of carbon, hydrogen and oxygen. Development and application of Agarose-g-PMMA sorbent based on microextraction methods were investigated. Several important extraction parameters were optimized comprehensively and analytical performances of the developed method were evaluated in the study. Agarose-g-PMMA-μ-SPE and Agarose-g-PMMA-D-μ-SPE methods were demonstrated to extract selected pesticides and heavy metals using

REFERENCES

Adams, S., Elias, A.J., and Cohen, P.S (Eds.). (1983). Recent Advances in Food Irradiation. *Elsevier Biomedical Press, Amsterdam*, 149.

Ahmadi, F., Shahsavari, A. A. and Rahimi-Nasrabadi, M. (2008). Automated extraction and preconcentration of multiresidue of pesticides on a micro-solid-phase extraction system based on polypyrrole as sorbent and off-line monitoring by gas chromatography-flame ionization detection. *Journal of Chromatography A*, 1193(1–2), 26–31.

Ajayan, P. M., Stephan, O., Colliex, C. and Trauth, D. (1994). Aligned carbon nanotube arrays formed by cutting a polymer resin–nanotube composite. *Science*, 265, 1212-4.

Allcock, H. R., Lampe, F. W. and Mark, J. E. (2003). *Contemporary Polymer Chemistry*. Upper Saddle River, N.J.: Pearson Education/Prentice Hall.

ALOthman, Z. A., Habila, M., Yilmaz, E. and Soylak, M. (2012). Solid phase extraction of Cd(II), Pb(II), Zn(II) and Ni(II) from food samples using multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo)resorcinol. *Microchemica Acta*. 177, 397-403.

Anastassiades, M., Lehotay, S. J., Stajnbaher, D. and Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC International*. 86(2), 412-431.

Arthur, C. L. and Pawliszyn, J. (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, 82, 2145-2148.

Athawale, V. D. and Lele, V. (1998). Graft copolymerization onto starch. II. Grafting of acrylic acid and preparation of it's hydrogels. *Carbohydrate Polymers*, *35*(1-2), 21-27.

Augusto, F., Carasek, E., Silva, R. G. C., Rivellino, S. R., Batista, A. D., and Martendal, E. (2010). New Sorbents for Extraction and Microextraction Techniques. *Journal of Chromatography A*, 1217, 2533–2542.

Aydin, F. A. and Soylak, M. (2007). A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples. *Talanta*. 73, 134-141.

Baek, J. B., Lyons, C. B. and Tan, L. S. (2004). Grafting of vapor-grown carbon nanofibers via in situ polycondensation of 3-phenoxybenzoic acid in poly(phosphoric acid). *Macromolecules,* 37, 8278-85.

Bailón-Pérez, M. I., García-Campaña, A. M., del Olmo-Iruela, M., Gámiz-Gracia, L. and Cruces-Blanco, C. (2009). Trace determination of 10 β-lactam antibiotics in environmental and food samples by capillary liquid chromatography. *Journal of Chromatography A*, 1216, 8355-8361.

Baltussen, E., Sandra, P., David, F. and Cramers, C. (1999). Stir Bar Sorptive Extraction (SBSE), a Novel Extraction Technique for Aqueous Samples: Theory and Principles. *Journal of Microcolumn Separation,* 11, 737–747.

Banci, L., Bertini, I., Cantini, F. and Ciofi-Baffoni, S. (2010). Cellular copper distribution: a mechanistic systems biology approach. *Cellular and Molecular Life Science,* 67, 2563-2589.

Basheer, C., Alnedhary, A. A., Rao, B. S. M. and Lee, H. K. (2009). Determination of carbamate pesticides using micro-solid-phase extraction combined with high performance liquid chromatography. *Journal of Chromatography A*, 1216, 211-216.

Basheer, C., Alnedhary, A. A., Rao, B. S. M., Valliyaveettil, S. and Lee, H. K. (2006). Development and application of porous membrane-protected carbon nanotube micro-solid phase extraction combined with gas chromatography/mass spectrometry. *Analytical Chemistry,* 78, 2853-2858.

Basheer, C., Chong, H. G., Hii, T. M. and Lee, H. K. (2007). Application of porous membrane protected micro-solid-phase extraction combined with HPLC for the analysis of acidic drugs in wastewater. *Analytical Chemistry*, 79(17), 6845–6850.

Basheer, C., Narasimhan, K., Yin, M., Zhao, C., Choolani, M. and Lee, H. K. (2008). Application of micro-solid-phase extraction for the determination of persistent organic pollutants in tissue samples. *Journal of Chromatography A*, 1186, 358-364.

Basheer, C., Wong, W., Makahleh, A., Tameem, A. A., Salhin, A., Saad, B. and Lee, H.K. (2011). Hydrazone-based ligands for micro-solid phase extraction-high performance liquid chromatographic determination of biogenic amines in orange juice. *Journal of Chromatography A*, 1218, 4332-4339.

Baskaran, D., Dunlap, JR., Mays, J. W. and Bratcher MS. (2005). Grafting efficiency of hydroxy-terminated poly(methyl methacrylate) with multiwalled carbon nanotubes. *Macromol Rapid Commun*. 26, 481-6.

Baskaran, D., Mays, J. W. and Bratcher, M. S. (2004). Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization. *Angewandte Chemie Internatinal Edition*, 43, 2138-42.

Bati, B. and Cesur, H. (2002). Determination of Copper in Edible Oils by Atomic Absorption Spectrometry after Lead Piperazinedithiocarbamate Solid-Phase Extraction and Potassium Cyanide Back-Extraction. *Analitical Science*, 18, 1273-1274.

Benhabib, K. and Town, R. M. (2012). Dynamic solid phase microextraction (SPME) of atrazine at PDMS and PA coated fibers. *Chemical Engineering Transation*,. 29, 151-156.

Bubb, J. M. and Lester, J. N. (1991). The impact of heavy metals on lowland rivers and the implications for man and the environment. *Science of the Total Environment*, 100, 207-233.

Cai, Y. Q., Jiang, G. B., Liu, J. F. and Zhou, Q. X. (2003).Multiwalled carbon nanotubes as a solid-phase extraction adsorbent for the determination of bisphenol A, 4-nnonylphenol, and 4-tert-octylphenol. *Analytical Chem*istry, 75, 2517-2521.

Camel, C. (2003). Review Solid Phase Extraction of Trace Elements, *Spectrochim. Acta B*. 58, 1177–1233.

Carletto, J. S., Roux, K. C., Maltez, H. F., Martendal, E. and Carasek, E. (2008). Use of 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of zinc(II) by F AAS. *Jounal Of Hazardous Materials*, 157, 88-93.

Cavaliere, B., Monteleone, M., Naccarato, A., Sindona, G. and Jagarelli, A. (2012). A solid-phase microextraction-gas chromatographic approach combined with triple quadrupole mass spectrometry for the assay of carbamate pesticides in water samples. *Journal of Chromatography A*, 1257, 149-157.

Celik, M. (2006). Preparation and characterization of starch-gpolymethacrylamide copolymers. *Journal of Polymer Research*, 13, 427–32.

Chao, C., Man, H. and Bin, H. (2011). Membrane solid phase microextraction with alumina hollow fiber on line coupled with ICP-OES for the determination of trace copper, manganese and nickel in environmental water samples. *Journal of Hazardous Materials*, 187, 379-385.

Chen, D. H., Hu, B. and Huang, C. Z. (2009). Chitosan modified ordered mesoporous silica as micro-column packing materials for on-line flow injection-inductively coupled plasma optical emission spectrometry determination of trace heavy metals in environmental water samples. *Talanta*, 78, 491-497.

Chen, J., Hamon, M. A., Hu, H., Chen, Y., Rao, AM., Eklund, P. C. and et al. (1998). Solution properties of single-walled carbon nanotubes. *Science*, 282, 95-98.

Chen, J., Rao, A. M., Lyuksyutov, S., Itkis, M. E., Hamon, M. A., Hu, H. and et al. (2001). Dissolution of full-length single-walled carbon nanotubes. *Journal of Physical Chemistry B*, 105, 2525-2528.

Ciucanu, I., Swallow, K. C. and Caprita, R. (2004). Micro-solid phase extraction with helical solid-sorbent in the presence of organic solvent for gas chromatography–mass spectrometry analysis of per-O-methylated mono- and disaccharides. *Analytica Chimica Act*a, 519(1), 93–101.

Crescenzi, V., Dentini, M., Risica, D., Spadoni, S., Skjak-Brak, G., Capitani, D., Mannina, L. and Viel S. (2004). C(6)-oxidation followed by C(5)-epimerization of guar gum studied by high field NMR. *Biomacromolecules*, 5, 537–46.

Cui, Y. M., Chang, X. J., Zhu, X. B., Jiang, N., Hu, Z. and Lian, N. (2007). Nanometer SiO_2 modified with 5-sulfosalicylic acid as selective solid-phase extractant for Fe(III) determination by ICP-AES from biological and natural water samples. *Microchemical Journal*. 86(1), 23-28.

Curyło, J., Wardencki, W., and Namieśnik, J. (2007). Green Aspects of Sample Preparation – a Need for Solvent Reduction. *Polish Journal of Enviromental Science*, 16, 5- 16.

Dagnac, T., Garcia-Chao, M., Pulleiro, P., Garcia-Jares, C. and Llompart, M. (2009). Dispersive solid-phase extraction followed by liquid chromatography-tandem mass spectrometry for the multi-residue analysis of pesticides in raw bovine milk. *Journal of Chromatography A*, 1216, 3702-3709.

Dallinger, D. and Kappe, CO. (2007). Microwave-assisted synthesis in water as solvent. *Chemical Reviews*, 107, 2563–91.

Dean, J.R. (1998). *Extraction Methods for Environmental Analysis*, Wiley, New York.

Ebdon, J. R. (1991). New methods for polymer synthesis. *Glasgow u.a: Blackie*, New York : Chapman and Hall, vol 2.

Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A. and Seiler, B. D., Shelton, MC., Tindall, D. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, 26, 1605–88.

El Tahlawy, K., and Hudson, S. M. (2003). Synthesis of a well-defined chitosan graft poly(methoxy polyethyleneglycol methacrylate) by atom transfer radical polymerization. *Journal of Applied Polymer Science, 89*(4), 901-912.

El-Hefian, E. A., Nasef, M. M., Yahaya, A. H. and Khan, R. A. (2010). Preparation and Characterization of Chitosan/Agar Blends: Rheological and Thermal Studies. *Journal of Chilean Chemical Society*, 55, 130-136.

El-Sheikh, A. H. (2008). Effect of oxidation of activated carbon on its enrichment efficiency of metal ions: comparison with oxidized and non-oxidized multi walled carbon nanotubes. *Talanta*. 75, 127-134.

El-Sheikh, A. H., Insisi, A. A. and Sweileh, J. A. (2007a). Effect of oxidation and dimensions of multi-walled carbon nanotubes on solid phase extraction and enrichment of some pesticides from environmental waters prior to their simultaneous determination by high performance liquid chromatography. *Journal of Chromatography A*, 1164, 25-32.

El-Sheikh, A. H., Sweileh, J. A. and Al-Degs, Y. S. (2007b). Effect of dimensions of multi-walled carbon nanotubes on its enrichment efficiency of metal ions from environmental waters. *Analitical Chimistry Acta*. 604, 119-126.

Escudero, L. A., Martinez, L. D., Salonia, J. A. and Gasquez, J. A. (2010). Determination of Zn(II) in natural waters by ICP-OES with on-line preconcentration using a simple solid phase extraction system. *Microchemical Journal*, 95, 164-168.

Ezoddin, M., Shemirani, F., Abdi, Kh., Saghezchi, M.K. and Jamali, M. R. (2010). Application of modified nano-alumina as a solid phase extraction sorbent for the preconcentration of Cd and Pb in water and herbal samples prior to flame atomic absorption spectrometry determination. *Journal of Hazardous Materials*. 178, 900-905.

Fagerquist, C. K., Lightfield, A. R. and Lehotay, S. J. (2005). Confirmatory and quantitative analysis of beta-lactam antibiotics in bovine kidney tissue by dispersive solid-phase extraction and liquid chromatography-tandem mass spectrometry. *Analitical Chemistry*, 77(5), 1473-82.

Fang, G. Z., He, J. X. and Wang, S. (2006). Multiwalled carbon nanotubes as sorbent for on-line coupling of solid-phase extraction to high-performance liquid chromatography for simultaneous determination of 10 sulfonamides in eggs and pork. *Journal of Chromatography A*, 1127, 12-17.

Fares, M. M., El-faqeeh, A. S. and Osman, M. E. (2003). Graft copolymerization onto starch. I. Synthesis and optimization of starch grafted with Ntert-butylacrylamide copolymer and its hydrogels. *Journal of Polymer Research*, 10,119–25.

Fernando, K. A. S., Lin, Y., Zhou, B., Grah, M., Joseph, R. and Allard, LF. (2005). Poly(ethylene-co-vinyl alcohol) functionalized single-walled carbon nanotubes and related nanocomposites. *Journal of Nanoscience and Nanotechnol*. 5, 1050-5.

Fontana, A. R., Camargo, A., Martinez, L. D. and Altamirano, J. C. (2011). Dispersive solid-phase extraction as a simplified clean-up technique for biological sample extracts. Determination of polybrominated diphenyl ethers by gas chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1218, 2490- 2496.

Galanos, C., Luderitz, O. and Himmelspach, K. (2004). The partial acid hydrolysis of polysaccharides: a new method for obtaining oligosaccharides in high yield. *European Journal of Biochemistry*, 8, 332–6.

Gilart, N., Cormack, P. A. G., Maarce, R. M., Borrull, S. and Fontanals, N. (2013). Preparation of a Polar Monolithic Coating for Stir bar Sorptive Extraction of Emerging Contaminants from Wastewaters. *Journal of Chromatography A*, 1295, 42-47.

González-Curbelo, M. Á., Herrera-Herrera, A.V., Hernández-Borges, J. and Rodríguez-Delgado, M. Á. (2013). Analysis of pesticides residues in environmental water samples using multiwalled carbon nanotubes dispersive solid-phase extraction. *Journal of Separetion Science,* 36, 556-563.

Górecki, T., Yu, X. and Pawliszyn, J. (1999). Theory of analyte extraction by selected porous polymer SPME fibres, *Analyst*, 124, 643–649.

Gref, R., Rodrigues, J. and Couvrceur, P. (2002). Polysaccharides grafted with polyesters: novel amphiphilic copolymers for biomedical applications. *Macromolecules*, 35, 9861–7.

Guan, W., Li, Z., Zhang, H., Hong, H., Rebeyev, N., Ye, Y. and Ma, Y. (2013). Amine modified graphene as reversed-dispersive solid phase extraction materials combined with liquid chromatography-tandem mass spectrometry for pesticide multi-residue analysis in oil crops. *Journal of Chromatography A*, 1286, 1-8.

Guilmeau, I., Esnouf, S., Betz, N., and Le , M.A. (1997). Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, *Elsevier*, 131, 270–275.

Gupta, B., Begum, Z. and Rajput G. (2007). Equilibrium and Kinetic Studies for the Adsorption of Mn(II) and Co(II) from Aqueous Media using Agar-agar as Sorbent. *Research Journal of chemistry and Environment*, 11, 2.

Gupta, S., Sharma, P. and Soni, P. L. (2004). Carboxymethylation of Cassia occidentalis seed gum. *Journal of Applied Polymer Science*, 94, 1606–1611.

Hemon, M. A., Chen, J., Hu, H., Chen, Y., Itkis, M. E., Rao, A. M. and et al. (1999). Dissolution of single-walled carbon nanotubes. *Advanceed Materials,* 11, 834-40.

Hu, N., Zhou, H., Dang, G., Rao, X., Chen, C. and Zhang, W. (2007). Efficient dispersion of multi-walled carbon nanotubes by in situ polymerization. *Polymere Internatinal*, 56, 655-9.

Hu, Y., S. Zhou, and Wu, L. (2009). Surface mechanical properties of transparent poly(methyl methacrylate)/zirconia nanocomposites prepared by in situ bulk polymerization. *Polymer*, 50, 3609-3616.

Huang, X. P., Chang, X. J., He, Q., Cui, Y. M., Zhai, Y. H. and Jiang, N. (2008). Tris (2-aminoethyl) amine functionalized silica gel for solid-phase extraction and preconcentration of Cr(III), Cd(II) and Pb(II) from waters. *Journal of Hazardous Materials*. 157(1), 154-160.

Iijima, S. (1991). Helical microtubules of graphitic carbon, *Nature*, 354, 56-58.

Ikhuoria, E. U., Folayan, A. S., Okieimen, F. E. (2010). Studies in the graft copolymerization of acrylonitrile onto cassava starch by ceric ion induced initiation. *International Journal of Biotechnology And Molecular BiologygResearch*,1,10-14.

Jia, Z., Wang, Z., Xu, C., Liang, J., Wei, B., Wu, D. and et al. (1999). Study on poly(methyl methacrylate)/carbon nanotube composites. *Mateialr Science Engineering A*, 271(1–2), 395-400.

Jiménez-Soto, J. M., Cárdenas, S. and Valcárcel, M. (2012). Evaluation of singlewalled carbon nanohorns as sorbent in dispersive micro solid-phase extraction. *Analitical Chimistry Acta*, 714, 76-81.

Jin, Z., Sun, X., Xu, G., Goh, S. H. and Ji, W. (2000). Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites. *Chemcal Physic Lett*ers, 318, 505-10.

Kaewtatip, K., and Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers,* 73(4), 647-655.

Kang, X., Ma, W., Zhang, H-L., Xu, Z-G., Guo, Y. and Xiong, Y. (2008). Vinyl-Carbon Nanotubes for Composite Polymer Materials. *Journal of Applied Polymer Science*, 110, 1915-1920.

Kanimozhi, S., Basheer, C., Narasimhan, K., Liu, L., Koh, S., Xue, F., Choolani, M. and Lee, H.K. (2011). Application of porous membrane protected microsolid-phase extraction combined with gas chromatography-mass spectrometry for the determination of estrogen in ovarian cyst fluid samples. *Analytica Chimica Acta*. 687, 56-60.

Karimipour , G., Ghaedi, M., Sahraei, M., Daneshfar, R. and Biyareh, M.N. (2012). Modification of gold nanoparticle loaded on activated carbon with bis (4 methoxysalicylaldehyde) -1,2-phenylenediamine as new sorbent for enrichment of sime metal ions. *Biological Trace Element Res*earch, 145, 109-117.

Kataoka, H. (2003). New trends in sample preparation for clinical and pharmaceutical analysis. *Trends in Analytical Chem*istry, 22, 232-244.

Kidwai, M., Misra, P. and Bhushan, K. R. (2001). Alumina-supported synthesis of thiadiazolyl thiazolothiones. *Synthtic Communication*, 31, 817-22.

Kim, S. W., Kim, T., Kim, Y. S., Choi, H. S., Lim, H. J., Yang, S. J. and Park, C. R. (2012). Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon*, 50, 3-33.

Koh, Y. (2001). Zinc and disease of the brain. *Mol. Neurobiol*. 24, 99-106.

Kong, H., Gao, C. and Yan, D. (2004a). Functionalization of multiwalled carbon nanotubes by atom transfer radical polymerization and defunctionalization of the products. *Macromolecules,* 37, 4022-30.

Kong, H., Gao, C. and Yan, D. (2004b). Constructing amphiphilic polymer brushes on the convex surfaces of multi-walled carbon nanotubes by in situ atom transfer radical polymerization. *Journal of Material Chemistry*, 14, 1401-5.

Kong, H., Gao, C. and Yan, D. (2004d) Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization. *Journal of American Chemistry Society*, 126(2), 412-3.

Kong, H., Li, W., Gao, C., Yan, D., Jin, Y. and Walton, D. R. M., et al. (2004c). Poly(Nisopropylacrylamide)-coated carbon nanotubes: temperaturesensitive molecular nanohybrids in water. *Macromolecules,* 37, 6683-6.

Kong, H., Luo, P., Gao, C. and Yan, D. (2005). Polyelectrolyte-functionalized multiwalled carbon nanotubes: preparation, characterization and layer-by-layer self-assembly. *Polymer*, 46, 2472-85.

Kurita, K., Inoue, M. and Harata, M. (2002). Graft Copolymerization of Methyl Methacrylate onto Mercaptochitin and Some Properties of the Resulting Hybrid Materials. *Biomacromolecules.* 3, 147-152.

Lagos, A., and Reyes, J. (1988). Grafting onto chitosan. I. Graft copolymerization of methyl methacrylate onto chitosan with fenton's reagent (Fe^{2+} $-H_2O_2$) as a redox initiator. *Journal of Polymer Science, Part A: Polymer Chemistry, 26*(4), 985-991.

Lee, T. P., Saad, B., Khayoon, W. S. and Salleh, B. (2012). Molecularly imprinted polymer as sorbent in micro-solid phase extraction of ochratoxin A in coffee, grape juice and urine. *Talanta*, 88, 129–135.

Li, Y. H., Wang, S., Luan, Z., Ding, J., Xu, C. and Wu, D. (2003). Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes, *Carbon.* 41, 1057-1062.

Liang, P., Liu, Y. and Guo, L. (2005). Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes. *Spectrochim. Acta B.* 60, 125-129.

Lin, Y., Zhou, B., Fernando, K. A. S., Liu, P., Allard, L.F. and Sun, YP. Polymeric carbon nanocomposites from carbon nanotubes functionalized with matrix polymer. *Macromolecules*. 36, 7199-204.

Liu, J, Rinzler, A. G., Dai, H., Hafner, J. H., Bradley, R. K., Boul, P. J. and et al. (1998). Fullerene pipes. *Science*, 280, 1253-6.

Liu, X. Y., Ji, Y. S., Zhang, Y. H., Zhang, H. X. and Liu, M. C. (2007). Oxidized multiwalled carbon nanotubes as a novel solid-phase microextraction fiber for determination of phenols in aqueous samples. *Journal of Chromatography A*, 1165, 10-17.

Liu, Y., Li, Y. and Yan, X. P. (2008). Preparation, characterization, and application of L-Cysteine functionalized multiwalled carbon nanotubes as a selective sorbent for separation and preconcentration of heavy metals. *Advanced Functional Materials,* 18, 1536-1543.

Liu, Z., Wu, G., and Liu, Y. (2006). Graft copolymerization of methyl acrylate onto chitosan initiated by potassium diperiodatoargentate (III). *Journal of Applied Polymer Science, 101*, 799-804.

Maggi, L., Zalacain, A. Mazzoleni, V., Alonso, G. L. and Salinas, M. R. (2008). Comparison of stir bar sorptive extraction and solid-phase microextraction to determine halophenols and halonisoles by gas chromatography-ion trap tandem mass spectrometry. *Talanta.* 75, 753-759.

Maiti, S., Ranjit, S., Biswanath, S. (2010). Polysaccharide-based graft copolymers in controlled drug delivery. *International Journal of Pharmacy and Technology*, 2, 1350–8.

Martin-Esteban, A. (2013). Molecular-Imprinted Polymers as a Versatile, Highly Selective Tool in Sample Preparation. *Trends Analytical Chem*istry, 45, 169-181.

Matahwa, H., Ramiah, V., Jarrett, WL., Mcleary, JB. and Sanderson, RD. (2007). Microwave assisted graft copolymerization of n-isopropyl acrylamide and methyl acrylate on cellulose: solid state NMR analysis and CaCO3 crystallization. *Macromolecular Symposia*, 255, 50–6.

Matyjaszewski, K. and Gaynor, S. G. (2000). Applied Polymer Science 21st Century, Ed. C.C. Craver and C.E. Carraher, Jr., *Elsevier, Amsterdam.*,929-977.

Mingos, D. and Baghurst, DR. (1991). Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chemical Society Reviews*, 20, 1–47.

Mishra, S. and Sen, G. (2011). Microwave initiated synthesis of polymethylmethacrylate grafted guar (GG-g-PMMA), characterizations and applications. *International Journal of Biological Macromolecules*, 48, 688-694.

Mishra, S., Sen, G., Rani, G. U., and Sinha, S. (2011). Microwave assisted synthesis of polyacrylamide grafted agar (Ag-g-PAM) and its application as flocculant for wastewater treatment. *International Journal of Biological Macromolecules*, *49*(4), 591-598.

Mishra, S., Sinha, S., Dey, K. P. and Sen, G. (2014). Synthesis, characterization and applications of polymethylmethacrylate grafted psyllium as flocculant. *Carbohydrate Polymers*, 99, 462-468.

Mitra, S. (2003). *Sample Preparation Techniques in Analytical Chemistry*. New Jersey: John Wiley & Sons, Inc.

Morel, F. M. M. and Price, N. M. (2003). The biogeochemical cycles of trace metals in the oceans. *Science*, 300, 944-947.

Munoz, J., Gallego, M. and Valcarcel, M. (2005). Speciation of organometallic compounds in environmetal samples by gas chromatography after flow preconcentration on fullerenes and nanotubes. *Analytical Chem*istry, 77, 5389-5395.

Neas, E. D. and Collins, M. J. (1988). Microwave heating: theoretical concepts and equipment design. In: Kingston HM, Jassie LB, editors. Introduction to microwave sample preparation: theory and practice. *Washington, DC: American Chemical Society*, 7–22.

Nishioka, N., and Kosai, K. (1981). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system - 1. Acrylonitrile and methyl methacrylate. *Polymer Journal*, 13(12), 1125-1133.

Nishioka, N., Matsumoto, K. and Kosai, K. (1983). *Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl* *sulphoxide/paraformaldehyde solvent system. II.* Characterization of graft copolymers.

Nishioka, N., Matsumoto, Y., Yumen, T., Monmae, K., and Kosai, K. (1986). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system. IV. 2-Hydroxyethyl methacrylate. *Polymer Journal, (Tokyo)*, 18, 323-330.

Nishioka, N., Minami, K., and Kosai, K. (1983). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system. III. *Methyl acrylate. Polymer Journal*, (Tokyo), 15, 591-596.

Niyogi, S., Hamon, M. A., Hu, H., Zhao, B., Bhowmik, P. and Sen, R. (2002). Chemistry of single-walled carbon nanotubes. *Accounts Chemical Research*., 35, 1105-13.

Ohya, Y., Maruhashi, S., Hirano, T. and Ouchi, T. (2001). Preparation of poly(lactic acid)-grafted polysaccharides as biodegradable amphiphilic materials. In: Chiellini E, Sunamoto J, Migliaresi C, Ottenbrite RM, Cohn D, editors. Biomedical polymers and polymer therapeutics. *New York: Kluwer Academic/Plenum publishers*, 139–48.

Ozcan, S. G., Satiroglu, N. and Soylak, M. (2010). Column solid phase extraction of iron(III), copper(II), manganese(II) and lead(II) ions food and water samples on multi-walled carbon nanotubes. *Food and Chemical Toxicology*. 48, 2401-2406.

Park, H., Zhao, J. and Lu, J. P. (2006). Effects of sidewall functionalization on conducting properties of single wall carbon nanotubes. *Nano Letters*, 6, 916-9.

Parkm, S. J., Chom, M. S., Lim, S. T., Cho, H. J. and Jhon, M. S. (2003). Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization. *Macromol Rapid Commun*, 24, 1070-3.

Pawliszyn, J. (1997). *Solid Phase Microextraction : Theory and Practise.* (1st ed.) New York : Wiley-VCH.

Pawliszyn, J. and Pedersen-Bjergaard, S. (2006). Analytical Microextraction: Current status and future trends. *Journal of Chromatographic Science*, 44, 291-307.

Plössl, F., Giera, M. and Bracher, F. (2006). Multiresidue analytical method using dispersive solid-phase extraction and gas chromatography/ion trap mass spectrometry to determine pharmaceuticals in whole blood. *Journal of Chromatography A*, 1135(1), 19-26.

Polshettiwar, V. and Varma, R. S. (2008). Microwave-assisted organic synthesis and transformations using benign reaction media. *Acc Chem Res*, 41, 629-39.

Poole, C. F. (2003). New Trends in Solid-Phase Extraction. *Trends Analytical Chem*istry, 22, 362-373.

Poole, C. F., Gunatilleka, A. D., and Sethuraman., R. (2000). Review – Contributions of Theory to Method Development in Solid-Phase Extraction, *Journal of Chromatography A,* 885, 17-39.

Poole, C.F. (2003). New trends in solid-phase, extraction. *Trends Analytical Chem*istry, 22, 362-373.

Posyniak, A., Zmudzki, J. and Mitrowska, K. (2005). Dispersive solid-phase extraction for the determination of sulfonamides in chicken muscle by liquid chromatography. *Journal of Chromatography A,* 1087(1-2), 259-64.

Pourreza, N. and Ghanemi, K. (2009). Determination of mercury in water and fish samples by cold vapor atomic absorption spectrometry after solid phase extraction on agar modified with 2-mercaptobenzimidazole. *Journal of Hazardous Materials*, 161, 982–987.

Pourreza, N., Mouradzadegun, A., and Mohammadi, S. (2011). Solid Phase Extraction of Zirconium as Arsenazo(III) Complex on Agar and Spectrophotometric Determination. *Journal of Iranian Chemical Society,* 8(4), 951-957.

Prasad, K., Meena, R. and Siddhanta, A. K. (2006a). Microwave-Induced Rapid One-Pot Synthesis of κ-Carrageenan-*g*-PMMA Copolymer by Potassium Persulphate Initiating System, *Journal of Applied Polymer Science*, 101, 161–166.

Prasad, K., Mehta, G., Meena, R. and Siddhanta, AK. (2006b). Hydrogel-forming agargraft PVP and k carrageenan graft-PVP blends: rapid synthesis and characterization. *Journal of Applied Polymer Science*, 102, 3654-63.

Prieto, A., Basauri, O., Rodil, R., Usobiaga, A., Fernández, L. A., Etxebarria, N., and Zuloaga, O. (2010). Stir-Bar Sorptive Extraction: A View on Method

Optimisation, Novel Applications, Limitations and Potential Solutions. *Journal of Chromatography A*, 1217, 2642–2666.

Pyrzynska, K. (1999). Functionalized cellulose sorbents for on-line preconcentration of trace metals for environmental analysis, *Critical Reviews Analytical Chem*istry, 29, 313-321.

Qin, S., Qin, D., Ford, W. T., Herrera, J. E. and Resasco, D. E. (2004). Grafting of poly(4- vinylpyridine) to single-walled carbon nanotubes and assembly of multilayer films. *Macromolecules*, 37, 9963-7.

Qin, S., Qin, D., Ford, W., Resasco, D. E. and Herrera, J. E. (2004). Polymer brushes on single-walled carbon nanotubes by atom transfer radical polymerization of n-butyl methacrylate. *Journal of the American Chemical Society*, 126(1), 170-176.

Qu, L., Veca, L. M., Lin, Y., Kitaygorodskiy, A., Chen, B., McCall, A. M. and et al. (2005). Soluble nylon-functionalized carbon nanotubes from anionic ringopening polymerization from nanotube surface. *Macromolecules*, 38, 10328-31.

Racamonde, I., Rodil, R., Quintana, J. B. and Cela, R. (2013). In-sample derivatization-solid-phase microextraction of amphetamines and ecstasy related stimulants from water and urine. *Analytical Chimistry Acta.* 770, 75-84.

Ramaprasad, A.T., Rao, V., Sanjeev, G., Ramanani, S.P. and Sabharwal, S. (2009). Grafting of polyaniline onto the radiation crosslinked chitosan. *Synthetic Metterials* ,159, 1983–90.

Rani, P., Mishra, S. and Sen, G. (2013). Microwave based synthesis of polymethyl methacrylate grafted sodium alginate: Its application as flocculant. *Carbohydrate Polymers*, 91(2), 686-692.

Richard, C., Balavoine, F., Schultz, P., Ebbesen, T. W. and Mioskowski, C. (2003). Supramolecular self-assembly of lipid derivatives on carbon nanotubes. Science, 300, 775-778.

Riggs, J. E., Guo, Z., Carroll, D. L. and Sun, Y. P. (2000). Strong luminescence of solubilized carbon nanotubes. *Journal of the American Chemical Society*, 122, 5879-80.

Ruan, S. L., Gaob, P., Yangb, X. G. and Yu, T. X. (2003). Toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes. *Polymer*, *44*(19), 5643-5654.

Salgueiro, M. J., Zubillaga, M., Lysionek, A., Sarabia, M. I., Caro, R., De Paoli, T., Hager, A. and Weill, R. (2005). Zinc as an essential micro nutrient: a review, Nutr. Res. *Journal of Boccio*, 20, 737-755.

Samiey, B. and Ashoori, F. (2012). Adsorptive removal of methylene blue by agar: effects of NaCl and ethanol. *Chemistry Central Journa*l, 6, 14.

Sand, A., Yadav, M., Mishra, D. K. and Behari, K. (2010). Modification of alginate by grafting of N-vinyl-2-pyrrolidone and studies of physicochemical properties in terms of swelling capacity, metal-ion uptake and flocculation. *Carbohydrat Polymer*, 80, 1147–54.

Sanghi, R. and Bhattacharya, B. (2005). Comparative evaluation of natural polyelectrolytes psyllium and chitosan for decolorisation of dye solutions. *Water Quality Research Journal*, 40, 97–101.

Sanghi, R., Bhattacharya, B. and Singh, V. (2002). Cassia angustifolia seed gum as an effective natural coagulant for decolourisation of dye solutions. *Green Chemistry*, 4, 252-254.

Santagada, V., Frecentese, F., Perissutti, E., Favretto, L., and Caliendo, G. (2004). The application of microwaves in combinatorial and high-throughput synthesis as new synthetic procedure in drug discovery. *QSAR and Combinatorial Science*, 23, 919-44.

Saracoglu, S., Soylak, M. and Elic, L. (2003). Determination of trace amounts of copper in natural water samples by flame atomic absorption spectrometry coupled with flow injection on-line solid phase extraction on ambersorb 563 adsorption resin. *Chemia Analityczna*. 48, 77-85.

Saraydın, D., Unver-Saraydin, S., Karada, E., Koptagel, E., Guven, O. (2004). In vivo biocompatibility of radiation crosslinked acrylamide copolymers. *Nuclear Instruments* and *Methods* in *Physics* Research *Section B*, 217, 281–92.

Schummer, C., Tuduri, L., Briand, O., Appenzeller, B. M. and Millet, M. (2012). Application of XAD-2 resin-based passive samplers and SPME-GC-MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxambourg. *Environmental Polluttion*, 170, 88-94.

See, H. H., Sanagi, M. M., Ibrahim, W. A.W. and Naim, A. A. (2010). Determination of triazine herbicides using membrane tip extraction prior to micro-liquid chromatography. *Journal of Chromatography A,* 1217, 1767-1772.

Sen, G., Singh, RP. and Pal, S. (2010). Microwave-initiated synthesis of polyacrylamide grafted sodium alginate: synthesis and characterization. *Journal* of *Applied Polymer Science,* 115, 63–71.

Sergi, M., Battista, N., Montesano, C., Curini, R., Maccarrone, M. and Compagnone, D. (2013). Determination of the two major endocannabinoids in human plasma by μ-SPE followed by HPLC-MS/MS. *Analytical and Bioanalytical Chemistry*, 405, 785-793.

Shams, E. and Torabi, R. (2006). Determination of nanomolar concentrations of cadmium by anodic-stripping voltammetry at a carbon paste electrode modified with zirconium phosphated amorphous silica. *Sensors and Actuators B*, 117, 86-92.

Sharma, B. R., Kumar, V. and Soni, P. L. (2003). Ce(IV)-ion initiated graft copolymerization of methyl methacrylate onto guar gum. *Journal of Macromolecul Science A*, 40, 49–60.

Silva, E. L., Roldan, P. S. and Gine, M. F. (2009). Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2- pyridylazo)-resorcinol and their determination by inductively coupled plasma optic emission spectrometry. *Journal of Hazardous Materials*, 171, 1133-1138.

Singh, R. P., Tripathy, T., Karmakar, G. P., Rath, S. K., Karmakar, N. C., Pandey, S. R., Kannan, K., Jain, S. K. and Lan, N. T. (2000). Novel biodegradable flocculants based on polysaccharides. *Current Science*,78, 798-803.

Singh, V. and Tripathi, DN. (2006). Microwave promoted grafting of acrylonitrile onto Cassia siamea seed gum. *Journal* of *Applied Polymer Science,* 101, 2384-2389.

Singh, V., Kumari, PL., Tiwari, A. and Pandey, S. (2010). Alumina-supported microwave synthesis of Cassia marginata seed gum-graftpolyacrylamide. *J Journal* of *Applied Polymer Science,* 117, 3630-8.

Singh, V., Sharma, A. K. and Maurya, S. (2009). Efficient cadmium(II) removal from aqueous solution using microwave synthesized guar-graftpoly(ethylacrylate). *Industrial & Engineering Chemistry Research,* 48, 4688-96.

Singh, V., Sharma, AK., Kumari, P. and Tiwari, S. (2008). Efficient chromium(VI) adsorption by Cassia marginata seed gum functionalized with poly(methylmethacrylate) using microwave irradiation. *Industrial & Engineering Chemistry Research*, 47, 5267-76.

Singh, V., Tiwari, A., Pandey, S. and Singh, SK. (2006b). Microwave-accelerated synthesis and characterization of potato starch-g-poly(acrylamide). *Starch/Starke*, 58, 536-43.

Singh, V., Tiwari, A., Tripathi, D. N. and Sanghi, R. (2004). Microwave assisted synthesis of guar-g-polyacrylamide. *Carbohydrate Polymer*, 58,1–6.

Singh, V., Tiwari, A., Tripathi, DN. and Sanghi, R. (2005). Microwave promoted synthesis of chitosan-graft-poly(acrylonitrile). *Journal* of *Applied Polymer Science,* 95, 820-5.

Singh, V., Tiwari, A., Tripathi, DN. and Sanghi, R. (2006a). Microwave enhanced synthesis of chitosan-graft-polyacrylamide. *Polymer*, 47, 254–60.

Singh, V., Tripathi, DN., Tiwari, A. and Sanghi, R. (2006c). Microwave synthesized chitosan-graft-poly(methylmethacrylate): an efficient Zn^{2+} ion binder. *Carbohydrate Polymer,* ;65, 35–41.

Smith, R. M. (2003). Review Before the Injection—Modern Methods of Sample Preparation for Separation Techniques. *J. Chromatogr. A.* 1000, 3-27.

Soylak, M. and Elic, L. (2000). Solid phase extraction of trace metal ions in drinking water samples from Kayseri – Turkey. *Journal of Trace and Microprobe Techniques.* 18, 397-403.

Soylak, M. and Tuzan, M. (2008). Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations. *Journal of Hazardous Materials.* 152, 656-661.

Spietelun, A., Marcinkowski, L., Guardia, M. and Namiesnik, J. (2014). Green Aspects, Developments and Perspectives of Liquid Phase Microextraction Techniques. *Talanta*. 119, 34-45.

Stafiej, A. and Pyrzynska, K. (2008). Solid phase extraction of metal ions using carbon nanotubes, *Microchemistry Journal,* 89, 29-33.

Stevens, M. P. (1999). Polymer chemistry: An Introduction (3rd Ed ed.). New York: Oxford University Press.

Streit, B. and Winter, S. (1993). Cadmium uptake and compartmental time characteristics in the freshwater mussel. *Chemosphere*, 26, 1479-1490.

Su, S., Chen, B., He, M., Hu, B. and Xiao, Z. (2014). Determination of trace/ultratrace rare earth elements in environmental samples by ICP-MS after magnetic solid phase extraction with Fe_3O_4@SiO_2@polyaniline–graphene oxide composite. *Talanta*, 119, 458-466.

Suleiman, J. S., Hu, B., Peng, H. and Huang, Ch. (2009). Separation/preconcentration of trace amounts of Cr, Cu and Pb in environmental samples by magnetic solid-phase extraction with Bismuthiol-II-immobilized magnetic nanoparticles and their determination by ICP-OES. *Talanta*. 77, 1579-1583.

Tasis, D., Tagmatarchis, N., Bianco, A. and Prato, M. (2006). Chemistry of carbon nanotubes. *Chemical Reviews*. 106,1105-36.

Tiwari, A. and Singh, V. (2008). Microwave induced synthesis of gum-acacia graft-polyaniline. *Carbohydrate Polymer*, 74, 427–34.

Trivedi, T. J., Rao, K. S. and Kumar, A. (2014). Facile preparation of agarose–chitosan hybrid materials and nanocomposite ionogels using an ionic liquid via dissolution, regeneration and sol–gel transition. *Green Chemistry,* 16, 320-330.

Tsuzuki, M., Hagiwara, I., Shiraishi, N., and Yokota, T. (1980). Characterization of products prepared by homogeneous grafting of styrene onto cellulose in a sulfur dioxide-diethylamine-dimethyl sulfoxide medium. *Journal* of *Applied Polymer Science*, 25, 2909 2924.

Tunali, S. and Akar, T. (2006). Zn(II) Biosorption Properties of Botrytis Cinerea Biomass. *Journal of hazardous materials.* 131(1-3), 137-145.

Tuncel, D. (2011). Non-covalent interactions between carbon nanotubes and conjugated polymers. *Nanoscale*, 3, 3545–3554.

Turiel, E., and Martín-Esteban, A. (2010). Molecularly Imprinted Polymers for Sample Preparation: A review. *Anaytical. Chimistry Acta*, 668 ,87–99.

Tuzan, M., Saygi, K. O. and Soylak, M. (2008). Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes. *Journal of Hazardous Materials*. 152, 632-639.

Tuzen, M., Saygi, K. M. and Soylak, M. (2008). Novel solid phase extraction procedure for gold(III) on Dowex M 4195 prior to its flame atomic absorption spectrometric determination. *Journal of Hazardous Materials*. 156, 591-595.

Velasco-Santos, C., Martínez-Hernández, A. L., Fisher, F. T., Ruoff, R, and Castaño, V. M. (2003). Improvement of Thermal and Mechanical Properties of Carbon Nanotube Composites through Chemical Functionalization. *Chemistry of Materials*, 15, 4470-4475.

Vellaichamy, S. and Palanivelu, K. (2011). Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture. *Journal of Hazardous Materials*, 185, 1131-1139.

Vijan, V., Kaity, S., Biswas, S., Isaac, J. and Ghosh, A. (2012). Microwave assisted synthesis and characterization of acrylamide grafted gellan, application in drug delivery. *Carbohydrate Polymers*, 90(1), 496-506.

Wan Ibrahim, W. A., Wan Ismail, W. N., Abdul Keyon, A. S. and Sanagi, M. M. (2011b). Synthesis and Characterization of a New Sol-Gel Hybrid Based on Tetraethoxysilane-Polydimethylsiloxane as a Stir Bar Extraction Sorbent Materials. *Journal of Sol-Gel Science and Technology*, 58, 602-611.

Wan Ibrahim, W.A., Abdul Keyon, A.S., Prastomo, N. and Matsuda, A. (2011a). Synthesis and Characterization of Polydimethylsiloxane-Cyanopropyltriethoxysilane-Derived Hybrid Coating for Stir Bar Sorptive Extraction. *Journal of Sol-Gel Science and Technology*, 59, 128-134.

Wang, W. B. and Wang, A. Q. (2010). Preparation, swelling and water retention properties of crosslinked supersorbent hydrogels based on guar gum. *Advance Materials Research*, 96, 177–82.

Wu, W., Zhang, S., Li, Y., Li, J., Liu, L., Qin, Y. and et al. (2003). PVK-modified singlewalled carbon nanotubes with effective photoinduced electron transfer. *Macromolecules*, 36, 6286-8.

Yang, B., Gong, Q., Zhao, L., Sun, H., Ren, N., Qin, J., Xu, J. and Yang, H. (2011). Preconcentration and determination of lead and cadmium in water samples with a MnO_2 coated carbon nanotubes by using ETAAS. *Desalination*. 278. 65-69.

Yang, K., and Xing, B. (2007). Desorption of Polycyclic Aromatic Hydrocarbons from Carbon Nanomaterials in Water. *Environmental Pollution*, 145, 529-537.

Yang, L., Zhang, X., Ye, M., Jiang, J., Yang, R., Fu, T., Chen, Y., Wang, K., Liu, C. and Tan, W. (2011). Aptamer-conjugated nanomaterials and their applications. *Advanced Drug Delivery Reviews,* 63, 1361-1370.

Yang, M., Gao, Y., Li, H. and Adronov, A. (2007). Functionalization of multiwalled carbon nanotubes with polyamide 6 by anionic ring-opening polymerization. *Carbon*, 45, 2327-33.

Yao, Z., Braidy, N., Botton, G. A. and Adronov, A. (2003). Polymerization from the surface of single-walled carbon nanotubes-preparation and characterization of nanocomposites. *Journal of the American Chemical Society,* 125, 16015-24.

Ying, L. S., Salleh, M. A. b.M., Yusoff, H. b. M., Rashid, S. B. A. and Razak, J. b. A. (2011). Continuous production of carbon nanotubes– a review. *Journal* of Industrial and *Engineering Chemistry*, 17, 367-376.

Zhang, N. and Hu, B. (2012). Cadmium (II) imprinted 3-mercaptopropyltrimethoxysilane coated stir bar for selective extraction of trace cadmium from environmental water samples followed by inductively coupled plasma mass spectrometry detection. *Analytical Chimistry Acta*, 723, 54-60.

Zhang, N., Peng, H. and Hu, B. (2012). Light-induced pH change and its application to solid phase extraction of trace heavy metals by high-magnetization Fe_3O_4@SiO_2@TiO_2 nanoparticles followed by inductively coupled plasma mass. *Talanta*, 94, 278-283.

Zhang, W. D., Shen, L., Phang, I. Y. and Liu, T. (2004). Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding. *Macromolecules*, 37, 256-9.

Zhang, X., Sreekumar, T. V., Liu, T. and Kumar, S. (2004). Properties and structure of nitric acid oxidized single wall carbon nanotube films. *Journal of Physical Chemistry B.,* 108, 16435-40.

Zhao, B., Hu, H., Yu, A., Perea, D. and Haddon, R, C. (2005). Synthesis and characterization of water soluble single-walled carbon nanotube graft copolymers. *Journal of the American Chemical Society,* 127, 8197-203.

Zhao, BX., Wang, P., Zheng, T., Chen, Cy. and Shu, J. (2006). Preparation and adsorption performance of a cellulosic-adsorbent resin for copper(II). *Journal of Applied Polymer Science,* 99, 2951–6.

Zhao, J. J., Buldum , A., Han, J., and Lu, J. P. (2002). Gas Molecule Adsorption in Carbon Nanotubes and Nanotube Bundles. *Nanotechnology.* 13, 195-200.

Zhao, P., Wang, L., Zhou, L., Zhang, F., Kang, S. and Pan, C. (2012). Multi-walled carbon nanotubes as alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method. Journal of *Chromatogrphy A,* 1225, 17-25.

Zhao, X. W., Song, N. Z. and Jia, Q. O. (2009). Determination of Cu, Zn, Mn and Pb by microcolumn packed with multiwalled carbon nanotubes on-line coupled with flame atomic absorption spectrometry. *Microchimca Acta*,166, 329-335.

Zheng, H., Chang, X., Lian, N., Wang, S., Cui, Y. and Zhai, Y. (2006). A pre-enrichment procedure using diethyldithiocarbamate-modified TiO_2 nanoparticles for the analysis of biological and natural water samples by ICP-AES. *International Journal of Environmental Analytical Chemistry*. 86, 431-441.

Zheng, M. M., Ruan, G. D. and Feng, Y. Q. (2009). Hybrid organic-inorganic silica monolith with hydrophobic/strong cation-exchange functional groups as a sorbent for micro-solid phase extraction. *Journal of Chromatography A*, 1216(45), 7739–7746.

Zheng, M., Jagota, A., Semke, E. D., Diner, B. A., McLean, R. S., Lustig, S. R., Richardson, R. E. and Tassi, N. G. (2003). DNA-assisted dispersion and separation of carbon nanotubes. *Natural Materials, 2*, 338-342.

Zhou, Q. X., Wang, W. D. and Xiao, J. P. (2006). Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography. *Analytical Chimistry Acta*, 559, 200-206.

Zhou, Q. X., Xiao, J. P. and Wang, W. D. (2006). Using multi-walled carbon nanotubes as solid phase extraction adsorbents to determine dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples by high performance liquid chromatography with UV detection. *Journal of Chromatography A*, 1125, 152-158.

Zorbas, V., Smith, A. L., Xie, H., Ortiz-Acevedo, A., Dalton, A. B., Dieckmann, G. R., Draper, R. K., Baughman, R. H. and Musselman, I. H. (2005). Importance