Nanotechnology & Environment

Mridula Chugh[1]
[1]Department of Applied Sciences,
Ganga Institute of Technology and Management, Kablana,
Jhajjar, Haryana, India

Abstract- **Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly improved using nanoparticles. Currently, the most widely used method for the removal and separation of toxic metal ions/organic compounds is the solid phase extraction technique. Recently, there have been reports in the literature on the enrichment and separation of trace elements and organic compound in the sample solutions by means of nanoparticles like TiO_2,Al_2O_3, ZrO_2, MnO and CeO_2. Nanoparticles have unique properties like large specific surface area, high adsorption capacity and low temperature modification, so they are promising solid-phase extractants and have contaminant scavenging mechanisms. This feature article includes application of nanoparticles in preconcentration, separation and determination of trace pollutants from various environmental samples.**

I. INTRODUCTION

Recent advancements suggest that many issues involving water quality could be resolved or greatly ameliorated using nanoparticles and other products resulting from the development of nanotechnology. In addition to obvious advantages for industrialized nations, the benefits for developing countries would also be enormous. Innovative use of nanoparticles for treatment of industrial wastewater is another potentially useful application. Many industries generate large amounts of wastewater. Removal of contaminants and recycling of the purified water would provide significant reductions in cost, time and energy to the industry and result in improved environmental stewardship. Aquifer and groundwater remediation are also critical issues, becoming more important as water supplies steadily decrease and demand continues to increase. Most remediation technologies available today, while effective, very often are costly and time consuming. The ability to remove toxic compounds from subsurface and other environments that are very difficult to access in situ, and doing so rapidly, efficiently and within reasonable costs, is the ultimate goal. Use of nanoparticles in analytical processes is the most extensively explored area of analytical nanotechnology. The objective is to exploit the excellent properties of nanoparticles to improve well established analytical methods or to develop others for new analytes or matrices. In addition to the typical advantages of nanoparticles, their use should lead to improved selectivity, sensitivity, rapidity, miniaturizability or portability of the analytical system. Nanoparticles can be incorporated or used in analytical methods either as such or chemically bonded. In the latter case, nanoparticles can be chemically bonded to a surface or functionalized with other organic or inorganic compounds in order to increase their solubility. Chemically unmodified nanoparticles can be used as raw randomized materials or as self-assembled raw materials. The explored nanoparticle properties can be electrical, optical, thermal, magnetic or chemical. Frequently, however, two or more properties are explored at once. Nanoparticles can be used for purposes such as sample treatment, instrumental separation of analytes, or even detection. In combination with the large variety of nanoparticles available, this provides a wide range of potential applications.The nanoparticles most widely used in analytical sciences at present include (a) silica nanoparticles, (b) carbon nanoparticles (mainly fullerenes and carbon nanotubes), (c) metallic nanoparticles and (d) supramolecular aggregates. Nanoparticles have two key properties that make them particularly attractive sorbents. On a mass basis, they have much larger surface area than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique properties of nanoparticles enable their development as high capacity and selective sorbents for metal ions and pollutants. Due to these reasons, now nanoparticles are designed and synthesized to act as either separation or reaction media for pollutants or scaffolds and delivery vehicles for bioactive compounds,thus providing unprecedented opportunities to develop more efficient and cost effective water purification processes and systems. Consequently, nanometer-sized material can selectively adsorb metal ions and have a very high adsorption capacity. Nanoparticles play a central role in purification and preconcentration of analytes from the sample matrix.Nanoparticles are used for the preconcentration and separation of pollutants from environmental sources. Investigation of the surface chemistry of highly dispersed metal oxides, e.g. TiO_2,Al_2O_3, ZrO_2, CeO_2 and MnO nanoparticles, indicates that these materials have very high adsorption capacity and give promising results when they are used for trace metal analytes of different types of sample. Thus, carbon nanotubes have been widely used as sorbents for solid-phase extraction. Ferric hydroxide is used to scavenge a variety of heavy metal contaminants.. This feature article deals with nanomaterials used in the separation and preconcentration of different pollutants from various samples.

A. Production techniques

There is a wide variety of techniques for producing nanoparticles.

B. *Vapour condensation*

This approach is used to make metal, metal oxide and ceramic nanoparticles. It involves evaporation of a solid metal followed by rapid condensation to formnanosized clusters that settle in the form of a powder. The main advantage of this approach is low contamination levels. The final particle size is controlled by variation of parameters such as temperature, gas environment and evaporation rate. This technique was developed originally in Russia.

C. *Chemical synthesis*

The most widely used chemical synthesis techniques consist essentially of growing nanoparticles in a liquid medium composed of various reactants. This is typified by the sol-gel approach, and is also used to create quantum dots. Chemical techniques are generally better than vapour condensation techniques for controlling the final shape of the particles. Scheme 1 represents the reactions involved in the sol-gel formation of nanoparticles.

D. *Solid state process*

Grinding or milling can be used to create nanoparticles. The milling materials, milling time and atmosphere affect the resultant nanoproperties· .The contamination from milling materials is one of the great disadvantages.

Biological process

This is a natural system to create almost atomically perfect nanostructures· .Yeast cells can create cadmium sulfide nanoparticles and viral proteins to create silver nanoparticles.

E. *Characterization*

Nanoparticles are characterized by different techniques, including structure analysis of nanostructure using the scattering effects of an e-beam., Early equipment did not have the required magnification or reflection capability to observe materials at the nanoscale. With the introduction of equipment like SEM, TEM, STM, AFM and SNOM, the hidden nano world is now before us to give us new materials which will change the world in the coming years. It may or may not be like the revolution brought about by information technology but it will be similar and it will help maintain the tempo of the IT revolution in addition to making the entry of nano to all other subjects including basic subjects like physics, chemistry, biology, medicine, biotechnology, materials science, electronics etc. SEM is now the most widely used technique in the characterization of nanomaterials. The revolution of SEM approaches a few nanometers and instruments can operate at magnifications that are easily adjusted from 10 to over 3 000 000 keV. Not only does SEM produce topographical information as optical microscopes do, it also provides chemical composition information near the surface. TEM uses a condenser lens system to accelerate electrons to 100 keV or higher, up to 1 MeV, projecting them onto a thin specimen (less than 200 nm) to penetrate the sample thickness undetected. Its greatest advantages are the high magnification, ranging from 50 to 106 keV, and the ability to provide both image and diffraction from a single sample. Scanning probe microscopy has emerged as the most effective tool for observation and manipulation at the nanoscale and is used effectively in advanced laboratories globally. Scanning probe microscopy is a general term used to describe a growing number of techniques and tools that use a sharp probe to scan over a surface and measure some property of that surface by observation of the interaction between the two and provide nanometre scale information concerning the sample. Some examples are STM, AFM and SNOM. SPM is avery important and versatile set of tools for nanotechnology. It operates in real space with A ° ngstrom to nanometre spatial resolution, in contrast to scattering techniques such as SEM that operate in reciprocal space. Rather than using a beam of light or electrons, SPM uses a fine probe that is scanned over a surface. The resolution obtained with this technique can resolve atoms, and true 3-D maps of surfaces are possible. STM is a tool for directly observing the positions of individual atoms in the reconstruction of a material. STM is one of a number of instruments that allow scientists to view and manipulate nanoscale particles, atoms and small molecules AFM is used to measure magnetic forces between a magnetized cantilever and the sample, if the sample is ferromagnetic. The interacting force between the probe and the sample is measured as an indication of the sample–probe distance. Since no current is involved, it can image both conducting and insulating surfaces. This is a major advantage over STM. Compared to a SEM, it has a simpler instrumentation set-up, it can be operated with the sample in the ambient air, and it is much cheaper, hence it is found commonly in laboratories. AFM has been widely used in research laboratories as an extremely high power microscope. It has a significant advantage over STM and SEM in that it can image insulating or semiconducting surfaces directly in ambient atmosphere or even liquids. In SNOM a tapered micropipette or optical fiber is used.It is a technique that can achieve spatial resolution performance beyond the classical diffraction limit by employing a sub-wavelength light source or detector positioned in close proximity to a specimen. Such a sub-wavelength source usually consists of an aperture at the end of a tapered probe, which functions basically as a wave guide. The resolution of SNOM is not high as STM and AFM.

$$Si(OR)_4 + H_2O \longrightarrow OH\,Si(OR)_3 + ROH$$

$$OH\,Si(OR)_3 + H_2O \longrightarrow (OH)_2\,Si(OR)_2 + ROH$$

$$(OH)_2Si(OR)_2 + H_2O \longrightarrow (OH)_3Si(OR) + ROH$$

$$(OH)_3\,Si(OR) + H_2O \longrightarrow (OH)_4Si + ROH$$

$$(OH)_4Si + (OH)_4Si \longrightarrow (OH)_3Si{-}O{-}Si\,(OH)_3 + H_2O$$

Scheme 1: Sol-gel formation of nanoparticles.

II. APPLICATION OF NANOPARTICLES FOR THE REMOVAL OF VARIOUS POLLUTANTS

The selective sorption of certain elements based on the stability of complexes formed with functional groups of sorbents has led to the use of these materials for selective enrichments and separation of inorganic ions from different natural and industrial sources. According to researchers at the Pacific North Laboratory (PNL), chemically modified nanoporous ceramics are used to remove contaminants from all types of waste streams faster and at a significantly lower cost than conventional techniques such as ion-exchange resins and activated carbon filters. These nanosponges could be used in a wide range of environmental applications, including drinking-water purification, wastewater treatment, site remediation and waste stabilization. Granular activated carbons (GACs) have been accepted as the industry standard for adsorbing unwanted chemical compounds from water. As a result, they have become ubiquitous throughout industry, wastewater treatment facilities and even in households for purification of drinking water. Scientists have developed robust filters composed entirely of multiwalled carbon nanotubes for the removal of benzene and ferrocene· These filters, shaped like hollow cylinders, are easy to clean and reusable. They can remove bacteria and viruses from water, eliminate heavy hydrocarbons from petroleum, and separate mixtures of benzene and naphthalene· Preconcentration of metal ions using nanoparticles.Recently, it has been found that iron sulfide (FeS) nanoparticles produced by certain bacteria act as excellent adsorbents for a wide range of metal ions in solution, such as As(III), Cd(II), Hg(II) and Pb(II). Waychunas et al. have discussed the structures and reactivity of goethite, akaganeite, hematite, ferrihydrite and schwertmannite nanoparticles (collectively referred to as FeOXnanoparticles). These are the important constituents of soil.Goethite nanoparticles are used for the adsorption of As(V),Cu(II), Hg(II) and Zn(II). The applicability of maghemite(g-Fe_2O_3) nanoparticles for the selective removal of Cr(VI), Cu(II)and Ni(II) from electroplating wastewater had been studied by Hu et al. Ceria nanoparticles supported on carbon nanotubes (CeO_2-CNTs) were used for the removal of arsenate from water by Peng et al. Allophane and boehmite are natural nanomaterials and do not pose much risk either to the physical environment or to human health Allophane has been used as a nanoscavenger for Cu(II) in environmental samples. Boehmite (ALOOH) nanoparticles have been used for the adsorption of arsenic by Anderson. The adsorption behaviour of toxic metal ions like Cu(II), Cr(III),Mn(II), Ni(II), Zn(II), Cd(II), Mo(VI) and rare earth elements on TiO_2 nanoparticles has been reported in environmental samplesThe adsorption properties of many oxides strongly depend on the characteristics of solids e.g. morphology, crystal structure, defects, specific surface area, hydroxyl coverage, surface impurities and modifiers and these factors can be controlled by using appropriate modification methods. The basic disadvantage of solid sorbents is the lack of selectivity, which results in interference with target metal ions. To overcome this problem, physical or chemical modification of the sorbent surface with some organic compounds, especially chelating ones, is required. Some examples are given in Table 1.

TABLE 1:
PRECONCENTRATION OF METAL IONS BY NANOPARTICLES

Nanoparticles	Analytical method	Analyte	LOD (mg/L)	Sample	Reference
TiO2	ICP-AES	Cu(II)	0.34	Environmental water samples	118
		Cr(III)	1.14		
		Mn(II)	0.52		
		Ni(II)	1.78		
TiO2	FAAS	Zn(II)	1.8	Environmental water samples	119
		Cd(II)	3.0		
TiO2	GFAAS	Se(IV)	0.16	Sediment, water samples	120
		Se(VI)	0.14		
TiO2	ICP-AES	Sm(III)	0.08	Stream sediments	121
		Ho(III)	0.1		
		Nd(III)	0.1		
		Tm(III)	0.06		
TiO2	ICP-AES	Au(III)	0.016	Geological samples	122
		Pd(II)	0.012		
		Ag(I)	0.006		
TiO2	ICP-AES	La(III)	0.124	Stream sediments	123
		Yb(III)	0.108		
		Y(III)	0.108		
		Eu(III)	0.28		
		Dy(III)	0.36		
TiO2	ICP-AES	Cr(III)	0.32	Water samples	124
MWCNs	ICP-OES	La(III) Yb(III) Eu(III) Dy(III) Y(III)	3–57	Water samples	125
Al2O3	ICP-MS	Mn(II)	0.006	Environment	126

			7	al water samples	
		Zn(II)	0.078		
		Pb(II)	0.027		
		Ni(II)	0.038		
		Co(II)	0.0082		
		Cd(II)	0.079		
ZrO2	ICP-OES	Mn(II)	0.012	Water samples	127
		Zn(II)	0.002		
		Cu(II)	0.058		
		Ni(II)	0.007		

III. CONCLUSIONS

Nanotechnology is a revolutionary science that will have a large impact on our life. A core piece of this technology is the production of nanomaterials for chemical, medical, and environmental applications. Nanomaterials have a number of key physicochemical properties that make them particularly attractive as separation media for purification of natural water and industrial effluents. Environmental application is an important avenue of nanomaterials research. Their capacity together with their relatively low cost and wide availability could increase the use of nanoparticles for environmental and heath protection.Nanoparticles have been found to be suitable replacements for organic solvents and reactive complexants in the extraction and preconcentration of trace metals and organic compounds from natural waters and environmental samples. Only small quantities of largely environmentally benign reagents are used in the synthesis of nanoparticles. No organic solvents are used in the application of nanoparticles as nanoscavengers. The physical advantages of the nanoscavengers approach over the conventional liquid–liquid extraction technique is that large numbers of samples can be rapidly treated with nanoscavengers. This can be carried out at the sampling site, stabilizing the analyte during transport and preanalysis storage. This leads to extractions being carried out without further intervention during the sampling excursion. The last but not least advantage of nanoparticles is that they are highly efficient in the preconcentration of toxic metals and organic compounds. They can be repeatedly used andthe matrix effects are low. There are different types of nanomaterials used for removal of environmental pollutants.

1) The applicability of carbon nanotubes for analytical purposes can be expanded. CNTs present a higher adsorption capacity toward organic pollutants and metal ions than commonly used activated carbon, and the analytes retained on this solid phase can be easily desorbed. Wider practical applications of carbon nanotubes may be hampered by their relatively high unit cost.

2) Zero-valent Fe0/Ni0 nanoparticles have given promising results for the removal of environmental pollutants, but background corrosion of iron particles not only limits the lifetime of these nanoparticles but also substantially decreases the reactivity of these nanoparticles.

3) Surface modifications of nanoparticles give good results for the preconcentration of environmental pollutants. Chemically modified nanoparticles of silica, titania, zirconia and magnesia are more effective, highly selective and more efficient for the preconcentration of the pollutants. Chemisorption of chelating molecules on silica surfaces provides immobility, mechanical stability and water insolubility, thereby increasing the efficiency,sensitivity and selectivity of the analytical application.

ABBREVIATIONS

AAS	atomic absorption spectrometry
CVAAS	cold vapor atomic absorption spectrometry
ESV	electrochemical stripping voltammetry
FAAS	flame atomic absorption spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
HPLC	high-performance liquid chromatography

REFERENCES

[1] K. A. D. Guzman, M. R. Taylor and J. F. Banfield,Environ.Sci.Technol, 2006, 40, 1401.
[2] C. L. Chun, R. L. Penn and W. A. Arnold, Environ.Sci.Technol,2006, 40, 3299.
[3] M. F. Hochella, Geochim.Cosmochim.Acta, 2002, 66, 735.
[4] A. Kay, I. Cesar and M. Gratzel, J.Am. Chem.Soc, 2006, 128, 15714.
[5] D. K. Kim, M. Mikhaylova, Y. Zhang and M. Muhammed,Chem.Mater, 2003, 15, 1617.
[6] D. E.Miser, E. J. Shin, M. R. Hajaligol and F. Rasouli, Appl. Catal.A., 2004, 258, 7.
[7] A. R. Turker, Clean, 2007, 35, 545.
[8] N. S.Wigginton, K. L. Haus and M. F. Hochella, J. Environ. Monit,2007, 9, 1306.
[9] K. Cottingham, Anal.Chem., 2003, 77, 51.
[10] M. Valcarcel, S. Cardens and B. M. Simonet, Anal.Chem, 2007, 79,4788.