

Polymeric nanocomposites as sorbents in environmental water analysis, a close view to the synthesis and potential applications

Jaime Millán-Santiago, Francisco Antonio Casado-Carmona, Rafael Lucena and Soledad Cárdenas

Abstract

Polymeric nanocomposites have been extensively used as sorbents to extract pollutants from environmental waters before their final instrumental analysis. These materials are highly versatile and can be adapted to a given analytical problem by selecting the polymer/nanomaterial combination adequately. The adaptability of the materials is strengthened by their easy preparation in the laboratory and the different formats (particles, membranes, monoliths, or fibers) in which they can be obtained. This article delivers a general overview of the potential of polymeric nanocomposites, emphasizing the practical aspects (synthesis and microextraction techniques). It aims to inspire researchers by showing the almost endless possibilities of these materials in sample preparation and the main trends in the near future.

Addresses

Affordable and Sustainable Sample Preparation (AS₂P) Research Group, Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (anexo), Córdoba, España

Corresponding author: Lucena, Rafael (rafael.lucena@uco.es)

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Keywords

Polymeric nanocomposites, Sorptive phases, Nanoparticles, Microextraction.

Introduction

Green Analytical Chemistry (GAC) identifies the sample preparation as a step with a potential environmental impact owing to the resources (reagents, solvents, and energy) it requires [1]. However, the direct analysis of

environmental waters is usually impeded by the complexity of the matrices and the low concentration of the target compounds, which usually falls below the sensitivity levels of the instruments. The isolation and preconcentration of the target pollutants before their analysis overcome these two limitations and reduce the exposure of the instrument to excessive soiling. Combining an efficient extraction technique and a sensitive instrument also allows responding to the increasingly restrictive environmental policies. The White Analytical Chemistry concept tries to frame the GAC, recalling that obtaining useful chemical information is the main aim of Analytical Chemistry [2]. Sample preparation is allowed in the scenario defined by GAC and White Analytical Chemistry because it is essential to solving many analytical problems.

Sorbent-based extraction is widely used in environmental water analysis owing to its high capacity and versatility (widely availability of commercial sorbents). In the last decades, the increasing environmental awareness of analytical scientists has driven the miniaturization of sorbent-based extraction, giving rise to two different groups of techniques: solid-phase microextraction (SPME) [3,4]; and micro-solid phase extraction (μ -SPE) [5,6]. Reducing the amount of sorbent challenges the capacity, and the design of very efficient material results key in this context. Polymeric phases have been extensively used as sorbents thanks to their high capacity, chemical and thermal stability, and versatility in interaction chemistries with the target analytes. Nanomaterials (NMs) emerged in the last decade as powerful sorbents thanks primarily to their high surface-to-volume ratio that accelerates the mass transference in the extraction [7,8]. Polymeric nanocomposites (PNCs) mix a polymer (or several polymers) with a nanostructured solid providing a distinct material that shares the properties of the individual ingredients [9]. For clarity, in this article, the term nanocomposite (NC) will be limited to those materials obtained by combining two or more NMs in the absence of a polymer.

The extraction selectivity of the PNCs is a relevant issue that will depend on the type of analysis. For nontargeted analysis, PNCs that extract compounds in a

List of abbreviations

CS-PNCs	Core-shell polymeric nanocomposites
E-PNCs	Embedded polymeric nanocomposites
GAC	Green Analytical Chemistry
NCs	nanocomposites
NMs	Nanomaterials
MEPs	Microextraction by packed sorbents
PNCs	Polymeric nanocomposites
SPME	Solid-phase microextraction
TFME	thin film microextraction
WAC	White Analytical Chemistry
μ -SPE	Micro-solid phase extraction

wide range of polarities are recommended to avoid the loss of information. In targeted analysis, however, two strategies can be possible. A more selective PNC is useful for extracting compounds with similar chemical characteristics. In contrast, a broader extraction PNC is required to extract a heterogeneous family of targets (e.g. endocrine disruptors) that contain compounds with different chemical compositions but similar action.

Type of polymeric nanocomposites: the main synthetic routes

PNCs can be ad-hoc synthesized, considering the analytical problem (e.g. target analyte or family of compounds) to solve and the scenario (e.g. in-lab, on-site) in which the extraction will be developed. Table 1 shows the wide variety of PNC types, their structures, synthetic approaches, and final formats. This general overview, supported by selected applications in water analysis, demonstrated the versatility of these materials in the field.

In the core–shell (CS) approach, the surface of the NM is coated with a polymer [10]. In this assembly, the NM acts as inert support, whereas the polymer is the actual sorptive phase. CS PNCs are usually obtained by covalent bonding of the polymer into the NM surface. The NM core, mainly when magnetic ones are used, is typically protected with a silica shell that also improves the anchoring of the polymer [11]. CS-PNCs are particulate materials with a nanometric size as the core is coated in a controlled way. The synthesis of CS-PNCs is usually a multistep procedure but produces materials with a high surface-to-volume ratio.

In the deposition approach, the NM is placed on the surface of the polymer, reducing its active surface. This aspect is critical when the polymer plays a primary role in the extraction of the analytes. The modification of commercial sorbents with cobalt ferrite NMs to provide a magnetic sorbent has been proposed to extract pollutants following this approach [12]. The deposition of

NMs over pre-existing membranes or monoliths is possible, but special techniques, like ionized jet deposition, are used to avoid a negative effect on the porosity, which is the main feature of these materials [13].

In the embedding approach, the NMs are introduced inside the polymer network. Although generally, the NMs are just physically entrapped, they can be eventually linked by covalent bonding. The synthesis procedures used to be simple, but some of the NMs are not accessible to the sample. However, the NM can improve the porosity of the PNC or provide properties like magnetism. Embedded PNCs (E-PNCs) can be obtained by several techniques as membranes, fibers, particles, and monoliths.

Electrospinning can be used for the synthesis of membranes and fibers. If an appropriate polymeric solution is electrospun over a planar collector (usually aluminum foil), E-PNCs membranes [14,15] are obtained. The NMs can be dispersed in the polymeric solution or can be spontaneously formed during the electrospinning step from the salt used as the electrolyte [16]. If a cylindrical and rotating collector is used, SPME fibers are produced [17]. The thickness of the fiber coating must be controlled as it affects the extraction capacity and kinetics.

Particulate E-PNC can be obtained by the precipitation (induced by evaporation of the solvent or its change-over) of the polymer in a precursor solution containing the dispersed NMs [18]. Planar sorptive phases can also be obtained by dip coating a planar substrate (e.g. filter paper) in the precursor solution [19] or by casting the solution in an appropriate holder [20].

Finally, E-PNC monoliths can be prepared by polymerizing suitable monomers in the presence of NMs that are finally entrapped in the network [21].

Polymeric nanocomposites as sorbents in microextraction

PNCs can be used in different extraction techniques (SPME and μ -SPE) and applied under two workflows (in-lab and on-site) for the determination of pollutants (inorganic and organic) in water samples. Figure 1 summarizes the use of PNCs in microextraction techniques and is designed to make more accessible the selection of the PNCs and the microextraction format depending on the analytical problem to be solved.

In-syringe-based microextraction permits to reduce the sample and eluent requirements, also being an easy to automate technique. Microextraction by packed sorbents (MEPS) consists of packaging the sorbent inside a special bin and passing through the sample to isolate the analytes [22]. In the case of particulate PNCs, the size is critical

Table 1

General overview of the synthetic approaches and format of polymeric nanocomposites (PNCs). The pictures represent the structure of the PNCs showing the nanomaterial (NM) in gray and the polymer in dark blue.




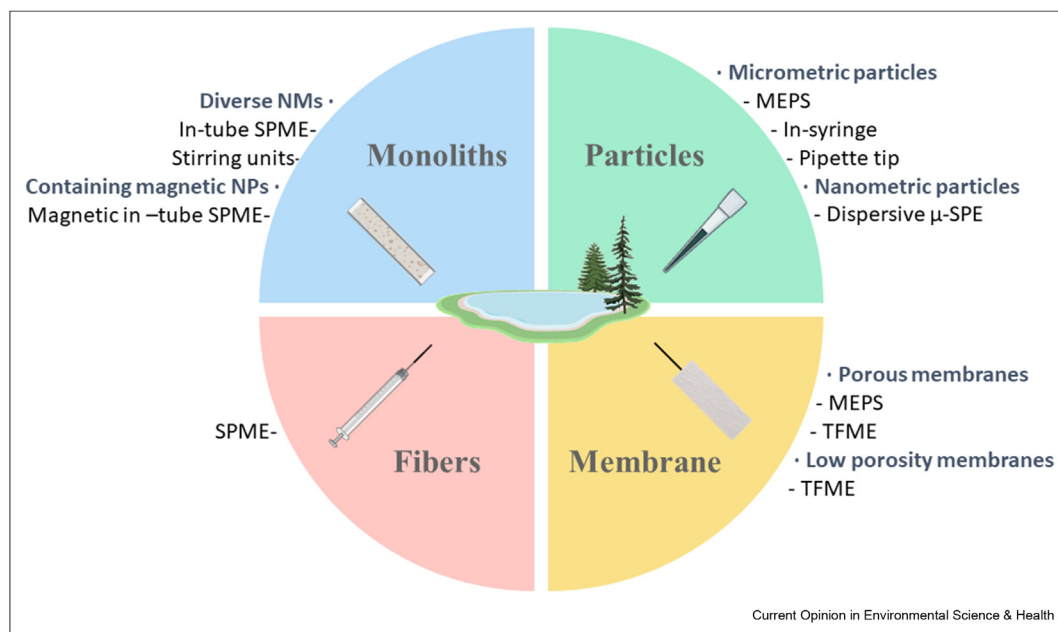
Type of PNC	Structure of the PNC	Synthesis technique	Process	Format of the resulting PNC	Comments	References
Core-shell		Covalent bonding	The polymer is anchored to the surface of an NM	Particulate	<ul style="list-style-type: none"> - The PNC presents a high surface to volume ratio. - Good stability of the coating. 	[10,11]
Deposition		Adsorption	An NM is grown or adsorbed over a polymer	Particulate	<ul style="list-style-type: none"> - The deposition reduces the active surface of the polymer affecting to the performance if the polymer plays a primary role. 	[12]
		Decoration	An NM is deposited over a pre-existing membrane	Membrane	<ul style="list-style-type: none"> - Special techniques are applied to avoid the membrane pores clogging. 	[13]
Embedding		Electrospinning	A precursor solution is electrospun over a flat collector	Membrane	<ul style="list-style-type: none"> - The NM can be dispersed in the precursor solution but can be also spontaneously formed. 	[14–16]
			A precursor solution is electrospun over a cylindrical and rotating collector	Fiber	<ul style="list-style-type: none"> - The thickness of the coating must be controlled. 	[17]
		Precipitation	The polymer of a precursor solution is precipitated	Particulate	<ul style="list-style-type: none"> - The resulting material is macroscopically homogeneous, but it can require grinding for better performance. 	[18]
			The polymer of a precursor solution is precipitated over a flat support	Membrane	<ul style="list-style-type: none"> - The flat support is dipped in the precursor solution. The number of dips and the concentration of the precursors define the thickness. 	[19]
			The precursor solution is cast in a holder	Thin film/membrane	<ul style="list-style-type: none"> - The volume of the solution defines the thickness of the resulting PNC. 	[20]
		Bulk polymerization	A polymer is synthesized in the presence of an NM	Monoliths	<ul style="list-style-type: none"> - The porosity of the PNC must be controlled to allow an efficient sample flow-through 	[21]

Figure 1



Schematic overview of the types of polymeric nanocomposites and the main extraction techniques in which they are applied.

to avoid excessive overpressure, and micrometric PNCs are selected [23–25]. Porous membranes prepared by a coating paper with PNCs have also been proposed in MEPS as sorbents [26]. In-syringe microextraction allows designing on-site extraction devices that integrate sampling and extraction in just one step. This alternative makes multisampling simpler (as only the sorbent containing the analytes is finally transported) and improves the representativeness of the results (the target pollutants are often more stable when they are trapped in a sorbent). These on-site devices can be built simply by placing the PNC in the adaptor of a needle [27]. In addition, PNCs are compatible with pipette extraction technique [28].

Particulate PNCs, especially those containing magnetic NMs, are also used in the dispersive μ -SPE [5], where the high surface-to-volume ratio of nanometric PNCs can be exploited to make the mass transference faster [10,29–31].

Porous PNCs membranes are used for filtering the samples increasing the processed volumes, which provides better enrichment factors. However, these membranes are prone to clogging and cannot be applied to process samples containing suspended particles. Nonporous or low-porosity membranes are helpful in the thin-film microextraction technique [14,15], where the material is incubated with the sample to extract the analytes. Thin-film microextraction minimizes the eluent volume and requires lower sample volumes to provide a good enrichment factor [32].

PNC fibers are used in classical SPME, where the fiber is immersed in the water sample [33] or its headspace [34–36].

PNC monoliths are mainly used in in-tube SPME [37]. In this case, the PNC monolith is *in-situ* synthesized in the inner volume of a capillary [38], and the sample is pumped through this tube to extract the analytes. The porous structure of the monolith guarantees a good sample flow increasing the analyte/sorbent interaction, and the potential integration of this capillary with liquid chromatography provides high enrichment factors [39]. Magnetic PNCs and external magnetic fields have been proposed to improve extraction performance [40,41].

Perspectives, envisioning a more sustainable preparation and application of polymeric nanocomposites

The definition of GAC principles demonstrates that the commitment of Analytical Chemistry to environmental protection goes beyond the simple development of analytical methods and considers all the steps developed in the laboratory. The synthesis of PNCs can be highlighted as a step with a potential environmental impact owing to the solvents and reagents used. Several strategies are envisioned to make this synthesis more sustainable.

The substitution of conventional solvents by environmentally friendly ones is an attractive alternative. Deep eutectic solvents, which can be obtained from natural precursors, have been used to prepare polymers and

NCs [42]. Reducing the solvent requirements is also an exciting option, and mechanochemical synthesis appears as a powerful technique. Mechanochemistry has been used for preparing PNCs in several fields [43] but, in the sample preparation context, it has been scarcely applied for the synthesis of PNCs [44,45] and NCs [46]. The use of natural polymers [19,47] and recycled polymers [48] as precursors in the preparation of PNCs is also a relevant research topic for the near future.

Environmental remediation eliminates pollutants from natural compartments by their simple retention on a solid trap or their degradation by catalytic (photocatalysis, electrocatalysis, or photoelectrocatalysis) processes. PNCs have been widely reported for catalytic degradation [49], and the design of PNCs based on lignocellulosic materials has started to be scrutinized [50].

Conclusions

PNCs are powerful sorbents in microextraction, and their appeal lies in their capacity and versatility. PNCs can be prepared with different compositions (providing several interaction chemistries with the target analytes), properties (magnetic and catalytic), formats (membranes, monoliths, particles, or fibers), and they can also be applied under several extraction workflows (SPME and μ -SPE). PNCs are also attractive because they can be ad-hoc synthesized, sometimes by affordable processes, and adapted to the analytical problem under study. The incorporation of new synthetic approaches and natural materials as precursors is identified as the main trend in the near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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