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Review

Nanomaterials for analysis and monitoring of emerging chemical pollutants

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A B S T R A C T

Emerging chemical pollutants (ECPs) are defined as new chemicals that have no regulatory status but may have an adverse impact on the environment and human health. Research on ECPs calls for new analytical tools. In this article, we review the applications of nanomaterials in analysis and monitoring of ECPs. We cover different types of nanomaterial (e.g., carbon nanotubes, graphene, metal nanoparticles, magnetic nanoparticles, and quantum dots) and different analytical techniques (e.g., sample-preparation techniques, electrochemical sensing, fluorescent detection, colorimetric detection, surface-enhanced Raman scattering, and mass spectrometry). We also discuss current challenges and give our perspectives on the future in this rapidly developing area.

Contents

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1. Introduction

Tremendous efforts have been made in prevention, control, and mitigation of environmental pollution caused by persistent organic pollutants (POPs) that are known to persist in the environment, resist biodegradation, bioaccumulate in organisms, and have adverse effects on the environment and human health. Nevertheless, it was recently recognized that risks to the environment and human health are not limited to classical POPs. More and more attention is being paid to emerging chemical pollutants (ECPs), which are defined as chemicals that are not covered by standard monitoring and regulatory programs but may pose potential threatens to the environment and human health [1–3].

The open list of ECPs encompasses a wide spectrum of chemicals (Table 1). Chemicals, such as polybrominated diphenyl ethers (PBDEs) and antibiotics, have been present in the environment for decades, but only recently did they emerge into the spotlight due to advances in monitoring techniques and increased knowledge of their toxicity. Some chemicals (e.g., ionic liquids) were even thought to be safe and "green", but are now considered potential pollutants with revelation of their ecotoxicity and health effects [4]. Despite that, recognition of the occurrence of ECPs in the environment is still limited, and reliable ecotoxicological data are only available for a small fraction of these chemicals.

To understand the potential biological impact of ECPs, it is urgent to develop reliable, practical methods for identifying and quantifying these compounds in the environment. However, analysis of ECPs is a great challenge due to:

(1) the complexity of the environmental matrices;
(2) the extremely low concentrations of these chemicals in the environment (usually at parts per trillion to billion level);
(3) the presence of multiple isomers or analogs (e.g., PBDEs have 209 congeners; and short-chained chlorinated paraffins (SCCPs), with thousands of isomers, enantiomers, and diastereomers, may be one of the most complex group of organic pollutants); and,
(4) the "emerging" nature, because, some ECPs have just been identified in the environment for a short period of time, and they still lack corresponding analytical methods.

Nanomaterials (NMs) have sparked intense research interest in almost all branches of analytical chemistry due to their intriguing chemical and physical properties (e.g., size, conductivity, mechanical strength, magnetism, and light absorption and emission). The application of NMs in environmental analysis has undergone rapid growth in recent years. Specifically, NMs have shown great promise for analysis of ECPs. Many papers have reported the use of NMs in analytical method development for ECPs. These works provide new analytical tools and push forward the research on ECPs. In electrochemical sensing, NMs can be used as molecular wires to enhance electron transfer or as catalysts to accelerate chemical reactions. In optical detection, NMs can serve as optical probes for designing novel detection systems. In separation science, NMs can often be used as stationary phases or adsorbents due to their large surface area and specific affinity for the pollutant molecules. Apart from that, the use of magnetic NMs can facilitate solid-phase extraction (SPE) and save time in sample preparation, which is usually the most laborious, tedious step in environmental analysis.

In this article, we review the applications of NMs in analysis and monitoring of ECPs. We focus on emerging pollutants, and do not cover classical pollutants. Due to the large number of publications on this topic, it is impossible for us to list exhaustively all the related papers, so we select only some of the most representative papers. Incidentally, it is necessary to clarify that NMs themselves are regarded as a class of ECPs. Although present in laboratories since the early 1980s, NMs became an environmental issue only recently with their increasing use in consumer products and continual release into the environment. Some papers have reviewed safety concerns about NMs [5–8].

2. Typical nanomaterials used in environmental analysis

Prior to discussing the applications, it is necessary to give a brief review on the most commonly used NMs in environmental analysis, including carbon NMs, gold nanoparticles (AuNPs), magnetic nanoparticles, and quantum dots (QDs).

2.1. Carbon nanomaterials

Carbon NMs comprise a number of allotropes. Among them, carbon nanotubes (CNTs) and graphene have been widely used in analysis of ECPs due to their large surface area, excellent electrical and optical properties, good chemical/physical stability, and relatively low cost.

CNTs can be synthesized in large quantities by various means, such as arc discharge, high-pressure carbon-monoxide disproportionation, or chemical-vapor deposition (CVD). Some of them are also applicable for graphene (e.g., CVD and arc discharge). Moreover, graphene can be produced from graphite by chemical methods [9], namely, exfoliation of graphite to graphene oxide (GO) by harsh oxidation and sonication, followed by reduction of the GO to the parent graphene state. Notably, GO is highly soluble in water and possesses a large number of reactive groups (e.g., carboxyl and hydroxyl), so it provides a versatile precursor for functional graphene and graphene composites.

There are some issues that should be paid attention to when applying carbon NMs, as below.

(1) ***Metallic impurities.*** CNTs contain a considerable amount of residual metallic impurities from the metal catalysts used in synthesis [10]. The same situation happens to graphene if metal catalysts are used in the synthesis; otherwise, the metallic impurities may also come from natural graphite (e.g., Fe, Co and Ni) [11]. These impurities are extremely difficult to remove and can be problematic for some

Table 1
Typical emerging chemical pollutants mentioned in this review

Classification	Typical compounds
Pharmaceuticals and personal-care products (PPCPs)[a]	Antibiotics; Steroids and hormones; Non-steroidal anti-inflammatory drugs (NSAIDs); Anticonvulsant and antidepressant drugs; β-Blockers; Lipid regulators; Triclosan; UV filters
Flame retardants	Polybrominated diphenyl ethers (PBDEs); Tetrabromobisphenol A (TBBPA); Tris(2,3-dibromopropyl) isocyanurate (TBC)
Perfluorinated compounds (PFCs)	Perfluorooctanoic acid (PFOA); Perfluorooctanesulfonic acid (PFOS)
Industrial additives	Bisphenol A (BPA); Alkylphenols; Phthalate esters; Methyl *tert*-butyl ether (MTBE); Short-chained chlorinated paraffins (SCCPs)
Others	Disinfection by-products (DBPs); Perchlorate; Nanomaterials (NMs); Algal toxins

[a] In this review, only papers that treated PPCPs as pollutants are discussed, so some medical-oriented applications are not involved.