

**Section V**

**New Trends in Environmental Analysis  
(Magnetic NMs, Nano-Sensors, Nano-Bio  
Sensors etc.,)**



# *Magnetic Nanomaterials for Environmental Analysis*

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## 19.1 Introduction

Magnetic nanomaterials (MNMs) have widespread applications in biotechnology, biomedical, material science, engineering, and environmental areas. Therefore, considerable attention has been given to their synthesis methods. MNMs as sorbents have been extensively exploited as materials of choice to separate biological cells and isolate proteins, enzymes or peptides. Separation techniques with magnetic nanomaterials are usually gentle and nondestructive to analytes, and even large complexes that tend to be broken up in the process of traditional column chromatography may remain active. Furthermore, magnetic separation can be easily and directly used for raw samples with several simple steps. Recently, different kinds of magnetic nanomaterials have been rapidly and extensively developed, and widely used in analytical techniques. MNMs are superparamagnetic so can attract a magnetic field, but retain no residual magnetism after the field is removed. Therefore, it is easy to isolate MNMs stuck to analytes from a sample solution or complicated matrices by simply applying an external magnetic field and this requires no filtration or centrifugation. In this chapter, factors

influencing contaminant removal by magnetic nanoparticles are reviewed and to reduce the treatment cost, the feasibility of the reuse and recovery of magnetic nanoparticles is also discussed.<sup>1,2</sup>

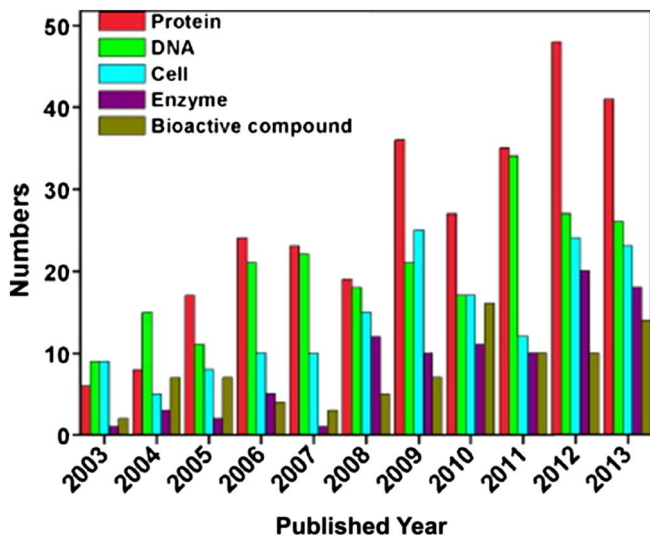
Compared with conventional separation techniques, there is no need for packing of the column with the sorbent, since the phase separation can be quickly and easily accomplished by applying an external magnetic field. There are a few problems associated with particles at the nano range, *i.e.*, their intrinsic instability, which tends to lead to formation of agglomerates. Moreover, uncovered metallic nanomaterials are chemically highly active and are easily oxidized in air, which results in loss of magnetism and dispersibility. The critical part is to develop shield approaches to chemically stabilize the isolated magnetic nanomaterials. Grafting or coating with an inorganic layer, like silica or carbon, or coating with organics, like surfactants and polymers, are a few shield approaches that have been utilized. In most of these approaches, the shielding shells not only stabilize the NMs but can also offer opportunity for additional functionalization. In summary, magnetic nanomaterials in environmental analysis are able to facilitate or accelerate many extraction and purification procedures and efficiently combine with the majority of other procedures used in environmental analysis.<sup>3,4</sup>

## 19.2 Properties and Format of Magnetic Nanomaterials

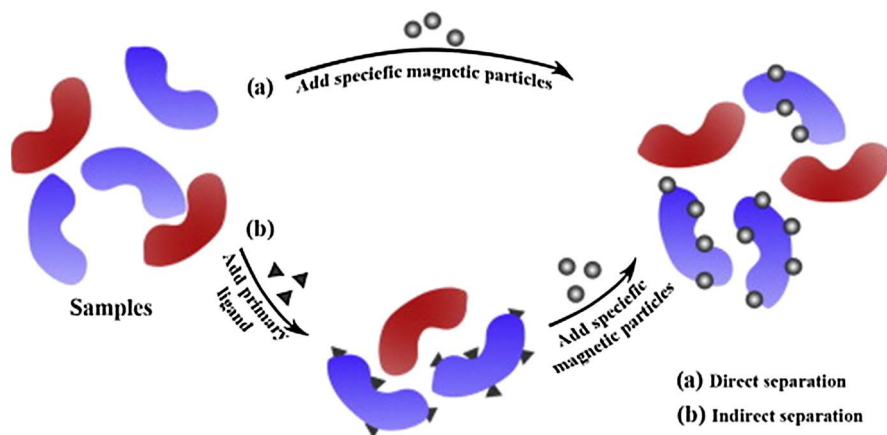
The properties of magnetic materials were identified early in the sixth century BC, but the first patent was filed by William Fullarton relating to the separation of iron minerals with a magnet in 1792. Application for the separation and analysis of various biologically active compounds and cells using magnetic materials was started in the 1970s. Since then, an increasing number of studies have focused on magnetic separation and analysis of biological samples using magnetic materials. Figure 19.1 shows the data of published articles on magnetic separation of proteins/peptides, nucleic acids, cells, and bioactive compounds and immobilization of enzymes from 2003 to 2013.<sup>5</sup>

There are two main ways of performing magnetic separation of analytes. In the first circumstance, no special modification of the target is needed when dealing with those exhibiting sufficient intrinsic magnetic moments involving some paramagnetic or ferromagnetic biomolecules or cells, such as ferritin, hemoglobin and deoxygenated erythrocytes (in plasma). In the second case, when coping with diamagnetic molecules and supramolecular structures, suitable magnetic modifications should be performed in order to attach magnetic labels to targets or immobilize targets to magnetic carriers or adsorbents. The linkage of magnetic labels to the targets is often mediated by affinity ligands or other types of interactions.<sup>5,6</sup>

In general, there are two modes for magnetic separation, *i.e.*, direct or indirect (Figure 19.2).<sup>5</sup> In the direct mode, magnetic affinity particles that possess appropriate affinity ligands and exhibit affinity toward the target



**Figure 19.1** Articles published on magnetic separation of proteins/peptides, nucleic acids, cells, and bioactive compounds, and immobilization of enzymes from 2003 to 2013. Reprinted from ref. 5, *Journal of Pharmaceutical and Biomedical Analysis*, 101, He J., Huang M., Wang D., Zhang Z. and Li G., Magnetic separation techniques in sample preparation for biological analysis: A review, 84–101, Copyright 2014 with permission from Elsevier.



**Figure 19.2** Direct and indirect modes of magnetic separation. Reprinted from ref. 5, *Journal of Pharmaceutical and Biomedical Analysis*, 101, He J., Huang M., Wang D., Zhang Z. and Li G., Magnetic separation techniques in sample preparation for biological analysis: A review, 84–101, Copyright 2014 with permission from Elsevier.

compound(s) are applied directly to the sample. After incubation, the target compounds or cells are bonded to the magnetic affinity particles and stable magnetic complexes are formed. In the indirect mode, free affinity ligands, such as appropriate antibodies, are firstly added to the solution or suspension to enable the interaction with target compounds. After the excess unbound affinity ligand is removed from the solution, the resulting labeled complex is captured by appropriate affinity magnetic particles. In both methods, the resulting complex of magnetic particles with the target structure is washed and recovered using an appropriate magnetic separator. The two methods perform equally well. Usually, the direct mode is faster, more easily controlled and requires fewer antibodies, while the indirect mode is more efficient, especially for affinity ligands with poor affinity for the target compounds or cells. However, the indirect mode usually needs excess antibodies or excess magnetic particles so the removal of free antibodies may be more difficult.<sup>7</sup>

### 19.3 Synthesis and Processing of Magnetic NMs

The most common techniques for MNMs synthesis include co-precipitation, thermal decomposition, microemulsion, vapor methods, sol-gel reaction, polyol method, flow injection synthesis, flame spray pyrolysis, laser pyrolysis, pulsed laser ablation, electrochemical methods and other wet chemistries. The most extensively used and most convenient method for the synthesis of ferrite NMs of controlled sizes and magnetic properties is co-precipitation. It is the simplistic way to synthesize MNMs. Metal oxides and ferrites are most commonly synthesized by this method. A wide range of surface chemistries have also been developed to enhance the biocompatibility of magnetic nanoparticles (MNPs). Additionally, several procedures have been developed for the formation of magnetic composites. Nanoferrites are the most commonly used MNMs, which become superparamagnetic when they are smaller than 128 nm. The stability of nanoferrites in solution is increased by chemically modifying their surface with surfactants, silicones or phosphoric acid derivatives. Metallic NPs have also been developed but they are difficult to handle and have unwanted side reactions. On the other hand, MNPs with a magnetic core (Fe or Co) but with a nonreactive shell, such as graphene, have been recently developed and have been demonstrated to have higher chemical stability (in acidic and basic solution, and organic solvents), and higher magnetization.<sup>8,9</sup>

A typical example of a top-down method of synthesis of magnetic nanomaterials is mechanical attrition, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. Often the major advantage is the possibility for easily scaling up to capacity quantities of material for various

applications. Typically, mechanical grinding is attained by using a high energy shaker, a planetary ball, or a tumbler mill. The energy transferred to the powder from refractory or steel balls depends on the rotational speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanomagnets are formed by the shear action during grinding.<sup>10</sup>

Wet chemical synthesis of nanomagnets is classified into two broad collections: firstly, top-down methods, where single crystals are imprinted in an aqueous solution for producing nanomaterials, *e.g.*, porous silicon synthesis by electrochemical etching. Secondly, bottom-up method, including precipitation and sol-gel method, where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution. In general, a sol-gel process comprises the evolution of inorganic networks through the formation of a colloidal suspension and gelation of the sol to form a network in a continuous liquid phase. The precursors for synthesizing these colloids usually consist of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol-gel transition controls the particle size and shape. Calcination of the gel produces the oxide. The sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps. Another extensively used method for the preparation of magnetic nano particles and films is laser ablation. A laser beam is used in this process as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications. The small dimensions of the particles and the possibility to form thick films make this method quite an efficient tool for the production of ceramic particles and coatings and also an ablation source for analytical applications, such as coupling to inductively coupled plasma emission spectrometry (ICP). The co-precipitation method is easy to do with a success rate from 96 to 99.9%. Chemical coprecipitation can produce fine, stoichiometric particles of single and multicomponent metal oxides. Templating is commonly employed for the controlled production of materials with ordered structure with desired properties. In the past, templates like aluminium oxide, carbon nanotubes, surfactants, polymer fibres, chitosan, cellulose, alginate and egg shell membranes have been employed.<sup>11,12</sup>

## 19.4 Environmental Applications of Magnetic Nanomaterials

Magnetic nanomaterials have been broadly used in environmental applications and have shown favorable performance for pollution removal and toxicity reduction. Among the most widely used magnetic nanoparticles, nano zero-valent iron, magnetite and maghemite nanoparticles have generated

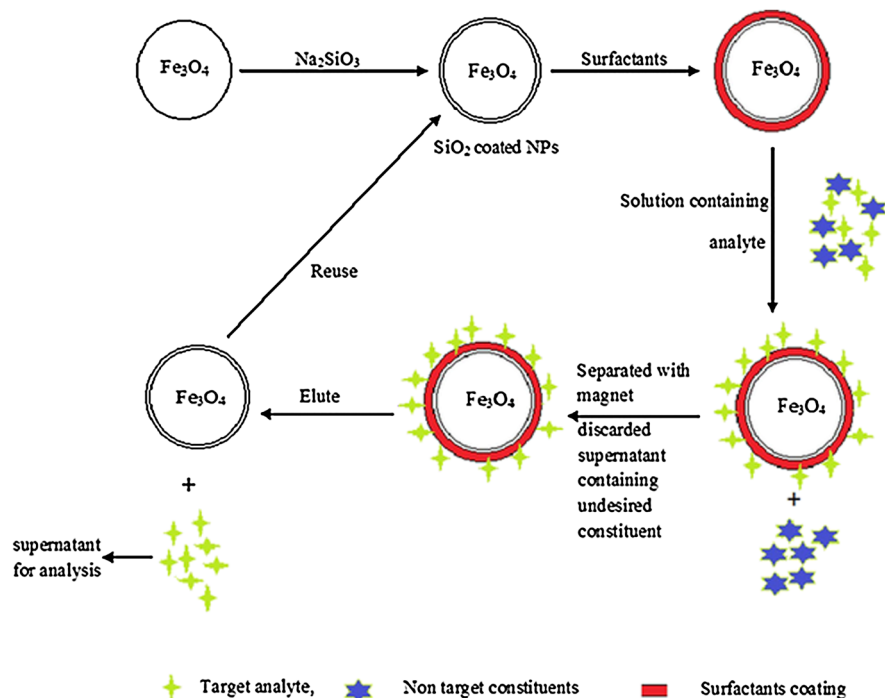
immense interest in research for environmental applications for treatment of contaminated water and subsurface environments. Heavy metals, such as arsenic and chromium, and organic pollutants, like chlorinated solvents, can be immobilized or reduced to less toxic species by nano zero-valent iron. The effectiveness of nano zero-valent iron is not just limited to laboratory findings. Many companies have been established for the manufacturing of nano zero-valent iron and its application for environmental protection.<sup>13,14</sup> In addition to the great removal performance, some researchers demonstrated the feasibility of reusing magnetic nanoparticles by desorbing the contaminants and regaining the removal capacity in successive treatment cycles. However, there are numerous conditions influencing the applicability of magnetic nanoparticles in a sustainable treatment process.<sup>15</sup>

Magnetic nanoparticles not only have a large removal capacity, fast kinetics and high reactivity for contaminant removal owing to their extremely small particle size and high surface-area-to-volume ratio, but they also have one more important property, magnetism. This is a useful property for water and wastewater treatment systems. A compact and efficient water or wastewater treatment system can take advantage of the high reactivity of the magnetic nanoparticles for pollutant removal. It is expected that magnetic separation could be a more cost-effective and convenient method for separating such tiny particles than sophisticated membrane filtration. Separation of magnetic nanoparticles from solution with a low-gradient magnetic field or a hand-held magnet has been frequently reported, showing the feasibility of separation and recovery of magnetic nanoparticles from water or wastewater, but no successful real applications of magnetic particles for water or wastewater treatment have yet been reported. On top of the high surface free energy, the magnetism of nanoparticles has been suspected to enhance the aggregation of nanoparticles and reduce the removal capacity, so acting as a great hindrance to the recovery and reuse of magnetic nanoparticles.<sup>16-19</sup>

A similarly important property of nanoscale iron particles is their huge flexibility for *in situ* applications. Modified iron nanoparticles, such as catalyzed and supported nanoparticles, have been synthesized to further enhance their speed and efficiency of remediation (Figure 19.3).<sup>20</sup> In spite of some still unresolved uncertainties associated with the application of iron nanoparticles, this material is being accepted as a versatile tool for the remediation of different types of contaminants in groundwater, soil, and air on both the experimental and field scales. In recent years, other MNMs have been investigated for the removal of organic and inorganic pollutants.<sup>20-25</sup>

MNMs have a high capacity for the removal of high concentrations of organic compounds. Dyes are present in the wastewater streams of many industrial sectors, such as in dyeing, textile factories, tanneries, and the paint industry. Therefore, the use of MNMs as an expensive or low efficient adsorbent for treatment of textile effluents can be a good platform, which needs more detailed investigations. A very important aspect in metal toxin removal is the preparation of functionalized sorbents for affinity or selective removal of hazardous metal ions from complicated





**Figure 19.3** Schematic illustration of preparation of surfactant-coated iron and silica NPs and their application as SPE sorbents. Reprinted from ref. 20 with permission from John Wiley and Sons. © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

matrices. MNMs are used as sorbents for the removal of metals like  $\text{Cu}(\text{II})$  (Table 19.1).<sup>26–28</sup>

Owing to their small size, magnetic MNMs offer a larger surface area-to-volume ratio than currently used microbeads, which results in good reaction homogeneity and faster reaction kinetics. Thus, the preparation of magnetic fluorescent particles, such as polystyrene magnetic beads with entrapped organic dyes/quantum dots, iron oxide particles coated with dye-doped silica shells, and silica MNMs embedded with iron oxide and quantum dots, is easier. The magnetic properties of the MNMs allow their manipulation by an external magnetic field without the need for centrifugation or filtration. Their optical characteristics (sharp emission, photostability, long lifetime) facilitate the implementation of internal calibration in the detection system. This introduces a unique internal quality control and easy quantification to multiplexed immunoanalysis. This method developed and enables a direct, simple, and quantitative multiplex protein analysis using conventional organic dyes and can be applied for disease diagnostics and detection of biological threats. In magnetic solid-phase extraction (MSPE) (Figure 19.4),<sup>29</sup> functionalized MNMs are added to sample matrices containing

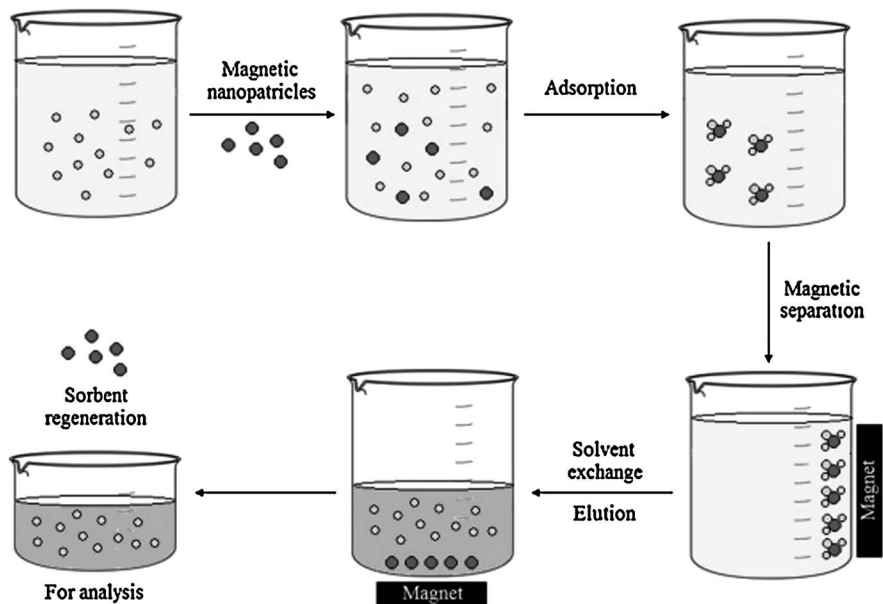
**Table 19.1** LOD, preconcentration factor and adsorption capacity of Cu(II) with different adsorbents. Reprinted from ref. 27, *Talanta*, 148, Abd Ali L. I., Ibrahim W. A. W., Sulaiman A., Kamboh M. A. and Sanagi M. M., New chrysin-functionalised silica-core shell magnetic nanoparticles for the magnetic solid phase extraction of copper ions from water samples, 191–199, Copyright 2015 with permission from Elsevier.

Sorbent	LOD (ng mL <sup>-1</sup> )	Preconcentration factor	Adsorption capacity (mg g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -N-chrysin	0.3	100	114.25
LIX-CNT-A	4.1	18.3	16.4
LIX-CNT	4.8	16.5	29.7
Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticle-based solid-phase extraction coupled with a functionalized gold nanoparticle probe	0.2	—	—
Magnetic nanoparticles coated with dithizone-modified chitosan	0.18	—	210
Morin-bound iron oxide magnetic nanoparticles	0.9	28	—
Amidoamidoxime silica	9	20	10.16
ZrO <sub>2</sub> /B <sub>2</sub> O <sub>3</sub>	3.3	10	46.5
Neocuproine modified magnetic microparticles	1.5	—	8

target analytes and untargeted compounds. After incubation or application of auxiliary irradiation agitation (*e.g.*, sonication) for an appropriate time until the target analytes are adsorbed by the adsorbent, the functionalized MNMs are easily isolated from the solution by applying an external magnetic field. When the external magnetic field is removed, the functionalized MNMs can re-disperse in solution, which is convenient for subsequent washing and desorption. Compared with commonly used sorbent materials, suspended magnetic nanomaterials can be separated from large-volume samples by use of a magnet instead of high-speed centrifugation or filtration; this simplifies and accelerates the isolation process.<sup>30–33</sup>

## 19.5 Conclusions and Perspectives

In summary, MNMs are highly stable and offer high extraction efficiency because of the high surface area-to-volume ratio of the extraction phase and faster separation, and they can conveniently synthesized and modified. Moreover, they also exhibit high selectivity for the target analytes from environmentally complicated matrices, reusability and excellent dispersibility in aqueous solutions. The application of MNMs in environmental analysis considerably reduces the duration of the analysis by decreasing the number of extraction steps. In addition, simultaneous isolation and enrichment of analytes and the use of an external magnetic field for separation of the sorbent with analytes adsorbed on the surface impact significantly on environmental



**Figure 19.4** The procedure used for functionalized magnetic solid-phase extraction (MSPE). With kind permission from Springer Science + Business Media, ref. 29, *Analytical and Bioanalytical Chemistry*, Application of functionalized magnetic nanoparticles in sample preparation, 406, 2, 2013, 377–399, Xie L., Jiang R., Zhu F., Liu H. and Ouyang G., © Springer-Verlag Berlin Heidelberg 2013.

analysis. Likewise, MNMs present opportunities for green analysis in chemistry as these can reduce usage of solvents, thus restricting the creation of hazardous waste.

MNMs are emerging materials that have attracted considerable attention from academics and researchers in multiple industries. Tools based on the usage of these are under active development as highly effective, efficient and economically viable options. Among the main advantages of these MNMs are the possibilities of surface modifications with different organic or inorganic coating agents to allow the removal of a wide range of target analytes. The application of MNMs in analytical methods is still incomplete and in the early stage and more research in the field is certainly necessary. Further development of MNMs for environmental analysis can be found in applications to more complex matrices and online analysis. The inclusion of MNMs promises new developments in the environmental analysis field with the design of new methods for synthesis and functionalization of the materials and enhancement of their physicochemical stability, lifespan, and selectivity. The development and design of new strategies will allow control of the interactions between the analyte and the surface, and improve the physicochemical properties of MNMs to prevent and reduce the background signal caused by non-specific binding. It is also necessary to develop appropriate analytical procedures to carry out synthesis and functionalization of MNMs,

and work on the conditions of the analysis process. Finally, there is still the challenge to develop on-site monitoring devices and apply MNMs for laboratory analysis of numerous samples.

## Websites of Interest

<http://pubs.rsc.org/en/content/articlelanding/2014/>  
<http://link.springer.com/article/>  
<http://nano.cancer.gov/>  
<http://journals.cambridge.org/>  
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