REVIEW ARTICLE

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Role of superparamagnetic nanoparticles in magnetic dispersive micro-solid phase extraction

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Abstract

The field of trace analysis of analytes in different samples has gained an increasing interest. This field of analysis gained many benefits by entering the era of nanomaterials and nanotechnologies. One aspect of nanotechnologies influence on the field of trace analysis is the development of magnetic dispersive micro-solid phase extraction (Magnetic D-µ-SPE) technique. Magnetic D-µ-SPE technique involves dispersion of an adsorbent phase with special magnetic properties as finely divided form; usually as nanoparticles, in sample solutions to adsorb target analytes. This is followed by adsorbent retrieval by external magnetic field. This technique provided several advantages including minimal use of solvents and adsorbent materials as well as procedures simplicity. An important key element in the preparation of Magnetic D-µ-SPE adsorbents is tailoring of its magnetic properties. Superparamagnetic nanoparticles had unique properties which fulfilled requirements of Magnetic D-µ-SPE procedures. This review discusses superparamagnetic behavior and its application in preparation of adsorbents for Magnetic D-µ-SPE technique.

Keywords: Magnetic dispersive micro-solid phase extraction, Superparamagnetic nanoparticles, Nanoparticles, Trace analysis, Micro-extraction.

1. Introduction

One of the most challenging tasks in analytical chemistry is the determination of trace compounds (e.g. contaminants, pharmaceuticals residues) in environment, food stuff and biological samples. Extraction techniques; either solid phase or liquid phase extraction modes, were applied for many decades for these tasks. However, several drawbacks of extraction techniques application in analytical field were encountered such as high consumption of organic solvents, high cost and labor time. These drawbacks have initiated the development of various alternative techniques to enable separation and pre-concentration of trace analytes with minimal solvents consumption and labor. Dispersive Micro-Solid Phase Extraction (D-µ-SPE) is an important technique that fulfilled this target. D-µ-SPE is the miniaturization of Dispersive Solid Phase Extraction (DSPE) previously described 2003 by Anastassiadis et al.

(Anastassiades et al. 2003). Both of DSPE and D-µ-SPE were based on the dispersion of adsorbent phase in the sample solution to increase contact area between sample and adsorbent phase. The adsorbent phase should be retrieved from sample solution for subsequent desorption of analytes. D-µ-SPE provided an advantage over DSPE by using minimal amounts of adsorbents in more divided particles (usually as nanoparticles) thus increasing adsorbent surface area and decreasing adsorbent amount needed for the process. Increasing the surface area accelerates mass transfer kinetics of the adsorbed analyte(s) and increases the adsorption capacity of adsorbent phase (Chisvert, Cárdenas, and Lucena 2018).

Dispersive Micro SPE (D-µ-SPE) gained benefits from application of nanomaterials. In D-µ-SPE; it is more convenient to apply the nanoparticles as a suspension or colloid directly to sample solution. The nanoparticles adsorb target analyte on their surfaces according to the affinity between the nanoparticles and the analytes. The nanoparticles could be retrieved to recover the target analyte (He et al. 2014).

Retrieving of adsorbent from sample solution could be done by filtration or centrifugation (Khezeli and Daneshfar 2017). However, application of magnetic nanomaterials enabled preparation of adsorbents as magnetic composites for much easier retrieval by an external magnetic field (Khezeli and Daneshfar 2017).

Although the apparent simplicity of the concept, challenges are still facing the technique regarding magnetic nanoparticles physical and chemical stability in extraction conditions as well as challenges to link the most suitable functionality to the target analyte.

This review provides a background for the challenges for application of magnetic nanoparticles on D-µ-SPE and the approaches to overcome these challenges. The following context gives special attention to magnetite nanoparticles synthesis, surface treatment and characterization.

An overview of the added value of nanomaterials and magnetic nanomaterials applications in D-µ-SPE was provided. This was followed by the key quality criteria for magnetic nanomaterials for suitability to D-µ-SPE applications. A literature review for examples of magnetic D-µ-SPE was also provided.

2. Superparamagnetic nanoparticles

2.1.Magnetic behavior of the materials

Magnetism results from the unpaired electrons in outer orbitals of some transition metals such as Fe, Ni and Co which produce a magnetic field around their atoms or molecules. This field causes alignment of the atoms or molecules within parallel to each other spontaneously without need of an external magnetic field forming a magnet. Such material is called a ferromagnetic material such as metallic Iron or Cobalt or ferrimagnetic such as Magnetite (Fe_3O_4) depending on proportion of atoms alignment to the same direction.

A bulk ferromagnetic or ferrimagnetic material does not configure its molecules magnetic axes in a single magnetic momentum and direction. Instead, the bulk material rearrange into smaller sub-microscopic units (magnetic domains) in a mosaic pattern, each domain has its own magnetic momentum and direction. This would result in saving of magnetostatic energy for this bulk material. Size of magnetic domains differs from a material to another and it is in the nanometers scale (Lu, Salabas, and Schüth 2007).

2.2.Superparamagnetic nanoparticles

When a ferromagnetic or a ferrimagnetic material exists in a volume less than the magnetic domain size of this material, the particle would be composed of only a single domain with a single magnetic axis (Lu, Salabas, and Schüth 2007). Each nanoparticle behaves as a huge paramagnetic atom as it has high magnetic moment with high magnetic susceptibility to external magnetic field (Lu, Salabas, and Schüth 2007)

In the absence of an external magnetic field, the magnetic momentum of the single domain magnetic nanoparticles flips rapidly in both axis directions on. Flipping speed increases by decreasing particles dimensions (Lu, Salabas, and Schüth 2007).

However, when a single domain magnetic nanoparticle is subjected to a magnetic field, the particle reorients to have its magnetic axis parallel to the applied magnetic field. This was followed by movement of the particle in the direction of magnetic field gradient. Removal of external magnetic field makes the magnetic nanoparticles free again to move and flip their magnetic momentum axis without remnance (residual magnetism). These particles are called superparamagnetic nanoparticles (Lu, Salabas, and Schüth 2007). Superparamagnetic nanoparticles share the following characteristics

- The particles respond to the external field.
- They have large magnetic moments
- No hysteresis loop in the magnetization curve.

2.3.Types of superparamagnetic nanoparticles

Superparamagnetic nanoparticles could be classified according to their chemical composition as follows:

- Pure metals such as iron nanorods and nanospheres (“Iron Nanorods and Nanospheres.pdf,” n.d.) and cobalt nanorods and nanospheres (Puntes 2001).
- Alloys of magnetic metals such as FePt and $CoPt_3$ (Shevchenko et al. 2002)
- Metal oxides such as:
  - Single metal oxides: such as Fe_3O_4(Magnetite), ɣ-Fe_2O_3 (Maghemite) (Sun and Zeng 2002; Grasset et al. 2002; Neveu et al. 2002)
  - Spinyl type oxides : such as $MnFe_2O_4$ or $MgFe_2O_4$ (Q. Chen et al. 1999).

2.4.Synthesis methods

2.4.1. Co-precipitation method

Co-precipitation is the most up-scalable technique for superparamagnetic nanoparticles synthesis. It is performed in reducing conditions to prevent atmospheric oxidation and at pH above 8.5 (Tombácz et al. 2015; Thanh, Maclean, and Mahiddine 2014). A great advantage of co-precipitation method is that the product have fixed characteristics for fixed experimental conditions (Lu, Salabas, and Schüth 2007).

Massart method (Massart 1981) is a scalable, high yield process that utilizes cheap non toxic chemicals (Colombo et al. 2012; J. Liu et al. 2011).The method follows the following Reaction equation:

$$Fe^{+2}+2Fe^{+3}+8OH^{-} \rightarrow Fe_3O_4+4H_2O$$

This method produces particles oh high magnetic saturation momentum with average diameter in the range of 3-17 nm. These particles have high magnetic saturation momentum. (Tombácz et al. 2015).

Co-precipitation method has the following limitations (He et al. 2014):

- The method requires careful adjustment of conditions.
- The product has wide particle distribution range.

2.4.2.Thermal decomposition methods

Thermal decomposition of metal salt in presence of a surfactant mixture and organic solvent results into monodisperse nanoparticles of metals or their oxides. Metal salts used are carbonyl, acetate, acetoacetate or carboxylate. The resulting nanoparticles average size is controllable in the range of 3-50 nm. (Lu, Salabas, and Schüth 2007).

Limitations of this process are the high temperature and pressure required. The method cost is high. The use of toxic reagents requires extra steps to purify the product before use in medical applications.

2.4.3.Microemulsion method

Reactants are provided as water in oil type microemulsions. The microemulsion droplet size is controlled by addition of surfactant. The reaction proceeds by mixing the two microemulsions so the droplet fuse together to start co-precipitation reaction. The reaction is stopped by addition of an organic solvent miscible in both phases (such as acetone or ethanol) (Bee, Massart, and Neveu 1995; Petit and Pileni 1999).

Limitations of microemulsion method: the reaction yield is low and consumes large volumes of organic solvents with polydisperse product (Bee, Massart, and Neveu 1995; Petit and Pileni 1999).

2.4.4. Hydrothermal/ solvothermal synthesis

Li et al. prepared magnetic nanocrystals from solvothermal process of metal linoleate in ethanol/oleic acid mixture and ethanol water solution (X. Wang et al. 2005). This was followed by reduction of metal ions by ethanol with the formation of magnetic nanocrystals at high temperature (>200°C) and high pressure (> 2000psi).The yield of the reaction is low.

2.5.Surface treatment

2.5.1. Protection

Application of uncoated superparamagnetic nanoparticles in microextraction processes has the following disadvantages:

- Chemical instability due to atmospheric oxidation (Lu, Salabas, and Schüth 2007).
- Agglomeration to reduce the high surface energy (Lu, Salabas, and Schüth 2007).

Superparamagnetic nanoparticles surfaces should be protected from atmospheric oxidation and acidic erosion. Protection layer should be by intact so that oxygen cannot penetrate it (Lu, Salabas, and Schüth 2007).

Protection could be achieved by one of the following protection methods:

2.5.1.1. *Protection by surface passivation*

Pure metal superparamagnetic nanoparticles could be protected by controlled surface oxidation. Several methods such as application of gas plasma were described for this task. For Example Peng et al. (Peng et al. 2000) and Boyen et al. (Boyen et al. 2003) passivated Co nanoparticles with gas plasma.

2.5.1.2. Surfactant coating

Surfactant addition to nanoparticles; either during or after preparation, prevents particles agglomeration by both electrostatic and steric repulsion. Example is magnetite nanoparticles stabilization by the addition of tetramethyl ammonium hydroxide (Massart 1981).

2.5.1.3. Polymer coating

Nanoparticle could be coated by polymers either during or after synthesis. Polymers protect nanoparticles from agglomeration by steric repulsion. Polymers applied for this task include polypyrrole (Butterworth et al. 1996), and polyaniline as well as other polymers.

Disadvantages of surfactant and polymer coating

Pure metals stabilized with surfactants and polymers are still liable to oxidation and acid erosion. Catalysis by metal core could disrupt coat integrity by reaction with the coat. Furthermore, coats are unstable at high temperatures (Lu, Salabas, and Schüth 2007). Accordingly, inorganic coatings provide better solution to this issue.

2.5.1.4. Precious metal coating

Superparamagnetic nanoparticles could be coated by inert metals such as Pt and Au. Inert metals coating could be performed by either chemical reduction (Park and Cheon 2001) or microemulsion method (Rivas et al. 1994).

Gold coated magnetic nanoparticles could be further reacted with Thiol compounds. This enables subsequent functionalization with various ligands for many applications.

2.5.1.5. Carbon coating

Carbon coating enables hydrophobic and π- π interactions between coat and target molecules. Carbon coating could be achieved by introduction of carbon precursor (e.g. glucose) to the nanoparticles surface then carbonization at high temperature (Geng et al. 2012).

2.5.1.6. Silica coating

Silica coating protects magnetic nanoparticles from chemical degradation. Silica coating is stable in acidic medium. The silica surface has free silanol (OH) groups. These groups could be easily modified and functionalized for many applications. Control of silica coating thickness enables prevention of particle agglomeration.

Silica coating has the following advantages:

- Availability of starting materials
- Thermal, chemical and mechanical stability of the product
- Ease of functionalization of surface silanol

On the other hand, silica coating has the following limitations:

- Silica coatings are unstable at High pH.
- Silica coated particles still have surface pores that enable oxygen penetration to some extent.
- The control of shell thickness is challenging.(Lu, Salabas, and Schüth 2007)
- Free silanol groups on silica coating

surface adsorbs polar compounds.

2.5.2. Surface funcionalization

Functionalization of magnetic nanoparticles aims to increase the affinity between the magnetic nanoparticles and the target analytes for application as an adsorbent. Functionalization could be directly performed to surface of magnetic nanoparticles or alternatively to the coating layer applied to the magnetic nanoparticles. In addition to the previously described materials used for surface protection of superparamagnetic surfaces, functionalization could also involve the following moieties:

- Chemical functional groups
- Binding sites or receptors
- Antibodies

2.6. Characterization of superparamagnetic nanoparticles

2.6.1. Superparamagnetism characterization

The superparamagnetism behavior could be characterized by VSM (Vibrating sample magnetometer): Superparamagnetic materials have a characteristic sigmoid magnetization curve which is with no hysteresis loops nor remnance magnetization in the tested material (Foner 1959).

2.6.2. Chemical composition

Raman spectrophotometry and FTIR can elucidate the chemical composition of the magnetic core through identification of bonding characteristic spectra.

Elemental analysis of nanoparticles is achieved by Energy Dispersive X-rays Spectrophotometry (EDS).

High resolution Transmittance Electron Microscope (HR-TEM) explores the crystalline structure of a single particle.

Combining EDS, FTIR and HR-TEM enables confirmation of successful modification to the nanoparticles (such as coating and fictionalization).

2.6.3 Shape and Size

Low resolution TEM explores particles dimensions, size, shape, and size distribution uniformity.

3. Application of superparamagnetic nanoparticles in Magnetic D-µ-SPE.

3.1. Magnetic Dispersive micro solid phase extraction (Magnetic D-µ-SPE)

The technique of D-µ-SPE was first described by Tsai et al. at 2009 (Tsai et al. 2009) by application of functionalized silica and polymeric adsorbents in extraction of tetracyclines from water samples. D-µ-SPE is based on the dispersion of minimal amount of finely divided adsorbent phase in the sample solution to increase contact area between sample and adsorbent phase. D-µ-SPE could be categorized as a type of microextraction and could be referred as "Dispersive SPME" (Chisvert, Cárdenas, and Lucena 2018).

The process of D-µ-SPE includes the following steps:

- Dispersion of adsorbent phase within the sample solution.

- Retrieving adsorbent phase form the sample solution.

- Desorption of target analytes form adsorbent phase.

Dispersion of adsorbent in the sample solution is the most crucial step in D-µ-SPE at it impacts precision and accuracy of the technique (Chisvert, Cárdenas, and Lucena 2018).

The major challenge in nanomaterial application in D-µ-SPE is the retrieval of the adsorbent nanomaterial after the end of microextraction process. Recovery of nanomaterials from solutions involves the use of high speed centrifugation (He et al. 2014). Beside the availability concerns of such utility, this process is time consuming and may involve non-reversible adsorption, sample loss or co-precipitation of contaminants (He et al. 2014).

Superparamagnetic nanoparticles helped to solve this issue as they could be retrieved after microextraction process by an external magnetic field. This technique is known as Magnetic D-µ-SPE (He et al. 2014)

3.2. Role of Superparamagnetic nanoparticles in Magnetic D-µ-SPE

When superparamagnetic nanoparticles are suspended in sample solution in absence of magnetic field the particles moves freely within the solution. Due to the superparamagnetic behavior, particle-particle magnetic interaction is minimal resulting in low tendency for magnetic aggregation. This helps distribution of the superparamagnetic adsorbent phase within the sample solution.

When an external magnetic field is applied to the sample solution containing the superparamagnetic nanoparticles, they will migrate rapidly towards the applied external magnet. The particles retrieval would be a very fast process (within seconds). This would facilitate recovery process and reduce extraction process time.

When the external magnetic field is removed, the nanoparticles lose their magnetization and become free to move in the desorption solution. This enables rapid re-dispersion of the adsorbent phase in desorption solvent and rapid recovery of analytes.

3.3.Requirements of superparamagnetic nanoparticles for D-SPME

The following quality criteria of superparamagnetic nanoparticles should be controlled for successful microextraction process:

- High magnetic saturation momentum value of the particles for easy particles retrieval.
- Small particle size to provide higher surface area, higher adsorption rates and higher capacity.
- Particles should have even particle size distribution to enable uniform magnetic behavior of the particles.
- Particles should hold functionality relevant to the target analytes.
- Particles should be stable against physical aggregation and chemical degradation in sample solutions. Stabilization of the particles could be achieved by coating.

3.4.Magnetic-D-µ-SPE advantage

Magnetic-D-µ-SPE techniques have the following advantages (L. Chen, Wang, and Tong 2011):

- Easy dispersion and retrieval of adsorbent phase.
- Does not require special instrumentation
- (e.g. centrifuges, filtration,..).
- Economic, fast and very convenient.
- Non-destructive to biological molecules such as peptides and proteins.

3.5.Challenges

Preparation efforts of a suitable adsorbent for Magnetic-D-µ-SPE applications encounter many challenges. The most common challenges could be summarized as follows:

- Chemical and physical stability issues of superparamagnetic nanoparticle components.
- Tendency of functional adsorbent nanomaterials to aggregate or sediment in their suspension thus impacting adsorbent suspension homogeneity and subsequently method precision.
- Challenges concerning linking of adsorbent functional molecules to the surface of superparamagnetic nanopareticles.

3.6.Examples of magnetic D-SPME in literature

Applications of superparamagnetic nanoparticles in Magnetic D-µ-SPE could be classified according to the type of surface coating or functionalization:

3.6.1. Silica coated superparamagnetic nanoparticles

Silica coated Superparamagnetic nanoparticles could be tailored for specific applications by derivatization of the surface free silanol groups as follows:

- Dithiocarbamide and Diphenylcarbazide functionalized silica coated magnetite nanoparticles were applied for adsorption of Hg from water samples (Zhai et al. 2010; Girginova et al. 2010).
- Silica coated magnetite nanoparticles functionalized with 3-mercaptopropyltrimethoxysilane (3-MPTMS) enabled extraction and analysis of heavy metals such as Cd, Cu, Hg, Pb and Te from water samples (Huang and Hu 2008).

- Functionalization of silica coated magnetite with β-cylcodextrin enabled
- Determination of Bisphenol A and diethylstilbesterol in water samples (Jang and Lim 2010).
- Modification of silica coated magnetite with diphenyl group enabled microextraction of Poly Aromatic Hydrocarbons (PAH) (Bianchi et al. 2012).
- Mesoporous silica was applied to extract sudan dyes from water samples (Y. Wang et al. 2013).
- Silica coated magnetite nanoparticles modified with FeO nanoparticles were applied for extraction of tetracyclines from river and tap water (Lian et al. 2018).

3.6.2. Octadecylsilane modified superpara-magnetic nanoparticles

Magnetic nanomaterials modified by silanization reaction with C18 hydrocarbon chains to enable extraction of many compounds according to their hydrophobicity. C18 modified magnetic nanoparticles have improved separation capacity and chemical stability

Examples are extraction of estrogens from water samples (Yaling Liu and Jia 2008) and polycyclic aromatic hydrocarbons (Y Liu, Li, and Lin 2009).

Modification of silica coated magnetites with C18 enabled extraction of Lidocaine from rat plasma (Chu et al. 2011).

Silica coated magnetite nanoparticles modified with C18 was applied by Synaridou et al. (Synaridou et al. 2014) for microextraction of endocrine disrupting compounds (EDCs) including some organochlorine pesticides and polychlorinated biphenyls from milk samples.

3.6.3. Polymer modified superparamagnetic nanomaterials.

For example; Asgharinezhad et al. applied polypyrrole coated magnetite for (D-µ-SPE) of the antidepressants; setraline and citalopram from biological fluids followed by HPLC-UV detection (Asgharinezhad et al. 2014). Another important modification is the functionalization. Molecular Imprinted Polymers (MIPs) are polymers which have molecular recognition functionalized surface cavities similar in shape and size to the target molecules. Coating of magnetic nanoparticles with MIPs enabled selective extraction of fluroquinolones from water samples (L. Chen et al. 2010) and bisphenol A (Ji et al. 2009).

3.6.4. Surfactant modified magnetic nanoparticles:

For example, Faraji et al. applied CTAB coated magnetite for preconcentration of Lead from water samples prior to analysis with Flame atomic absorption spectrophotometer (Faraji et al. 2016). Water samples were first treated 1-(2-pyridilazo)-2-naphthol to complex with iron then the whole complex was extracted with CTAB-Magnetite nanoparticles.

3.6.5. Carbon coated magnetic nanoparticles:

Olga et al. developed activated Carbon coated magnetite for microextraction of Bisphenol A from Milk samples followed by HPLC-UV (Filippou, Deliyanni, and Samanidou 2017).

Ma et al. applied hydrophilic modified magnetic-MWCNTs for selective extraction of trans-resveratrol from vegetable oils samples (Ma et al. 2015).

Another Carbon material is Graphene (G). G exists in 2D nanostructures as sheets of fused benzene ring with extended conjugation. He et al. prepared Magnetite-G nanopartoicles for extraction of seven fluoroquinolones from milk, eggs and chiken muscles.

Yan et al. synthesized reduced graphene oxide (RGO) - magnetite composite for microextraction of isocarbophos residues from crop samples prior to GC detection (Yan et al. 2014).

4. **Conclusion:**

Magnetic D-µ-SPE has found growing potential applications in the field of trace analysis. Superparamagnetic nanoparticles were considered as a crucial element for preparation of competent adsorbents for Magnetic D-µ-SPE.

Overcoming the challenges of the preparation and linkage of to both components of D-µ-SPE; the superparamagnetic core and the functional surface, are necessary to fulfill this task. selected as a magnetic core for the proposed D-µ-SPE application.

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