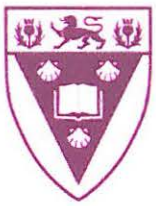

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Electrospun Sorbents for Solid Phase Extraction (SPE) and Colorimetric Detection of Pesticides

A thesis submitted to Rhodes University in fulfillment of the requirements for the degree of

Master of Science

by

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Dedication

This thesis is dedicated to my King for the constant motivation and my incredible family for their endless support, understanding and unconditional love despite the long absence.

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Abstract

The thesis presents the evaluation of polysulfone sorbents for solid phase extraction (SPE) and the development of colorimetric probes for pesticides analysis in water. Through electrospraying and electrospinning techniques, different morphologies of sorbents (particles, beaded fibers and bead-free fibers) were fabricated. The sorbents were morphologically characterized by scanning electron microscopy. Adsorption capacities of sorbents were evaluated by conducting recoveries studies for model pesticides; atrazine, chlorpyrifos and DDT using batch and column SPE modes. Better recovery results were achieved by employing the batch mode of fibers, as values ranged from 98 to 105%. Further sorbent evaluation was conducted using breakthrough experiments and static experiments. The breakthrough studies indicated that 1700 μL was the sample volume that could be percolated with no breakthrough of the analyte that correspond to a concentration of 150 mg/g of sorbent that can be extracted without any loss of analyte. From static studies, quantities of each model compound adsorbed into the fiber at the equilibrium time were evaluated. The adsorbed atrazine was 65, chlorpyrifos 250 and DDT 400 mg/g of sorbent. Kinetic studies suggested retention mechanism following pseudo first and second order model observed by high correlation coefficients (> 0.96), demonstrating the fiber affinity to retain both polar and non-polar compounds opening a possibility to be used as sorbent for sample preparation of different classes of pesticides in water. For the second part of the study simple strategies for colorimetric sensing based on silver nanoparticles and polivinylpyrrolidone capped nanoparticles were developed, respectively for atrazine and chlorpyrifos detection. The limits of detection of the methods were 3.32 and 0.88 mg/L for atrazine and chlorpyrifos respectively. The applicability of the probe in real samples was demonstrated by the recoveries studies of tap water varying from 94 to 104 %. The versatility of the probe was demonstrated by affording a simple, rapid and selective detection of atrazine and chlorpyrifos in the presence of other pesticides by direct analysis without employing any sample handling steps. Attempt to incorporate the probes in a solid support was achieved by using nylon 6 as solid support polymer proving to be fast and useful for on-site detection.

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Abbreviations and symbols

EP	European Pharmacopoeia
FEPCA	Federal Environmental Pesticide Control Act
BHC	Benzene hexachloride
DDT	Dichlorodiphenyltrichloroethane
2,4-D	2,4-Dichlorophenoxyacetic acid
OCP	Organochlorine pesticide
ONP	Organonitrogen pesticide
OPP	Organophosporus pesticide
g	Gram
mg	Miligram
L	Litre
GC	Gas chromatography
HPLC	High performance liquid chromatography
TLC	Thin-layer chromatography
ECD	Electron capture detector

DAD	Diode array detector
MS	Mass spectrometry
LLE	Liquid – liquid extraction
FMASE	Focused microwave – assisted soxhlet extraction
MAE	Microwave – assisted extraction
SDME	Single – drop microextration
ASE	Accelerated solvent extraction
SFE	Supercritical fluid extraction
SPE	Solid phase extraction
SPME	Solid phase microextration
MSPD	Matrix solid phase dispersion
SBSE	Stir bar sorptive extraction
MIP	Molecularly imprinted polymer
AgNPs	Silver nanoparticles
AuNPs	Gold nanoparticles
PS-DVB	Polystyrene divinyl benzene

ELISA	Enzyme linked immunosorbent assays
DMF	Dimethylformamide
THF	Tetrahydrofuran
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
PTFE	Polytetrafluoroethylene
kV	Kilovolt
mL	Milliliter
TGA	Thermogravimetric analysis
r	Correlation coefficient
SPR	Surface plasmon resonance
FIA	fluoroimmunoassay
SERS	Surface – enhanced Raman scattering
NSEF	Normalized scattering electric field
PVA	Polyvinyl alcohol
PVP	Polivinylpyrrolidone

BSA	Bovine serum albumin
AChE	Acetylcholinesterase
ATCh	Acetylthiocholine
LD	Limit of detection

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Chapter 1 General Introduction

1.1 Background

Chemical substances and their derivatives are widely used in many economic sectors including industry, agriculture, mining, water purification, public health and infrastructure development. Immense benefits have been brought to humankind through the use of chemicals and, at the same time the chemicals have had a negative impact on human health and safety [1]. Various organic and inorganic chemical pollutants discharged from different sources get into the environment. The sea, rivers, dams or lakes have become the immediate environmental reservoirs for organic pollutants, consequently pollutants can now be found in air, surface, ground and drinking water, sediments, soil, food systems as well as in aquatic and marine organisms [2, 3]. One group of such chemicals are the pesticides that are employed worldwide for the control, prevention and elimination of plagues, that attack plantations and herbs, as well as vector of diseases in human beings [4].

Preservation of the environment for a better quality life is increasingly becoming of great concern to the society. Pesticide use has increased worldwide so as to secure adequate food supply to the worlds ever-increasing population [1]. Intensification of agriculture, especially in the tropical regions, has led to high level of pesticides consumption. On the other hand it is reported that pesticides have saved millions of lives and prevented hundreds of millions of incidence of serious illnesses due to malaria, typhus, dysentery and more than 20 other insect-borne diseases[5, 6]. Ideally pesticides should be highly selective, destroying only target organisms but in reality, most pesticides are not so selective. In considering the use of pesticides, the benefits must be weighed against the risk to human health and environmental quality.

The major risk of pesticides is environmental contamination, especially translocation within the environment where pesticides might enter by both food chains and natural water systems. Factors to be considered in this regard are persistence in the environment and potential for bioaccumulation [7]. The

pesticides generally applied nowadays are regarded as some of the most dangerous contaminants of the environment. Their presence especially in water is hazardous because they cause human beings to become more susceptible to disease [5].There is growing concern about possible environmental contamination from pesticides. In this respect, it's important to develop strategies and methodologies for pesticides determination, which could be used to inform on the state of the environment so as to contribute for better life.

1.2 Pesticides and Classification

1.2.1 Pesticides

Pesticide is a generic term used to describe a large number of widely differing biological, inorganic and organic compounds, including positional, geometric and optical isomers, employed in the control, prevention and elimination of plagues, that attack plantations and herds, as well as vectors of diseases in human beings [4, 8]._However, there are more precise definitions, such as those provided by the European Pharmacopoeia (EP) or the Federal Environmental Pesticide Control Act (FEPCA). The European Pharmacopoeia defines a pesticide to be "any substance, or mixture of substances, intended for preventing, destroying or controlling any pest, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of vegetable drugs." The item includes substances intended for use as growth regulators, defoliants or desiccants and any substance applied to crops either before or after harvest to protect the commodity from deterioration during transport and storage[6]. The FEPCA definition is similar to the EP, in addition it lists some classes of plants and animals[9].

The use of pesticides started with the application of Arsenic to kill insects[10]. The use of arsenical compounds has continued and, during the early part of the 20th century, large quantities of compounds such as lead arsenate were used to control insect pests[11]. Another arsenical compound, Paris green (copper aceto-arsenite), was extensively applied to pools and standing water in the tropics in an attempt to control malaria-transmitting mosquitoes [11, 12]. Inorganic compounds, which

were used as insecticides and fungicides, contained antimony, boron, copper, fluorine, manganese, mercury, selenium, sulfur, thallium, and zinc as their active ingredients and were not found to be very effective as insecticides [13]. However, many such compounds were persistent in the soil and there were instances of crops being damaged by inorganic residues in the soil. The era of synthetic organic pesticides began about 1939 [6, 14]. These chemicals were found to be very effective in controlling pests, so their adoption was extremely rapid. Several new chemicals such as BHC, chlordane, aldrin, dieldrin, endrin, endosulfan, isobenzene and carbamates were developed and used as pesticides [6, 10, 15].

To date, thousands of chemical and biological substances are used for many different applications [16, 17] that include:

- eliminate, control the numbers of or attract all manner of pests destroying plants and plant products;
- destroy weeds, foliage and excessive numbers of flowers;
- increase the production of animal and plant biomass;
- combat the pathogens of humans, animals and plants;
- regulate the growth of plants or their parts;
- combat micro-organisms causing the rotting of agricultural products;
- combat insect pests and other animals;
- protect textiles in textile mills and dry-cleaning establishments;
- prevent the development of algae in swimming pools;
- combat fungi in paints and paper products;
- protect museum exhibits from pests; and,
- combat the growth on algae on ships and boats;

1.2.2 Pesticides Classification

Pesticides can be classified according to:

a) Chemical structure
b) Their use

c) Hazard they cause

Table 1.1 presented classification of pesticides using the criteria's mentioned above and respective examples [18].

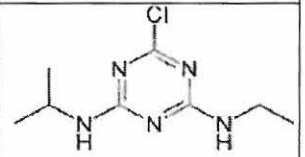
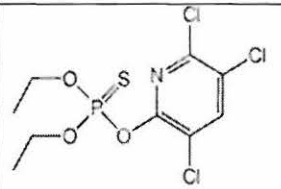
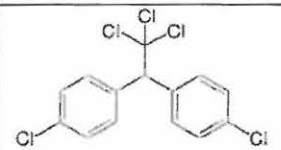
Table 1.1: Classification of pesticides

Criteria	Group	Examples
Chemical structure	Organochlorines	DDT, Aldrin, Endosulfan
	Organophosphorous	Malathion, Chlorpyrifos
	Organonitrogen	Atrazine, Bitertanol,
	Carbamates	Pyridaben
	Dithiocarbamates	Carbaril, carbofuran
	Carboxilic acid derivates	Thiram
	Substituted Ureias	2,4-D
	Triazines	Diuron
	Pyrethroids	Atrazine, Simazine
	Neem Products	Cypermethrin
	Organometallics	Nimbidin
	Thiocyanates	Phenylmercury acetate
	Fhenol	Lethane 60
Use	Acaricides	Abemectin, diazinon
	Fungicides	Benomil, Oxime copper
	Herbicides	Atrazine, Aminocarb
	Insecticides	Lindane, Ethion
Hazards	Class I (highest hazard class)	
	Ia (extremely hazardous)	Aldicarb, Parathion
	Ib (highly hazardous)	Acrolein, Methiocarb
	Class II (moderately hazardous)	DDT, Diazinon, Chlorpyrifos
	Class III (slightly hazardous)	Atrazine, Carboxin

1.3 Identity and properties of the selected pesticides

Table 1.2 presents some properties and identity of selected pesticides based on polarities and chemical structures [6, 19].

Table 1.2: Identity and physicochemical properties of model pesticides

Common name	IUPAC name	Group	Class	Molecular weight(g/mol)	Solubility (mg/L) (20°C)	pKa	pK_{ow}	structure
Atrazine	6-Chloro-N-ethyl.N'-isopropyl-1,3,5-triazine-2,4-diamine	herbicide	ONP	215.7	33	1.7	2.7	
Chlorpyrifos	O,O-Diethyl.O-3,5,6-trichloropyridin-2-yl phosphorothioate	Insecticide	OPP	350.6	1.05		4.7	
DDT	1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane	Insecticide	OCP	354.5	0.006		6.91	

1.4 Pesticides effect on the environment

The effects of pesticides on the environment are defined by the composition and properties of pesticides, as well as the conditions of the environment.

1.4.1 Organochlorine pesticides (OCPs)

The OCPs are divided into three groups:

- DDT related compounds,
- Cichlodienes insecticides (Aldrin, endrin, heptachlor and endosulfan) and,
- Isomers of Hexachlorocyclohexan HCH [15]

Organochlorine pesticides have been used extensively in the past two decades to combat pests in agriculture, industry and even to control diseases such as typhus and malaria [7]. Some examples of OCPs that have been commonly used in the past include toxaphene (Toxakil), endrin (Hexadrin), aldrin (Aldrite), endosulfan (Thiodan), BHC (hexachlorocyclohexane), dienoclor (Pentac), heptachlor (Heptagran), dicofol, mirex (Declorane), chlordane, and DDT. In additional to their use as insecticides in agricultural and forestry settings, OCP compounds have also been widely used as structural protection against termites in the past. Some of these compounds are still commonly used in developing countries. Their physicochemical properties (lipophilicity, low vapor pressures and slow rate of degradation) make OCPs highly resistant to biological degradation and therefore are highly persistent and bioaccumulate in the environment.

Due to their wide spectrum of distribution, they reach for example the aquatic environment from different sources (agricultural through atmospheric precipitation or transport, dredging, infiltration and soil erosion, also traces of pesticides are dispersed after spraying, accidental spills, and their direct application in fields situated near aquatic systems or when applied to rivers or ponds to kill fish) and its lower biodegradation, these compounds pose a serious threat to public health and most forms of life, since OCPs may behave as pseudo hormones, disrupting the endocrine system in wildlife, humans, as well as aquatic biota [8, 20].

Many health or developmental problems are linked to these endocrine disrupters, such as neurological damage, Parkinson's disease, birth defects, respiratory illness, early sexual development, behavioral changes, breasts cancer, lowered sperm counts and immune system dysfunction [20].

Some OCPs are environmentally very stable, can be transported long distances, accumulate in living organisms, and can be deposited in sediments at the bottom of water basins. Numerous publications have confirmed the presence of such pesticides in not only surface waters and groundwater's but also in drinking water, rain water, and even in the water and ice from mountainous and polar regions. That is why OCPs, whose range of activity turned out to be wider than at first thought, were gradually withdrawn [16]. Therefore, monitoring trace levels of OCPs in food and waters is still imperative for health protection and environmental control because of their difficult degradation, easy accumulation and high toxicity [20].

1.4.2 Organophosphorus pesticides (OPPs)

Organophosphorus pesticides comprise a fundamental group of compounds used for plant protection including all phosphorus containing organic compounds, they act as insecticides. Structurally, they are usually esters and decompose quite quickly; they are very poorly soluble in water, but are more so in organic solvents and fats. Thus these compounds, in contrast to the OCPs, do not represent a serious challenge as contaminants of soil and water and rarely enter the human food chain. Being esters, the compounds are susceptible to hydrolysis, and their breakdown products are generally nontoxic. Direct contamination of food by concentrated compounds has been the cause of poisoning episodes in several countries [7].

OPPs are widely used as replacements for more persistent OCPs in agriculture by virtue of their biodegradable nature and short persistence. In fact, chlorpyrifos, an organophosphate compound, has become a widely used termiticide, serving as a substitute for the more persistent OCPs used in the past. However, because of the acute toxicity of some of the organophosphate compounds, another class of pesticide—pyrethrin— has become more widely used. Examples of commonly

used organophosphates include Dursban (chlorpyrifos), Knox Out 2FM (diazinon), and Vapona (dichlorvos) [8].

OPPs are toxic because of their inhibition of the enzyme acetylcholinesterase[21]. The enzyme inhibition results in the accumulation of acetylcholine in nerve tissue and effector organs, with the principal site of action being the peripheral nervous system. In addition to acute effects, some OP compounds have been associated with delayed neurotoxicity, known as organophosphorus-induced delayed neuropathy [7].

The use of OPPs can provide benefits for increasing agricultural production. The improper use of OPPs, however, may also result in the presence of their residues in agricultural products and thus eventually in animals and humans. Moreover, OPPs are mostly sprayed over crops or applied to soils, leading to the direct transfer of OPPs from drainage of agricultural lands to other parts of surrounding environments, including ground and surface water [22].

1.4.3 Organonitrogen pesticides (ONP)

Since the 1960s, atrazine and dichlobenil have been used extensively as broad-spectrum herbicides both in agriculture and in urban areas. Their use has been based on the assumption that they are either retained in the upper soil or degraded by microorganisms and hence do not penetrate into the groundwater. However, dichlobenil is mainly degraded to 2,6-dichlorobenzamide (BAM) by biotic or abiotic processes in the hydrosoil and is extremely resistant to further degradation[23-25]. Consequently, dichlobenils has been banned in many countries since its discharge into groundwater has resulted in the widespread presence of BAM in the drinking water both in Europe and in the United States of America [26]. Furthermore, an increasing presence of atrazine and its degradation products in groundwater supplies has also been reported [27]. Atrazine's half-life degradation in soil ranges from 1.5 months to 5 years and its intensive use in agriculture has led to the accumulation of atrazine, polluting the soil and the water at levels exceeding the permissible limits with varying concentrations (e.g., 1 to

>130 μg/L). The uses of cyanazine were halted in 2001 and no further use was permitted after 2002[7].

Dichlobenil and atrazine have well documented mutagenic, teratogenic and carcinogenic effects, and hence pose a potential risk factor for public and environmental health[26]. The resistance of atrazine to microbial degradation, and its slow hydrolysis, low vapor pressure, and moderate aqueous solubility enhance its presence as a groundwater contaminant. It has recently been reported that atrazine can induce hermaphroditism and demasculinization in African frogs, while in humans; the effects in this sense are not clear yet [28]. Considering these facts, it is not surprising that many efforts have been focused in developing efficient remediation treatments to clean atrazine from groundwater[27].

OPPs and ONPs act on living organisms as receptor inhibitors. They bind with the receptor of acetylcholinesterase, an enzyme essential for the proper functioning of the nervous system. The bind with acetylcholinesterase gives rise to characteristic symptoms of nervous-system irritation. Such a xenobiotic-receptor bond can block an important metabolic step, cause metabolism to take a dangerous course, accelerate or retard transmission of nerve signals. It can also lead to severe poisoning, and catalyze teratogenic or carcinogenic processes [16].

1.5 Methods for the determination of pesticides in water

The need to determine numerous contaminants present in the environment at trace levels means that laboratories have to be capable of applying the relevant analytical procedures. Laboratories also have to be equipped with the necessary tools for obtaining reliable results, not to mention state-of-the-art apparatus enabling large numbers of compounds to be quickly and reliably determined in multifarious matrices.

A large number of multiresidue extraction methods have been developed over the years. The most frequently used methods employ solvent extraction followed by liquid–liquid partitioning chromatographic clean-up and gas chromatography (GC), where at least 60% of the registered pesticides and/ or their metabolites can

be analysed by using GC with selective detection. GC equipped with electron capture detector (ECD) is the most widely used technique especially for the determination of OCPs in different matrices[10]. The tentative identification is by comparison of the retention times of standard reference material (SRM) with sample extracts, and confirmation using thin-layer chromatography (TLC), by analysis using different polarity columns, and most recently through mass spectrometry (MS) [6, 29].

Chromatographic analysis usually is preceded by sample preparation to extract the pollutants from environmental matrices (i.e. soil, sediment, air, water). In the isolation of the target compounds from matrices, various extraction and clean-up procedures have been employed. Table 1.3 shows some techniques of sample extraction and clean-up of pesticides in different matrices, some characteristics for comparison and applications [16, 20, 22, 30, 31]. Other methods that can be found in the literature for pesticides analysis are Capillary Electrophoresis, Immunochemical Methods, Spectrophotometric methods (Spectrofluorometry, Chemiluminescence) and Electrochemical Methods (Voltammetry) [6].

Table 1.3: Techniques of sample extraction and purification

Technique	Extraction	purification	Short characteristics	Applications
LLE (liquid-Liquid extraction)	++	_	Laborious, highly time-consuming, large solvent volume, purification step needed	OCP, OPP and ONP
Soxhlet and soxtec extraction	++	_	Laborious, highly time-consuming, large solvent volume, no filtration required	PCB, OCP,OPP
FMASE (Focused microwave-assisted Soxhlet extraction)	++	_	low solvent volume, but solvent must be able to absorb microwaves, purification step needed	Pesticides residues
USE (Ultrasound Assisted Extraction)	++	_	Large solvent volume, purification step needed	OPP,OCP
MAE (microwave – assisted extraction)	++	_	Evaporated temperature, low solvent volume, but solvent must be able to absorb microwaves purification step needed	OCP, OPP and ONP
SDME (Single - drop microextration)	++	_	low solvent volume, easy automation	OCP
ASE (accelerated solvent extraction)	++	_	Evaporated temperature, low solvent volume, purification step needed	PCB

SFE (supercritical fluid extraction)	++	+	Many parameters to optimize, decreased or no use of solvents, evaporated temperature, concentrated extracts	OPP and OCP
Membrane extraction	++	+	Highly time-consuming easily automated, decreased or no use of solvents, direct introduction of sample	OPP
SPE (Solid Phase Extraction)	++	+	Easily automated, low solvent volume	OPP, ONP, 4 Triazine, carbamates
SPME (Solid Phase Micro Extraction)	++	_	Decreased or no use of solvents, easily automated, no sensitivity to suspended matter, problems with reproducibility and optimization	OPP, triazine, Carbamates, anilide, cloroacetamide
MSPD (matrix solid phase dispersion)	++	+	Low solvent volume, not suitable for dry samples or sample with high lipid content – adsorbent consumption is then high and MSPD requires un additional clean-up step	
SBSE (Stir Bar Sorption Extraction)	++	_	Significant increase in amount of extracting medium (PDMS) as compared to SPME, with results in high degree of recovery	ONP and OPP
MIP (Molecularly Imprinted Polimer)	++	_	Higher specificity and better stability	OPP

++ main application, +secondary application, _generally no application

1.6 Aim of investigation

The aim of the study presented in this thesis was to evaluate particle or fiber based polymeric sorbent for SPE of pesticides in water by chromatographic analysis as well as to develop a colorimetric method based on AgNPs for point of use pesticides analysis in aqueous media.

The specific objectives were:

i) To fabricate polysulfone particles or fibers through electrospraying or electrospining technique

ii) To test the adsorption capacity of the particles or fibers on three model pesticides Atrazine, Chlorpyrifos and DDT

iii) To evaluate the properties of the fabricated sorbents

iv) To develop colorimetric methods for pesticides analysis based on AgNPs for Atrazine and Chlorpyrifos

Chapter 2 Polysulfone sorbents for pretreatment of Pesticides in water

Overview

This chapter presents background information on solid phase extraction. The emphasis is on the use of polymeric material to extract three model pesticides from water. It has been configured to provide details of the general reagents and equipment that were used as well as experimental procedures for the three important components of the chapter which were; i) fabrication and characterization of the sorbents, ii) quantification for recoveries studies by GC-μECD and iii) evaluation of the characteristics of the sorbents by static and dynamic experiments employing HPLC-DAD. It concludes by reporting the experimental aspects of the studies that were carried out in this section of the thesis.

2.1 Introduction

2.1.1. Adsorption process

Adsorption is the process that involves trapping of atoms or molecules that are incident on the surface by result of attractive potential of atom or molecule that binds onto the surface under proper circumstances. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent or simply sorbent. This surface accumulation of adsorbate on sorbent is called adsorption or sorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology [32].

Charcoal was the first sorbent to be used for the extraction of organic compounds from water. The advantage of this material was the high retention of low-molecular-mass polar pesticides and their metabolites [33].

2.1.2 Solid phase extraction

SPE is an extraction method that uses a solid phase and a liquid phase hosted in a solid support to isolate one, or one type of analytes from a solution [34]. It is usually used to clean up a sample before chromatographic analysis or other analytical technique so as to identify as well as quantify the amount of analyte(s) in the sample. SPE was first introduced in the mid-1970s [35]. It became commercially available in 1978, and to date SPE cartridges and disks are available from many suppliers [36]. SPE is currently one of the most widespread extraction methods for environmental [37-41], food [42] and biological samples [43, 44].

SPE is based on selective retention of analytes on a sorbent and subsequent elution with a suitable solvent. Two different approaches can be used to develop the extraction protocol. As in the traditional SPE approaches, the extraction column can operate in "normal phase" mode or "reverse phase" mode. In the first approach the analyte is selectively retained by the extraction column by non-covalent interactions between the analyte molecules and the sorbent binding sites, whereas interfering molecules are not retained by these sites. Then, elution of the analyte is obtained by increasing the strength of the mobile phase. In the reverse phase mode, the analyte and any other interfering substance are retained by the hydrophobic polymeric matrix that acts as a reverse phase material without any apparent specificity towards the target analyte. The elution of the interfering substances is obtained by increasing the hydrophobicity of the mobile phase, while the target analyte is not eluted because of its ability to bind the sorbent binding sites [45].

The general procedure is to load a solution onto the SPE sorbent phase (adsorption), wash away undesired components (clean-up), and then wash off (desorption) the desired analytes with another solvent into a collection tube [46].

SPE is particularly suited for the isolation of organic micropollutants from water and has now become the method of choice in order to carry out simultaneously the extraction and concentration of many pesticides and metabolites in aqueous samples [47].

SPE possesses distinct advantages over other extraction techniques (see Table 1.3 of the chapter1) that include:

(1) Requires a lower volume of solvent than traditional liquid–liquid extractions;

(2) Involves simple manipulations which are not time consuming and makes it possible for field treatment of samples;

(3) The SPE cartridges can be used for short-term storage of the sample;

(4) Provides high enhancement factors proportional to the volume of water passed through the SPE cartridge [48].

2.1.3 Sorbents for SPE

The selection of an appropriate SPE extraction sorbent depends on understanding the mechanism(s) of interaction between the sorbent and the analyte of interest. That understanding in turn depends on the knowledge of the hydrophobic, polar and inorganic properties of both the solute and the sorbent. Solid phase sorbents (SPS) retain solutes by mechanisms such as Van der Waals and electrostatic interactions [49].

Non-polar sorbents with silica base were the first materials tested in SPE of phenols in water, of which, C18 is the most popular [50]. The most widely used sorbents are C8 and C18 chemically bonded to silica, carbon black and polymeric resins. But in the last years, new styrene–divinylbenzene packing materials have been developed allowing greater π–π interactions between analytes and the sorbent [47].

After more than 20 years of development, the variety of SPE sorbents has increased significantly and thus a wide range of SPE columns are commercially available. However, the conventional sorbents such as silica, graphitized carbon black and macro porous

polystyrene divinylbenzene (PS-DVB), show low retention for polar compounds that is characterized by the small breakthrough volume for highly polar molecules in water making them inadequate for quantification [48].

In order to improve the extraction efficiency for polar compounds, the development of new sorbents modified by introducing polar groups has become a major research direction. Some examples of the modifications include the use of cyano, diol, or mino, octadecyl, octyl, cyclophenyl or phenyl groups. With the modifications achieved, non-polar to moderately polar analytes are extracted from polar solutions onto non-polar silica sorbents (e.g. C18, C8, C2, C1, CH, PH, CN) [49].

Silica sorbents contain a low concentration of ionized silanol groups capable of retaining basic solutes by ion-exchange mechanism. Low recovery of these compounds can result from inability of eluting solvents to displace the analytes from the ion-exchange sites. Sometimes the addition of a competing base to eluting solvent can solve this problem. However, silica based sorbents are unstable at pH extremes 2>pH>8. Porous polymers and graphitic carbon sorbents offer a potential solution as they are stable throughout the full pH range and do not possess silanol groups. Those porous polymer sorbents are generally copolymers of styrene [51].

The copolymer styrene-divinylbenzene, an example of styrene copolymer, is well known as a hydrophobic sorbent with retentions equal or higher than on octadecyl-bonded silica. So only non-polar to moderately polar analytes can be retained on that polymer [49]. Some of other polymers applied for pesticides analysis are: Amberlite XAD-2 and XAD-4, PRP- 1, acrylate polymers (Amberlite XAD-7 and XAD-8 [36], Separon SE), 2,6-diphenyl-p-phenylene oxide (Tenax GC), ethylvinylbenzene-divinylbenzene (Porapak Q), amide esters (polyurethane foam) and organic polymeric sorbents without functional groups (Wolfatit Y77) [33].

Tested polymers showed interesting characteristics to preconcentrate the majority of pollutants. Retention experiments showed that PRP-1 was better suited for trace enrichment purposes than octadecyl-bonded silica material. Similarly positive results were

achieved also with the other type of polymeric material, PLRP-S, which was proven to be a good compromise between sufficient retention and limited additional band broadening. It was also found to be suitable for preconcentration of a wide range of pesticides [52].

Another aspect that is a disadvantage for silica based sorbents is related to the size of the particles. Silica microparticles were shifted to the use of silica nanoparticles due to their large specific surface area and intrinsic surface reactivity. However, the use of silica nanoparticles for packed sorbent SPE still remains a challenge chiefly because of high back pressure, which explains why to date the smallest microparticles that has been used for packed sorbent SPE has a diameter of 8 μm. Due to the fact that the simple electrospinning set-up allows the collection of nanofibers in the form of a porous nonwoven mesh, it follows that porous electrospun nanofiber based SPE sorbent formats could be easily fabricated. Therefore, it is anticipated that electrospun silica nanofibers would be used for packed sorbent SPE, thus overcoming the high back pressure limitation associated with silica nanoparticles [53].

Chemically modified resins containing different polar functional groups (acetyl, hydroxymethyl, benzoyl or o-carboxybenzoyl), have been developed and used in the SPE of polar compounds from environmental waters. Several other highly crosslinked polymers such as Envi-Chrom P [54], LiChrolut EN [55, 56] or Isolute EN [57, 58] have become available. These sorbents have a higher degree of crosslinking and so have an open structure (high porosity material), which increases their specific surface area and allows greater π–π interactions between analytes and sorbents that increases the breakthrough volumes of analytes [52].

Another class of sorbents that is based upon molecular recognition is used. One of the approaches uses antibodies to facilitate a high degree of molecular selectivity. Extraction, concentration and isolation are possible in a single step. Single analytes can be targeted but due to the cross-reactivity of antibodies, immunoextraction sorbents have been also designed to target groups of structurally related analytes. Some examples of the application of Enzyme Linked Immunosorbent Assays (ELISA) have been reported in literature [59,

60]. Another approach deals with molecular imprinted polymers (MIPs), which avoids the inherent instability of biological materials. ELISA and MIPs based SPE materials are now emerging from laboratory studies and their development was confirmed by Zao et al. and Zhu et al. [61, 62].

During the search for the best SPE material it became obvious that there is no universal sorbent suitable and optimum for all groups of pesticides. Each material was found advantageous for certain applications but the drawbacks were reported when used with other compounds, matrices or techniques. Therefore, the drive to find the best material slowly turned into the efforts to find the optimum solution for a particular problem. Simultaneously, the major attention of analysts has been gradually shifted to technological issues. However, some technical problems such as undesired dilution and possibility of sample contamination still remain. This scenario suggest the need for new materials to be used, considering the properties of the analyte, as well as the properties of the sorbents, as the main way to improve on the efficiency of the extraction process.

The advent of nanotechnology has been a major boost in the research area of polymer-based sorbents as it opened up possibilities for new classes of materials that could be used. Polymers can be transformed into nanoscale structures for example nanofibers and nanoparticles which can offer enhanced responses and rapid procedures for SPE due to the large surface area by volume ratio, small interfibrous pore sizes, penetrability and interaction with other compounds.

On the basis of the hypothesis that the large surface areas of nanocomposites facilitate interaction between nanocomposites with target molecules, reducing the scale of materials used in SPE is gradually attracting interest. Some examples of the use of nanomaterials for SPE were reviewed by Núria Fontanals [63]. With the same perspective, a polymer (polysulfone) was chosen for the studies conducted in this thesis.

2.1.4 The formats and procedures in SPE

There are many ways of packing sorbents for SPE. The most common are the standard SPE cartridges, also called columns.

2.1.4.1 Cartridges

Typical cartridge devices consist of short columns (generally an open syringe barrel) containing a sorbent with a nominal particle size of 50-60 μm, packed between porous plastic or metal frits [64]. The size of the cartridge depends on the amount of sorbent that is controlled by the expected mass of the analyte or of the analytes in the sample that will also be extracted. Cartridges are available with sorbent mass of 10 mg, 10 g or more [65]. Limitations of packed SPE conventional cartridges include restricted flow-rates and plugging of the top frit when handling water-containing suspended solids such as surface water or wastewater. Therefore, the typical volume of sample is 500 ml if it has not been carefully filtered. In the case of filtered sample the volume can be higher (see Figure 2.1).

2.1.4.2 Discs

Disc is a variation of the extraction cartridge were the sorbent is placed into a web of Teflon or other inert polymer then is trapped in a glass fiber of paper filter. The discs can be placed in a syringe barrel or other housing, and the resulting hybrid "disc cartridge" (see figure 2.1) [66]. Glass fiber discs are thicker and more rigid, providing higher flow-rates than with PTFE membranes. The sorbent particles embedded in the disks are smaller than those found in the cartridges (8 μm diameter rather than 40 μm). The short sample path and small particle size allow efficient trapping of analytes with a relatively high flow-rate through the sorbent, as compared to the cartridges. The disks are primarily used to reduce analysis time when handling large volumes of aqueous environmental samples. The extraction disk cartridges come in three diameters: 4 mm/1 ml, 7 mm/3 ml and 11 mm/6 ml. One of the disadvantages of using disks instead of cartridges is the decrease in the

breakthrough volume, mainly for more polar compounds. For this reason, disks are used when there is a strong interaction between the analyte and the sorbent [46, 66].

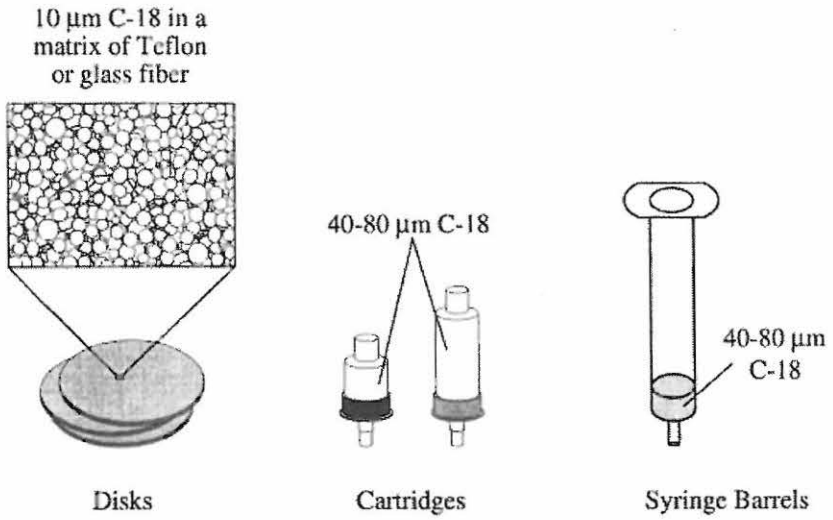


Figure 2.1: Examples of SPE formats

2.1.5 Nanomaterials

Nanomaterials may exhibit unique mechanical, optical, magnetic and electronic properties as a result of their nanoscale dimensions [67]. Nanofibers are an important class of nanomaterials with lengths and diameters from a few nanometers to micron size which have a high surface area to volume ratio, as a result, nanofibers are good candidates to be used as sorbents and extracting media [68].

Various techniques have been employed to fabricate polymeric nanofibers and nanoparticles and these include; polymerization, preformed polymers or ionic gelation [38, 69], drawing, template synthesis, phase separation, self-assembly and electrospraying/electrospining [70].

2.1.6 Methods for producing nanoparticles and nanofibers

Polymeric nanofibers/nanoparticles can be fabricated by a number of techniques such as drawing, template synthesis, phase separation, and self-assembly. Despite their advantages, these conventional methods have difficulties in producing fibers/particles with diameters smaller than 10 μm and controlling fiber orientations. In addition, fiber dimensions cannot be controlled easily with drawing and self-assembly techniques. It should be noted that self-assembly is a complex and inconvenient method. Phase separation and self-assembly techniques are limited to be effective with only few specific polymers with low yields. Melt blowing is another promising technique that has been shown to be capable of producing nanofibers in a single stage. However, due to the underlying driving mechanism, the attenuation rate is essentially slow, and thus numerous very small orifices are required to obtain nanofibers with significant throughput [71]. Another approach to produce polymer nanofibers/ nanoparticles in a single stage is electrospinning/electrospraying [72-74].

Electrospraying/electrospinning provides a simple and versatile method for generating ultrathin fibers and particles from a rich variety of materials that include polymers, composites and ceramics. While the electrospinning process still suffers from low throughput, relatively high attenuation rates can be achieved with some process modifications [75]. The modifications eventually result in increased throughputs thus positioning electrospinning as an attractive candidate to address the industrial demand. Specifically, electrospinning technique has been found to be a unique and cost-effective approach for fabricating large surface area mats for a variety of applications.

2.1.6.1 Electrospraying/ Electrospinning

In recent years, electrospraying and electrospining have been used to fabricate polymer surfaces with controlled morphology, such as beads and fibers with diameters in the range of micro- to nanometer. Either of the electroprocesses involves the application of an electric field on an injected polymer solution or melt to produce a jet. More precisely, a polymer solution flows through a thin nozzle under the influence of high electric field. The

electric field is applied between the nozzle and a collector. As a result of surface tension, viscoelastic force and electrostatic repulsion between charges on the jet surface, small droplets or particles are generally formed in electrospraying with a polymer solution of low viscosity, whereas fibers are formed in electrospining with a highly viscous polymer solution or melt. [76].

A typical setup of the electrospraying/electrospinning is shown on the Fig 2.2.

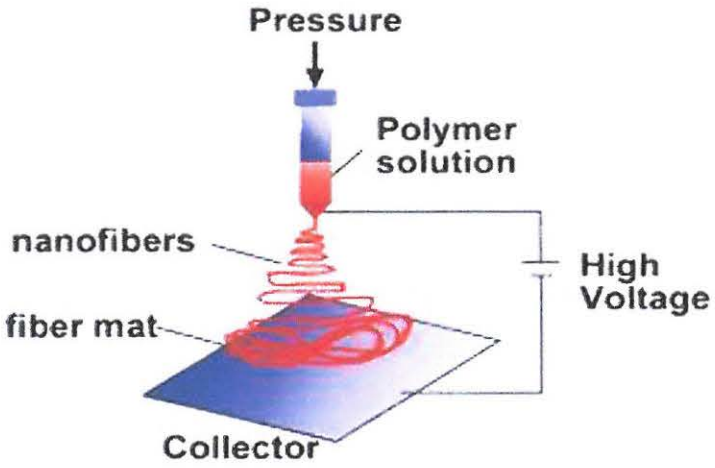


Figure 2.2: Typical electrospinning set-up [77]

Depending on the polymer solution properties (such as viscosity, conductivity, and surface tension) and the process conditions (such as applied voltage, flow of the polymer solution, and nozzle-to-collector distance), materials with different morphologies can be produced. Formation of nanofibers through electrospinning is based on the uniaxial stretching of a viscoelastic solution thus without any disruption to the electrospinning jet the formation of the fiber would be continuous [78]. The morphology can be purely fibrous (electrospinning), composed of particles (electrospraying), or composed of both fibers and particles. Also, the mean fiber or particle size can be controlled[70].

Since the electrosprayed/electrospun mats exhibit remarkable features of high surface area and large porosity, considerable efforts have been made to explore the method to

produce functional surfaces with special characteristic and properties used for a variety of applications [76, 79-81].

2.1.6.2 Parameters that affect the electrospinning/electrospraying process

2.1.6.2.1 Polymer solution parameters

Viscosity, conductivity, surface tension and dielectric constant of the solvent are the polymer solution parameters that affect the electrospraying/electrospinning process. Experiments have shown that a minimum viscosity for each polymer solution is required to yield fibers without beads. At a low viscosity, it is common to find beads along the fibers deposited on the collection plate due to high surface tension of the solution and the insufficient viscosity and electrical conductivity of the solution. When the viscosity increases, there is a gradual change in the shape of the beads from spherical to spindle-like until a smooth fiber is obtained [82].

Surface tension has the effect of decreasing the surface area per unit mass of a fluid. When there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to congregate and adopt a spherical shape due to surface tension. A higher viscosity will mean that there is greater interaction between the solvent and polymer molecules thus when the solution is stretched under the influence of the charges, the solvent molecules will tend to spread over the entangled polymer molecules thus reducing the tendency for the solvent molecules to come together under the influence of surface tension [70].

Electrospinning involves stretching of the solution caused by repulsion of the charges at its surface. If the conductivity of the solution is increased, more charges can be carried by the electrospining jet. Beads will be formed if the solution is not fully stretched. The increase in the stretching of the solution will tend to yield fibers of smaller diameter [70].

A solution with a greater dielectric property reduces the beads formation and the diameter of the resultant electrospun fiber. Solvents such as N,N-Dimethylformamide (DMF) may be

added to a solution to increase its dielectric property to improve the fiber morphology. The bending instability of the electrospinning jet also increases with higher dielectric constant.

2.1.6.2.2 Processing parameters

The processing parameters (voltage, feed rate, temperature, collector, diameter of the needle and the distance tip to collector) also affect the electrospraying /electrospinning process.

The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. Generally, both high negative or positive voltage of more than 6 kV is able to cause the solution drop at the tip of the needle to distort into the shape of a Taylor Cone during jet initiation.

As both the voltage supplied and the resultant electric field have an influence in the stretching and the acceleration of the jet, they will have an influence on the morphology of the fibers obtained. In most cases, a higher voltage will lead to greater stretching of the solution due to the greater electrostatic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers and also encourage faster solvent evaporation to yield drier fibers. When a solution of lower viscosity is used, a higher voltage may favor the formation of secondary jets during electrospinning. This has the effect of reducing the fiber diameter. Another factor that may influence the diameter of the fiber is the flight time of the electrospinning jet. A longer flight time will allow more time for the fibers to stretch and elongates before it is deposited on the collection plate. Thus, at a lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrospinning jet which may favor the formation of finer fibers. In this case, a voltage close to the critical voltage for electrospinning may be favorable to obtain finer fibers [70].

The feed rate will determine the amount of solution available for electrospinning. For a given voltage, there is a corresponding federate, if a stable Taylor cone is to be maintained.

A lower feed rate is more desirable as the solvent will have more time for evaporation. However the temperature of the solution has both the effect of increasing its evaporation rate and reducing the viscosity of the polymer solution.

There must be an electric field between the source and the collector for electrospinning to initiate. Thus in most electrospinning setup, the collector plate is made out of conductive material such as aluminum foil which is electrically grounded so that there is a stable potential difference between the source and the collector.

The internal diameter of the needle or the pipette orifice has a certain effect on the electrospinning process. A smaller internal diameter was found to reduce the clogging as well as the amount of beads on the electrospun fibers.

In several cases, the flight time as well as the electric field strength will affect the electrospinning process and the resultant fibers. Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength. For independent fibers to form, the electrospinning jet must be allowed some time for most of the solvents to be evaporated. When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the collector plate. Moreover, the electric field strength will also increase at the same time and this will increase the acceleration of the jet to the collector. As a result, there may not have enough time for the solvents to evaporate when it hits the collector.

2.1.6.2.3 Ambient parameters

Any interaction between the surrounding and the polymer solution may have an effect on the electrospun fiber morphology. High humidity for example was found to cause the formation of pores on the surface of the fibers [70]. Since electrospinning is influenced by external electric field, any changes in the electrospinning environment may also affect the electrospinning process.

2.1.7 Chemistry of the sorbent material

There are several sorbent material types that can be employed to produce electrospun based SPE material. For example polysulfone was the polymer of choice for the studies conducted in this thesis.

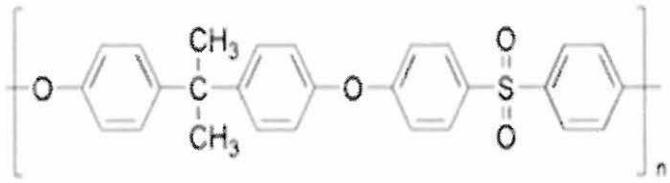


Figure 2.3: Chemical structure of polysulfone

The structural unit of polysulfone (Figure 2.3) is composed of phenylene units linked by three different chemical groups – isopropylidene, ether, and sulfone – each contributing specific properties to the polymer. The complex repeating structure imparts inherent properties to the polymer that conventionally are gained only by the use of stabilizers or other modifiers. The most distinctive feature of the backbone chain is the diphenylene sulfone group.

The sulfur atom (in each group) is in its highest state of oxidation. Furthermore, the sulfone group tends to draw electrons from the adjacent benzene rings, making them electron-deficient.

Thermal stability is provided by the highly resonant structure of the diphenylene sulfone group. This high degree of resonance imparts high strength to the chemical bonds. Substances stable to oxidation strongly resist the tendency to lose their electrons to an oxidizer. It then follows that the entire diphenylene sulfone group is inherently resistant to oxidation [83].

2.1.8 Characterization of the morphology of the fibers and particles

Scanning Electron Microscopy (SEM) is used to characterize the morphology of the particles and fibers. In SEM the area of the sample to be analyzed is targeted by a narrowly

focused electron beam that can be swept across the surface of the specimen to form an image or may target one place only to analyze a particular position. The image is produced due to the interaction of the electron beam with atoms at or near the surface of the samples. SEM can also produce very high resolution images (1 to 5 nm). SEM specimens are required to be conductive at the surface to avoid accumulation of electrostatic charge at the surface. For imaging non-conductive specimens, the surface is coated with a thin film of conducting metal like gold.

2.1.9 Thermal properties of the sorbent

Thermogravimetric analysis (TGA) is used to evaluate the stability of a certain material.

In this technique, the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. The objective is to determine the temperature at which the substance starts to decompose.

From TGA of polysulfone is known that no significant evolution of volatiles from polymer degradation occurs below about 800°F (426°C) conferring to this polymer, good thermal stability [84].

2.1.10 Theoretical aspects of the characterization of a sorbent material

2.1.10.1 Physicochemical properties of the sorbent

Initial evaluation of new sorbent materials for SPE application can be achieved without complete characterization of the physicochemical properties of the sorbent. Progress can be made by relying on the theoretical prediction of physicochemical properties of the sorbents. This is normally achieved through batch experiments as they enable one to generate information about sorbent adsorption characteristics, in particular adsorption kinetics derived from the equilibrium isotherms.

The amount of pesticides adsorbed q_s (mg/g) is evaluated employing Eq.1:

$$q_s = \frac{V(C_0 - C_s)}{m} \quad (1)$$

where C_0 (mg/L) and C_S (mg/L) are the initial real-time concentrations of the analyte in the liquid phase, respectively V (L) is the volume of the solution; and m (g) is the mass of the sorbent.

The linear pseudo-first and pseudo-second order and Elovich models corresponded to Eqs. 2, 3 and 4, respectively, and are used to investigate kinetic behavior of the analytes [85].

$$\ln(q_e - q_t) = lnq_e - K_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 - q_e^2} + \frac{t}{q_e} \quad (3)$$

$$q_t = \alpha + \beta \ln t \quad (4)$$

Where q_e (mg/L) and q_t (mg/g) are the adsorption amount at equilibrium and at time t (min), respectively; α (mg/g.min), K_1 (1/min) and K_2 (g/(mg.min)) are the corresponding rate constants and β (g / mg) adsorption constant.

The moving boundaries models are used to distinguish the relative roles of adsorption steps involved to complement the information about the kinetic of the analyte. If the adsorption is controlled by liquid film diffusion, interparticle diffusion or chemical interaction, the rate constant can be expressed by Eqs. 4, 5 and 6, respectively [85].

$$k = -\ln(1 - F) \quad (4)$$

$$k = 1 - 3(1 - F)^{2/3} + 2(1 - F) \quad (5)$$

$$k = 1 - (1 - F)^{2/3} \quad (6)$$

where F is the adsorption fraction (q_t/q_e), and k is the adsorption rate constant. By plotting a linear relationship of k versus contact time t (min), the regression coefficient (R^2) for the three adsorption steps are obtained, of which the one with the highest R^2 value is assumed to be the controlling rate step.

2.1.10.2 Flow based properties of the sorbent

Given that the major sorption parameters characterizing a SPE sorbent are efficiency (analyte recovery) and breakthrough volume, which may influence some of the main analytical parameters of a determination process (selectivity, concentration ratio, and sample loading capacity). From this point of view, one of the most important parameters is the breakthrough volume, which influences the maximum volume of aqueous sample that can be loaded into a cartridge (adsorption capacity)[86]. A flow through based screening experimental approach relies on breakthrough profile.

Breakthrough volume (V_B) can be defined as the volume giving an assumed breakthrough level (the ratio of the outlet to inlet concentration). The breakthrough volume depends on kinetic parameters of sorbent and on retention parameters as well as on the flow rate of the sample [86].

Assuming that there is measurable analyte retention, the breakthrough curve forms a sigmoid shape that gives an indication of the analyte mass transfer kinetics as a function of the sorbent retention characteristics. In addition to the breakthrough volume, two important parameters that are obtained from the breakthrough curve are holdup volume (V_M) and retention volume (V_R).

These three parameters: (V_B), (V_M) and (V_R), can be defined as points corresponding (on the breakthrough curve) to 1%, 99% and 50% of the maximum concentration of analyte in the eluate. From these parameters, two important chromatographic characteristics of a sorbent bed; theoretical plates (N) and retention factor (k) are calculated [53].

The number of theoretical plates corresponds to the extraction efficiency and it depends on the physicochemical properties of the sorbent, particularly the available surface area for analyte retention. While the retention factor gives an indication of the quantity of sorbed analyte and it is directly related to the sorbent recovery efficiency.

One method that has been employed for the calculation of theoretical plates for conventional SPE sorbents, was proposed by Werkhoheve-Goëwie and co-workers [87] as described in Eq.7.

$$V_B = V_R * (\frac{\sqrt{N}-2}{\sqrt{N}}) \quad (7)$$

The retention factor (k) is calculated from the fundamental equation of chromatography expressed as;

$$V_R = V_M(1+k) \quad (8)$$

Given that the equations for calculating (N) and (k) have been applied to microparticle based sorbents (commercially available sorbents), the same equations can be used for nanofibrous sorbent bed material. More so, bearing in mind that the research work on electrospun nanofiber based SPE sorbents is a step towards the development of electrospun nanofiber based SPE devices, it is necessary to have a fundamental understanding of their kinetic and thermodynamic properties in relation to retention characteristics.

The best mathematical function used to fit the experimental data for a breakthrough curve is the Boltzmann's equation, written in the form used by Origin program:

$$Y = A_2 + \frac{A_1-A_2}{1+e^{\frac{x-x_0}{dx}}} \quad (9)$$

Where Y represents the analyte concentration in effluent, x is the volume of percolation using a single sorbent bad, A_1 and A_2 are two regression parameters, and x_0 is the inflexion point where Y become $\frac{A_1+A_2}{2}$. The maximum value of Y is A_2, obtained for $x \rightarrow \infty$, while the minimum value of Y is approximately A_1, obtained for $x \rightarrow 0$. By means of these parameters one can calculate the characteristic points of the breakthrough curve as following:

$$Y = \frac{99}{100} * A_2 \text{ for hold-up volume} \quad (10)$$

$$Y = \frac{1}{100} * A_2 \text{ for breakthrough volume} \quad (11)$$

and $V_R = x_0$ for retention volume.

The direct estimated parameter is however V_R, where the analyte concentration in effluent is $\frac{A_1+A_2}{2}$ [86].

Pesticides exhibit a wide range of polarities as they fall into the highly polar, medium polar and non-polar category with octanol-water partition coefficient (logKow) between 2.7 and 6.9 for Atrazine and DDT respectively. Because pesticides have some affinity for binding on solid surfaces, the most commonly used sorbents are charcoal, silica as well as porous polymers. The sorptive capacity of a given sorbent depends in part on the treatment or manufacturing conditions and on the composition of the sorbent. Additionally the extraction ability of sorbents in the SPE bed depends also on: (i) the bed capacity; (ii) the loaded volume of sample, (iii) the nature and volumes of conditioning solvents and eluents [86]. Considering the characteristic of polysulfone mentioned on the section 2.1.4 fabrication and evaluation of polysulfone particles and fibers are proposed in this work.

2.2 Experimental

2.2.1 General materials and reagents

Polysulfone (Mw = 22000g/mol) was obtained from Sigma Aldrich (St. Louis, MO USA), atrazine (99%), DDT (98.5%) and chlorpyrifos (9%) from Dr.Ehrenstorfer GmbH. Dimethylformamide (DMF), tetrahydrofuran (THF) were obtained from Merck Chemicals (Wadeville, South Africa).

Hexane, methanol, ethyl acetate, acetone, methylene chloride and acetonitrile, all of pesticide grade were obtained from Sigma Aldrich (South Africa).

2.2.2 Instrumentation and measurements

2.2.2.1 Electrospinning set-up

The electrospinning set-up consisted of a polypropylene 20 ml syringe and a 21 gauge, 90° blunt and stainless steel needle that was clamped horizontally on a syringe pump. The metal electrode and the collector plate were made of copper. The grounded static collector plate was covered with aluminum foil. The stainless steel needle was connected to the tip of the syringe via polytetrafluoroethylene (PTFE) tubing. The anode of the high voltage power supply was connected to the needle. All polymer solutions were delivered by a syringe pump at controlled flow rates. Electrospraying/electrospinning was carried out at room temperature (25 °C). The typical electrospraying electrospinning set-up used in this study is shown in Figure 2.4.

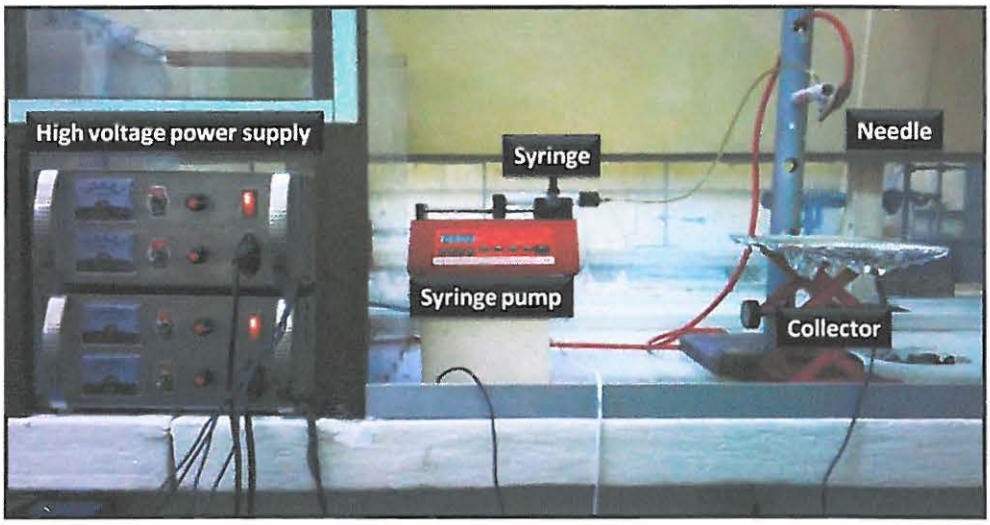


Figure 2.4: The electrospraying/electrospinning set-up that was used for the fabrication of nanoparticles and nanofibers for the thesis

2.2.2.2 Fabrication of electrosprayed particles and electrospun nanofibers

A solution for electrospining was prepared by dissolving 0.5, 1 and 2 g of polysulfone pellets in 10 mL of DMF, THF or both and stirred for 3 h to obtain a homogeneous solution. After loading the polymer solution into a 20 mL syringe, it was mounted on a

programmable syringe pump (New Era, NE-1000). The solution was pumped and particles and fibers were collected on aluminium foil.

The surface modification of a polymer can be achieved via electrospryaing/electrospinning process by varying the conditions that affect the process. For this study condition tested for particles and fibers fabrication are presented in the table 2.1.

Table 2.1: Parameter used on the electrospraying/electrospinning process

Parameter	Levels
Polymer concentration % (m/v)	5, 10 and 20
Solvent system DMF:THF	(100:0, 50:50 and 0:100)
Voltage applied (kV)	12.5, 15, 20
Flow rate (mL/h)	1.2, 4 and 10
Distance tip to colector (cm)	15

2.2.2.3 Characterization of the obtained particles and fibers

The morphology of the nanofiber mats were studied by the Tescan (TS5136ML) Scanning Electron Microscope (SEM) operating at an accelerated voltage of 20 kV and a JEOL JSM-7001F Field Emission Scanning Electron Microscope operating at 2 kV after gold sputter coating.

2.2.2.4 SPE Applied Methods

The adsorption studies were conducted using batch experiments in the column format (see scheme of the Fig. 2.5).

The sorbents were tested using the batch mode, where 10 mL of water spiked with the analytes was placed in a sample vial. A magnetic stirrrer bar and a piece of fiber

(conditioned with hexane) of known mass was added to the solution. The solution was stirred for 1 h and subsequently the fiber was taken out, left to dry in laboratory ambient air for 4 h. When dry it was placed in a vial, the eluting solvent was added, and the solution was stirred for 1 h to let the extraction to take place. The solution was transfered to a round flask, 2 mg of sodium sulfate was added, subsequently it was evaporated in a rotaevaporator until dryness and then reconstituted in 2 mL of methanol. The separation and quantification was achieved employing a GC-μECD or HPLC with a UV-Vis detector.

The column was prepared placing 100 mg of fiber or particles in a clean SPE cartrige, within two teflon frits. Cartridges were loaded on a vacuum manifold, to which a pressure of 15 mmHg was applied for all samples. The packed column was conditioned with 2 mL of hexane and then equilibrated with 2 mL of water. A spiked water sample was loaded into the column then the column was left to dry under a constant air flow. The analytes were eluted and the solution was transferred to a round flask, to which 2 mg of sodium sulfate were added, evaporated in a rotary evaporator to dryness and then reconstituted in 2 mL of methanol. The separation and quantification was achieved on a GC-μECD or HPLC with UV-Vis detection.

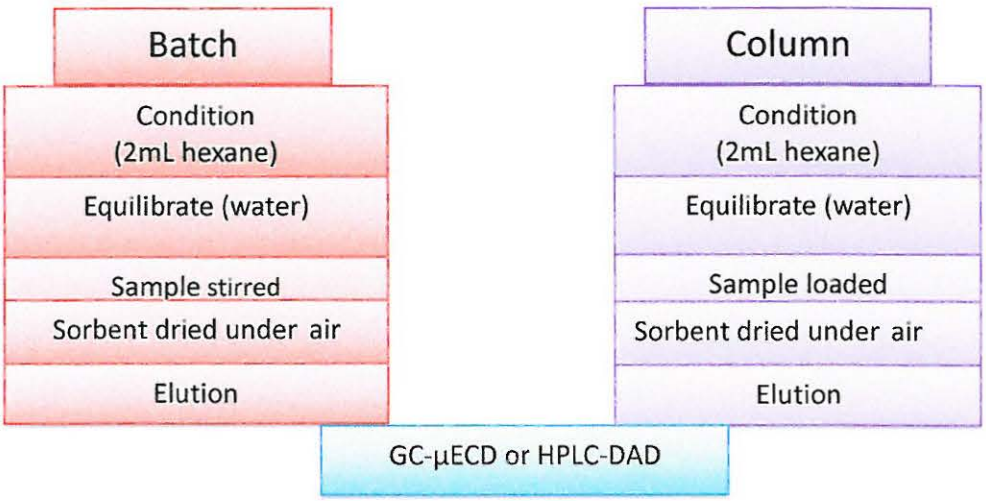


Figure 2.5: Schematic representation of the SPE methods used in this study

2.2.2.5 Optimization of the parameters for SPE

Elution solvent and fiber mass are some of the keys parameters defining SPE that was optimized in this work.

The solvents evaluated for the elution optimization were hexane, ethyl acetate, acetonitrile and dichloromethane and the sorbent mass used for optimization are presented on the Table 2.2.

Table 2.2: Sorbent mass (g) used for optimization of SPE

SPE batch	-	0.0057	0.1000	0.5000
SPE column	0.0037	0.0318	0.1077	0.3091

2.2.2.6 Gas Chromatography with micro Electrochemical Detector (GC-μECD)

For this work an Agilent 6890N version of GC equipped with μECD detector was used for separation and quantification of pesticides for all the recoverie studies. The column used was DB-35ms (30m x 0.32mm id, 0.25μm), the carrier gas was Argon, injection was conducted in the splitless mode at 250 °C, and nitrogen was the makeup gas at a constant flow of 30 mL/min. The oven temperature program is presented in the Table 2.3.

Table 2.3: GC-μECD oven parameters used in the static and beacktrough studies

Stage	Temperature	Hold time(min)	Time(min)
initial	80 °C	1.0	
Ramp1	12°C/min-210°C	0	
Ramp2	15°C/min-230°C	0	
Ramp3	3°C/min-250°C	0	
Ramp4	40°C/min-300°C	10	
Post run	300°C	2.0	
Total			33.08

2.2.2.7 Preparation of standard solutions for calibration of GC-μECD

The internal standard addition method was used for calibration prior to conducting adsorption experiments employing GC-μECD. Stock solutions of Atrazine, DDT and Chlorpyrifos (1000 mg/L) were prepared by dissolving 5 mg of the solid standard in acetone:methanol (1:9) in a volumetric flask of 5 mL. Working solutions of 0.005, 0.01, 0.025, 0.050, 0.100, 0.25, 0.500, 1.00, 5.00 and 10.00 mg/L of mixed pesticides was prepared in methanol for the calibration, and to each standard was added 0.5 mg/L of cypermetrin employed as an internal standard.

2.2.2.8 Preparation of the sample for adsorption experiments

From the stock solution of 1000 mg/L each pesticides, was prepared a solution of 10 mg/L of the mixed pesticides in deionized water added cypermetrin for a final concentration of 0.5 mg/L after elution. 10mL of this solution was used for recoveris studies.

2.2.2.9 Parameters considered for HPLC-DAD

An Agilant 1200 HPLC with UV detector and a column Agilant eclipse plus C18 (4.6 x 75mm, 3.5 μm) was used for the characterization of the fibers by conducting break through experiments. Conditions used for the HPLC are presented in Table 2.4.

Table 2.4: HPLC set parameters

Mobile phase	Column temperature	Flow rate	Wevelegnth	Injection volume
Methanol: water (80:20)	50 °C	0.8 mL/min	210-230 nm	1 μL

2.2.2.10 Preparation of standard and test solutions for HPLC

From stock solutions of 1000 mg/L was prepared standards of of 0.5, 1.0, 50, 100 and 250 mg/L for atrazine and DDT and 0.5, 1.0, 10 and 100 mg/L for Chlorpyrifos.

The optimum adorption and desorption time was confirmed through static studies, were 100 mL solutions were spiked with 500 mg/L of each pesticide were prepared, extracted using batch mode with 0.1 g of the fiber. 1.5 mL was collected from the extration flask at (15, 25, 35 and 45 min) and 1 µL was injected into the HPLC. The same procedure was used to determine the maximum amount sorbed per mass of fiber.

For breackthrough experiments, 0.01g of fiber was packed in a 1 mL pipete tip attached to a syringe barrel. The syringe was mounted on a syringe pump and solutions of 10 mg/L of each pesticides were pumped at a flow rate of 1 mL/min. A fraction of 100 µL was collected separatly and 1 µL was injected into the HPLC.

2.2.2.11 Thermogravimetric Analysis

In this work a TGA analysis of the fibers was performed with an Perkin Elemer 2000 TGA 7.

2.3 Results and Discussion

2.3.1 Selection of the sorbent

A variety of sorbents have been used as SPE sorbents for pesticides. Particularily polymer based nanostrutured material have shown to be a good platform for efficient separation, extraction and enrichment of different kind of analytes from complex matrices, due to the high surface area-to-volume ratio, small interfibrous pore sizes, strong permeability and interaction with other compounds providing a great deal of active sites for adsorption. Although the full potential of the polymers have not been explored.

Based on the aplication of polysulfone: Changsheng Zhao et al., reported the use of polysulfone beads for removal of endocrine disruptors [88, 89] and Schmidt and Fritz used sulfonated cation-exchange resin for separation of ionic and neutral organic componds **[90-92]**. However, polysulfone was selected studies reported this thesis.

2.3.2 Fabrication and characterization of the sorbents

Since the objective was to prepare nanomaterial with different morphologies, the parameter was set for concentration (5-20%w/v), voltage (12.5-20kV), flow rate (1.2-10mL/h) and the distance from the tip to the collector was kept constant. In addition, diferent solvents were evaluated with solutions prepared in DMF, THF and a mixture of DMF:THF (1:1).

Different morphologies were obtained by varying the concentration of the polymer solutions. For concentration up to 5 %(m/v) particles were observed (see figure 2.6 A). For 10 and 20 %(m/v) beaded fibers and beads free fibers were obteined respectively (see figure 2.6 B and C).

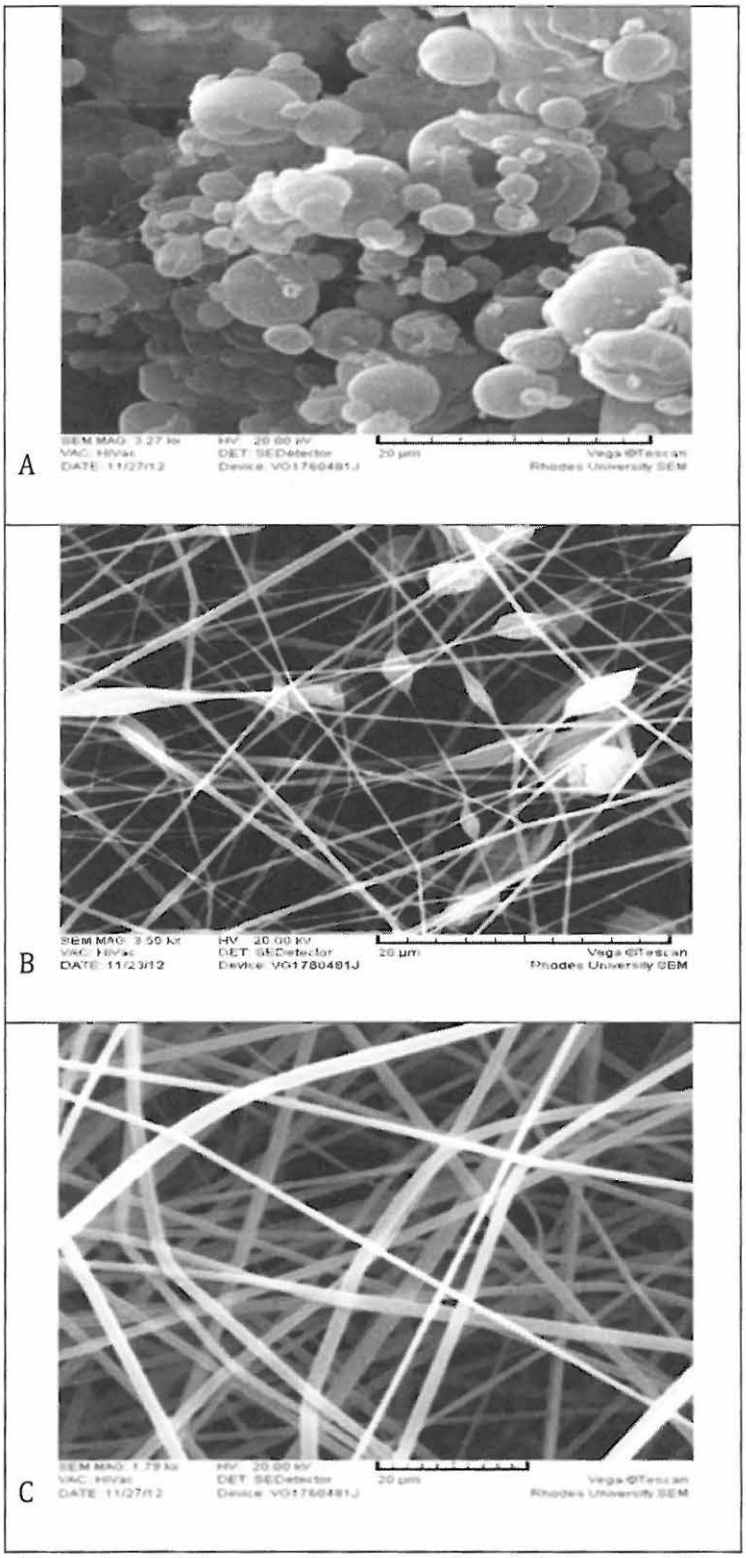


Figure 2.6: SEM images; A particles, B beaded fibers and C beads free fibers

It was found that the only factor influencing the morphology of the fibers was the concentration of the polymer solution.

2.3.3 Quantification for recoveries studies by GC-μECD

2.3.3.1 Calibration Method

The calibration method used for GC was the method of internal standard because the normal calibration method was conduting to results with lower precision. The tested concentration range was 0.025-10 mg/L for atrazine, 0.01-1 mg/L for chlorpyrifos and 0.005-1 mg/L for DDT. The obtained calibration graphs for all analytes were linear at the selected ranges with satisfatory regression coeficient r^2 >0.98

2.3.3.1 Sorbent mass optimization

The sorbent mass obtained from preliminary experiments was found to be 0.1 g for both SPE batch and column as can be seen on the Figures 2.7a and 2.7b.

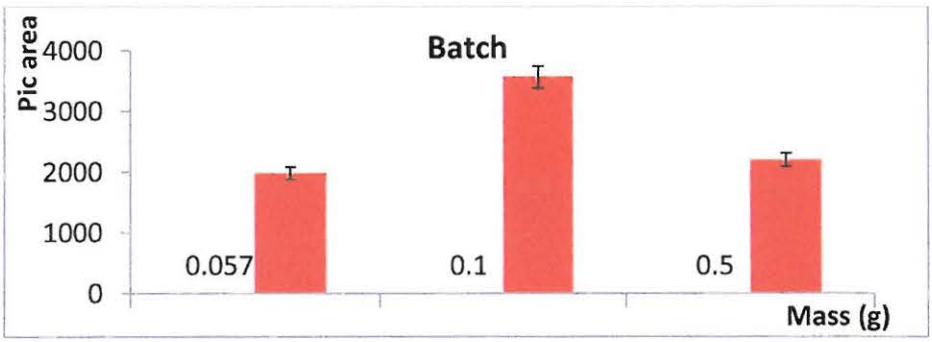


Figure 2.7a: Sorbent mass optimization (SPE batch)

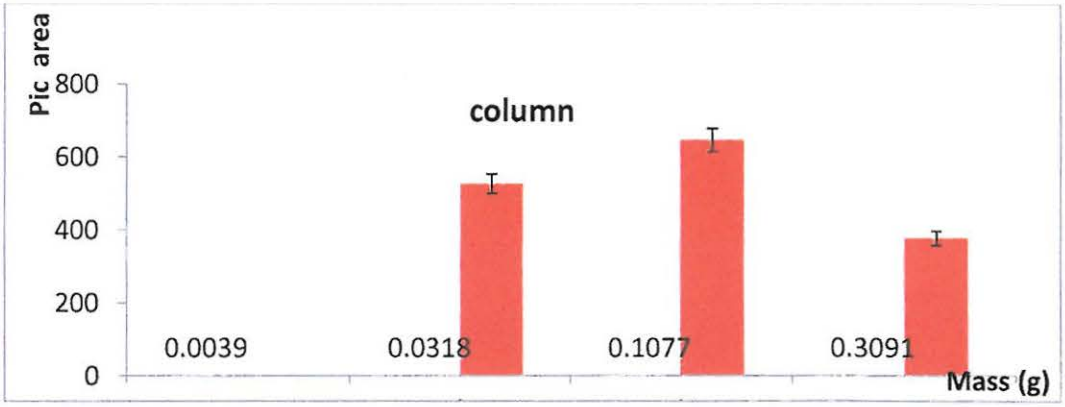


Figure 2.7b: Sorbent mass optimization (SPE column)

2.3.3.3 Selection of the eluent for Pesticides analysis

Many solvents have been reported as SPE eluents. In increasing order of expected elutropic strength, based on their polarity, include: acetic acid, methanol, acetonitrile, acetone, ethyl acetate, diethyl ether, methyl butyl ether, dichloromethane, benzene and hexane. From the list, 4 solvents (acetonitrile, ethyl acetate, dichloromethane and hexane) were selected for elution optimization for both the batch and column SPE modes (see figures 2.8a and 2.8b). The fibers and particles were partially soluble in dichloromethane, hence the pseudo recoveries for the solvents exceeded 100%.

For all analytes and for both SPE modes, hexane showed to be the best elution solvent due to its high elutropic strent. The trend hexane > ethil acetate > acetonitrile observed experimentaly follow the predicted trend based on polarities. Therefore hexane was used as the elution sovent for the next experiments.

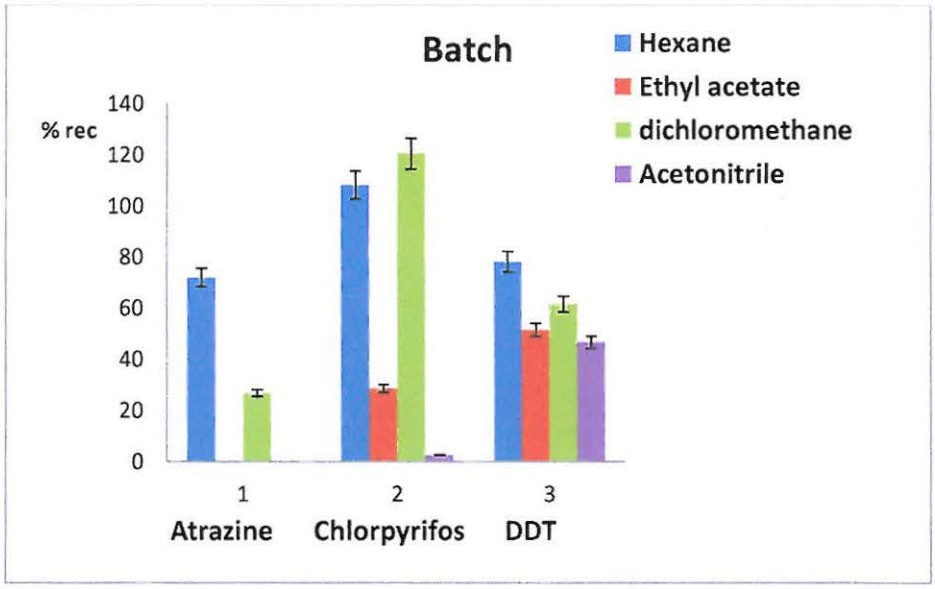


Figure 2.8a: Recoveries obtained for different solvent elution on SPE batch mode

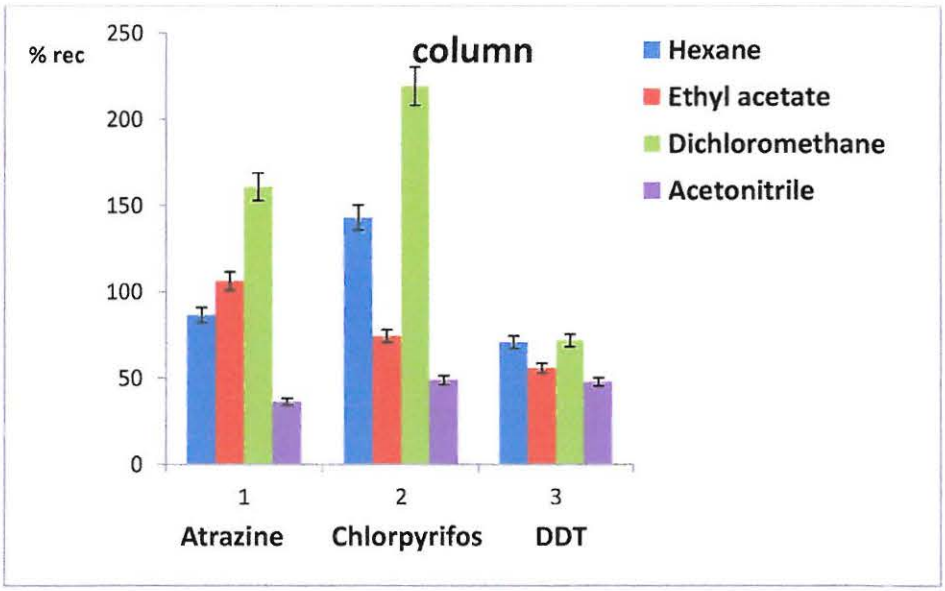


Figure 2.8b: Recoveries obtained for different solvent elution on SPE column mode

2.3.3.4 Comparison of the different sorbent morphology and different formats of SPE

Comparison of adsoption capacity of the sorbents was achieved by recoverie stadies with the results presented on the Table 2.5 where n is the number of replicate and s the standard deviation.

Table 2.5: Percentage recoveries obtained for spiked water samples

% Recovery ± n*s					
	Particles	Beaded fibers		Fibers	
	column	column	batch	column	Batch
Atrazine	25±0.01	76±0.03	102±0.05	57±0.03	105±0.06
Chlorpyrifos	27±0.52	87±0.68	98±1.29	52±0.89	99±1.89
DDT	32±1.24	79±1.83	101±3.82	77±1.52	98±2.30

For different morphologies, it was observed that better results were obtained for beaded fibers and beads free fibers for all analytes. It can be seen clearly that the nanofibers that is assumed to have large surface area to volume ratio performed better than particles. In the electrospraying/electrospinning process, when a low concentration is used, more solvent is separated from the mixture due to vapor-induced phase separation. During electrospraying the rapid evaporation sovent results in a less polymer-rich phase and a more solvent-rich phase. For 5 w/v% concentration solution, the polymer-rich phase was insufficient to form a rigid matrix of particles when electrosprayed; therefore, porous particles collapsed and aggregated together. This could be the reason why particles showed lower sorption capacity.

The recoveries for beaded fibers and bead-free fibers achieved using the column method were lower than the batch method. The packed design exhibited some disadvantages for water analysis. For example, the cross-sectional area was small, therefore sample

processing rates were slower and the tolerance to blockage by particles or fibers and adsorbed matrix components is lower, and channeling reduced the capacity to retain analytes.

2.3.4 Evaluation of the characteristics of the sorbents by static and dynamic experiments for the sorbent using HPLC-DAD

2.3.4.1 Calibration Method

The method used for calibration for HPLC was normal calibration. The analytes showed good linearity with $r^2 > 0.98$.

2.3.4.2 Confirmation of the adsorption and desorption optimization time

It was observed that for all analytes, the adsorption equilibrium is reached at 35 min when more than 90% of the analytes is extracted. The profile for adsorption was also similar to that of desorption (see the plots on the figures 2.9a and 2.9b).

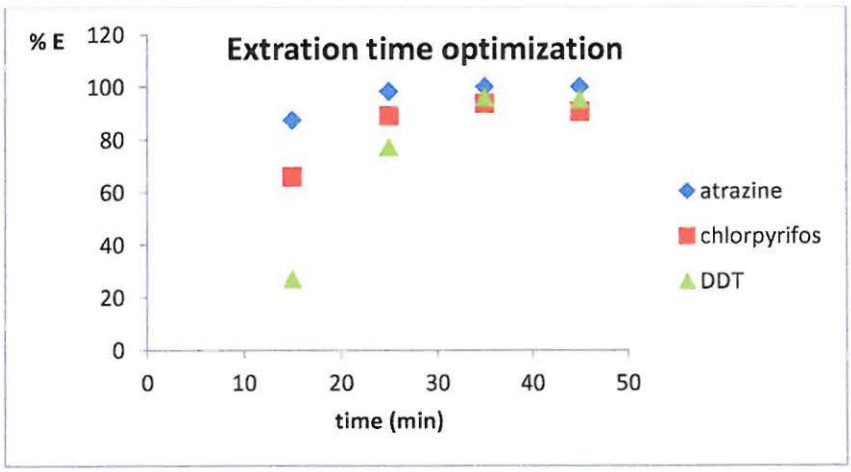


Figure 2.9a: Extraction time optimization plot

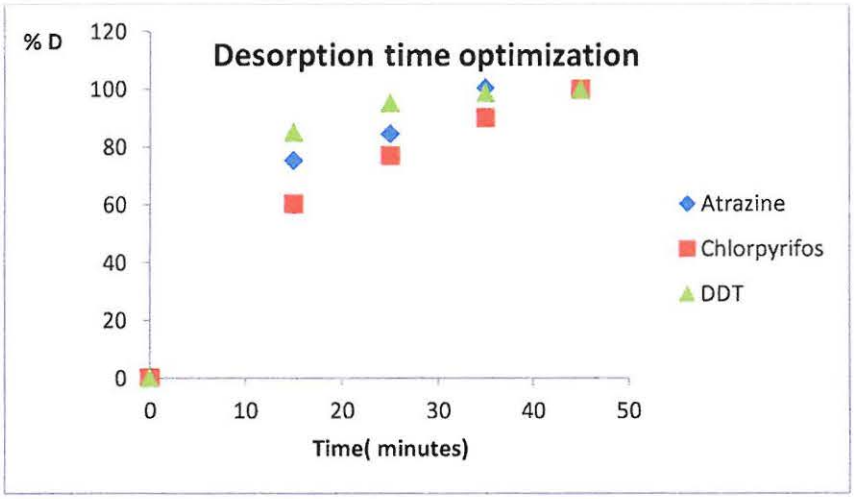


Figure 2.9b: Desorption optimization plot

2.3.4.3 Characterization and properties of polysulfone

From static studies (batch experiments) it was possible to calculate the quantities of each model compound adsorbed (Eq. 1) into the fiber at the equilibrium time. The adsorbed atrazine was 65 mg/g of the sorbent, Chlorpyrifos 250 mg/g of sorbent and DDT 400 mg/g of sorbent.

The quantities of each analyte indicate that the retention of the analytes differed due to the different polarities of the compounds as atrazine is the most polar, chlorpyrifos is moderately polar and DDT is non-polar.

The highly and moderate hydrophobic compounds, DDT and chlorpyrifos, respectively, showed higher mass retention thus suggesting a mechanism based on π-π interactions and for the polar (atrazine), less mass retention and a mechanism based on electrostatic and Van der Waal attractions, since this compound has acidic character (pka = 1.7) and contain nitrogens in its structure that create a possibility to form hydrogen bonds with the sorbent.

This observation was confirmed by the results obtained from breakthrough experiments presented in the section 2.3.4.5.

2.3.4.4 Adsorption kinetics

2.3.4.4.1 Atrazine

The kinetics for atrazine followed the pseudo-second order model, indicated by the high correlation coefficient (see Table 2.6), meaning that it is a chemsorption process probably based on hydrogen bond formation.

Table 2.6: Adsorption kinetic models for atrazine

Model	Equation	Correlation coefficient
Pseudo-first order	Y = - 0.1363X + 4.969	0.992
Pseudo-second order	Y = 0.0044X + 0.0105	0.999
Ellovich	Y = 20.547X + 138.85	0.843
Liquid film diffusion	Y = -0.1365X - 0.3913	0.943
Interparticle diffusion	Y=7.703X+165.7	0.945

2.3.4.4.2 Chlorpyrifos

The kinetic model that better fit Chlorpyrifos was pseudo-first order as it was characterised by the high correlation coefficient (see table 2.7).

An adsorption process consists of several sucessive kinetic steps, viz. transport in the bulk solution, diffusion across the film sorrounding the sorbent particles, diffusion across the pores of the sorbent and finaly adsorption on solid surface [93, 94]. The first three steps are driven mainly by mass balance or Fick diffusion [95], belonging to physical adsorption process, and reasonably reflects the nature of first order kinetcs that is usually governed by the concept of driving force.

The coefficient rate (k, from pseudo-first order model) is $0.057min^{-1}$ and is comparable to the liquid diffusion mechanism which also has $k = 0.057min^{-1}$. The apparent adsoption rate

constant is equivalent to the diffusion rate constant that confirms that it is a physical adsorption process.

Table 2.7: Adsorption Kinetic models for chlorpyrifos

Model	Equation	Correlation coefficient
Pseudo-first order	Y = - 0.057X + 5.671	0.999
Pseudo-second order	Y = 0.002X+0.027	0.994
Ellovich	Y = 109.6X-30.47	0.990
Liquid film diffusion	Y = 0.057X-0.3	0.999
Interparticle diffusion	Y=42.73X+104.2	0.992

2.3.4.4.3 Dichlorodiphenyltrichloroethane (DDT)

From data given in Table 2.8, DDT kinetics fits the pseudo-second order model reflecting that it is some form of chemical reaction[93]. The applicability of the second-order kinetic model is dependent to the availability of adsorption sites on the surface of the sorbents. It's plausible that DDT could interact with polysulfone via π-π interactions, enabling the polymer to bind to the adsorbate molecules so that the degree of fit for the second order kinetic model is acceptable.

Table 2.8: Adsorption Kinetic models for DDT

Model	Equation	Correlation coefficient
Pseudo-first order	Y = -0.106X+4.783	0.946
Pseudo-second order	Y = 0.003X+0.017	0.964
Ellovich	Y = 25.30X+193.5	0.894
Liquid film diffusion	Y = -0.106X-0.875	0.946
Interparticle diffusion	Y=9.565X+226.2	0.843

2.3.4.5 Dynamic adsorption experiments (breakthrough)

One of the most important parameters in establishing the suitability of an SPE sorbent for extracting target analytes is the breakthrough volume (V_B) as it gives an indication of the sorbents loading capacity (adsorption capacity).

The experimental breakthrough curves for studied compounds, which are fitted by Boltzmann's function are given in Fig. 2.10

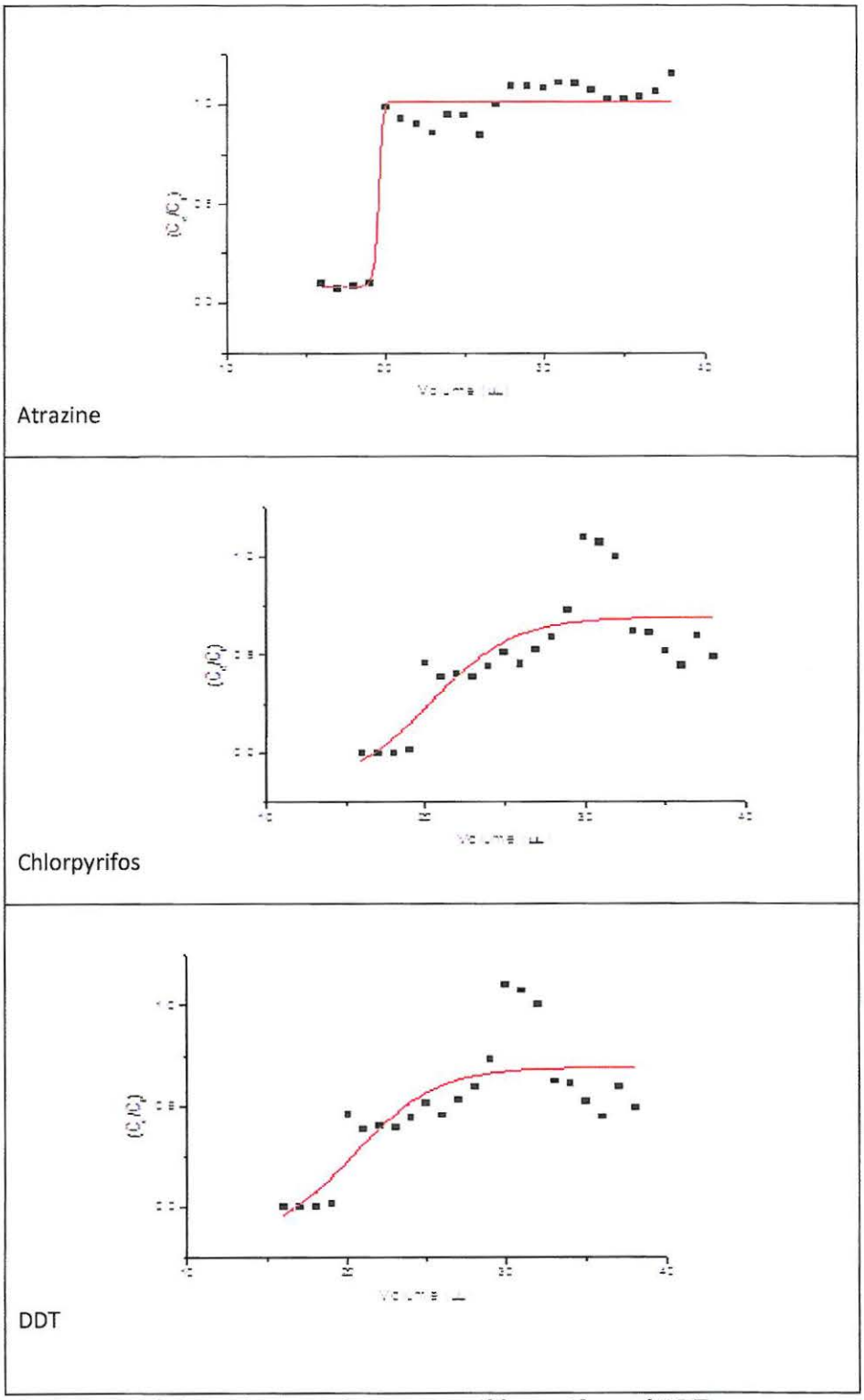


Figure 2.10: Breakthrough curves for atrazine, Chlorpyrifos and DDT

The values of V_B, V_M, V_R, N and k calculated from observed value of V_B are given on the table 2.9.

Table 2.9: Values of VB, VM, VR, N and K

Analyte	V_B(μL)	V_M(μL)	V_R(μL)	N	k
Atrazine	1700	1900	2000	22.2	0.053
Chlorpyrifos	1700	2200	2700	3.65	0.22
DDT	1700	2300	2600	4.17	0.13

The retention characteristcs of polysulfone was confirmed by breakthrough volumes assumed to be higher than 1700 μL. The adsorption capacity of sorbent was calculated using the V_B, and found to be 150mg/g of sorbent for all analytes. This value suggests that the saturation occurred after all atrazine was retained (the maximum amount retained by batch experiments for atrazine on the static studies was 65mg/g of sorbent), meaning that for Chlorpyrifos and DDT, the breakthrough volume could be 2 or 3 times higher than 1700 μL.

Theoretical plates are a function of the available surface area for analyte interaction, it could be concluded that due a larger surface area of the sorbent material, may exhibit a larger number of theoretical plates and consequently a large retention capacity as mass transfer kinetics would be enhanced. Therefore, a larger number of theoretical plates would correspond to a steeper slope of the breakthrough curve as a result of fast mass transfer kinetics observed on breakthrough curve of atrazine.

2.3.4.6 Thermostability of the sorbent

The information about the thermal stability of a sorbent is important for the characterization of the sorbent material. The results presented in Fig 2.11 confirm that the thermal properties of polysulfone remain constant (decomposition starting at 490°C) after the morphological modification of the polymer by electrospraying or electrospinning processes.

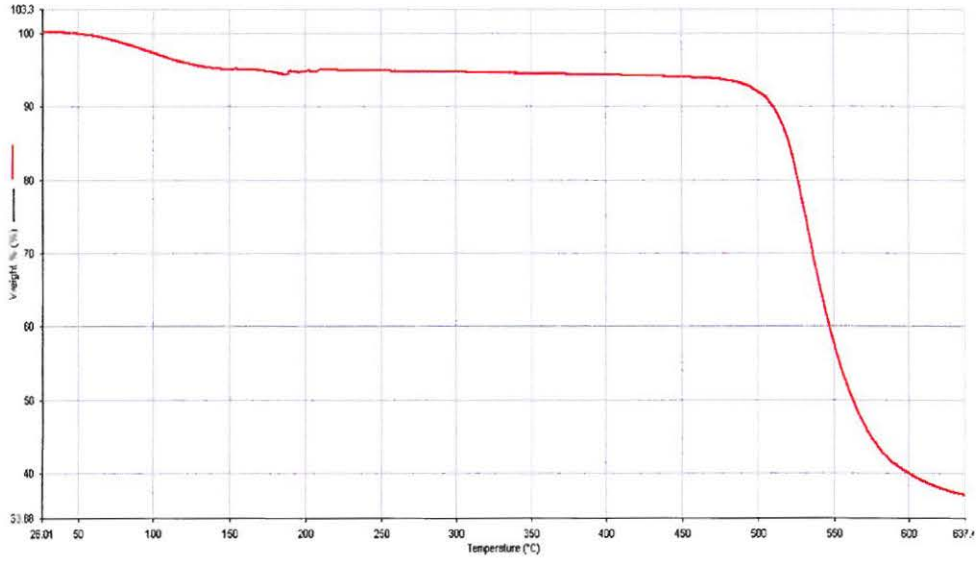


Figure 2.11: TGA diagram of polysulfone fibers

2.4 Conclusions:

This chapter presented the evaluation of polysulfone particles and fibers as sorbents for pesticides sample in water.

With the need for development of more efficient, accessible and economically viable techniques for sample preparation for detection of pesticides in water, current research developments in the field of nanotechnology offer promising solutions. Nanomaterials, such as electrospun nanofibers and electrosprayed particles offer an alternative method to produce sorbents with high surface area and porosity and the ease of fabrication allow for

the development of polymeric nanofibers with a wide range of characteristics that can be used for sample pretreatment prior to GC or HPLC analysis.

Different sorbent morphologies were obtained after varying the electrospraying and electrospinning conditions. From our results the morphology of the sorbent was mainly influenced by the concentration of polymer solution were for (5% m/v) particles were obtained, 10% beaded fiber and 20% beads free fibers were formed.

From the studies conducted for evaluation of adsorption of analytes with different polarities and structures (atrazine, DDT and chlorpyrifos) into particles, beaded fibers and bead free fibers showed significant differences between particles and fibers where better results was obtained for fibers with recoveries varying from 52 to 100%.
Two SPE modes applied (batch and column), showed differences were batch experiments conducted to better results than packed sorbent method.
Polysulfone fibers with confirmed retention capacity and following pseudo first and second order model, demonstrated to have affinity to retain both polar and non-polar compounds opening a possibility to be used as sorbent for sample preparation of different classes of pesticides in water for further analysis by GC or HPLC.

Chapter 3 Colorimetric based methods for pesticides analysis in aqueous media

Overview

This chapter presents background information of colorimetric based methods with emphasis on metal nanoparticles. The experimental parts, gives descriptions of how the AgNPs were synthesized, characterized and subsequent interaction with the analytes. The chapter concludes by reporting the experimental aspects of the studies that were carried out in this section of the thesis.

3.1 Introduction

3.1.1 Colorimetric probes

Colorimetric probes could be defined as molecules of biotic and abiotic origin that bind selectively with the analyte with concomitant change in color [96].

Colorimetric detection method is gaining increased attention due to its simplicity, rapidity, high sensitivity and ease of measurement. It is simple to use in comparison with other spectroscopic methods as it can give simple visual results for "naked-eye" detection [97]. Colorimetric probes, as the name would suggest, are based upon the detection of an analyte-induced color change in the materials [98-100]. Hence they can overcome the limitations caused by the traditional instrumental methods because no sophisticated instrumentation or sample preparation is required in their procedures. To efficiently analyze large numbers of samples, accurate, reliable, rapid and relatively inexpensive analytical methods are required. Colorimetric probes are extremely attractive since signaling the targeted event can be visualized and thus can make on-site, real-time detection possible [101, 102]. Not only does the obvious color change of the sample make the testing direct and convenient, the linear relationship between the concentration of the analyte and the absorbance also gives steady, quantitative results [103].

A number of materials such as chemo-responsive dyes, ligands and metal nanoparticles have been used for the development of colorimetric probes.

Chemosensors utilizing color and/or fluorescence intensity have been developed to be useful tools for sensing various analytes [104]. A typical optical chemosensor contains a receptor (the recognition site), linked to a fluorophore (the signal source), which translates the recognition event into the fluorescence signal. Compared to small organic compounds, polymer based optical sensors display several important advantages. For instance, signal amplification could be one of the most important advantages of polymer-based colorimetric sensing [105].

3.1.2 Colorimetric probes for pesticides

Recent years have witnessed considerable progress in analytical methods for the determination of pesticide residues. In parallel with typical chromatography, immunochemical assay and noble metal nanoparticles based colorimetric probes has been confirmed as alternatives for pesticide measurement by virtue of its high selectivity, sensitivity, and reliability as well as its rapidity [22].

Colorimetric sensing platforms based on metal nanoparticles, especially silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs), have received considerable interests in recent years due to their unusual optical and electrical properties. These properties have been exploited in pesticide detection systems, which are most often based on colorimetric techniques or fluorescence (see Table 3.1). The metal nanoparticles based colorimetric assays do not utilize organic co-solvents, enzymatic reactions, light-sensitive dye molecules, lengthy protocols, or sophisticated instrumentation thereby overcoming some of the limitations of more conventional methods.

Table 3.1: Optical Strategies for Pesticide Detection

Pesticide	Nanomaterial	DL	Detection technique	Sample	ref
Dipterex	AgNPs	0.18 ng/mL	Colorimetric	Spiked water	[106]
Carbaryl, diazinon, malathion, and phorate	AuNPs	0.1, 0.1, 0.3, and 1 μg/L	Colorimetric	River water and spiked apple juice	[107]
Methamidophos	AuNPs	1.40 ng/mL	Colorimetric	Spiked vegetables	[108]
Carbofuran/triazofos	AuNPs	0.14/0.0012 μM	Colorimetric competitive LFIA	Spiked, tap, surface and groundwater	[109]
Atrazine	AuNPs	5 pM	SPR	acetonitrile	[110]
β-endosulfan	AgNPs	50 μM	SERS		[111]
organophosphate	AgNPs-Eu^{3+}	1 μM	NSEF		[112]

SPR, surface plasmon resonance; FIA, fluoroimmunoassay ; SERS, surface-enhanced Raman scattering; NSEF, normalized scattering electric field

3.1.3 Metal nanoparticles

Metal nanoparticles are very attractive because of their size and shape dependent properties. Metal nanoparticles particularly silver and gold nanoparticles with well-controlled size have recently been the focus of great interest because of their color changes. The color changes are associated with their surface Plasmon absorption band which is dependent on a number of parameters such as the size and shape of the particle, the adsorbed species, the dielectric properties of the medium, and the distance between particles [113].

Some studies showed that very small particles have a big fraction of their atoms located on the surface. This has a very big influence on the properties of the particles, e.g. giving an increase in both reactivity and vapor pressure for decreasing particle sizes, as a result of the very high percentage of the atoms situated on the surface for silver particles 10 nm in diameter and less. The nanoparticles will in this case have a large number of unsaturated bonds and hence a very high surface energy. This can be directly related to the chemical reactivity, which has been shown to increase sharply for particles smaller than 10 nm[114].

Recently, the color changes associated with aggregation of the ligand-functionalized AuNPs upon binding its target have been exploited in the development of colorimetric assays. Some examples are presented on the Table 3.1. Compared to AuNPs, AgNPs have some advantages over AuNPs since they possess higher extinction coefficients relative to Au NPs of the same size [115]. However, few reports have focused on AgNP-based colorimetric assays due to the susceptibility of the silver surface to oxidation [116]. Therefore, the interface functionalization plays a crucial role in increasing the stability and analytical applicability of Ag NPs.

3.1.3.1 Silver Nanoparticles

Ag exhibits the high efficiency of Plasmon excitation. Moreover, optical excitation of Plasmon resonances in nanosized Ag particles is the most efficient mechanism by which light interacts with matter. A single Ag nanoparticle interacts with light more efficiently than a particle of the same dimension composed of any known organic or inorganic chromophores. The light-interaction cross-section for Ag can be about ten times that of the geometric cross-section, which indicates that the particles capture much more light than is physically incident on them. Silver is also the only material whose Plasmon resonance can be tuned to any wavelength in the visible spectrum [117].

3.1.3.2 Colloid stability

A crucial aspect of colloid chemistry is the means by which the metal particles are stabilized in the dispersing medium, since small metal particles are unstable with respect to agglomeration to the bulk. At short interparticle distances, two particles would be attracted to each other by van der Waals forces. Without the aid of any counteracting repulsive forces, a sol would coagulate. There are in general two methods for achieving counteraction, electrostatic and steric stabilization.

In the case of the reduction of silver nitrate by sodium borohydride, the formed colloidal silver particles are surrounded by an electric double layer arising from the adsorbed borohydride ions and the cations which are attracted to them (an excess of sodium borohydride is essential for proper particle stabilization). This results in a electrostatic repulsion between the particles that decays exponentially with increasing interparticle distance. Thus, if the electric potential associated with the electrostatic repulsion of the double layer is sufficiently high, agglomeration is prevented [118]. If too much sodium borohydride is added however, the overall ionic strength of the sol will increase, leading to a compressed double layer and a shortened range of the repulsion. Ultimately the sol coagulates as the particles can no longer be kept apart.

The second way of preventing colloidal particles from aggregating is by the adsorption of large molecules, also known as steric stabilization. The adsorbed particles, such as polymers or surfactants, provide a protective layer preventing the metal particles from approaching. There are mainly two effects responsible for steric stabilization. By the entropic effect, the approach of two particles is restricted due to the low configurational freedom of the polymer chains resulting in a lowering of the entropy. And due to a rise in the local concentration of polymer chains between two approaching particles, equilibrium is reestablished by an osmotic repulsion leading to separation of the particles (osmotic effect) [118].

3.1.3.3 Stabilizing agents

Previously, stabilizing agents were low-molecular organic compounds (carbonic acids, alcohols, amides) and natural polymers (gelatin, agar-agar, starch, cellulose and so on). To date, synthetic polymers are more frequently employed. Synthetic polymers solve the limitations of nanoparticle stabilization and introduction of a polymer ingredient into the nanocomposite. Some examples are: polyvinyl alcohol (PVA), polivinylpyrrolidone (PVP), Bovine serum albumin (BSA) citrate and cellulose [119]. PVP is a polymer that binds strongly to the silver nanoparticle surface. It provides greater stability than citrate or tannic acid, but is more difficult to displace. PVP is used to protect the silver nanoparticles from growing and agglomerating [119].

As stabilizing agents for nanoparticles, polymers provide several possible advantages over small molecules. Because polymers consist of multiple repeating units, each of which can display ligand functionality, they have a much greater potential degree of multivalency and also allow for the ready incorporation of multiple types of ligand functionality. While small molecule ligands typically require very strong affinities for nanoparticle surface sites to ensure nanoparticle stability[114].

3.1.4 AgNPs fabrication methods

The most widely employed techniques to fabricate metal nanostructures, with focus in silver are: chemical synthesis, physical metal deposition and lithographic techniques [114]. The choice of the technique is mainly based on the final application. For studies conducted in this thesis, the chemical synthesis was chosen.

3.1.4.1 Chemical synthesis of AgNPs

Wet chemical nanoparticle preparation is based on the reduction of metal salts (chemical reduction or photo reduction), electrochemical pathways or controlled deposition of metastable organometallic compounds [114, 119]. Chemical reduction methods to produce AgNPs vary in the choice of silver precursor, the reducing agent and their relative

quantities and concentrations, the temperature, mixing rate, and duration of reaction. By the use of different reagents and conditions for the synthesis of large variations in the particle shape, size and size distributions may be expected. As for the source of silver, several salts have shown to be applicable but silver nitrate is by far the most adopted. Table 3.2 lists the most commonly used reducing agents for fabricating silver nanoparticles from silver salts together with the conditions for the synthesis[120].

Table 3.2: List of the most common reducing agents and the reaction conditions in the precipitation of silver nanoparticles from uncomplexed silver salts

Reducing agent	Conditions	Rate
Organic acids, alcohols, polyols	≥ 70 °C	Low
Aldehydes, sugars	< 50 °C	Moderate
Citrate	> 70 °C	Moderate
Hydrazine, H_2SO_4, H_3PO_2	Ambient	Fast
$NaBH_4$, boranes	Ambient	Very fast

Many chemical reduction methods have been used to synthesize silver nanoparticles from silver salts [119, 121-126]. Sodium borohydride and the reduction of silver nitrate were adopted in this study to synthesize AgNPs. The method was primarily chosen based on the possibility to produce particles of different size regimes, but also because of the synthesis simplicity, requiring simple laboratory setup and including few reactants which potentially may cause interferences.

AgNPs and PVP AgNPs were synthesized by reduction with sodium borohydride and used as colorimetric probe for atrazine and chlorpyrifos.

3.2 Experimental

3.2.1 Reagents and material

Polyvinyl pyrrolidone PVP (Mw = 360 000), Nylon-6 (Mw = 10 000), $NaBH_4$ and $AgNO_3$ were of analytical grade and were used as obtained from Sigma Aldrich (St. Louis, MO USA).

Formic acid (90%), Glacial acetic acid (100%), and Sodium hydroxide (NaOH) were obtained from Merck Chemicals (Wadeville, South Africa).

Sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$) and Potassium hydrogen phthalate ($C_8H_5KO_4$) were obtained from Saarchem Analytic (Krugersdorp, South Africa). All experimental manipulations and data collection were performed at room temperature unless otherwise stated. Standard solutions were freshly prepared by dissolving known quantities of metal salts in ultrapure water obtained from a Millipore system.

3.2.2 Instrumentation and measurements

3.2.2.1 Characterization techniques

In this section of the work, are described the two characterization techniques used to confirm the successful formation of products for the synthesis as well as morphology. Characterization instruments used in this work are briefly described below.

3.2.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy is the most useful imaging technique for nanoparticles. In case of transmission electron microscopy (TEM) a beam of electrons is transmitted through an electronically transparent specimen interacting with the atoms to produce one image. To obtain TEM image, the sample is required to be dispersed on TEM grids (carbon coated copper grid or molybdenum grid). For this work, TEM images were recorded by a JEOL-JEM 2010 electron microscope operating at 100 kV and a JEOL JEM 2100 LaB6, working in STEM and HAADF (High Angle Annular Dark Field Mode). Samples for TEM

were prepared by placing a drop of colloidal sample on carbon coated copper grid and dried at room temperature.

3.2.2.3 UV-VIS absorption spectroscopy

In this technique a beam of light of wavelengths in the visible and ultraviolet region passes through the specimen and its intensity before and after interacting with a sample is measured to determine the light transmitted through or absorbed by the sample. For metal nanoparticles absorption peaks can be correlated to their surface plasmon resonance peak. Absorption peaks can also indicate type of bonds in a given molecule. In this work, electronic absorption spectra were recorded on a Perkin Elmer Lambda 25 UV/VIS spectrophotometer in a quartz cell (1 cm).

3.2.3 AgNPs based methods development

3.2.3.1 Silver nanoparticles synthesis

A 1 mL volume of 1.0 mM silver nitrate was added drop wise (about 1 drop second) to 10 mL of 1.0 mM sodium borohydride solution. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned bright yellow when all of the silver nitrate had been added.

3.2.3.2 Colorimetric probes for Atrazine

The prepared silver nanoparticles were tested for atrazine using the following procedure:

1 mL of the prepared silver nanoparticles solution was mixed with 10 mg/L of atrazine the absorption spectra were registered immediately.

3.2.3.2.1 Optimization of the pH of the AgNPs probe for atrazine

The optimization was carried in the range of pH from 2 to 13.

The buffer solutions used were potassium hydrogen phthalate-hydrochloric acid (pH 2.2-4.0), sodium acetate-acetic acid (pH 3.7-5.6), sodium dihydrogen phosphate-sodium hydroxide (pH 6.0-8.0), Sodium bicarbonate-sodium hydroxide (pH 9.60 - 11.00) and potassium chloride-sodium hydroxide (12-13). The pH of the solutions were monitored by use of a digital pH-meter; A Jenway 3510 pH meter (London, UK) calibrated with standard buffers of pH 9, 7 and 4 at 21±1 °C.

To 1 mL of the probe, was added 1 mL of the buffer and atrazine to a final concentration of 10 mg/L, diluted to 5 mL and the absorbance spectra was recorded after 15 min.

3.2.3.3 Colorimetric probe for Chlorpyrifos

Synthesis of PVP capped AgNPs followed the same procedure described for the uncapped AgNPs. Addition of PVP occurred after half of the solution of the silver salt was added.

3.2.4 Incorporation of the probe in a solid support

Nylon-6 was used as a solid support to incorporate AgNPs and PVP capped AgNPs and employed as a solid probe for detection of atrazine and chlorpyrifos.

Nylon-6, silver nitrate, $NaBH_4$ and PVP were used as electrospinnable polymer, silver precursor, reducing agent and stabilizer respectively. Nylon-6 pellets were dissolved in a mixture of acetic acid and formic acid in the ratio of 1:1 to make a solution with a concentration of 15 wt/wt%. The mixture was stirred with a magnetic stirrer for 1 h until the lumps of the nylon-6 pellets were broken and well dispersed. 42.3 mg of $AgNO_3$ were then added to the nylon-6 solution. The mixture was allowed to stir for an hour after which, 20.1 mg of $NaBH_4$ were added to the mixture. After stirring for about 5 min 2.0 mg, of PVP was added (in the case where the capping agent was used).

3.2.4.1 Fabrication of electrospun nanocomposite fibers

The homogenous nanocomposite solution was loaded into a 20 mL plastic syringe. The syringe was then mounted on a programmable syringe pump (New Era, NE-1000). The

solution was delivered at a flow rate of 0.5 mL/h through a steel needle of 0.584 mm internal diameter. Nanofibers were collected on an aluminum foil collector with the distance between the needle tip and the collector of 12 cm and the applied voltage at the needle tip was 22.5 kV. The electrospun fiber mats were cut into uniform strips and without any further treatment the strips were placed in the various test solutions.

3.3 Results and discussion

3.3.1 Synthesis of AgNPs

The general chemical reduction reactions involve reducing agents that are reacted with a salt of the metal according to equation 12:

$$mMe^{n+} + nRed \longrightarrow mMe^{0} + nO_x \qquad (12)$$

In a study of metal ion reduction by borohydride system, it was reported that BH_4^- ions functions not only as a reducing agent but also as a stabilizer that prevents the nanoparticles from aggregating [114]. Adsorption of borohydride onto the surface plays a key role in stabilizing growing nanoparticles by providing particle surface charge leading to electrostatic repulsion that keeps them from agglomerating (see Figure 3.1). Therefore, there had to be enough borohydride in solution to reduce the metal ions as well and to stabilize the particles as the reaction proceeded.

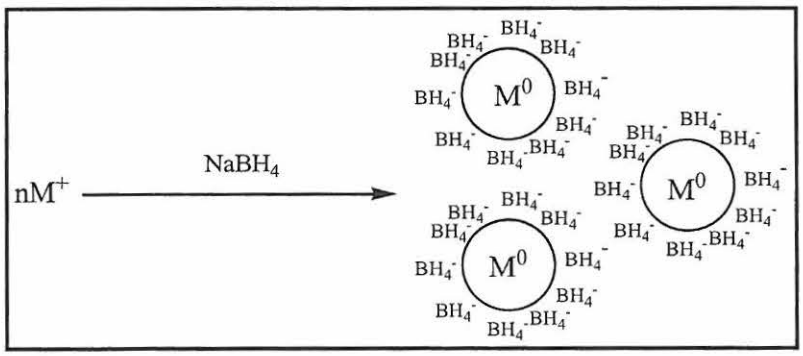


Figure 3.1: Separation of nanoparticles by repulsive forces induced by adsorbed borohydride

Well dispersed AgNPs with sizes varying from 5-10 nm were synthesized. The UV-spectra of the yellow colored solution and the TEM images are presented in the Figs. 3.2 and 3.3.

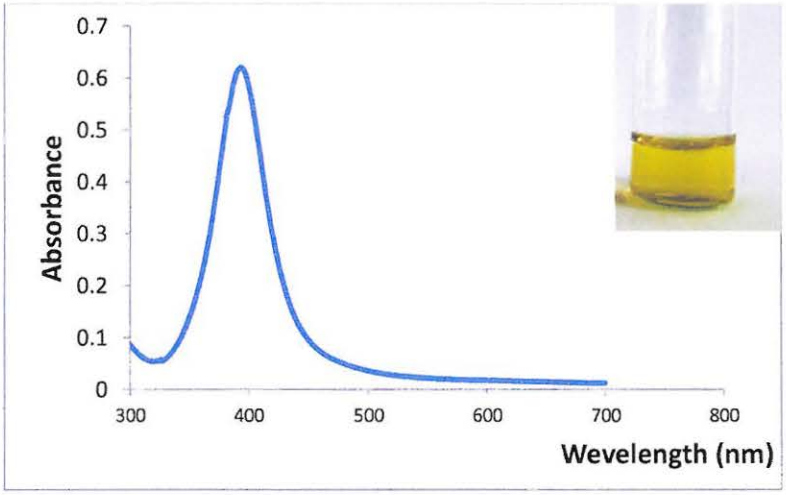


Figure 3.2: Absorption spectra of the solution of AgNPs showed on the picture, prepared by reduction of $AgNO_3$ with $NaBH_4$

Figure 3.3: TEM image of dispersed AgNPs

3.3.2 Detection principles of Atrazine using AgNPs as colorimetric probe

The principle of Raman spectroscopy is associated to vibration energy levels of the molecule, so it is a fingerprint of the molecule. Conventional Raman scattering has small cross section and requires large number of molecules or strong incident light to give adequate signals. Surface-enhanced Raman spectroscopy (SERS) led to renewed interest in the exploration of Raman spectroscopy for ultrasensitive analysis. The common SERS substrates are silver nanoparticles AgNPs and gold nanoparticles AuNPs in colloidal solution or film [127]. The Raman scattering cross-section of a molecule can be increased by factors up to 10^{14}–10^{15}, comparable to fluorescence. This great enhancement is presumably from the large electromagnetic (EM) field produced by hot spots, which reside in the interstices in metal nanostructures such as dimers or aggregates [128].

In this work, enhancement of the signal of atrazine was observed when a solution of atrazine was mixed with the AgNPs (see Figure 3.2). No color change was observed. The enhancement of the intensity of the yellow color of the probe was believed to be due to SERS principle.

It is known that some molecules have strong chemical affinity for Ag and Au metal surfaces, forming strong covalent bonds. Molecules with thiol or triazole moieties in their structure are such typical examples [129].

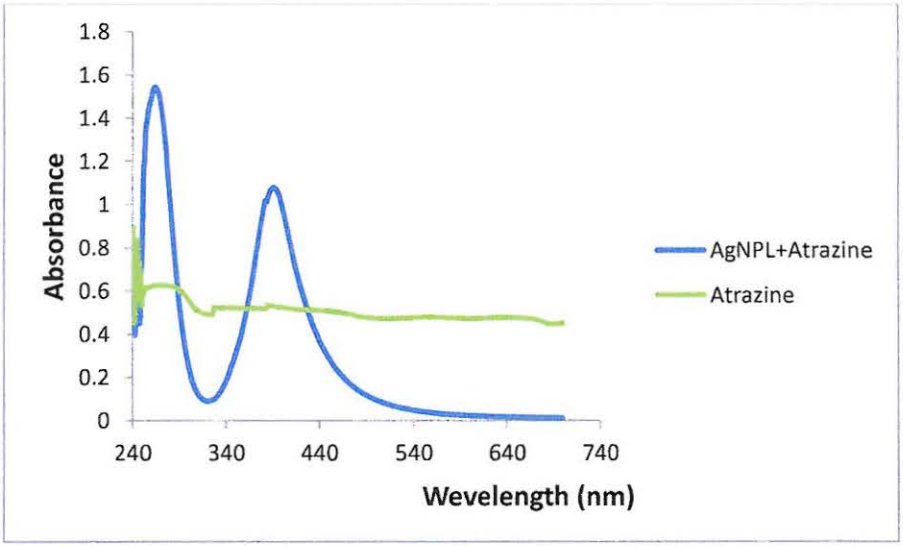


Figure 3.4: In green the absorption spectra of atrazine (50 mg/L) and in blue the spectra of AgNPs with atrazine (10 mg/L)

Atrazine is a molecule that contains two exocyclic amino groups (-NH_2) and tree-nitrogen hybrid ring. Two possible combinations can result from the addition of AgNPs. Formation of a covalent bond of the AgNPs with the exocyclic amino groups and electrostatic attraction by the negatively-charged borohydride ion with the protonated atrazine, since the atrazine molecule is a weak acid. These combinations can cause enhancement of the absorption of the compound, increasing the sensitivity of the analyte that can be used for quantitative determination (see Figures 3.5 and 3.6).

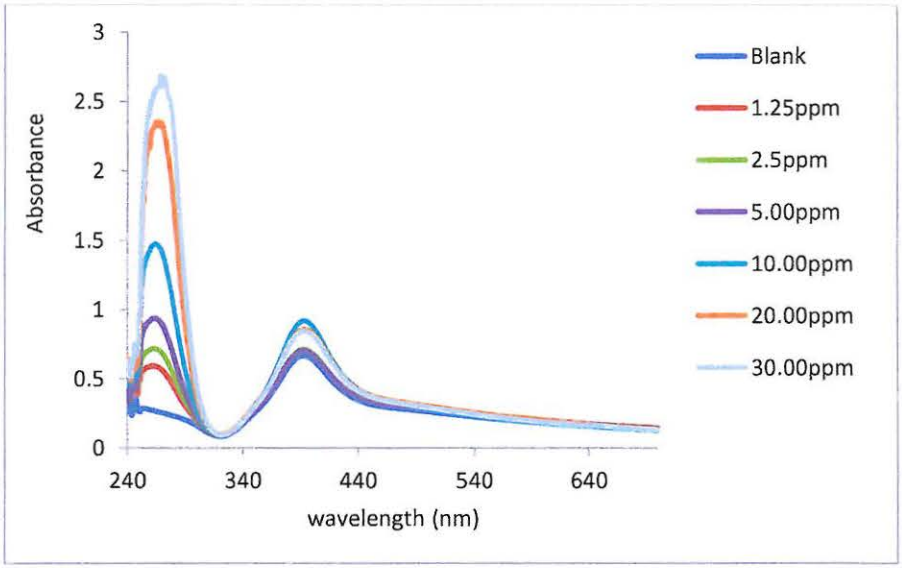


Figure 3.5: Increasing concentration of atrazine spectra for the test probe of AgNPs

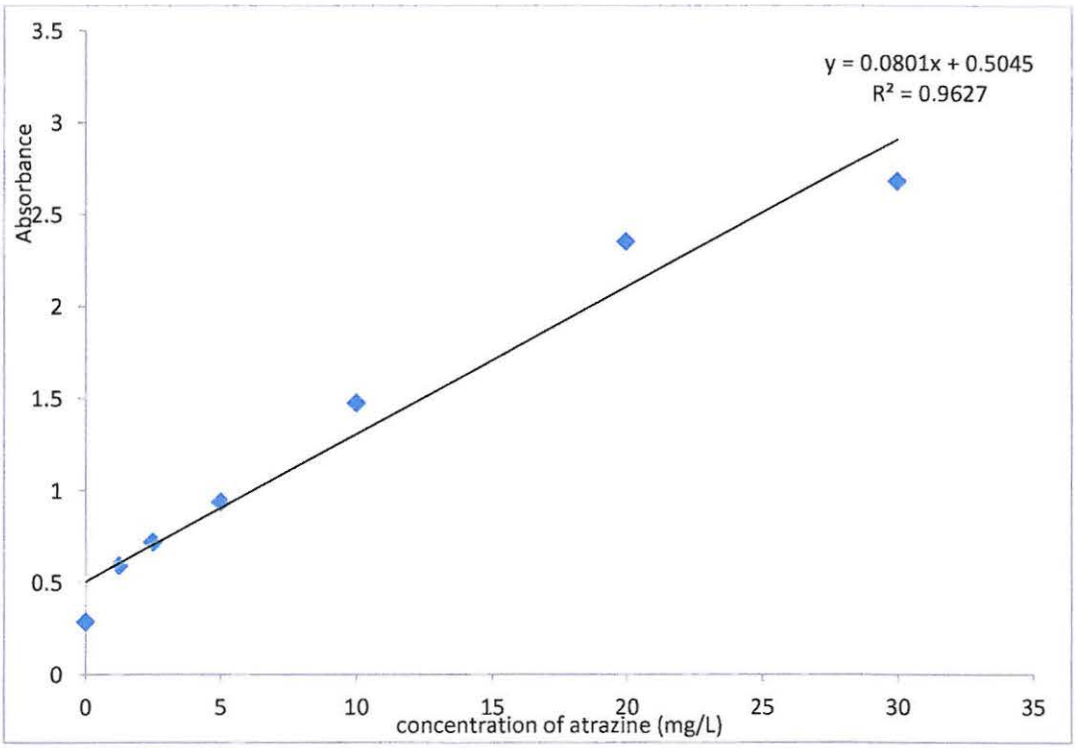


Figure 3.6: Calibration curve of atrazine

After 2 days, the solution prepared with atrazine changed the color from yellow to pink and the spectra were recorded (see Figure 3.7), a new band appeared in the region of 550 nm. This means that atrazine induced the aggregation of AgNPs (see Figure 3.8), but in these conditions, with a very low reaction rate, the analysis time was a limiting factor. However, by optimization the media pH, the reaction time can be increased.

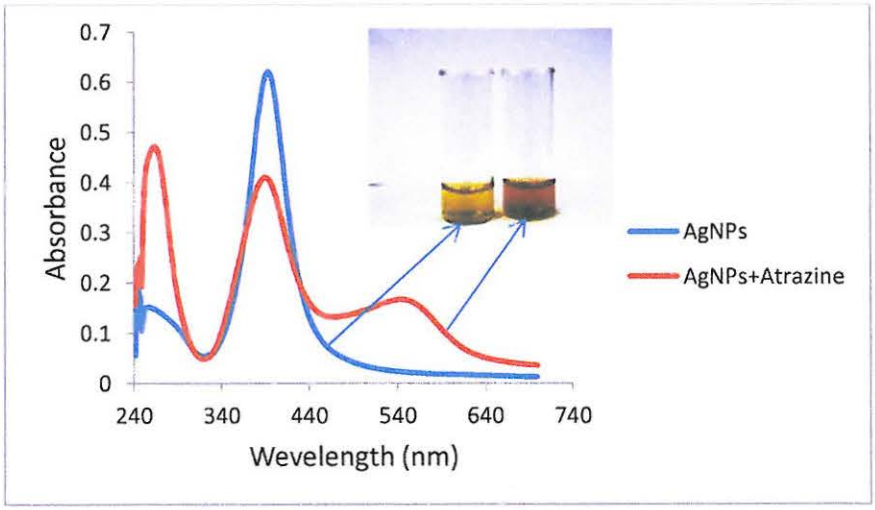


Figure 3.7: UV spectra of AgNPs and AgNPs with atrazine recorded after 2 days

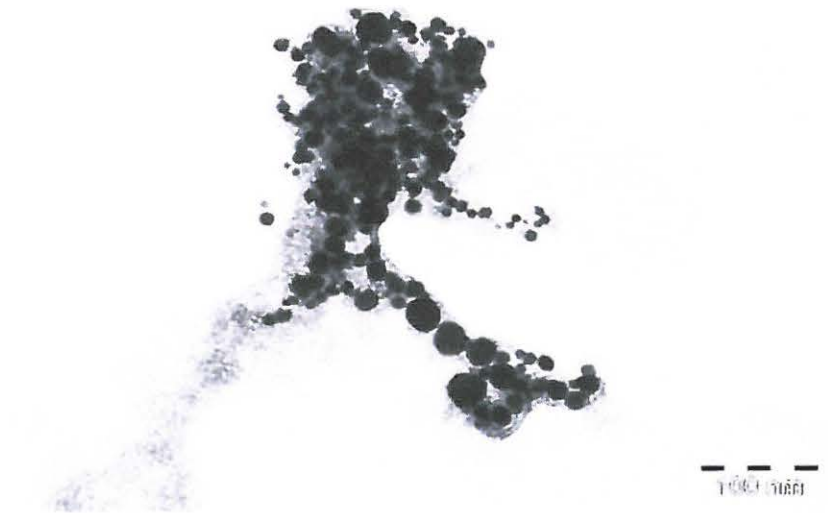


Figure 3.8: Aggregation of AgNPs induced by atrazine

3.3.2.1 Optimization of assay condition

The interaction of AgNPs and Atrazine can be affected by media pH. Atrazine is a weak base (pKa = 1.7) and the media pH can affect the form of atrazine in aqueous solution. The media pH was investigated in the range from 2 to 13. The pH change of the media was accompanied with color change at basic pH>11 as can be seen in Fig. 3.9. The color change resulted from the aggregation induced by atrazine at the point where hydrolyses does not occur.

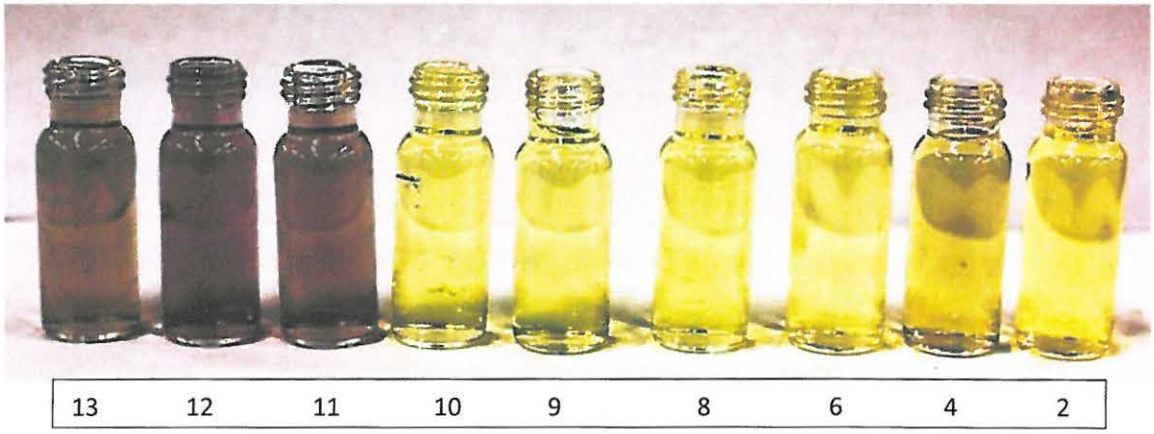


Figure 3.9: pH effect on AgNPs colorimetric probe for atrazine

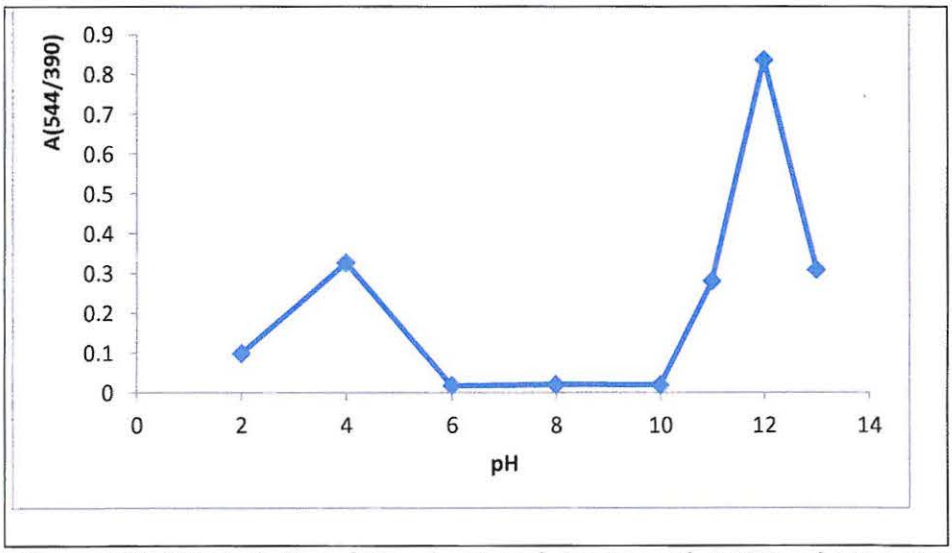


Figure 3.10: Effect of pH on determination of atrazine with AgNPs colorimetric probe.

Taking the advantage of the color change developed during the pH optimization studies, a second probe was tested for this analyte, based on visual color change.

Different concentration of atrazine were tested on the probe with a fixed pH of 12 were the maximum absorbance was obtained and the results showed the aggregation started at a minimum concentration of atrazine of (5 mg/L) as can be seen Fig 3.8.

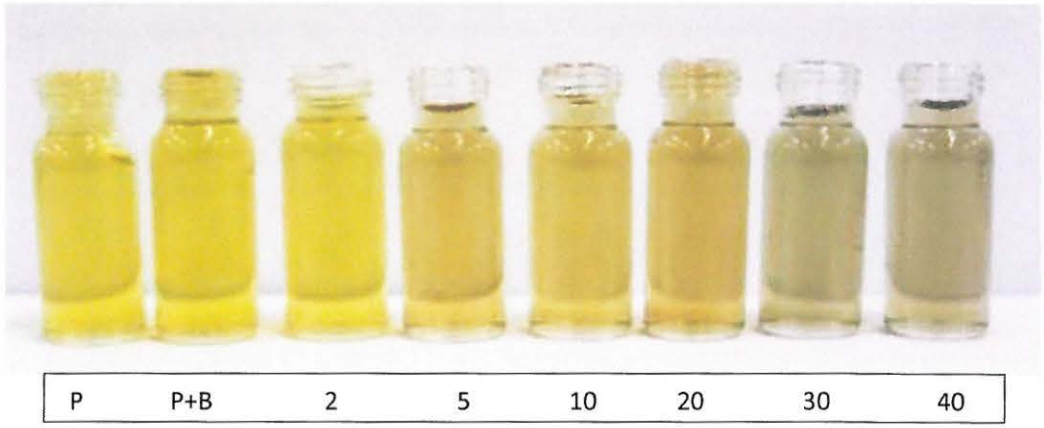


Figure 3.11: Color change observed with addition of atrazine (2, 5, 10, 20, 30 and 40 mg/L), P the probe without buffer and P+B probe with buffer (pH =12)

The development of the color starts 5 min after addition of the analyte with a concentration of 5 mg/L and the limit of detection calculated from the calibration curve (see Figure 3.12) was 3.32 mg/L.

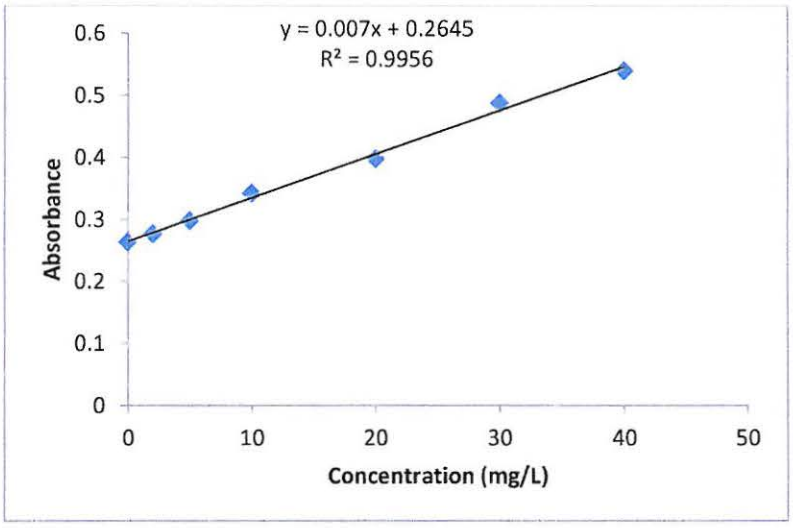


Figure 3.12: Calibration curve for atrazine at optimized pH of 12

3.3.3 Detection principles of Chlorpyrifos using PVP stabilized AgNPs

3.3.3.1 Background chemistry and chemical analysis of OPP in the presence of AgNPs

Organophosphorus pesticides are known to have the capacity to irreversibly inhibit the activity of Acetylcholinesterase (AChE) by combining the hydroxyl group in the active serine site on AChE. Similarly, acetylthiocholine (ATCh) can be converted to thiocholine (TCh) by the AChE catalyst. The process produces a reactive thiol group (-SH) in the TCh molecule and the SH can readily react with heavy metals, such as Au, Ag, Cd and Hg. This is the principle that guides most of the assays based on AgNPs. In this work we decide to explore different functionalities for molecular recognition.

Silver nanoparticles without the capping agent were found to aggregate rapidly in the presence of Chlorpyrifos. Yellow solution first turns a darker yellow, then violet, and eventually grayish, after which the colloid breaks down and particles settle out.

During the synthesis of AgNPs by reduction with $NaBH_4$, the addition of PVP , Ag^+ coordinate with PVP and form a complex $[Ag(PVP)]^+$ that create electrostatic repulsion and strongly stabilize the nanoparticles due to its high molecular weight.

The addition of this functional group will limit the reaction of AgNPs with Chlorpyrifos, making possible to use as colorimetric probe for this analyte with a limit of detection of 0.88 mg/L.

3.3.3.2 Optimization assay conditions for chlorpyrifos

3.3.3.2.1 Effect of stabilizing agent

Two stabilizing agents with different functionalities (with counteraction achieved by electrostatic and steric stabilization) were used.

AgNPs were stabilized in solution by coating them with negatively charged citrate ions, and the electrostatic force counteract the effect of Van de Waals force between the molecules with the result of homodisperse of AgNPs. The molecules of chlorpyrifos have highly reactive groups and when in contact with AgNPs will rapidly induce the aggregation of nanoparticles until they collapse. For this reason they cannot be used for quantitative analysis.

On the other hand the complex $[Ag(PVP)]^+$ formed by stabilizing AgNPs with PVP will prevent the fast aggregation of the AgNPs, thus creating a suitable environment for the AgNPs to bind the molecule of chlorpyrifos and promote the color change due to the aggregation of the nanoparticle and at the same time maintaining the color of the solution stable for some time.

Figure 3.13 presented the UV spectra of the interaction of chlorpyrifos with uncapped AgNPs, citrate capped and PVP capped.

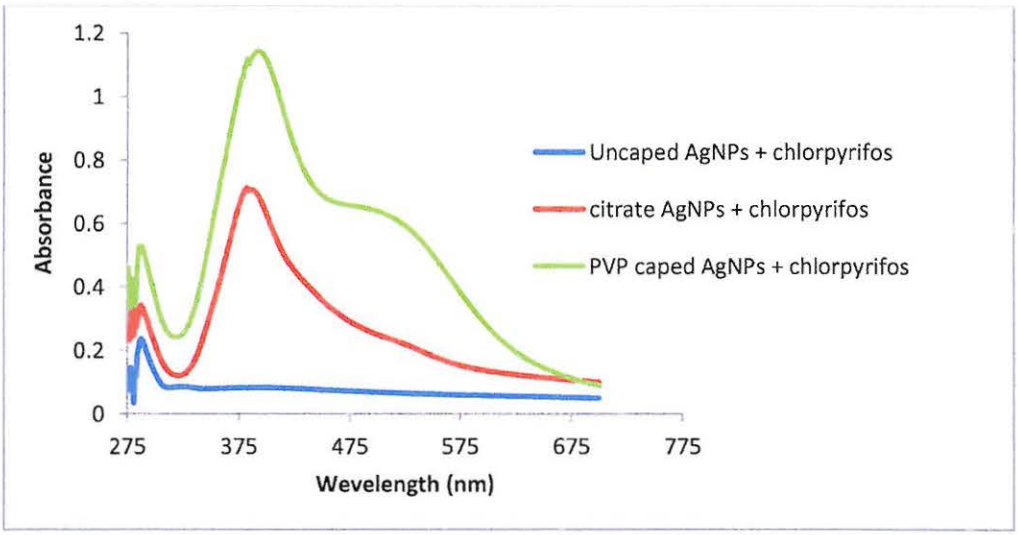


Figure 3.13: UV spectra of the interaction of chlorpyrifos with uncapped AgNPs, citrate capped and PVP capped

3.3.3.2.2 pH effect of on the determination of chlorpyrifos using PVP capped AgNPs

The pH of the media affects the interaction of AgNPs with chlorpyrifos. The pictures and the absorption UV spectra on the Figure 3.14 clearly show that the probe is only sensitive on interval of pH between 10 and 12 with the optimum at pH 11.

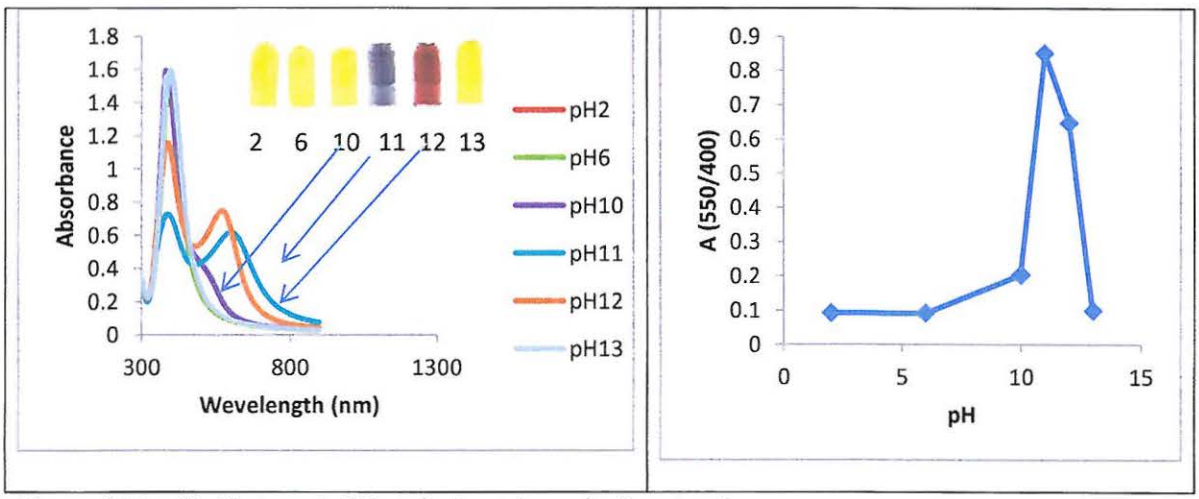


Figure 3.14: pH effect on AgNPs colorimetric probe for atrazine

3.3.3.3 Sensitivity of the probe

Increasing concentration of chlorpyrifos was used to plot the calibration curve in the interval of concentration of (0.4 to 12 mg/L). The calibration graph showed a linear trend with good coefficient correlation 0.996.

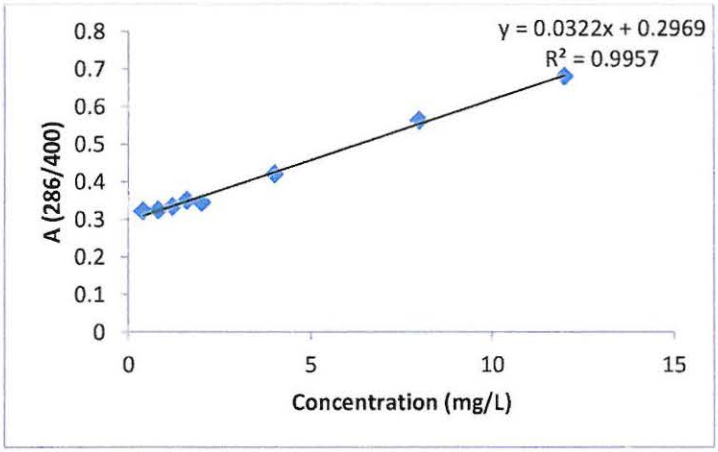


Figure 3.15: Calibration curve of chlorpyrifos at optimized pH of 11

3.3.4 Interferences studies

The developed probes were tested for other pesticides (1 Aldrin, 2 Chlordane, 3 DDT, 4 Dieldrin, 5 Endrin, 6 Endosulfan, 7 Heptachlor, 8 Hexachlorbenzene, 9 Lindane and 10 Toxafene) and no color change was observed for the conditions tested for chlorpyrifos.

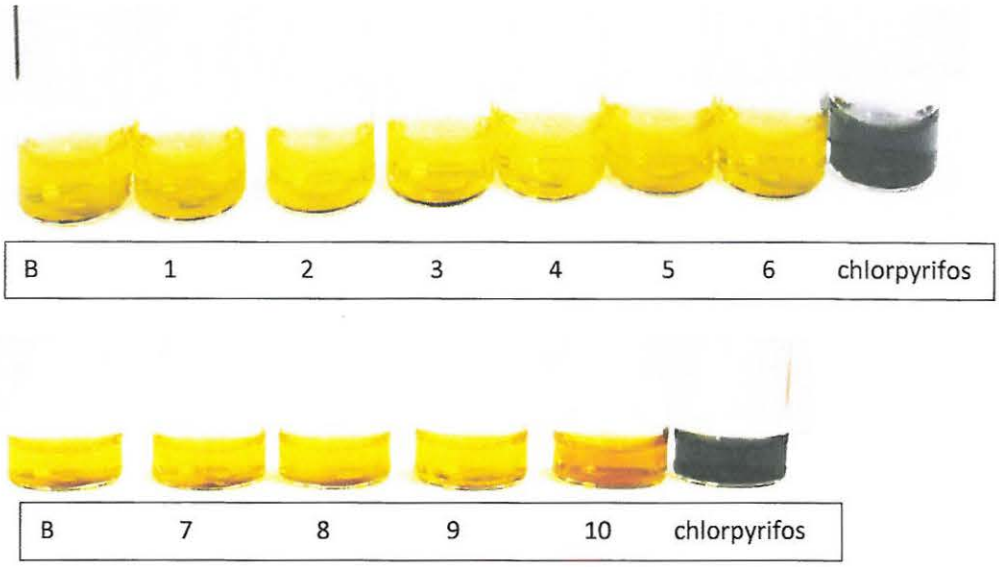


Figure 3.16: Responses of PVP capped AgNPs to different pesticides (1 Aldrin, 2 Chlordane, 3 DDT, 4 Dieldrin, 5 Endrin, 6 Endosulfan, 7 Heptachlor, 8 Hexachlorbenzene, 9 Lindane and 10 Toxafene)

3.3.5 Analysis in real samples

The proposed method was applied in the determination of the concentration of atrazine and chlorpyrifos in a water sample; tap water from the F12 research lab at Rhodes University was used. For this purpose, the tap water was spiked with atrazine (10.06 and 30.26 mg/L) and with chlorpyrifos (0.98 and 10.23 mg/L). The results (see table 3.3) showed that it was not possible to detect any of the analyte, probably because the concentration of analytes in the sample was lower than the limit of detection. However the applicability of the probe in real samples was demonstrated by the recoveries obtained from these experiments.

Table 3.3: Recoveries and limits of detection of atrazine and chlorpyrifos on tap water samples

Analyte	Spike level (mg/L)	%Rec ±n*s	Concentration in the sample	LD(mg/L)
Atrazine	10.06	103.57±2.01	-	3.32
	30.26	92.92±0.99	-	
Chlorpyrifos	0.98	99.40±0.002	-	0.88
	10.23	101.06±0.002	-	

3.3.6 Incorporation of the AgNPs and PVP capped AgNPs in a solid support for rapid detection of atrazine and Chlorpyrifos in aqueous media

Attempt to incorporate the AgNPs into a solid support showed from preliminary results, to be a very good alternative for using colorimetric probes based on AgNPs on site. However the results presented in this work are limited. More detailed studies for optimization of the probe synthesis would be necessary for quantification purposes.

The synthesized solid probe AgNPs and PVP capped AGNPs was sensitive for atrazine (color change from yellow to green) and chlorpyrifos (color change from light brown to dark brown) respectively as can be seen on the Figures 3.17 and 3.18. The morphology of the fiber slightly changed as a result of aggregation.

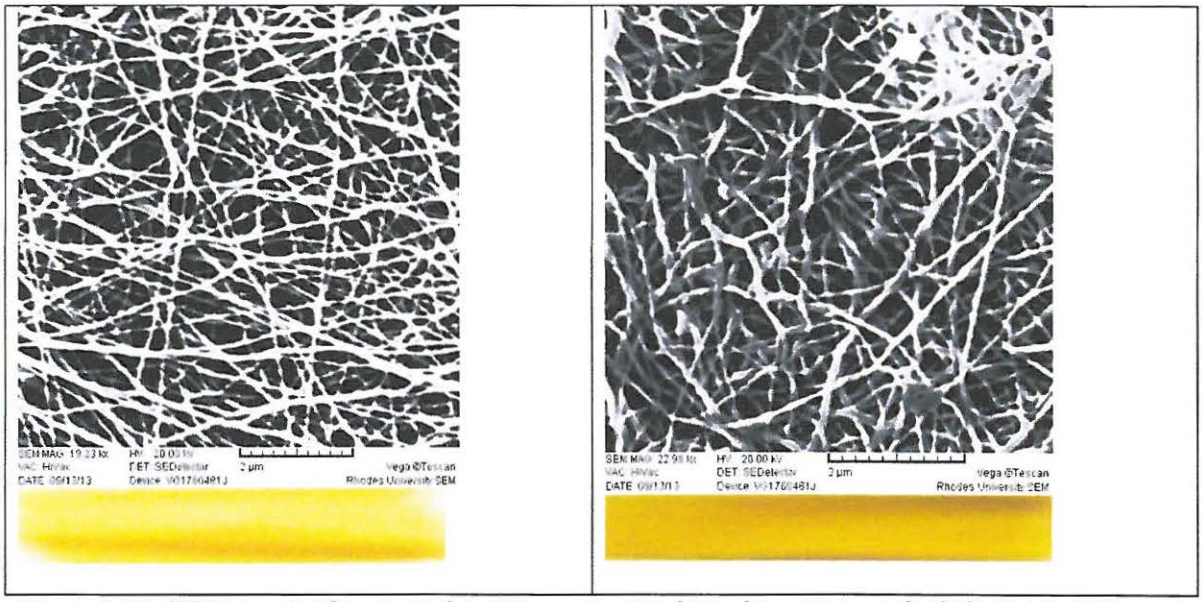


Figure 3.17: SEM images of uncapped AgNPs composite dipped in water on the left, and AgNPs dipped in a solution of atrazine on the right

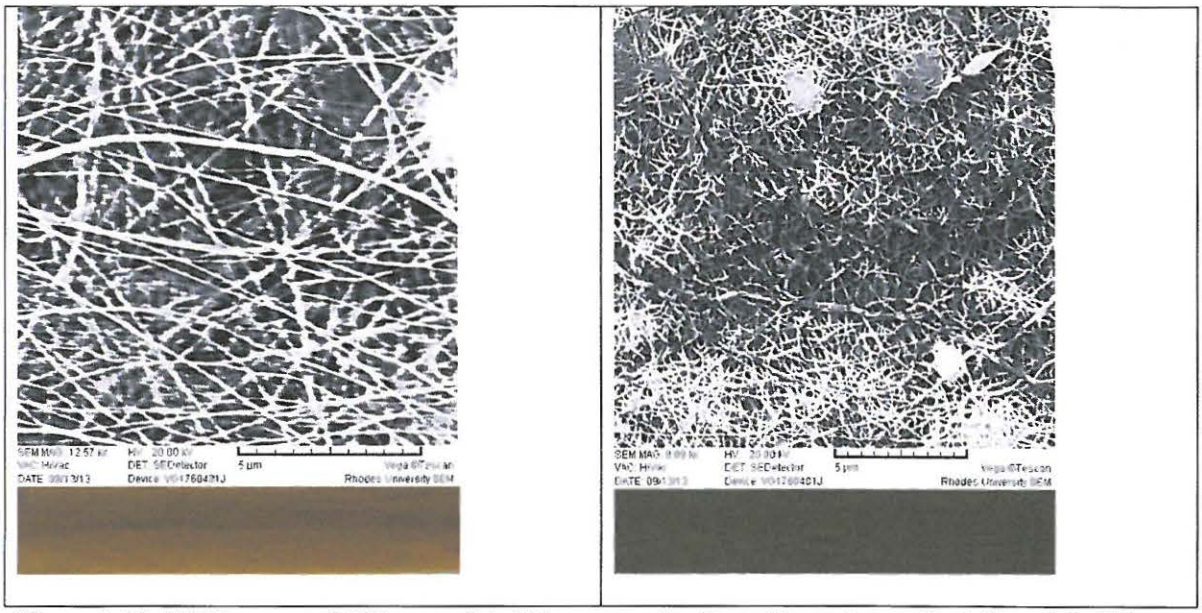


Figure 3.18: SEM images of PVP capped AgNPs composite dipped in water on the left, and AgNPs dipped in solution of Chlorpyrifos on the right

3.4 Conclusions

AgNPs and PVP capped AgNPs were synthesized characterized and applied as colorimetric probes for atrazine and chlorpyrifos respectively. The principles of Surface-enhanced Raman and induced aggregation by specific conditions of the analytes were explored in the achievement of this goal. The proposed methods can be used for detection of atrazine and chlorpyrifos in water samples with detection limits of 3.32 and 0.88 mg/L. Attempt to incorporate the probe in a solid support was achieved by using nylon 6 as solid support polymer. The detection could be observed by necked eyes.

Chapter 4 General Conclusions and recommendation

The work presented an evaluation of particle or fiber based polymeric sorbent for solid phase extraction and the development of colorimetric assays based on silver nanoparticles for pesticides analysis in water. In the light of the urgent need for development of new, more efficient, accessible, economically viable and environmentally friendly techniques for pesticides detection in water, current research developments in the field of nanotechnology and the versatility and exceptional properties of nanomaterials offer promising solutions. Nanomaterials, such as electrosprayed/electrospun nanofibers offer alternative choices for development of rapid and cheap extraction systems for trace enrichment for further analysis by chromatographic or other detection techniques. The potential for nanomaterials, such as metal nanoparticles can be used to develop easy efficient alternatives for pesticides detection.

The results obtained demonstrated that polymeric nanofibers are attractive as extraction media based on the enormous possibilities that exist to tailor their chemical and physical characteristics.

The methods presented in the studies conducted in this thesis demonstrated the possibility of having alternative ways to complement the conventional methods for detection and quantification of pesticides in water which often include; the use of large sample volumes, extensive sample preparation steps and the use of expensive instrumentation. The AgNPs are one example presented in this work that demonstrated to have great potential to be used for rapid assays of pesticides with the advantage that can be incorporated in a solid support and be used as cheap and efficient alternative of conventional methods; however more investigation on this field is needed.

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