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Dendrimers based sorbents: Promising materials for analytical extractions

Muhammad Sajid

Center for Environment and Water, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

Dendrimers are macromolecules with highly repetitive branched structures resembling with a tree. Their size, shape, inner core and outer functionalities can be tailored and modified per required molecular design, which encourages their use as a selective extracting phase in analytical extractions. Their multifunctional architecture can provide high selectivity as well as enrichment factors. To date, these materials have been widely used in biomedical applications such as drug delivery, gene and cancer therapy, and tissue engineering. Recently, an emerging trend has been seen for using dendrimers based sorbents in analytical extractions such as solid phase extraction, solid phase microextraction, capillary microextraction, dispersive micro solid phase extraction, and stir-bar sorptive extraction. This review intends to provide a brief overview of this trend to analytical community.

1. Introduction

Dendrimers are macromolecules with highly repetitive branched structures that resemble with a tree. In general, dendrimers have radially symmetrical shape around the core (dendrin). Dendrimers are characterized by their homogeneous and monodisperse structures that are very well-organized like the branches of a tree. They are also known as “cascade molecules” and “arborols” but these names are not as frequently used as “dendrimers” [1].

Properties of the dendrimers are dependent mainly on the functional groups on the molecular surfaces and sometimes on the internal cores. The overall architecture of dendrimers can be built in a careful and controllable manner. As their end groups can be tailored and modified with desired functionalities, dendrimers with a broad range of physicochemical and biological properties can be synthesized [2].

Dendrimer chemistry can be visualized in between molecular chemistry and polymer chemistry. Their step-by-step controlled synthesis has greater resemblance with molecular chemistry while formation of repetitive structure from monomers is related to polymer chemistry. However, dendrimers are different from the conventional macromolecular structures that their synthesis allows formation of monodisperse and highly controllable structures very similar to the molecules in biological systems. Dendrimer chemistry has its own nomenclature. In general, the core molecule is made to react with the monomers that contain one reactive and two dormant groups. This reaction leads to first generation dendrimers. The end groups (periphery) are further activated to react with new monomers to generate next generation dendrimers. The process is repeated step by step leading to increasing generations of dendrimers [3]. In comparison to linear polymers, dendrimers can by synthesized with a better control leading to monodisperse structure that contain a large number of peripheral groups [1]. Dendrimer synthesis allows very controllable tailoring of molecular design parameters such as size, shape, inner core and outer functionalities. There are three main components in a dendrimer structure; core, interior shells (generations) and outer end groups (Fig. 1 shows general structure of dendrimers).

Dendrimers are synthesized either by divergent (inside out) or convergent (outside in) strategy [1]. The most noticeable difference between these two strategies is the direction of the dendrimer growth. In divergent method, dendrimer grows from the core toward the periphery, while in convergent method, it starts from the periphery toward the core. The divergent method employs synthesis from a multifunctional core, which is extended outward by a series of reactions. It allows fast creation of a library of several generation dendrimers owing to the opportunity of ending the reaction at any step or automating the repetitive steps [2]. The other advantages are fast synthesis, use of cost-effective reagents, step wise and exponential growth, and opportunity to prepare

E-mail addresses: msajid@kfupm.edu.sa, analyticalchemist508@gmail.com.

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higher generation dendrimers [5]. In convergent approach, dendrimers are synthesized from small molecules that end up at the surface of the periphery, and reactions continue inward and are ultimately attached to a core. The final generation is predetermined by the size of the dendrons [1]. In this strategy, addition of same dendrons to the different cores (inorganic or organic) leads to a variety of new dendrimers. Moreover, different types of dendrons can be linked together to get a final dendrimer product having properties of a few dendrimers. The synthesis of big building blocks or higher generations is somehow complicated [5]. Most of the commercially available dendrimers are synthesized by divergent method due to its obvious advantages [2].

Dendrimers have shown exciting applications in biomedical research. They have been extensively used in drug delivery, gene and cancer therapy applications [6,7]. They are also considered as ideal candidates for tissue engineering applications [8]. Recently, they are emerging as novel adsorbents for removal of organic and inorganic pollutants from water as well as materials for other water treatment technologies owing to their tunable architectures and thus selectivity [9–41].

The sorbents that can show excellent performance in removal applications due to their reasonably good selectivity and efficiency can also be explored for their potential use in analytical extractions [42]. Therefore, most of the sorbents serve the purpose both in removal and analytical extractions. The selectivity is key factor in both applications; the amount of the sorbent to be used can differ significantly, because removal is an exhaustive process while most of the extractions rely on time dependent equilibrium.

Dendrimers are good candidates as sorbent materials for extraction of inorganic and organic species because.

(i) They are a new class of adsorbents that consist of highly branched exceptional type of macromolecules, with modifiable surface, accessible internal cavities, three-dimensional architecture with high functionality and high capabilities for capturing pollutants.
(ii) They can provide excellent selectivity due to the extended network of peripheral functional groups.
(iii) More importantly, end groups of dendrimers can be tailored per the nature of the target compounds.
(iv) The other sorbents of excellent adsorption capacity owing to their high surface areas can be grafted with dendrimers to increase their selectivity toward certain class of target analytes.
(v) Especially, higher generations of dendrimers possess open and vacuous structures characterized by channels and pockets. In this way, higher generations have greater internal surface area compared with the external surface area. Consequently, third and higher generation dendrimers can be tested for applications where high surface area (both internal and external) is a prerequisite [43].
(vi) Their unique structure and features can open new windows in accomplishing enhanced selectivity, sensitivity, and performance in sample preparations and chromatographic separations.

This is the first article where the potential of the dendrimers as sorbents in analytical extractions have been reviewed. The coming sections are classified based on the type of analytical extraction where dendrimers were employed as sorbents.

2. Solid phase microextraction

Solid phase microextraction (SPME) was introduced by Pawliszyn et al. in 1990 [44]. It provided a new direction to research and development in area of sample preparations. It has been widely used in environmental [45], food [46] and biological analysis [47]. In SPME, a small amount of sorbent material is coated on the fused silica or metal support which can be used for extraction of target analytes from liquids and gases. It can be performed both in direct immersion (DI) or headspace (HS) mode. The target analytes are partitioned between the sorbent and the sample and equilibrium is established after a certain time. After the concentration equilibrium is achieved, further exposure of fiber to the sample will not enhance any extraction. The extraction can take place through absorption or adsorption depending on the extraction phase [48,49]. The extracted analytes are desorbed thermally or by the suitable solvent. It can be coupled/hyphened offline or online with gas and liquid chromatography [50]. If the sorbent and target analytes have good affinity, SPME can provide very high enrichment factors as

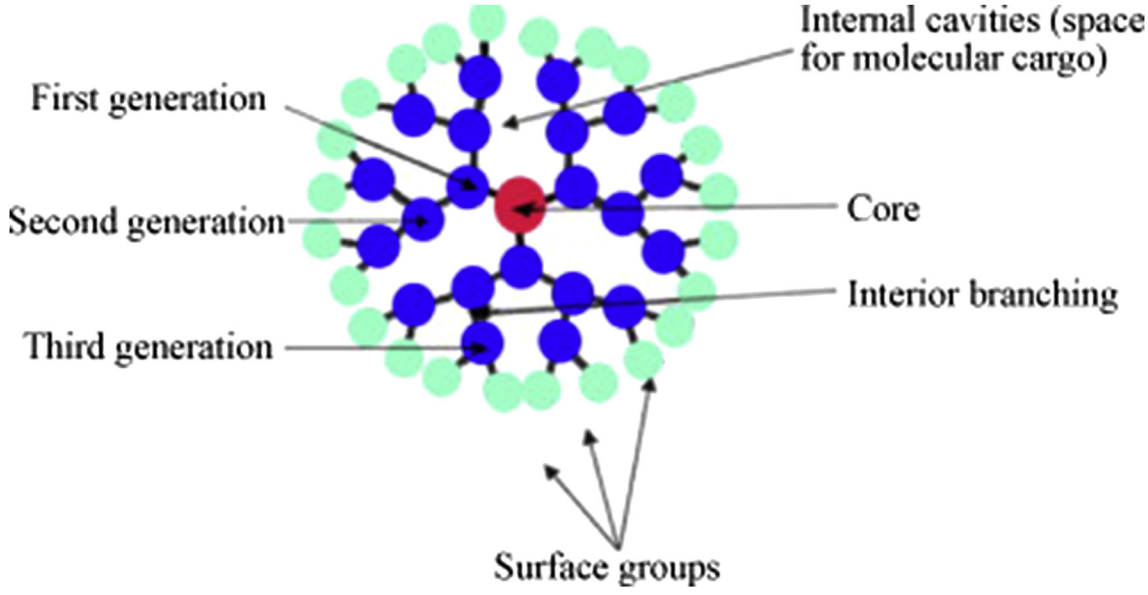

Fig. 1. The general structure of dendrimers.
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