

# **Use of Polydimethyl Siloxane Microparticles for the Sequestering of Model Pollutants in Water**

by

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## **ABSTRACT**

Polymer micro and nanoparticles are an emerging type of material with promising applications for remediation and degradation of environmental contaminants in water, due to their enhanced surface area and chemical reactivity. Such benefits have also raised public concern due to the impending risk for nanomaterials to exacerbate a variety of conditions similar to those shown by natural micro and nanoparticles like suspended particulate matter. In this work, the selection of organic compounds was made searching structural similarities with model contaminants common of waters in Puerto Rico. These organic compounds entered in contact with colloidal polydimethylsiloxane (PDMS) microparticles and polystyrene nanoparticles (PNP) to study their sequestration power. The interaction process was monitored by high performance liquid chromatography with diode array detection. The results showed that PDMS microparticles can sequester over 90% of these organic compounds forming an easily filterable coagulate; while PNP sorptive properties were negligible. Exposing the samples to UV-VIS radiation showed that although the limited sorption of PNP, their enhanced surface area increase the photodecomposition of the analytes under aerobic conditions.

## RESUMEN

Polímeros en micro y nanoestructuras son un tipo de materiales emergentes con prometedoras aplicaciones para remediación y degradación de contaminantes en agua, debido a su aumento en área de superficie y a su reactividad química. Tales beneficios también han despertado la inquietud pública debido al riesgo inminente por nanomateriales a exacerbar una variedad de condiciones similares a aquellas mostradas por micro y nanopartículas naturales como lo son las partículas suspendidas. En este trabajo, la selección del modelo de contaminantes orgánicos se basó en la búsqueda de similitudes estructurales con contaminantes comunes en aguas de Puerto Rico. Estos compuestos orgánicos entraron en contacto con partículas coloidales de polidimetilsiloxano (PDMS) y nano partículas de poliestireno (PNP) para estudiar su poder de secuestación. El proceso de interacción fue monitoreado por cromatografía líquida de alta resolución (HPLC por sus siglas en inglés) con un sistema de detección de arreglo de diodos. Los resultados mostraron que micro partículas de PDMS pueden secuestrar sobre el 90% de los compuestos orgánicos estudiados, dando como resultado coágulos de tamaño fácilmente filtrables; mientras que las propiedades de secuestación de nano partículas de PNP fueron insignificantes. La exposición de muestras a radiación UV-VIS mostró que aunque la secuestación de PNP es limitada, su aumento en área de superficie incrementa la foto descomposición de los analitos bajo condiciones aeróbicas.

*To my family, who supports and believes in me*

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# CHAPTER I

## 1.1. An overview of micro and nanoparticles

Advances in technology have created a demand for new nanomaterials for a variety of applications. Over the past decades, the use of micro and nanostructured materials for chemical sensing and remediation has become an important area of research in science and engineering.<sup>1</sup> These materials are characterized based on their size, shape, particle densities and inherent properties such as the surface to volume ratio. This has resulted in a plethora of size dependent properties which can be markedly diversified from their related bulk counterparts. Despite their current vogue, several of these materials have been available for centuries; giving astonishing colors to vases, pottery, and medieval cathedral windows among others.<sup>2</sup>

Modern micro and nanostructured materials have been adapted in several applications including magnetic supports, enzymatic immobilization, immunoassays, cells isolation, DNA and RNA purification. Micro and nanoparticles can be classified in two major groups: suspended particles such as colloids, and sol gels<sup>1</sup>; and static (fixed) particles that are physically or chemically attached to a substrate. While suspended particles are in solution, static particles are physically or chemically bound to the substrate. Generally, suspended particles are more economical and easily fabricated. However, attaining controlled size and shape is difficult to obtain requiring several controlled chemical steps. Alternatively, static particles are fabricated with

various shape, size, and densities either by sophisticated methods like electron beam lithography (EBL) or by immobilizing suspended particles by a variety of techniques like spot and dry, self assembly, Langmuir blotting, and a combination of suspended and static methods. Suspended and static methods have been employed to generate a significant number of metal and polymer micro and nanoparticles for various applications. For instance, micro or nanospheres can be charged with a magnetic fluid in the synthesis process, to improve their selectivity for chemical separations.<sup>3</sup> Microspheres are also coupled in nanolithography to form periodic arrays on a thin substrate film that is subsequently employed to construct periodic arrays of metal nanoparticles.<sup>4</sup> Metallic nanoparticles such as colloidal gold (Au) on top of silica (SiO<sub>2</sub>) nanoparticles, results in an optic and highly active substrate for Surface Enhance Raman Spectroscopy (SERS).<sup>5</sup> Alternatively, polymeric micro and nanoparticles have been used in the controlled release of drugs, genes and other bioactive agents by coating or encapsulation of these agents to the particles, thus providing significant benefits such as selective targeting, controlled release rate, reduced therapeutic dosing, decreased decomposition and prolonged biological activity.<sup>1</sup> Cosmetics, sensors (highly specify) and electrolytic cells are additional examples of the extended applicability of micro and nanoparticles.<sup>6, 7</sup> The increase in global energy demand have extended the applicability of these technologies toward the fabrication of various photovoltaic and fuel cells assemblies with the potential for producing cleaner, yet cost effective, energy in a environmentally friendly manner.<sup>8</sup>

## 1.2. Fabrication of micro and nanoparticles

The main challenge of micro and nanotechnology involves the systematic adjustment of physical properties such as shape, size, and particle density to tailor the chemical properties of the material for a specific application. Current research on micro and nanoparticles focused is on two types of materials: metallic and polymeric. The most common metals employed for these applications include silver, gold, iron palladium, and lithium.<sup>2, 9-11</sup> Polyurethane, lactic acid, polystyrene, and methylacrylate are among the most commonly used polymers for micro and nanofabrication applications.<sup>12-14</sup>

Colloidal metal nanoparticles are prepared by mixing an aqueous solution with a reducing agent often stabilized with organic polymers, ligands that provide a protective coating to prevent their rapid oxidation. Citrates, and borohydrides are common reducing agents used for these applications.<sup>15, 16</sup> Similarly, colloidal nanopolymers often requires vigorous agitation of the aqueous solution during their synthesis. Additional to the monomer and its initiator, the aqueous suspension should have a dispersing agent such as fine particles or a water soluble polymer and a stabilizing agent on a surfactant. Variation in the size of the polymeric cluster is dependent on pH and temperature.<sup>17</sup> For instance, carboxyl functionalized polystyrene nanospheres were obtained by Li, Zhi-Wei in solution with a combination of controlled temperature and convection.<sup>18</sup> Conversely amphiphilic polyurethane nanoparticles were obtained by emulsification without surfactant since it could affect their removal application.<sup>12</sup> Alternatively, polymeric nano-networks of

polyethylene glycol with modified urethane acrylate were fabricated by chemical emulsification.<sup>13</sup> The key aspects in these fabrication procedures are the convection and dispersion of solid particles in a liquid support where Brownian movements of suspend particles promote their systematic adhesion and growth. Amphiphilic polyorganosiloxane with core shell nanospheres were fabricated via sol gel which are useful to study the sequestration and encapsulation of small hydrophilic molecules in organic solvents.<sup>19</sup>

Immobilized particles can be formed by a variety of processes including chemical vapor deposition (CVD), physical vapor deposition (PVD), photolithography (PL), and a self assembly to a solid support.<sup>2</sup> Chemical Vapor Deposition (CVD) occurs when a solid material is ionized by a reactive gas forming a vapor that is deposited at the surface of a substrate. Precursor gases normally diluted within the chamber are delivered into a vacuum evaporating chamber where they react with the target compound. Once vaporized the heated material condenses at the surface of the substrate forming a solid coating at its surface. Some of these methods are the result of the various methods. Examples of the above mentioned techniques include the fabrication of iron nanoclusters employing a sputtering gun, and the formation of polystyrene microspheres bound to a silicon substrate by self assembly technique.<sup>20</sup>

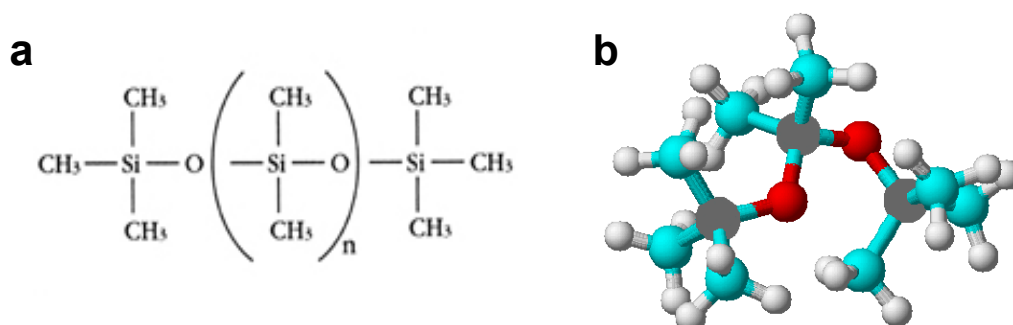
### **1.3. Polymer micro and nanoparticles**

Polymer micro and nanoparticles are a type of reinforced polymers with low quantities of micro or nanofillers resulting in a polymer matrix with enhanced performance. In early days, fillers (bulking agents) were added to reduce fabrication cost; however, today fillers are introduced into the polymer matrix to create new functional properties such as increased elasticity, glass point or conductivity.<sup>21</sup> The purpose of the fillers is to reduce fabrication costs, while preserving the physical and mechanical properties of the polymer. However an excess of these agents could compromise the polymer performance. An important effect of particulate fillers is their ability to act as a nucleation agents, while some fillers show strong nucleation effects others do not. The nucleation effect of fillers depend on their particles characteristics. The probability of aggregation also is affected by fillers; decreasing the size fillers increases the probability to aggregation. Some fillers characteristics affect particles properties. However, the most important are size distribution, specific surface area, particle size, and particle shape.<sup>21</sup> Some of the polymers widely employed as micro and nanoparticles are polydimethylsiloxane (PDMS) and polystyrene (PS).

#### **1.3.1 Polydimethylsiloxane (PDMS) Polymer:**

PDMS makes part of the polyorganosiloxanes, which contain Si-O-Si bonds of similar nature as in silicates. Organic radicals are attached on the

silicon; which imparts on PDMS its dual inorganic and organic character and its enhanced optical properties.<sup>22, 23</sup>

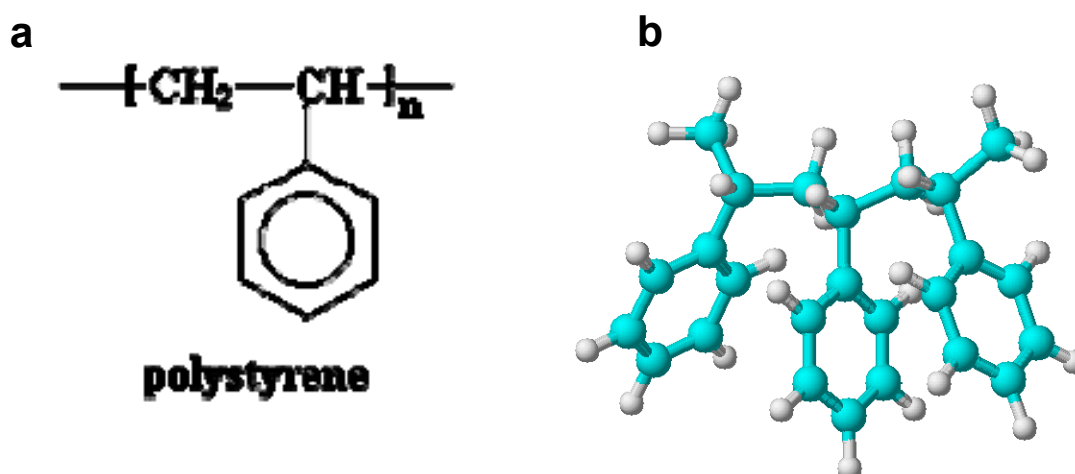


**Figure 1. Polydimethylsiloxane (PDMS) a. Chemical structure;<sup>24</sup> b. Spatial distribution**

PDMS is optically clear, generally considered to be inert, non-toxic, non-flammable. It is also viscoelastic which means that at high temperatures acts like a viscous fluid, while at low temperatures acts like an elastic solid. PDMS is rather water insoluble and exhibits a low surface tension, high compressibility, and resistance to thermal and oxidative stress. The polymer has been widely used in a variety of applications including chromatographic phases, adhesives, silicone grease, lubricants, defoaming agents, heat transfer fluids, polishes, and cosmetics.<sup>25</sup> It also has been used as a filler fluid in breast implants, and as food additive. PDMS is also regularly used as a sorbent material in solid phase micro extraction, solid phase extraction, as stamp resin for soft lithography, and as substrate for microfluid chips.

## Polystyrene (PS) Polymer:

Polystyrene polymer is fabricated by the polymerization of styrene, to form a long hydrocarbon chain with aromatic groups extending from it. At room temperature it exists in solid state; however, it is melted if heated above 240°C and solidifies again when the temperature is below 108°C.



**Figure 2. Polystyrene (PS) a. Chemical structure;<sup>26</sup> b. Spatial distribution**

Polystyrene is a colorless, low cost polymer with limited flexibility. It has low impact strength, poor weatherability and chemical resistance. Polystyrene is used in a variety of applications ranging from food packing, light switches, dining plates, cars, airplanes, and toys. The research applications of polystyrene include substrates for nanosphere lithography, core shell nanospheres for sorption of small hydrophilic molecules and standards for the calibration of transmission and scanning electron microscopes.<sup>4, 14, 18, 27</sup> A modified polystyrene called expanded polystyrene foam is of special environmental concern since takes approximately 900 years to decompose.



PDMS and polystyrene polymers have been widely used in digital electronics and engineering applications. PDMS has been routinely employed in solid phase extraction, for a broad spectrum of analytes. Its powerful sorption properties make it attractive for remediation process, and water treatment. In addition to this, these polymers have been. The development of synthetic procedures to construct micro and nano scale particles of these polymers can potentially enhance their extracting properties.

#### **1.4. Related Works**

Environmental remediation is one of the most important problems of our time and the use of micro and nanotechnology based methods are a promising alternative, not only in cleanup processes, but also in pollution prevention.<sup>28, 29</sup> For instance, the use of heavy metals could be eliminated from computer displays if carbon nanotubes are used as their replacement. Carbon emissions also can be reduced by 200 million tons per year if nanotechnology based home lighting is employed.<sup>11</sup>

Despite current investigations about micro and nanoparticles, most of the current research has been focused on their properties, and applications rather than their potential toxicity and impact to the environment. The use of metal nanoparticles such as those of zero valent iron are aggressively investigated due to their ability to reduce anions like perchlorate, nitrate and dichromate, and heavy metals such as nickel and mercury. In addition to this, bimetallic particles like iron/palladium, and iron/silver may act as potent reducer and catalysts for a

variety of common environmental contaminants such as organochlorine, pesticides and halogenated organic solvents. Xiao-quin Li at Lehigh University<sup>11</sup> found that zerovalent iron nanoparticles with a core-shell structure exhibit hydrous iron oxides and metallic iron characteristics. This provides reduction power for permanent stabilization/immobilization of nickel II by forming a surface complex and its subsequently reduction to metallic nickel on the nanoparticles surface. The nanoscale size of the particles offers an enhanced surface area and superior reactivity for sorption and reduction reactions. These makes them suitable candidates for the separation and transformation of Ni(II), organoarsenics, and nitroaromatic compounds.<sup>11</sup>

Bao-Wei Zhu and Teik-Thye Lim, at the School of Civil and Environmental Engineering in Singapore,<sup>10</sup> evaluated the catalytic reduction of chlorobenzenes with Pd/Fe nanoparticles. Dechlorination of monochlorobenzenes and dichlorobenzenes with Pd/Fe nanoparticles was complete, leaving only benzene as the only product detected via GC-MS. In this work the rate of dechlorination for the positional isomers of dichlorobenzene (DCB) followed the order of, 1,4-DCB > 1,3-DCB ≥ 1,2-DCB. The lower dechlorination rate of 1,2-DCB compared with 1,4-DCB was indicative of steric effects.

Metallic nanoparticles often need controlled conditions in order to avoid their oxidation. Notwithstanding the inherent benefits of this technology; the use of colloidal metal nanoparticles in environmental remediation, is of concern due to their potential toxicity and difficult removal from the applied sample.

Ju-Young Kim et al, at Cornell University,<sup>12</sup> evaluated the potential for novel amphiphilic polyurethane (APU) nano-network particles for extraction of sorbed phenanthrene. The results showed that APU nano-network emulsions extracted a very high level (95%) of the sorbed phenanthrene from aquifer sand with extremely low loss of the applied particles, 97-98% of the applied APU particles can be recovered from column experiments with a small volume of wash water.

In addition, Warapong Tungittiplakorn et al.,<sup>13</sup> developed polymeric nano network particles made from poly(ethylene)glycol modified urethane acrylate (PMUA). These nanoparticles showed an enhanced rate of phenanthrene (PHEN) crystals in water, PHEN sorbed on aquifer material, and PHEN dissolved in a model nonaqueous phase liquid (NAPLs) (hexadecane) in the incidence of aquifer media. The increased PHEN mineralization rate during the first few days is interpreted to be the result of the enhanced desorption rate from the aquifer media in combination with the greater accessibility of PMUA bound PHEN to *Comamonas testosteroni* bacteria present in a mineral salt media. The accessibility of contaminants in PMUA particles to bacteria also suggests that particle function may be effective to enhance the in-situ biodegradation rate in remediation through natural reduction of contaminants. Results also showed that these PMUA nanoparticles are not toxic for these bacteria as a result of the similarities of PMUA to micelle structures. These nanoparticles have hydrophilic poly(ethylene glycol) chains extending out from their hydrophobic surface of polyurethane acrylate. As a result, their cross

linked form will not break up upon contact with soil and are not expected to interact with the microorganism.

Navid Saleh et al., at Carnegie Mellon University in Pittsburgh Pennsylvania,<sup>30</sup> demonstrated the ability of iron nanoparticles modified with a novel triblock copolymer (poly(methacrylic acid)-block-poly(methyl methacrylate)-block-poly(styrenesulfonate)) to promote colloid stability in aqueous suspension and absorb contaminants such as trichloroethylene (TCE), and reduce it to nontoxic nonchlorinated compounds such as acetylene or ethane, in contrast, unmodified iron nanoparticles were not capable to reduce these contaminants.

Nadja Jungmann et al., at Mainz university in Germany,<sup>19</sup> performed the synthesis of novel amphiphilic core-shell poly(organosiloxane) nanospheres using a chemical system where organosilane monomers are condensed via the sol-gel process in aqueous dispersion, followed by the sequential addition of the monomers to the formation of spherical core-shell colloids with diameters of 5 nm up to about 100 nm.

Other nanomaterials have been studied for environmental remediation, which is the case of Meagan S. Mauter et al, at Yale University,<sup>7</sup> who reported that carbonaceous nanomaterials work as a sorbent for environmental contaminants like natural organic matter, clays, trihalomethanes, polycyclic aromatic hydrocarbons and naphthalene. Rapid equilibrium rates and high sorbent capacity were some of the benefits of these carbonaceous

nanomaterials. Direct sorption of organic contaminants to the nanomaterials surface is driven by basic hydrophobic, dispersion, and weak dipolar forces that determine their sorption energies.

As outlined in our previous discussion, the small size of nanostructured materials represents a major milestone for its use in environmental remediation. For instance, a considerable number of nanoparticles show limited aggregation, which makes them difficult to remove by existing filtration and water treatment methods.

## **1.5. Applications and Characterization Techniques**

### **1.5.1. Environmental Remediation:**

In general, the term environmental remediation is associated to the removal of pollutants from an environmental media such as soil, groundwater, surface water, etc. The growing demand for clean water have resulted in the development of several remediation techniques including pump and treat, surfactant enhanced aquifer remediation, in situ oxidation, soil vapor extraction, and solid phase extraction. The majority of these techniques are assessed based on their efficiency to remove emerging pollutants as manifested by the decrease availability of the pollutant in water. This process is governed by sorption theory.

### 1.5.2. Sorption Theory<sup>31</sup>

Sorption can occur by one of two mechanisms: adsorption and absorption. Absorption involves the distribution (partitioning) of the solute within a material, consisting of the taking up of a constituent called absorbate by a liquid or solid (absorbent), while adsorption is the process by which a solute adheres to a solid surface, it is manifest in changes of concentration of a surface in the boundary layer between two neighboring phases and depends both on the properties of the adsorbing body, as well as the adsorbent body.

The Langmuir and Freundlich isotherms are the traditional models to describe most of adsorption phenomena. The Langmuir model assumes that adsorbent have definite sites to fix one molecule for site. In this model a solid-liquid adsorption is represented by:

$$C_s = Q^0 - \frac{C_s}{bC_l}$$

Where:

$C_s$  = Equilibrium concentration of adsorbate(solute) in the sorbent

$C_l$  = Equilibrium concentration of adsorbate in solution

$b$  = Langmuir constant (represent: affinity between the adsorbate and the sorbent)

$Q^0$  = Langmuir constant (represent: adsorbate concentration in the sorbent, considering a complete coverage of available sites).

In contrast, the Freundlich model assumes a heterogenic surface with sites and energy exponential distribution; thus:

$$C_s = K_f C_l^{\frac{1}{n}}$$

Where:

$K_f$  = Freundlich constant (Relative indicator of adsorption capacity)

$1/n$  = Freundlich constant (Represent: sorption behavior)

This model is the one that commonly describe the interaction process between polymeric materials and organic compounds in aqueous phase. Partition between immiscible phases is described by:

$$K = \frac{C_s}{C_l}$$

Where:

$K$  = Partition Coefficient

$C_s$  = Equilibrium concentration of solute in the sorbent

$C_l$  = Equilibrium concentration of solute in solution

Usually, quantification of removal pollutants is performed by separation analytical techniques since matrix sample is often complex. The analytical techniques most commonly used are liquid chromatography, gas chromatography, supercritical fluid chromatography and electrophoresis.

Although these techniques are good tools for separations, high performance liquid chromatography has been widely employed for environmental analysis since it allows the analysis of organic complex samples of semi volatile and no volatile pollutants with high reproducibility.

### **1.5.3. High Performance Liquid Chromatography (HPLC)<sup>31</sup>**

In the beginning HPLC was known as High Pressure Liquid Chromatography to differentiate from traditional liquid chromatography (LC) which used gravity or a peristaltic pump for solvent delivery. Modern HPLC or simply LC, as currently known, employs small size, densely packed stationary phases to enhance elution efficiency and resolution.

HPLC offers excellent separations of complex mixtures in a relative short period of time. The technique also allows for the analysis of a wide range of compounds of environmental interest such as pesticides, pharmaceuticals and other emerging pollutants. This makes of HPLC the tool of choice for the analysis of a wide range of chemicals like polystyrenes, dyes, phthalates, proteins, peptides, nucleotides, tetracyclines, corticosteroids, antidepressants, barbiturates, polyaromatic hydrocarbons, inorganic ions, herbicides, amino acids, vitamins, homocysteine, lipids, and antioxidants

HPLC is widely used in pharmaceutical and environmental sciences for the analysis of organic compounds like polyaromatics hydrocarbons as well as emerging pollutants such as estrogens, antimicrobial drugs and dyes. The technique is capable to analyze complex samples even those with extremely



high molecular weight as long as they are soluble in the elution media. Once separated, sample components flow to detector that usually is a non destructive device such as a UV-VIS or fluorescent detector. Where the individual sample components are detected and measured. To ensure good chromatographic peak shapes, target analytes should be totally dissolved and free of any particulate matter. HPLC is a powerful tool for environmental remediation since it allows the extraction and quantification of trace pollutant levels. The separation process should be carefully monitored and must be highly reproducible to establish the separation efficiency.

Efficiency of chromatography separations depends on several parameters. The retention factor ( $k'$ ) gives a relation between the time that a solute spends in the stationary phase and in the mobile phase.

$$k' = \frac{t_R - t_M}{t_M}$$

Where:

$k'$  = Retention Factor

$t_R$  = Retention Time (Time between injection of a sample and appearance of a solute peak at the detector)

$t_M$  = Dead Time (Time that takes unretained species to pass through the chromatographic column).

A good separation usually shows retention factors in a range of 1 to 5.

The selectivity factor ( $\alpha$ ) for two analytes defines the ratio of the distribution constant of the more retained solute with the distribution constant for the less retained solute.

$$\alpha = \frac{k_B}{k_A} \quad \text{or} \quad \alpha = \frac{(t_R)_B - t_M}{(t_R)_A - t_M}$$

Where:

B = More retained solute

A = Less retained solute

Selectivity factor value must be greater than unity.

The efficiency of a chromatographic column is also determined by the plate count or number of theoretical plates (N). It provides the ratio between the retention time for a compound and width its eluted peak. As the plate count becomes greater, the efficiency of the column increases.

$$N = 16 \left( \frac{t_R}{W} \right)^2$$

Where:

W = width of the peak in units of time

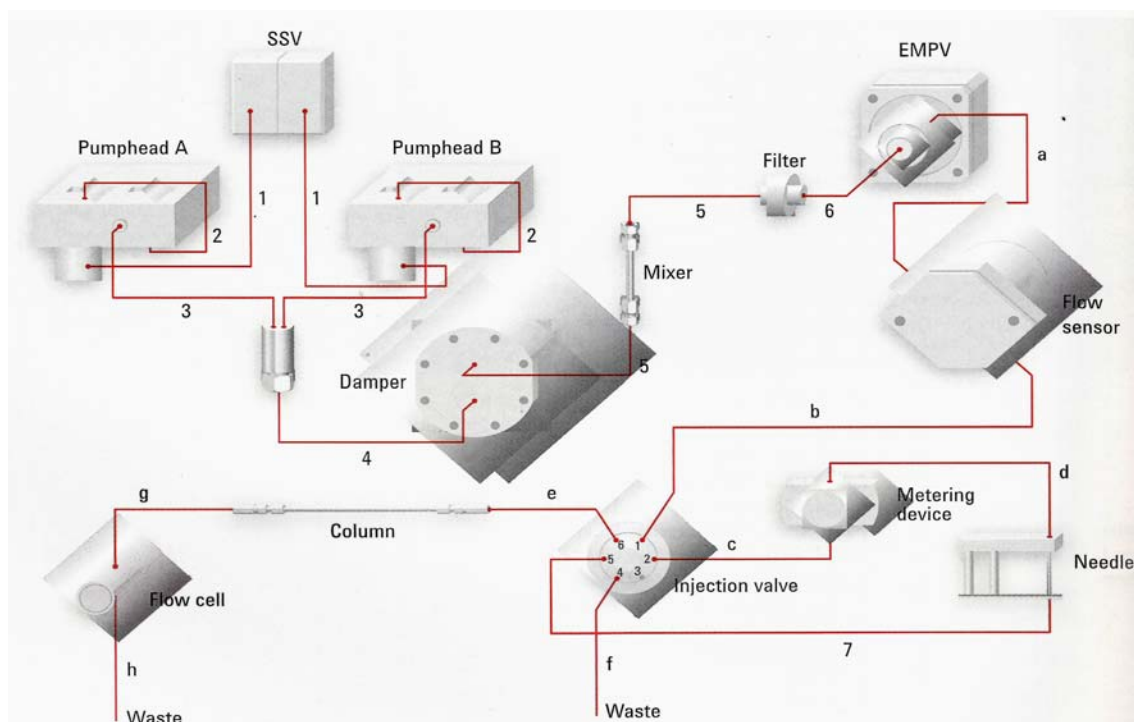
Efficiency in terms of plate numbers may fluctuate from a few hundred to several hundred thousand.

The resolution ( $R_s$ ) expresses a quantitative measure of chromatographic column to separate two analytes.

$$R_s = \frac{2(\Delta t_R)}{(W_1 + W_2)}$$

A separation of approximately 99.7% is given by a value resolution of 1.5 and values greater than 2 represent complete separations.

Figure 3 shows the main components of a high performance liquid chromatograph. In general terms it consist of a mobile phase reservoir, which should have an inlet frit to trap particulate matter; the solvent delivery system must provide accurate and constant flow, an exact mobile phase composition and the necessary force to push the mobile phase through the tightly packed column. The injector must deliver the sample without disturbing or stopping the mobile phase flow through the column. The Column should separate each sample component in the trajectory to the detector system.



**Figure 3. Diagram of a Modern High Performance Liquid Chromatography System.**<sup>32</sup>

#### 1.5.4. Raman Spectroscopy<sup>33, 34</sup>

Raman spectroscopy provide in relative short time information that can be used to elucidate structural information about organic and inorganic compounds. Raman takes place when monochromatic light of  $h\nu_0$  encounters matter (molecule). Electromagnetic radiation scattered by the molecule could be of three types. Most of the scattered radiation presents the same frequency of incident radiation; this type is known as Rayleigh scattering and does not provide any information of sample composition. If scattered photon possess different frequency of incident one, the collision is inelastic given place to Raman scattering. If the scattered photon is lower in energy by an amount

equal to a vibrational transition  $h\nu_1$ , it is called Stokes Raman scattering. If the molecule is in an excited vibrational state when the incident photon is scattered, the photon may gain energy giving place to anti-Stokes Raman scattering. Figure 4 presents these possible light scattering events, where virtual energy states can be considered an electron cloud distortion of a very short lived which is caused by the oscillating electric field of the light. A Raman spectrum consists of the scattered intensity plotted versus the shift of the Raman signal in wavenumbers. The Stokes and anti-Stokes Raman peaks are symmetrically positioned about the Rayleigh peak. The Maxwell-Boltzmann distribution establish that 99% of molecules are in the lowest possible vibrational state or ground vibrational state at room temperature, giving a result a greater probability of occurrence for Raman Stokes scattering than Raman anti-Stokes scattering.

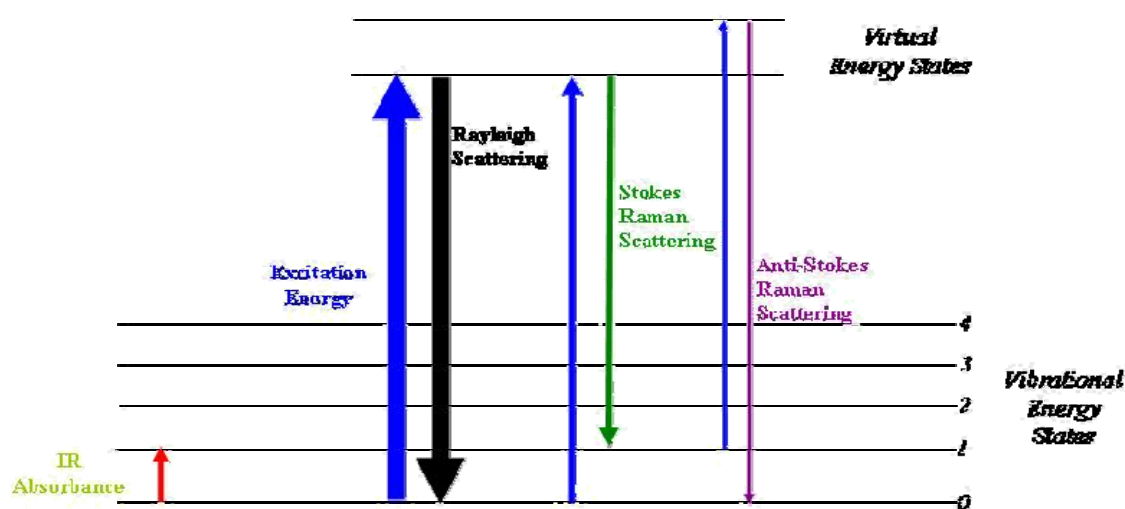


Figure 4. Energy diagram for Raman scattering<sup>35</sup>

The key factor of the Raman effect is the polarizability ( $\alpha$ ) of the molecule and it depends on the orientation of the molecule with respect to the applied electric field.

$$E = E_0 \cos(2\pi\nu_i t)$$

Where:

$E$  = Electromagnetic field

$E_0$  = Amplitude of the electromagnetic wave

$\nu_i$  = Frequency of the incident beam

$t$  = time

A dipole moment ( $\mu$ ) is generated by interactions between oscillating field and electron distribution of the analyte.

$$\mu = \alpha E \quad \text{or} \quad \mu = \alpha E_0 \cos(2\pi\nu_i t)$$

This equation only represents an approximation of the general deformability of the molecule as a result of the electromagnetic field incidence.

The molecular vibrations are composed of normal modes, ( $Q_j$ ), of which there are  $3N-6$  (or  $3N-5$  for a linear molecule) in a molecule with  $N$  atoms.

$$Q_j = Q_j^0 \cos(2\pi\nu_j t)$$

Where:

$\nu_j$  = characteristic harmonic frequency of the  $j^{\text{th}}$  normal mode.

The polarizability of electrons in the molecule will be governed by the molecular vibration.

$$\alpha = \alpha_0 + \left( \frac{\delta\alpha}{\delta Q_j} \right) Q_j + \dots$$

As a result:

$$\mu = \underbrace{\alpha_0 E_0 \cos(2\pi\nu_0 t)}_{\text{(Rayleigh term)}} + \underbrace{\frac{E_0}{2} Q_j^0 \left( \frac{\delta\alpha}{\delta Q_j} \right) \cos[2\pi(\nu_0 + \nu_j)t]}_{\text{(Stokes term)}} + \underbrace{\frac{E_0}{2} Q_j^0 \left( \frac{\delta\alpha}{\delta Q_j} \right) \cos[2\pi(\nu_0 - \nu_j)t]}_{\text{(Anti-Stokes term)}}$$

Raman spectroscopy is a powerful technique for the analysis of polymers, biophysical, biomedical and environmental analysis since it requires low amount of samples and the presence of water does not interfere with the structural information of analyte.

### 1.5.5. Scanning Electron Microscopy (SEM)<sup>34, 36</sup>

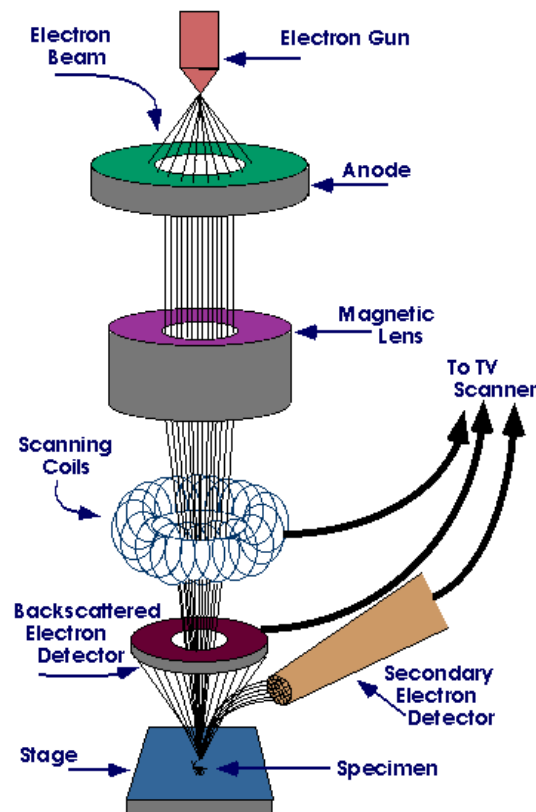
SEM utilizes electrons rather than light to form a surface image. This image is acquired by scanning the surface with a high energy electron beam. The electron beam follows a vertical course through the microscope. The beam

goes through lenses and electromagnetic fields which have the function to focus the beam down in the direction of the specimen (sample). Once the beam reaches the sample, primary backscattered electrons, secondary electrons, Auger electrons and X-rays can be generated based on the applied voltage. Where backscattered electrons are those scattered with no appreciable loss of energy as a result of an elastic collision. These backscattered electrons show the spatial distribution of elements or compounds. Secondary electrons are generated by inelastic collision between electron beam and atoms in the sample, the electron imparts some of its energy to a lower energy electron in the sample, causing a slight energy loss and path change in the incident electron and ionization of the electron in the sample. These show the topography of the surface. When an electron from an inner shell is root out, this vacancy could be filled with an electron from an external shell resulting in extra energy that could be liberated by emission of X-ray or could be taken by other electron and emitted like an Auger electron.

The SEM produces images of high resolution, allowing the examination of closely spaced specimens at a high magnification. There is more control in the degree of magnification. The SEM has a large depth of field, which makes it able to focus more at a specimen at one time. This technique is useful in the characterization of micro and nanoparticles. Its high resolution and the possibility to generate images with depth fields could determine the size and shape of these particles.



Vacuum conditions and the use of electrons to form an image are reasons for the total water elimination of the sample and for its conversion in conductive sample with a thin layer of conductive material.



**Figure 5. Scanning Electron Microscopy System.**<sup>36</sup>

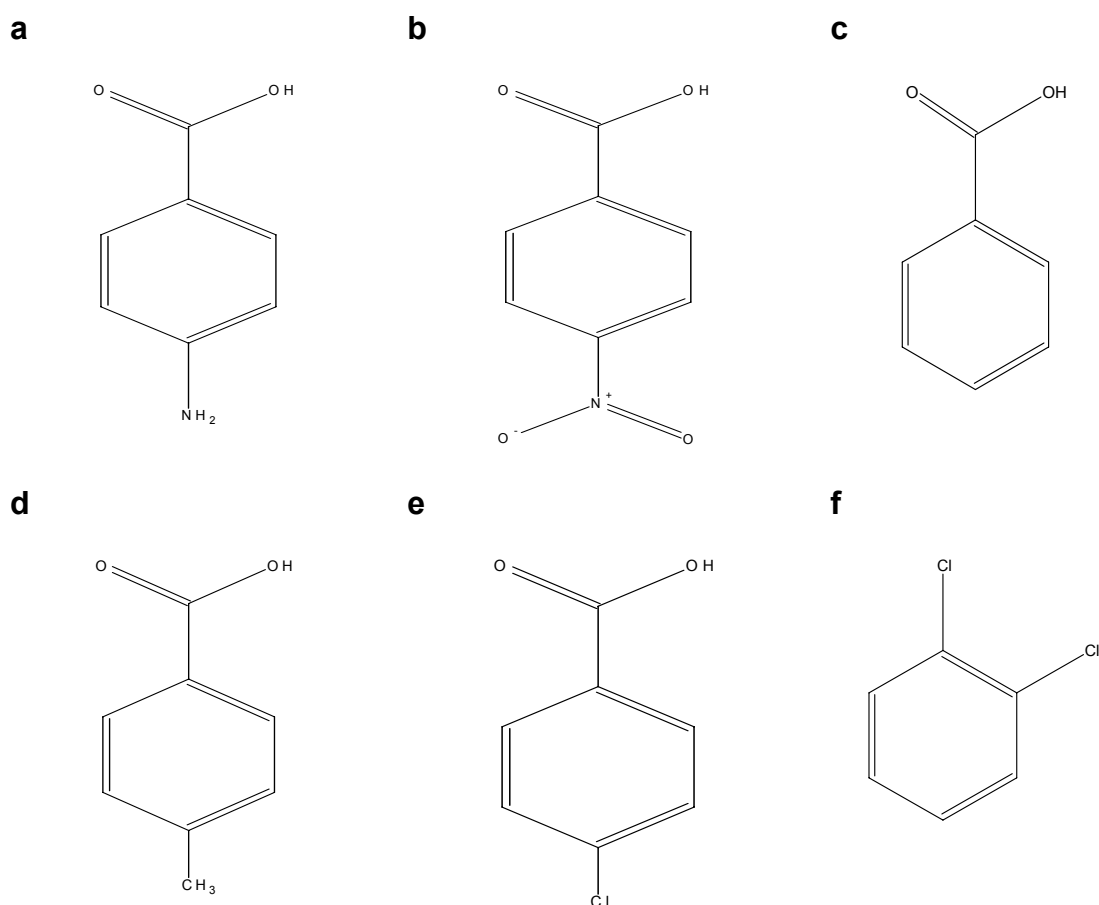
## 1.6. Statement of the problem

Over the past years, the emergence of several diseases and extinction of significant number of animal species related to environmental pollution have proven the necessity to pursue a more responsible and sustainable use of our natural resources. In the world, 300,000 people die every day due to lack of water, and less than 0.4% of the total water is readily available.<sup>37</sup> In addition, effects like global warming, and the growing population increases the demand

for the limited clean water resources. In Puerto Rico the water demand is approximately of 750 million gallons per day and natural disasters like hurricanes can lead to severe damages to the water and sewer infrastructure. Moreover, in the Caribbean the population is growing at a rate of 2.17% per year. New facilities for water treatment are being constructed with approximate costs of 300 millions of dollars. As a result, the development of new, cost effective and more rapid water purification methods are being required; however, re-designing of the water treatment facilities is expensive and unattractive. The cited studies demonstrate the potential benefits of using micro and nano scale materials for environmental remediation and water treatment applications; since the enhanced physical and reactive properties of these materials could provide a faster, yet more efficient purification of this limited resource.

Notwithstanding, the merits of micro and nanotechnology in environmental remediation, regulatory agencies such as the Environmental Protection Agency (EPA) are concerned about micro and nanoparticles into the environment, since the size of these materials make them difficult to remove from the environment. In addition to this, the lack of data about the influence of these micro and nanoparticles in the decomposition and photolytic degradation of environmental contaminants has required a more proactive approach for the implementation of these technologies; particularly, when recent studies linked cellular death and cardiovascular problem to certain micro and nanoparticles exposition.<sup>38-40</sup> Therefore, there is a need for the preparation of new micro and nanostructured materials that are easily removed after treatment.

This work investigates the chemical reactivity and sorption capacity of colloidal PDMS microparticles and PNP to model organic pollutants. The model organic pollutants (Figure 6) were chosen based on their similarities chemicals commonly found in the natural waters of Puerto Rico. Polymer micro and nanoparticles employed in this investigation, where selected by their solid phase extracting properties and their recent use in micro and nanotechnology. The impact of the polymeric material on the photolytic reactivity of model pollutants was also investigated.



**Figure 6. Chemical structure of model organic pollutants, a. 4-aminobenzoic acid (4-ABA); b. 4-nitrobenzoic acid (4-NBA); c. benzoic acid (BA); d. 4-toluic acid (4-TA); e. 4-chlorobenzoic acid (4-CBA); f. 1,2-dichlorobenzene (DCB).**

Successful results were observed for removal of carboxylic acids studied by PDMS microparticles with the benefit of forming an easily filterable aggregate which is a promising tool for water treatment. The efficiency of this process was monitored via HPLC. The development HPLC protocol were highly reproducible and with a reasonable efficiency for the quantitative analysis of a broad range of analytes and photodecomposition products.

## CHAPTER 2

### 2.1. Introduction

Micro and nanoparticles are an emerging type of material with promising applications in pharmaceutical and environmental sciences. Current research has demonstrated the potential of these advanced materials comprise in the construction of high performance sensors, catalyst, substrates for optical spectroscopy, enzymatic processes, controlled drug delivery and environmental remediation.<sup>3, 5-7, 41</sup> Most of the remediation technologies available today, while effective, are often expensive and time consuming, particularly at the water treatment facility. From an environmental standpoint, the ability to remove toxic compounds from wastewaters, Brownfields and potential hazardous environment is the ultimate goal.<sup>41</sup> Advances in micro and nanotechnology are providing unprecedented opportunities to develop more cost effective and environmentally acceptable remediation strategies.<sup>28</sup>

The most notable parameter of these advanced materials is their enhanced surface areas, which improve the extractive and catalytic properties of these nano structured agents. The extracting properties of polymer particles combined with their enhanced micro and nanoscale features make them ideal candidates for fast acting agents to remove organic compounds. Such agents are needed to cope with the increasing demand for clean water due to population growth, pollution, and rigorous environmental standards. Despite the need, the successful removal of organic pollutants in this complex mixtures

have been a major challenge for water treatment applications.<sup>42</sup> Reasonable costs, high extraction yields, rapid action and the ability to be employed in situ are among the desirable properties for the removal of organic compounds, particularly hazardous materials and emerging pollutants.

A majority of the remediation technologies available today, while effective, are time consuming and costly; particularly pump-and-treat methods.<sup>42</sup> Among treatment technologies that are commercially available, the use of polymeric formulations have been explored since they are a relatively new class of materials that offers the benefits of low costs, decreased toxicity, enhanced selectivity and improved performance especially for the extraction of pollutants that are difficult and often impossible to eliminate by traditional methods.

Several studies are focused toward the removal of organic matter (OM) since its presence in water results in a number of problems including undesirable color, odor, and taste.<sup>41</sup> In addition, OM can react with residual chlorine from the waste water treatment processes generating trihalomethanes, which have been linked with human carcinogenesis. OM also affects the performance of the membrane filtration process when it attaches or blocks the filtration membranes resulting in differential pressures and incomplete pollutant removal. The effective removal of OM prior to these treatments could represent major improvement in the waste water treatment process. Carbonaceous nano materials have proven effective to promote the sorption of a variety of compounds including OM, clays, naphthalene, trihalomethanes and poly aromatic hydrocarbons. The sorption on the surface of nanomaterials is driven

by fundamental electrostatic hydrophobic dispersions, and weak dipolar forces that determine sorption energies of the conventional system.<sup>41</sup> A key aspect for the successful implementation of these materials in remediation is the need for the effective removal of the nanoparticle upon treatment preferably by forming an easily filterable precipitate or flocculate that can be rapidly removed by existing methods.

Environmental remediation processes typically combine several techniques to ensure the effective removal of specific contaminants. The use of micro and nanomaterials in remediation offers the benefit of easy functionalization and enhanced specificity for the removal of particularly difficult and persistent pollutants, like chlorinated compounds. Waste of organochlorine pesticides, fungicides, and herbicides composed by 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene have been effectively treated by positive dechlorination with Pd coated iron nanoparticles. Zero-valent iron nanoparticles are also used in remediation studies where Ni(II) forms a surface complex on  $\text{Fe}^0$  and is subsequently reduced to metallic nickel.<sup>10-12</sup> However the rapid oxidation of the nanoparticles requires the in situ generation of the nanoparticles which is difficult in a water treatment facility. Effective water treatment additives are expected to be directly transferred to the treatment containers without the need for additional steps or modifications.

Even though the inherent benefits of micro and nanotechnology for water treatment, there is growing concern about the environmental fate and transport of these new materials. Recent investigations show that carbon nanotubes can

increase the number of ischemic and cardiovascular cases and induce atherosclerosis due to the accumulation of peroxidative products, and a total depletion of the reserve of antioxidants. Similar effects are observed by the interaction with micro and nano particles primarily by lipid oxidation.<sup>39, 40, 43</sup> Consequently, there is a need to develop new strategies that allow the safe and effective use of this technology for the removal or neutralization of water contaminants without further toxicological concerns.

This study evaluates the effectiveness of colloidal polydimethylsiloxane (PDMS) and polystyrene (PNP) particles to serve as additives for the removal of model aromatic contaminants in water. Target compounds are a family of five carboxylic acids and one dichlorinated compound representing groups of pollutants (i.e. phenols, nitroaromatics, etc.), commonly present in Puerto Rican natural waters. The efficiency of the remediation process was monitored by reversed phase high performance liquid chromatography with diode array detection (HPLC-DAD).

## **2.2. Experimental**

### **2.2.1. Preparation and characterization of PDMS and PNP particles**

The synthesis of colloidal PDMS was performed by preparing a mixture containing 90% w/w of deionized water, 2.1% w/w of powder surfactant (Dry Clean, Fisher), 0.05% w/w of NaOH (95% Fisher), 5.7% w/w of Sylgard® 184



silicone elastomer base and 0.63% w/w of curing agent (Dow Corning Corporation). The elastomer base and curing agent were slowly titrated to the solution. The polymerization reaction was performed in an ice bath to reduce the kinetics of the polymerization and reduce the particle size. Once mixed, the suspension was stirred for 24 hours in a method similar to that employed by Jungmann and collaborators.<sup>19</sup> Standard, carboxyl and aldehyde terminated polystyrene nanoparticles were acquired from Duke Scientific Corporation with a PNP concentration of 4% w/w and a standard particle size of  $97(\pm 3)$  nm.

The size and shape of both PN and PDMS particles were determined by the spot and dry method using a JEOL scanning electron microscope (SEM) model JSM-5410LV. The samples were coated with a thin film of gold by sputtering the metal at 20 mÅ/s for 2 min with an EMS 550X sputter. Scanning electron micrographs were acquired at a magnification of 3,500 and 5,000X and an accelerating voltage of 3 and 15 KV respectively. The SEM micrographs were used to determine size and shape of the obtained particles. The chemical composition of each polymer was corroborated by Raman spectroscopy. The spectroscopic data was acquired using a Renishaw RM2000 Raman spectrograph with 514 nm excitation, and 100 mW of power at the source. Each spectrum was collected with an integration time of 10 seconds using a 50X, infinity corrected objective.

### 2.2.2. Sample preparation

1mM stocks of 4-aminobenzoic acid (4-ABA) (99% Acros), benzoic acid (BA) (99.6% Fisher), p-nitrobenzoic acid (p-NBA) (99% Sigma), p-toluic acid (p-TA) (98% Sigma), 4-chlorobenzoic acid (4-CBA) (99% Sigma) and 1,2-dichlorobenzene (DCB) were prepared in deionized water. A series of 0.1 mM standard mixtures containing the five carboxylic acids in (0.18%) PDMS, and (0.05%) PNP, respectively were prepared. Individual and mix control standards (0.1 mM each) of 4-ABA, 4-CBA and DCB were also prepared.

### 2.2.3. Sorption Studies

Sorption capacity of PDMS microparticles and PNP particles were determined by exposing the compounds to micro and nano particles for 24 hours (in concentrations samples of part 2.2.2.), followed by filtration with a 0.45 $\mu$ m nylon filter. The filtrate was analyzed with an HPLC (Agilent, model 1100). The sorption capacity was then establish by differential concentrations of analyte. Calibration curves were obtained in a concentration range of  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$ M.

### 2.2.4. Photolytic Studies

A series of 0.1 mM standard mixtures containing the five carboxylic acids and individual samples of 4-ABA, 4-CBA, and DCB with same concentrations of part 2.2.2. were used to perform these photolytic studies. Samples were placed

under aerobic conditions in an antireflective box under long ultraviolet light (312 nm) for 10 days followed by filtration with 0.45 $\mu$ m pore size filter. HPLC chromatography was employed to study the effect of micro and nanoparticles in photodecomposition process of studied compounds.

### **2.2.5. Anaerobic studies**

Sample preparation, sorption studies and photolytic studies were performed as above described, although only 4-ABA was employed for these studies. Anaerobic conditions were obtained by degassing the sample for 3 minutes using nitrogen gas.

### **2.2.6. Instrumentation**

An Agilent HPLC chromatograph series 1100 with a diode array detector monitoring the 254nm line for the sorption and photolytic analysis of carboxylic acids was employed. The separation of the carboxylic acid derivatives was performed with a Zorbax RX-C18 column, under isocratic conditions (65%:35% water:acetonitrile respectively), and a flow rate of 1mL/min. Samples containing DCB were analyzed by monitoring at 270 nm under 70%:30% methanol:water elution at a flow rate of 1mL/min.

Results were evaluated from three sets of experiments with triplicate measurements. Sorption models of PDMS can be finding as specifications for SPE by Sigma Aldrich.

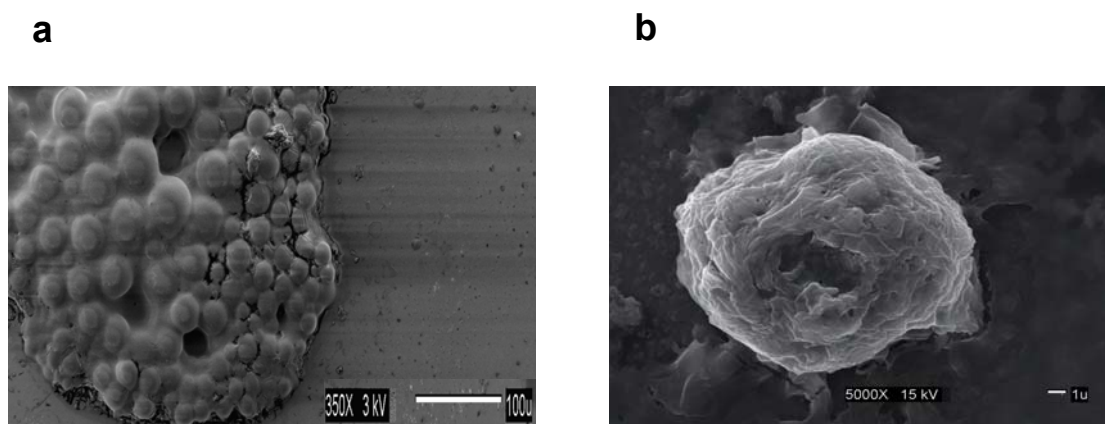
## 2.3. Results and Discussion

The addition of a surfactant, under alkaline conditions and continuous convection were key factors to optimize the preparation of colloidal PDMS particles. The addition of sodium hydroxide was the first factor that allowed the formation of small spheres. This hydrophilic environment allowed for the outer PDMS, dimethyl groups to point toward the inner core of the micro-particle while its corresponding siloxane groups were pointing toward the aqueous surroundings. The rapid convection of solution further improved formation of small clusters stabilized by the surfactant to prevent its coagulation. Moreover, the polymerization was initiated under ice to reduce the reaction kinetics and promote the formation of small PDMS particles. The absence of an appropriate control of the system temperature and surfactant ratio leads to the rapid coagulation and substantial growth of the PDMS particles, resulting in the formation of macro-spheres typically 2-3 mm in diameter. Optimum preparation conditions were obtained with a 5.7%:0.63% polymer to surfactant ratio under iced water. The process forms globular microparticles of 10-50  $\mu\text{m}$  in diameter.

The viscous and highly hydrophobic nature of the polymer suspension makes it prone to aggregation (Figure 7a). This micrograph shows a large PDMS cluster, formed after spot-drying a drop of the colloid on a glass slide.

The average particle size in the cluster is of 25.6  $\mu\text{m}$  with particles as small as 15  $\mu\text{m}$  in diameter (Figure 7b). The oblong shape and hollow center of

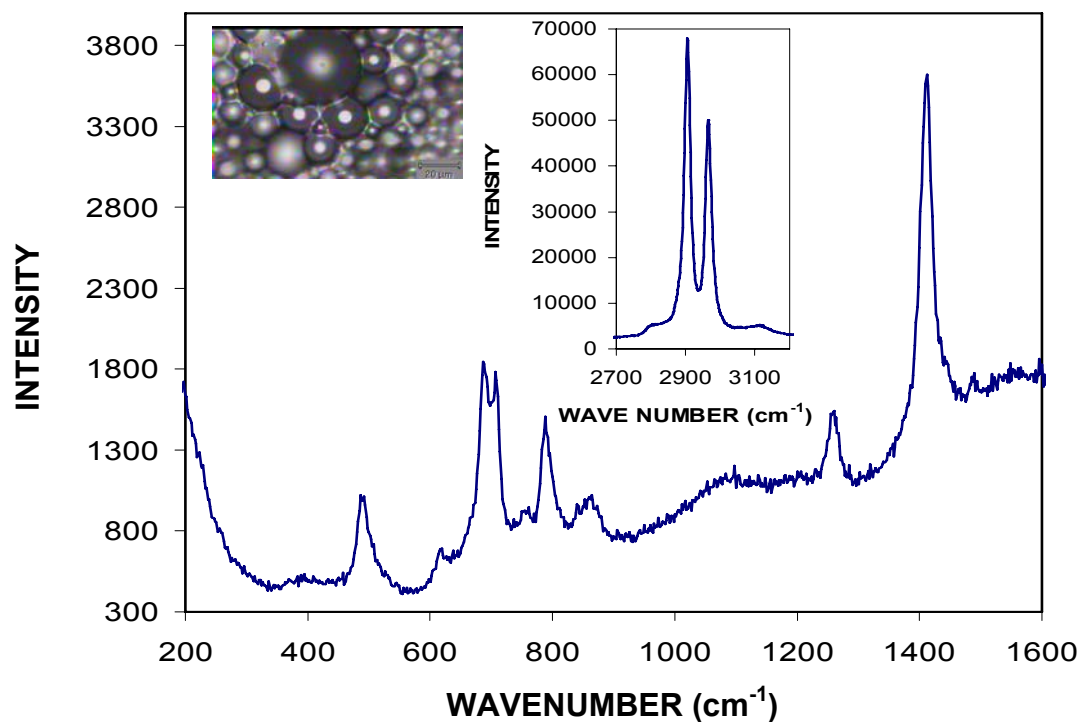
this particle suggests that they are formed through a layer by layer addition of the polymer.



**Figure 7. SEM micrograph of colloidal PDMS microparticle: a. PDMS cluster; b. Individual particle.**

An analysis of the Raman spectrum of the cluster confirmed that the particles are composed of PDMS (Figure 8). The spectroscopic data shows PDMS characteristic bands at  $200\text{-}1600\text{ cm}^{-1}$  and  $2700\text{-}3200\text{ cm}^{-1}$  as detailed in Table 1.

The spectrum shows the characteristic Si-O-Si symmetric stretching ( $489\text{ cm}^{-1}$ ), and the  $709\text{ cm}^{-1}$  band which corresponds to the symmetric stretch of the bonds C-Si-C groups of the polymer. The symmetric and asymmetric bending of methyl groups occurred at  $1263$  and  $1411\text{ cm}^{-1}$  respectively, in agreement with previous PDMS studies.<sup>25, 44, 45</sup>



**Figure 8. Raman spectrum of colloidal PDMS suspension at 254nm and 10 seconds of acquisition time.**

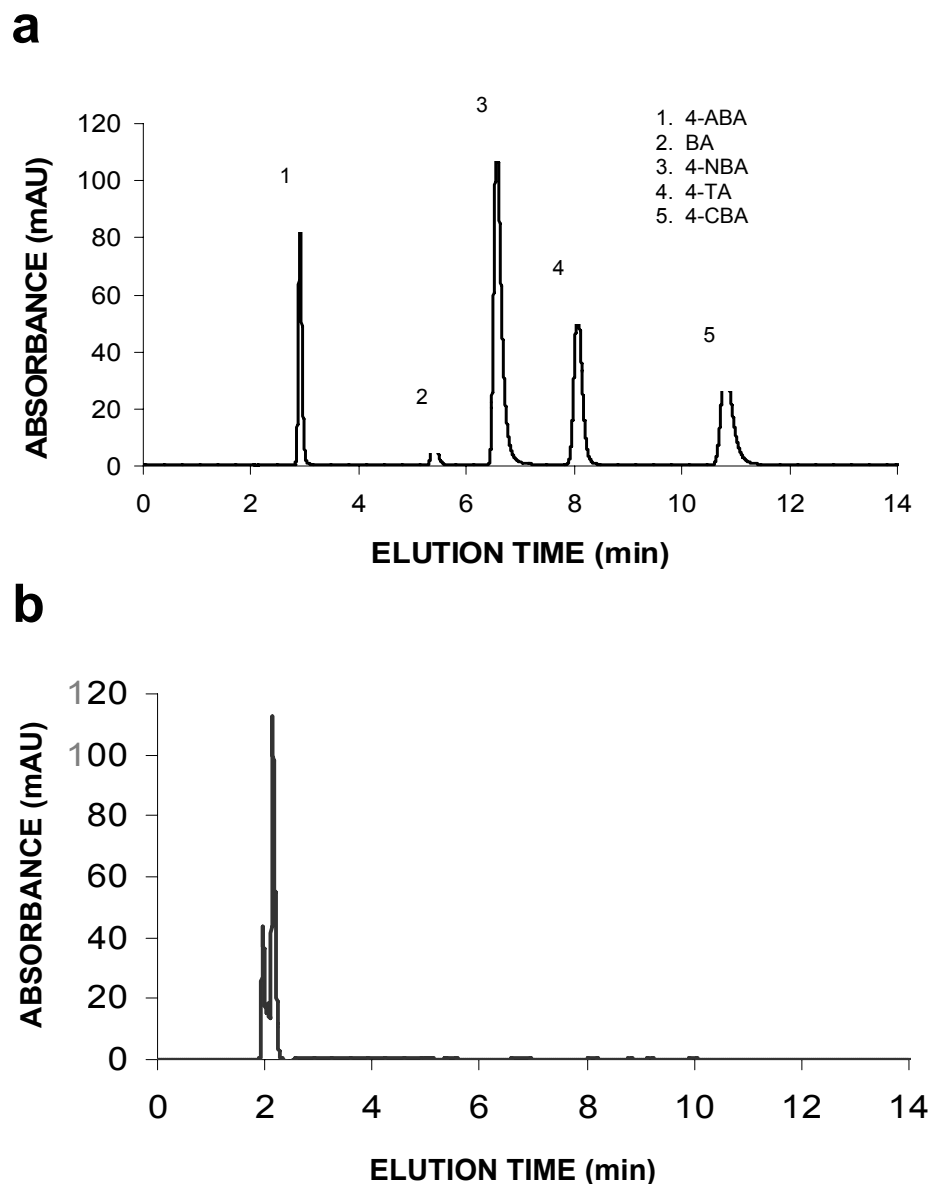
**Table 1. Characteristic Raman shifts of PDMS microparticles**

EXP. WAVENUMBER (cm <sup>-1</sup> )	MODE
489	Si-O-Si Sym Stretch (Str)
709	C-Si-C Sym Str
788	C-Si-C Asym Str
1263	CH <sub>3</sub> Sym Bend
1411	CH <sub>3</sub> Asym Bend
2802	CH <sub>3</sub> Asym overtone
2906	CH Sym Str
2965	CH Asym Str

Once characterized, the PDMS suspension was used as a sorbent agent for the removal of a group of benzoic acid derivatives. The sorptive and chemical reactivity of the micro colloids was compared against that of commercial polystyrene nanoparticles (PNP).

The family of benzoic acids used in this study includes benzoic acid (BA) and its para substituted derivatives (4XA), where X is a chlorine, hydroxyl, methyl and nitro groups respectively (4-ABA, 4-NBA, 4-TA, 4-CBA). These model pollutants were selected due to their reasonable solubility in water, and their structural similarities with pesticides, herbicides and phenolic compounds commonly present in superficial water and waste waters. Laboratory standards of these chemicals were prepared in the  $1 \times 10^{-3}$  –  $1 \times 10^{-6}$  M range. Careful adjustment of the elution conditions resulted in an optimum separation with an isocratic elution of 65%/35% water/Acetonitrile ratio and water pH of 2.88.

Figure 9a shows the elution of a standard 0.10 mM mixture of each benzoic acid derivative under the above mentioned conditions. The ascending elution order of the analytes was 4-ABA, < BA, < 4-NBA, < 4-TA, < 4-CBA with retention times of 2.944( $\pm 0.002$ ), 5.29 ( $\pm 0.01$ ), 6.48( $\pm 0.02$ ), 7.98( $\pm 0.02$ ), 10.75( $\pm 0.04$ ) minutes, respectively.



**Figure 9. a. Standard chromatogram showing the successful separation of five carboxylic acids (0.10 mM each) at 254 nm; b. Elution after treating the sample with colloidal PDMS.**

The developed procedure is able to separate all the components within the mixture with a resolution greater than 7.8 (Table 2). The capacity factor data also demonstrates that the separation can be accomplished within a reasonable time ( $k' < 4.27$  for all the components). Moreover, the column exhibited a reasonable selectivity toward the separation of this group of benzoic



acids derivatives, showing a selectivity factor greater than 1.334 and over  $2 \times 10^4$  theoretical plates.

**Table 2. Elution parameters for selected model pollutants.**

COMPOUND	AVERAGE ELUTION TIME (min)	K'	N	Sym	R <sub>ab</sub> *	$\alpha^*$
4-ABA	2.944( $\pm 0.002$ )	0.439	$2.9 \times 10^4$	0.7603	N/A	N/A
BA	5.29 ( $\pm 0.01$ )	1.637	$4 \times 10^4$	0.7193	26.7	3.73
4-NBA	6.48( $\pm 0.02$ )	2.18	$2 \times 10^4$	0.5077	7.8	1.334
4-TA	7.98( $\pm 0.02$ )	2.93	$4 \times 10^4$	0.7233	8.9	1.338
4-CBA	10.75( $\pm 0.04$ )	4.27	$3 \times 10^4$	0.5777	13.1	1.460

\*Values calculated in reference to the adjacent left band

Validation of quantitative conditions showed that the method implemented in this work is highly reproducible with a percent relative standard deviation (%RSD) of less than 0.410% for the elution time and 1.78% for the band areas. Table 3 shows working curves obtained under current elution conditions and some highlights on the validation parameters. The curves were linear within the working range of  $10^{-4}$  and  $10^{-6}$  M with a limit of detection (LOD) and a limit of quantification (LOQ) values below than  $5.90 \times 10^{-6}$  and  $1.97 \times 10^{-5}$ , respectively.

**Table 3. Validation parameters for the quantitation of selected compounds.**

ANALYTE	CALIBRATION CURVE EQUATION	R <sup>2</sup>	%RSD t <sub>r</sub>	%RSD AREA	LOD	LOQ
4-ABA	$y = 1.135 (\pm 0.003) \times 10^6 X + 1.10 (\pm 0.77)$	0.99(±0.73)	0.015	0.55	1.20E-06	3.99E-06
BA	$y = 2.563 (\pm 0.004) \times 10^5 X + 0.21 (\pm 0.09)$	0.99(±0.14)	0.410	1.78	1.07E-06	3.58E-06
4-NBA	$y = 3.009 (\pm 0.004) \times 10^6 X + 1.00 (\pm 1.14)$	1.00(±2.22)	0.156	1.30	1.14E-06	3.80E-06
4-TA	$y = 1.753 (\pm 0.001) \times 10^6 X - 1.40 (\pm 0.42)$	0.99(±0.62)	0.194	0.46	7.19E-07	2.40E-06
4-CBA	$y = 2.166 (\pm 0.003) \times 10^6 X + 0.10 (\pm 0.62)$	1.00(±1.21)	0.260	1.37	8.64E-07	2.88E-06
DCB	$y = 7.20 (\pm 0.02) \times 10^4 X - 0.90 (\pm 0.10)$	1.00(±0.13)	0.100	0.95	5.90E-06	1.97E-05

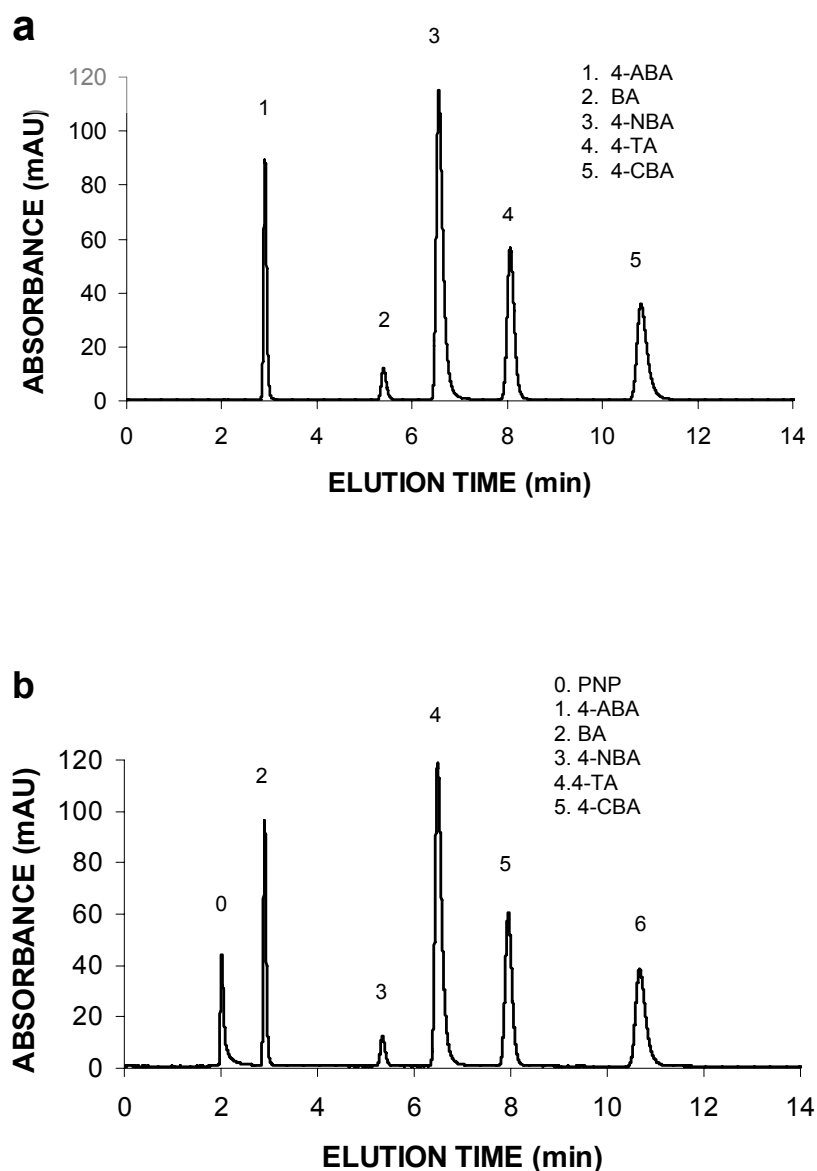
The extraction efficiency of the PDMS and PNP colloids were studied by adding  $1 \times 10^{-4}$  M of each compound to a 0.18% w/w suspension of the micro and nanoparticles, respectively. The collected data showed that PDMS was able to remove over 98% of the studied compounds at the submillimolar concentration range, where 4-TA was the least removed compound with a 1.3(±0.2)% of this analyte present in aqueous phase (Table 4) as a result of a steric effect of methyl group. As shown in figure 9b, the signal for the corresponding carboxylic acids after exposing them to the PDMS micro particles is negligible. Two new and unresolved bands appeared at 1.978(±0.007) and 2.094(±0.009) respectively, the former corresponding to the free PDMS identified by its UV spectrum and the later is attributed to a residual trace of Benzoic acids sorbed within sub 0.45 µm PDMS particles.

**Table 4. Performance of PDMS micro particles and PNP on the removal of model pollutants.**

COMPOUNDS	PERCENT OF COMPOUND IN AQUEOUS PHASE (%)	
	SAMPLE WITH PNP	SAMPLE WITH PDMS
<b>4-ABA</b>	99.4( $\pm$ 0.8)	0.1( $\pm$ 0.5)
<b>BA</b>	100.2( $\pm$ 0.8)	-0.2( $\pm$ 0.7)*
<b>4-NBA</b>	97.3( $\pm$ 0.2)	0.5( $\pm$ 0.3)
<b>4-TA</b>	99.1( $\pm$ 0.2)	1.3( $\pm$ 0.2)
<b>4-CBA</b>	95.6( $\pm$ 0.1)	1.0( $\pm$ 0.2)

\* Complete removal of the analyte, the reported value falls within the specified uncertainty.

A comparison of the PDMS sequestering potential against that of commercially available colloids like PNP shows that colloidal polystyrene sequesters less than 5% of the analytes under similar conditions (Figure 10). The collected chromatograms show little difference with that of the standard mixture (figure 10a, b). This indicates that the sorption of these chemicals by PNP is negligible.



**Figure 10. a. Chromatogram of the standard  $1 \times 10^{-4} \text{M}$  solution of the five carboxylic acids at 254 nm; b. Chromatogram of an equimolar sample after interaction with PNP at 254nm.**

The reduced sorption of the analytes by PNP relative to that of PDMS suggests that the PNP interaction with the analyte is dominated by adsorption and that of PDMS by absorption. The amount of analyte removed by PDMS far exceeds that for a complete coverage of the available surface area of the

microparticles. The amount of analyte removed and the coagulation of the particles are strong indicators of the absorption of the analyte into the polymer. This is consistent with available literature which shows that PDMS is the most frequently applied polymer for the SPME of hydrophobic organics, since it provides well-defined absorptive retention.<sup>46-47</sup> The difference in the distribution coefficients of the analytes when exposed to each polymeric suspension are in agreement with these observations (Table 5). The results indicated that PDMS has a sequestering power over 4 orders of magnitude greater than PNP. The data also shows that the PDMS sequestering power was in the order of BA > 4-ABA > 4-CBA > 4-NBA > TA.

**Table 5. Distribution coefficients (K) obtained for the carboxylic acids under study with selected polymer particles.**

COMPOUND	K <sub>PNP/WATER</sub>	K <sub>PDMS/WATER</sub>
4-ABA	1.8E-02	403
BA	1.1E-02	—*
4-NBA	3.4E-02	90.4
4-TA	5.0E-04	76.0
4-CBA	5.5E-02	103

\* Completely removed

Analyses performed with individual carboxylic acids under study with polymer particles confirm the high sorption capacity of PDMS and the reduced sorption capacity of PNP (Table 6). Table 6 shows a removal of chlorinated aromatic compounds such as 1,2-dichlorobenzene (DCB) by PDMS of 55.44% with a 44.56% of analyte present in aqueous phase, this suggest that the

analyte is poorly partitioned into the polymer; which implies that this class of chemicals are adsorbed rather than partitioned within the nanoparticles. PNP nanoparticles were more effective on the removal of DCB, where 64.91% of the DCB was removed by the polymer (Table 6). The improved extraction of the chlorinated compound by PNP is attributed to the stacking interactions between aromatic groups of the DCB and PNP which is facilitated by its aromatic chain. The removal of DCB by PDMS and PNP does not reach the law for human consumption water, where U.S. Environmental Protection Agency establish a concentration of 0.6 mg/L of 1,2-dichlorobenzene as safe concentration in drinking water .

**Table 6. Performance of micro PDMS and PNP particles on the removal of individual model pollutants.**

SAMPLE	PNP (%)	PDMS (%)
4-ABA	100.5( $\pm$ 0.8)	0.3( $\pm$ 0.5)
4-CBA	96.47( $\pm$ 0.05)	0.00( $\pm$ 0.2)
DCB	35.09( $\pm$ 0.06)	44.56( $\pm$ 0.06)

These results open the door to explore the use of PDMS microparticles as a complementary step to secondary water treatment process to remove carboxylic acids and other moderately polar pollutants. This allows aggregation for carboxylic acids onto the PDMS colloid forming an easily removed precipitate that can be delivered to a recycling facility. The PDMS microparticles offer the benefits of being a rather simple, low cost and effective procedure that can be easily adapted into current water treatment protocols.

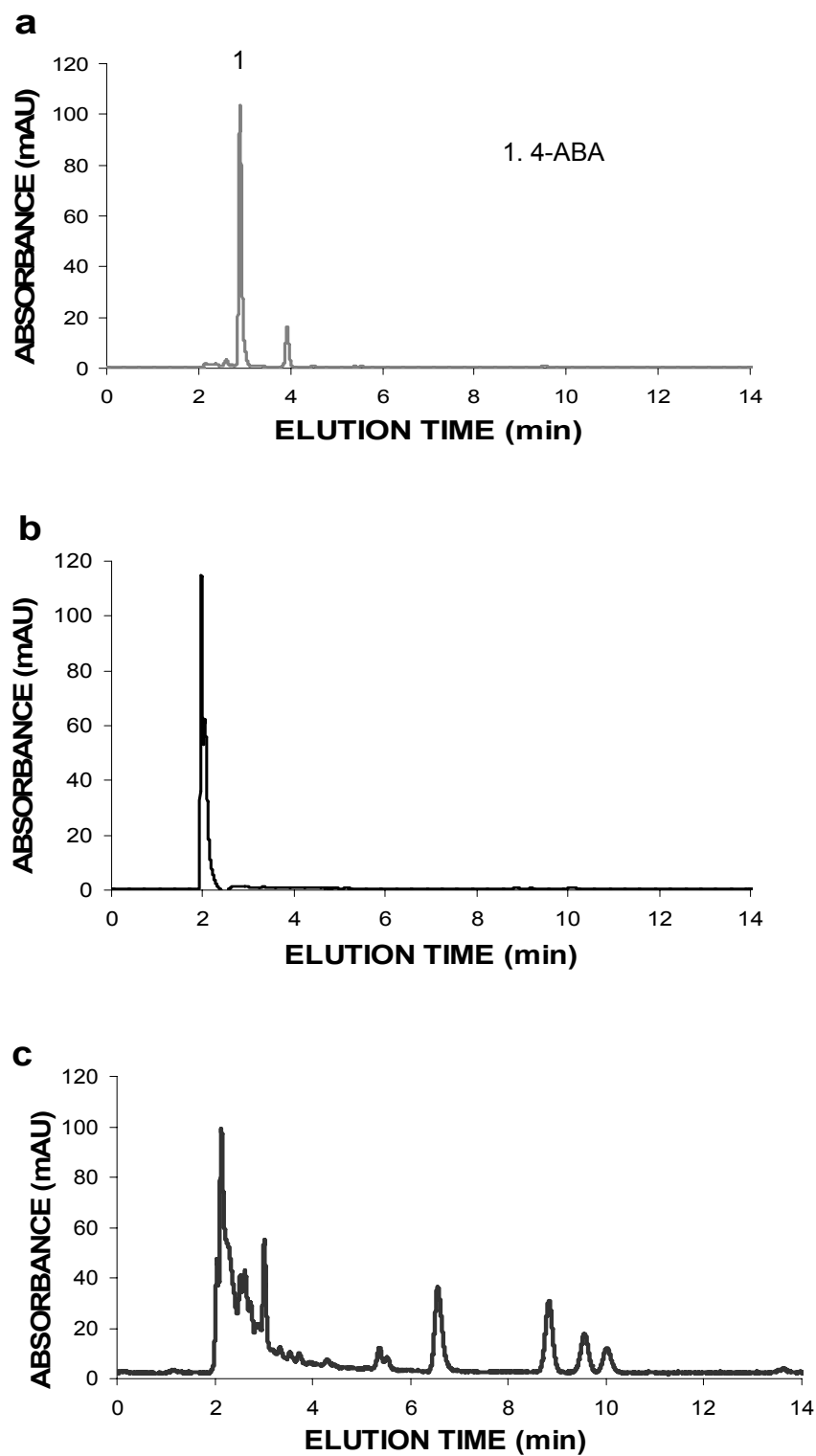
Since the size of micro and nanoparticles enhance its available surface area, this could potentially augment its chemical reactivity as well. As a result, the persistence of aggregated and the free polymer particles in the treated water could represent a potential risk to public safety since the products of these interactions can lead to the formation of more toxic and reactive products than original contaminants. In contrast with PNP, the ability of colloidal PDMS to form easily filterable coagulates could in principle prevent this problem. However, it is important to demonstrate that the polymer is capable to sequester not only the analytes of interest but also their decomposition products. As part of this investigation, a series of equimolar solutions of the analytes were prepared to determine the effects that diluted PDMS and PNP particles could exert on the photo-decomposition of the investigated analytes.

**Table 7. Performance of micro PDMS and PNP particles on the removal of model pollutants ( $1 \times 10^{-4} \text{M}$ ) after exposition to UV radiation at 312nm.**

COMPOUNDS	PERCENT OF COMPOUNDS IN AQUEOUS PHASE (%)		
	CONTROL SAMPLE AFTER UV	SAMPLE WITH PNP AFTER UV	SAMPLE WITH PDMS AFTER UV
<b>4-ABA</b>	65.7( $\pm 0.3$ )	44.6( $\pm 0.2$ )	0.2( $\pm 0.4$ )
<b>BA</b>	105.9( $\pm 0.5$ )	112.2( $\pm 0.8$ )	-0.2( $\pm 0.6$ )
<b>4-NBA</b>	98.91( $\pm 0.09$ )	108.2( $\pm 0.1$ )	0.9( $\pm 0.1$ )
<b>4-TA</b>	102.3( $\pm 0.1$ )	98.9( $\pm 0.2$ )	1.1( $\pm 0.1$ )
<b>4-CBA</b>	98.58( $\pm 0.07$ )	92.52( $\pm 0.05$ )	0.4( $\pm 0.2$ )

Results for the PDMS microparticles show the effective removal of both analytes in question as well as their photo decomposition products (Figure 11b). Moreover, the exposure to UV-radiation did not compromise PDMS extraction performance and did not improve PNP sequestering properties (Table 7). Instead, exposure of PNP particles exacerbated the decomposition of the analytes under study as evidenced by the appearance of new chromatographic bands and the increase of existing ones (Figure 11c). A similar trend was also observed for halo-aromatic compounds like DCB (Table 8). The data reveals that although PNP does not remove the analyte effectively it augments its chemical reactivity. Therefore, it is evident that PNP nanoparticles could catalyze undesirable chemical reactions under environmental conditions, rendering inadequate for remediation on water treatment applications.





**Figure 11. Representative chromatograms of 4-ABA upon exposure to UV-VIS radiation at 312 nm (long wave). a. Control sample; b. 4-ABA ( $1 \times 10^{-4}$  M) with 0.18% of PDMS; c. 4-ABA ( $1 \times 10^{-4}$  M) with 0.05% of PNP.**

Individual standards of the analytes, exposed to UV radiation, contained 68.5( $\pm$ 0.5)%, 80.43( $\pm$ 0.06)% and 85.8( $\pm$ 0.1)% of 4-ABA, 4-CBA and DCB respectively remains in its native form in water (Table 8). Such reduction is the result of the photo-degradation of the analyte by the incident UV radiation (Figure 11a). The exposition to UV-VIS radiation toward sample composed by 4-ABA and PNP resulted in an enhanced of photodegradation products with an 8.15( $\pm$ 0.08)% of 4-ABA in its native form in water (figure 11c). This increase in photodegradation products is also observed for 4-CBA and DCB with influence of PNP (Table 8). Thus, PNP works as a substrate that facilitates chemical reaction on its surface.

**Table 8. Performance of micro PDMS and PNP particles on the removal of individual model pollutants after exposition to UV radiation.**

COMPOUNDS	PERCENT OF COMPOUNDS IN AQUEOUS PHASE (%)		
	SAMPLE AFTER UV	SAMPLE WITH PNP AFTER UV	SAMPLE WITH PDMS AFTER UV
4-ABA	68.5( $\pm$ 0.5)	8.15( $\pm$ 0.08)	0.2( $\pm$ 0.4)
4-CBA	80.43( $\pm$ 0.06)	55.2( $\pm$ 0.1)	0.4( $\pm$ 0.1)
DCB	85.8( $\pm$ 0.1)	1.88( $\pm$ 0.08)	1.88( $\pm$ 0.08)

Figure 11b shows the chromatogram of 4-ABA with PDMS after exposition to UV-VIS radiation. It shows the total absence of both analyte and photo-degradation products. A similar result was observed for 4-CBA with PDMS influence.

The extraction efficiency of PDMS and PNP colloids upon 4-ABA under anaerobic conditions were also studied by adding  $1 \times 10^{-4}$  M of 4-ABA to a 0.18%

and 0.05% w/w suspension of micro and nanoparticles, respectively. The collected data showed that PDMS was able to remove over 99% of the 4-ABA at this submillimolar concentration range (Figure 12b). The chromatographic data shows no appreciable signal of the analyte at its corresponding elution time. An identical trend was observed for the PDMS samples investigated under anaerobic conditions. In contrast, the elution data for PNP showed that it has a low sequestering potential, since it removed less than 4% of the original content of the analyte (Figure 13b).

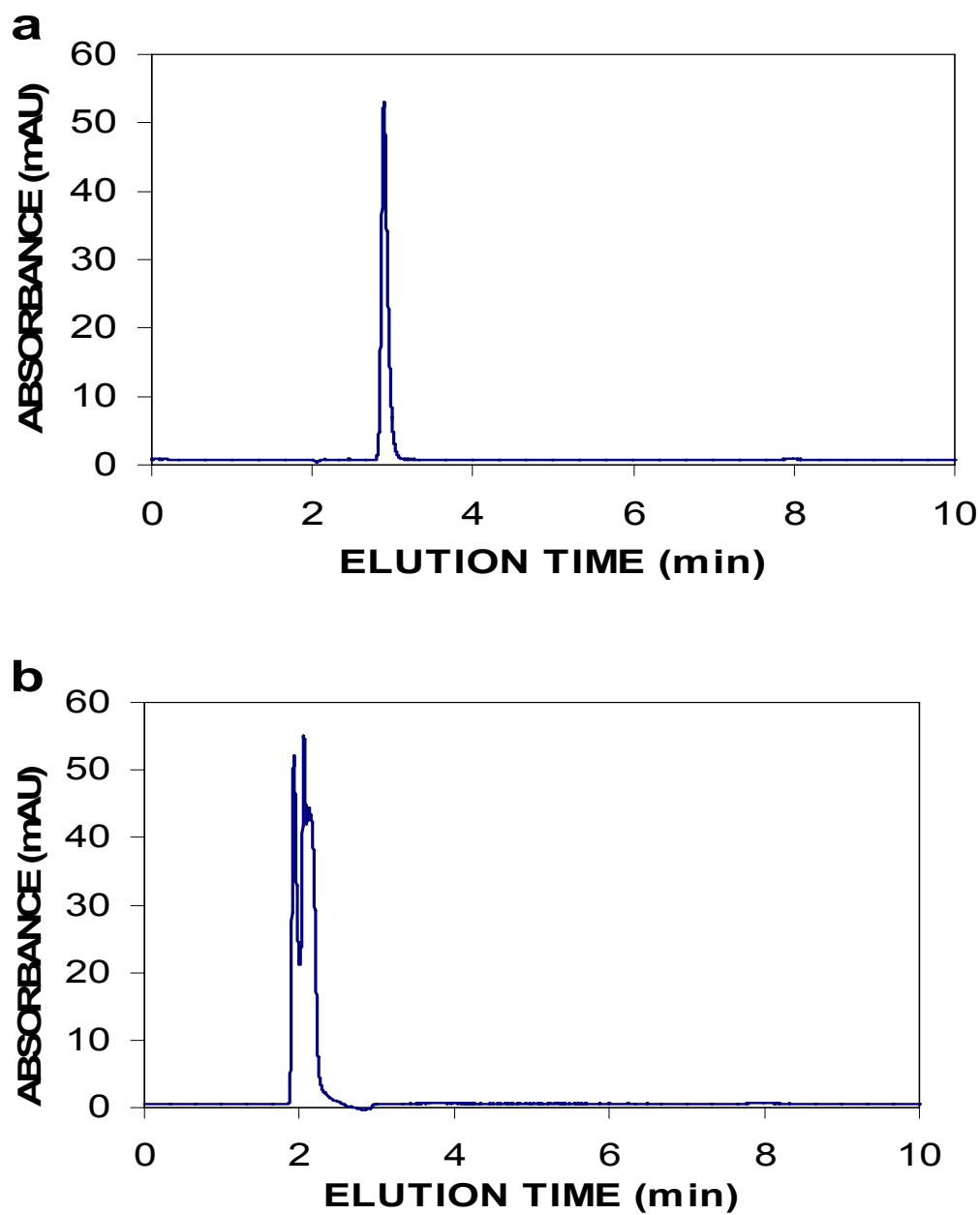
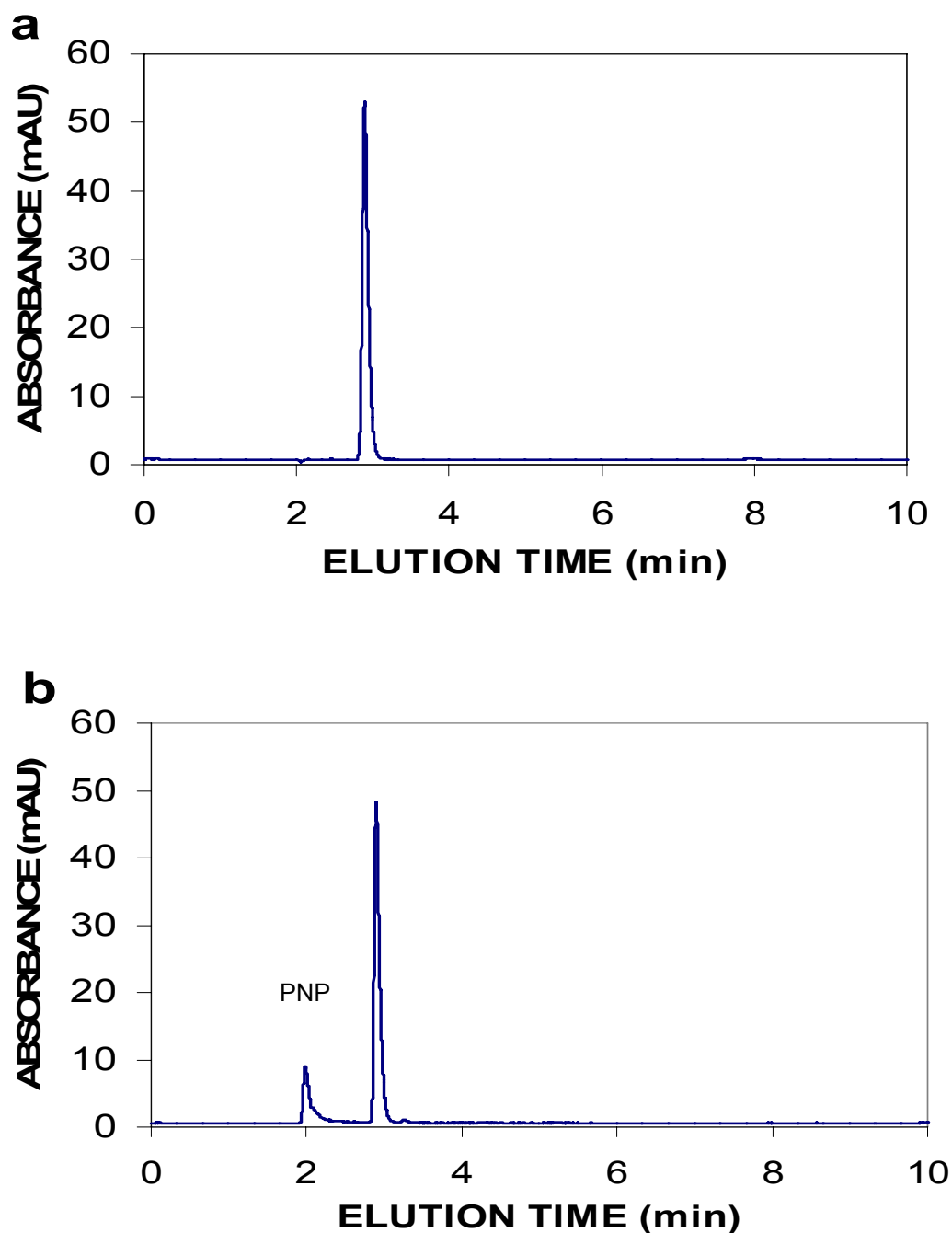


Figure 12. a. Standard chromatogram of 4-ABA (0.10 mM) at 254 nm; b. Elution after treating the sample with colloidal PDMS.



**Figure 13. a. Standard chromatogram of 4-ABA (0.10 mM) at 254 nm; b. Chromatogram of an equimolar sample after interaction with PNP at 254 nm.**

By comparing the results of the anaerobic studies with those under aerobic conditions, it is clear that the PDMS sequestering process involves the

absorption (partitioning) of the analyte into the polymer. This is confirmed by the splitting of the residual PDMS band into two unresolved signals upon its interaction with this model pollutant. That is not the case for PNP where the interaction is dominated by the adsorption of the analyte onto the surface of the polymer. This is supported by the difference in the distribution coefficients of 4-ABA when is exposed to each polymeric suspension. (Table 9).

**Table 9. Performance and distribution of micro PDMS and PNP particles on the removal of 4-ABA.**

COMPOUND	PERCENT OF COMPOUND IN AQUEOUS PHASE (%)		$K_{\text{PDMS/WATER}}$	$K_{\text{PNP/WATER}}$
	SAMPLE WITH PDMS	SAMPLE WITH PNP		
4-ABA	0.3( $\pm$ 0.2)	96( $\pm$ 3)	362	3.4E-02

Under anaerobic conditions, the experimental results demonstrated that PDMS microparticles are capable to sequester not only the carboxylic acids under study, but also its decomposition products. However, although exposing these model pollutants to PNP particles did not lead to a significant removal of the analytes. The presence of the nanoparticles within the UV-VIS irradiated samples exacerbated the decomposition of analytes (Figure 14).

The absence bands within the PDMS sample confirms that polymer is capable to remove 4-ABA as well as its degradation products; thus reducing the risks of leaving in solution products that could be more toxic and reactive than the original contaminant.

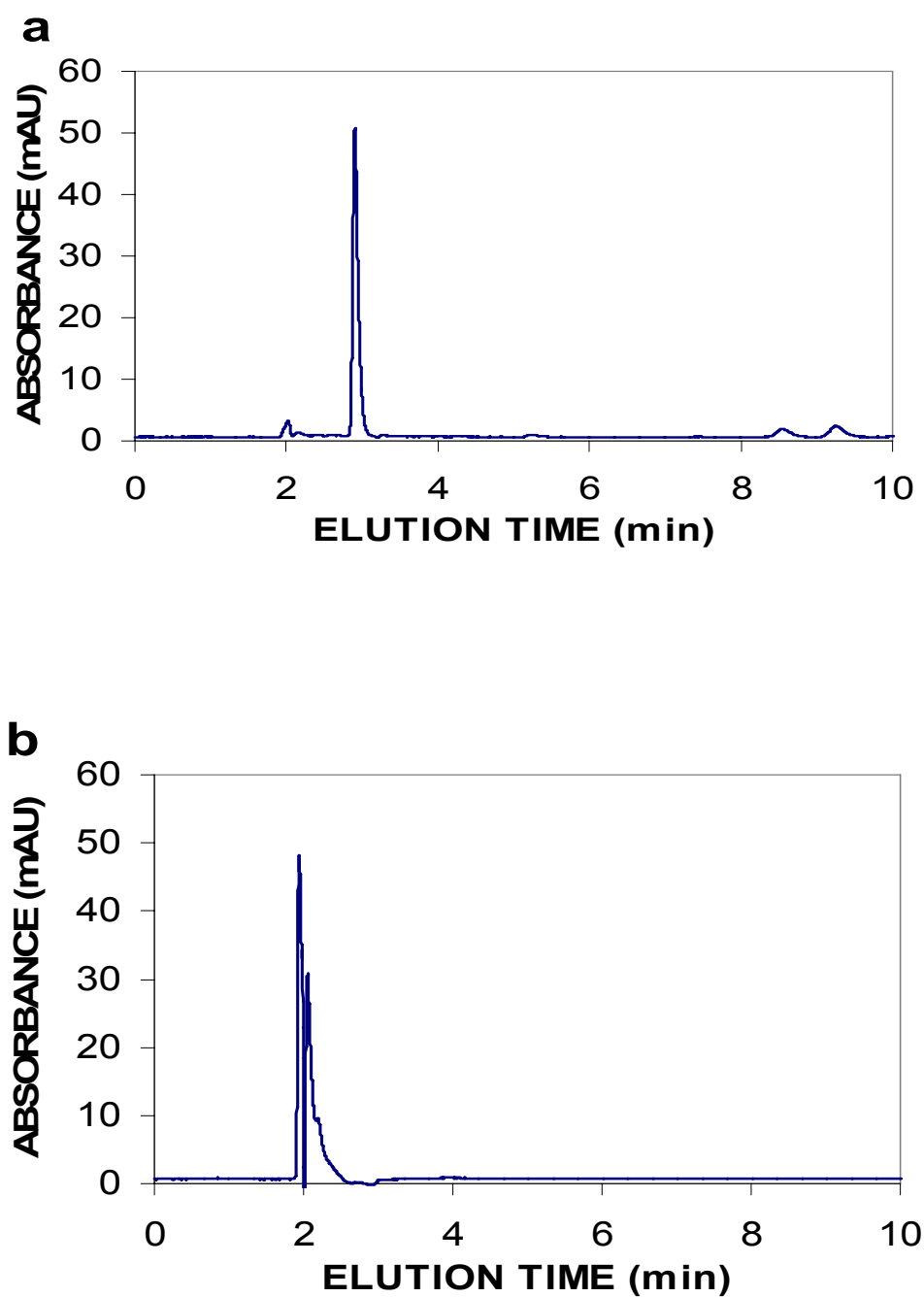


Figure 14. Representative chromatograms of 4-ABA upon exposure to UV-VIS radiation at long wave; a) 4-ABA ( $1 \times 10^{-4}$  M) with 0.05% of PNP; b) 4-ABA ( $1 \times 10^{-4}$  M) with 0.18% of PDMS.

## CHAPTER 3

### 3.1. Conclusions

Fabrication of PDMS microparticles was performed by the colloidal suspension method. This method demonstrated to be a feasible way to obtain easily and cost effective polymeric colloidal. Characterization of this polymer suspension was performed by Raman spectroscopy which revealed all PDMS functional groups for its identification. Scanning electron microscopy was a powerful tool to establish the shape and average size of the colloidal PDMS microparticles.

Reversed phase liquid chromatography with diode array detection is a widely used technique used in environmental analysis as a result of its capacity to detect pollutants in traces amounts. The use of this chromatographic technique to evaluate the effectiveness of colloidal polydimethylsiloxane (PDMS) and polystyrene (PNP) particles for the removal of model aromatic contaminants in water was successfully demonstrated. The developed high performance liquid chromatography protocols prove suitable for the separation, detection and quantitation of trace amounts of halogenated, acid and basic aromatic compounds in water. The developed procedures also provide a simple, cost effective, analytical method to determine the sequestering power of emerging pollutants by polymers. Although the method used for this study proved efficient for the target compounds, additional improvements could be performed to further optimize the efficiency of the separation. Future



investigations on the matter could consider the use of rapid resolution columns to reduce the elution time and improve the costs and performance of the polymer validation process.

In terms of the effectiveness of using PDMS microparticles for the removal of model pollutants, the colloidal microparticles can effectively remove carboxylic acids by absorbing them into the polymer matrix and triggering the precipitation coagulation and subsequent precipitation of the polymer. This is a key benefit for its use in water treatment since it allows the use of a microstructured material that can be easily removed by current water treatment protocols, thus reducing the concerns on the fate and transport of micro and nanostructured materials upon use in water treatment procedures.

The studies on the use of PDMS for the removal of DCB in water strongly suggest that the polymer microparticles are considerably less selective and efficient for the removal of halogenated pollutants in water. The continuation of this project could focus on the functionalization or synthesis of new polymeric blends whose properties have been tailored for a particular class or group of chemicals. The study of additional polymer formulations could also lead to identify an even more efficient broad spectrum extractor for remediation applications.

The significance of properly selecting a polymer for water treatment and environmental remediation processes was demonstrated on the PNP studies. PNP prove to be ineffective for the removal of the studied analytes in water. In

addition the polymer nanoparticles are considerably more resilient to aggregation which makes it extremely difficult to effectively remove the polymer upon contact with the water matrix.

Exposing the above mentioned pollutants to UV-VIS radiation results in the rapid photodecomposition of the analytes under both aerobic and anaerobic conditions. Degradation products of carboxylic acids were effectively removed by the addition of PDMS microparticles while the presence PNP nanoparticles results in an increase in the number and the amount of photodecomposition products. This combination with its difficulty remove from solution confirms that in order to adequately use a micro or nanostructured agent in a water purification process, care must be taken to ensure that it is safely removed from the sample matrix to minimize its potential risk to the environment and to public safety. The methods and analytical protocols established in this research serve as an initial step toward gathering new knowledge and to develop new research strategies to investigate the safe use and disposal of micro and nanomaterials for scientific applications.

Although these findings demonstrate that micro and nanoparticles properties could make them very useful in remediation process, there is a need to carefully regulate the adequate use and disposal of micro and nanostructured materials since the release of these materials in the environment could result in the increase of photolytic reactivity of pollutants present in water. This is a major point of concern in environmental sciences, since an irresponsible use of these advanced materials could results in the emergence of potentially harmful

pollutants that could have a profound effect in the sustainable protection of our environment.

## REFERENCES

- (1) Wang, Y.; Dave, R. N.; Pfeffer, R. *J. Supercrit. Fluids* **2004**, 28, 85-99.
- (2) Armelao, L.; Barreca, D.; Bottaro, G.; Gasparotto, A.; Gross, S.; Maragno, C.; Tondello, E. *Coord. Chem. Rev.* **2006**, 250, 1294-1314.
- (3) Liu, X.; Y., G.; Ma, Z.; Liu, H. *Langmuir* **2004**, 20, 10278-10282.
- (4) Tan, B. J.; Sow, C. H.; Lim, K. Y.; Cheong, F. C.; Chong, G. L.; Wee, T. S.; Ong, C. K. *J. Phys. Chem.* **2004**, 108, 18575-18579.
- (5) Wang, W.; Ruan, C.; Gu, B. *Anal. Chim. Acta.* **2006**, 567, 121-126.
- (6) Sun, Y.; Li, A.; Qi, M.; Zhang, L.; Yao, X. *Mater. Sci. Eng., B* **2001**, B86, 185-188.
- (7) Mauter M.; Elimelech, M. *Environ. Sci. Technol.* **2008**, 42, 5843- 5859.
- (8) Correa, M. A.; Kosiorek, A.; Kandulski, W.; Giersig, M.; Liz-Marzan, L. *Chem. Mater* **2005**, 17, 3268-3272.
- (9) Sostaric, J. Z.; Pandian, R. P.; Weavers, L. K.; Kuppusamy, P. *Chem. Mater* **2006**, 18, 4138-4189.
- (10) Zhu, B. W.; Lim, T. T. *Environ. Sci. Technol.* **2007**, 41, 7523-7529.
- (11) Li, X.; Zhang, W. X. *Langmuir* **2006**, 22, 4638-4642.
- (12) Kim, J. Y.; Cohen, C.; Shuler, M. L. *Environ. Sci. Technol.* **2000**, 34, 4133-4139.
- (13) Tungittiplakorn, W.; Cohen, C.; Lion, L. W. *Environ. Sci. Technol.* **2005**, 39, 1354-1358.
- (14) Cui, J. Q.; Kretzschmar, I. *Langmuir* **2006**, 22, 8281-8284.
- (15) Anton, N.; Benoit, J. P.; Saulnier, P. *J. Controlled Release* **2008**, 128, 185-199.
- (16) Zhang, W. X. *J. Nanopart. Res.* **2003**, 5, 323-332.
- (17) Shaw, D. J. *Introduction to Colloid and Surface Chemistry*, 4th ed.; Elsevier Science: Burlington, 1992.
- (18) Li, Z. W.; Zhou, J. F.; Zhang, Z. J.; Dang, H. X. *Chin. J. Chem.* **2004**, 22, 1133-1137.

- (19) Jungmann, N.; Schmidt, M.; Maskos, M.; Weis, J.; Ebenhoch, J. *Macromolecules* **2002**, 35, 6851-6857.
- (20) Jiji, A.; Nutting, J.; Baer, D. R.; Meyer, D.; Sharma, A.; Qiang, Y. *Journal of Nanomaterials* **2006**, 1-4.
- (21) Móczó, J.; Pukánszky, B. *J. Ind. Eng. Chem.* **2008**, 14, 535-563.
- (22) Wang, Y.; Lai, H. H.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. *Anal. Chem* **2005**, 77, 7539-7546.
- (23) Song, J.; Duval, J. F. L.; Cohen, M. A.; Hillborg, H.; Gunst, U.; Arlinghaus, H. F.; Vancso, G. J. *Langmuir* **2007**, 23, 5430-5438.
- (24) De Vries, A.; Turnhout, J. V. Silicone Arteries. <http://www.delftoutlook.tudelft.nl/info/indexedcb.html?hoofdstuk=Article&ArtID=3655>.
- (25) Jayes, L.; Hard, A. P.; Sene, C.; Parker, S. F.; Jayasooriya, U. A. *Anal. Chem* **2003**, 75, 742-746.
- (26) Lon, M. Polymer Crystallinity. <http://pslc.ws/macrogcss/crystal.html>.
- (27) Tsuji, H.; Sasaki, H.; Utsumi, Y.; Sato, H.; Gotoh, Y.; Ishikawa, J. *Surf. Coat. Technol.* **2002**, 158-159, 620-623.
- (28) Savage, N. D., M. S. *Journal of Nanoparticle Research* **2005**, 7, 331-342.
- (29) Masciangioli, T.; Zhang, W. X. *Environ. Sci. Technol.* **2003**, 102A-108A.
- (30) Saleh, N.; Phenrat, T.; Sirk, K.; Dufour, B.; Ok, J.; Sarbu, T.; Matyjaszewski, K.; Tilton, R. D.; Lowry, G. V. *Nano Lett.* **2005**, 5, 2489-2494.
- (31) Skoog; West; Holler; Crouch *Fundamentals of Analytical Chemistry*, 8th ed.; Thomson Learning Inc: Belmont, CA, USA 2004.
- (32) Technology, A., Ed.: USA, 2005.
- (33) McCreery, R. L. *Raman Spectroscopy for Chemical Analysis*; A John Wiley & Sons: New York, 2000.
- (34) P. Atkins, J. D. P. *Atkins' Physical Chemistry*, 8th ed.; Oxford University Press: New York, NY, 2006.
- (35) Bhupalpally, A. P. C.V. Raman. <http://sumannotebook.blogspot.com/2008/07/c-v-raman.html>.
- (36) Schweitzer, J. Scanning Electron Microscope (SEM). <http://www.purdue.edu/REM/rs/sem.htm>.

- (37) Suchorsky, A.; McGill University: Montreal, Canada, 2007.
- (38) L. K. Limbach, P. W., P. Manser, R. N. Grass, A. Bruinink, W. J. Stark *Environmental Science and Technology* **2007**, 41, 4158-4163.
- (39) Shvedova, A. A.; Castranova, V.; Kisin, E. R.; Schwegler, D.; Murray, A. R.; Gandelsman, V. Z.; Baron, A. M. P. *J. Toxicol. Environ. Health* **2003**, 66, 1909-1926.
- (40) Araujo, J. A.; Barajas, B.; Kleinman, M.; Wang, X.; Bennett, B. J.; Gong, K. W.; Navab, M.; Harkema, J.; Sioutas, C.; Lusk, A. J.; Nel, A. E. *Circ. Res.* **2008**, *Published online*.
- (41) Weber, W. J.; Tang, J.; Huang, Q. *Environ. Sci. Technol.* **2006**, 2006, 1650-1656.
- (42) Yue, Z.; Economy, J. J. *Nanopart. Res.* **2005**, 7, 477-487.
- (43) Jia, G.; Wang, H.; Yan, L.; Wang, X.; Pei, R.; Yan, T.; Zhao, Y.; Guo, X. *Environ. Sci. Technol.* **2005**, 39, 1378-1383.
- (44) Pryce, H. G.; Casserly, T. B.; Gleason, K. K. *J. Electrochem. Soc.* **2001**, 12, F212-F220.
- (45) Langford, S. A.; Sugden, J. K.; Fitzpatrick, R. W. *J. Pharm. Biomed. Anal.* **1996**, 14, 1615-1623.
- (46) Witt, G.; Liehr, A.; Borck, D.; Mayer, P. *Chemosphere.* **2009**, 74, 522-529
- (47) Watson, J. M.; Zhang, G.S.; Payne, P. A. *J. Membr. Sci.* **1992**, 73, 55-71