Separation and Purification Technology 191 (2018) 400–423

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Review

Removal of heavy metals and organic pollutants from water using dendritic polymers based adsorbents: A critical review

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ARTICLE INFO

Keywords:
Dendrimers
Adsorption
Water treatment
Heavy metals
Modified adsorbents

ABSTRACT

The contamination of water resources with inorganic and organic pollutants is the greatest challenge of the modern age. These contaminants pose serious health risks to the human health and wildlife. Different strategies have been developed for water remediation to make it clean and reusable, and to meet the increasing demands of fresh water. The adsorption technology is one of the famous strategies for water treatment. The significant efforts have been made over the years to develop highly selective and efficient adsorbent materials. Despite the great achievements, researchers are now focusing on developing the materials that are non-toxic, biocompatible, cost-effective and efficient at the same time. Dendritic polymers are hyperbranched macromolecules with unique three-dimensional structures decorated with a huge number of reactive end groups. They are relatively cheap, less-toxic, easy to functionalize over other substrates and highly efficient. They have been widely employed as adsorbents for removal of inorganic and organic pollutants from water. In this review, we critically reviewed the applications of dendrimers and other dendritic polymers in water treatment, the mechanism of their interaction with target pollutants, the key parameters that affect their performance and finally the opportunities for their future potential in water treatment.

1. Introduction

Fresh water is a basic requirement for the sustainability of human and wild life on the earth. The availability of clean drinking water is paramount to maintain a healthier life. Intensive industrialization and urbanization have resulted in pollution of the natural water resources with inorganic and organic pollutants [1–2]. These pollutants include but not limited to heavy metals, polyaromatic hydrocarbons, and dyes. The toxicity and health risks of these pollutants are well-understood, and their presence in drinking water above a certain limit can pose serious health risks to the human body. This is the reason that removal of these pollutants from water is a great subject of research nowadays [3]. Among different removal technologies, adsorption has been widely adopted [4]. In this regard, a wide range of adsorbents has been studied that include materials based on carbon [5], silica [6], polymers [7], natural adsorbents [8–9], and others. The development of new adsorbents that are cost-effective, efficient, and non-toxic in nature is a hot topic of research in the area of water treatment and purification.

Dendritic polymers are highly branched polymers that contain three-dimensional architectures. They can be classified at least into the following six subclasses based on some structural differences; dendrimers, hyperbranched polymers, multi-arm star polymers, dendronized or dendrigrafts polymers, hypergrafts or hypergrafted polymers, dendritic-linear block polymers [10–12]. Schematic diagram of different classes of dendritic polymers is given in Fig. 1. Among these classes, dendrimers are most widely used for water purification applications. Although other dendritic polymers have also been employed in some reports, most of the authors used term “dendrimer” even for other subclasses of dendritic polymers.

Dendrimers are novel nanostructured synthetic polymers that possess a highly branched structure with a unique three-dimensional molecular configuration and a large number of (reactive) end groups [13–15]. They are complex monodisperse macromolecules with a regular and well-defined chemical structure, and are excellent structurally ordered systems. Their functional groups can react with different functional moieties of other molecules at the nanoscale. This reactivity comes from multifunctional architecture and empty internal cavities. Dendrimers have received special attention for functionalization over various substrates as they possess many superior properties compared to linear polymers. They are unique in their viscosity, density

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http://dx.doi.org/10.1016/j.seppur.2017.09.011
Received 3 June 2017; Received in revised form 1 September 2017; Accepted 5 September 2017
Available online 06 September 2017
1383-5866/

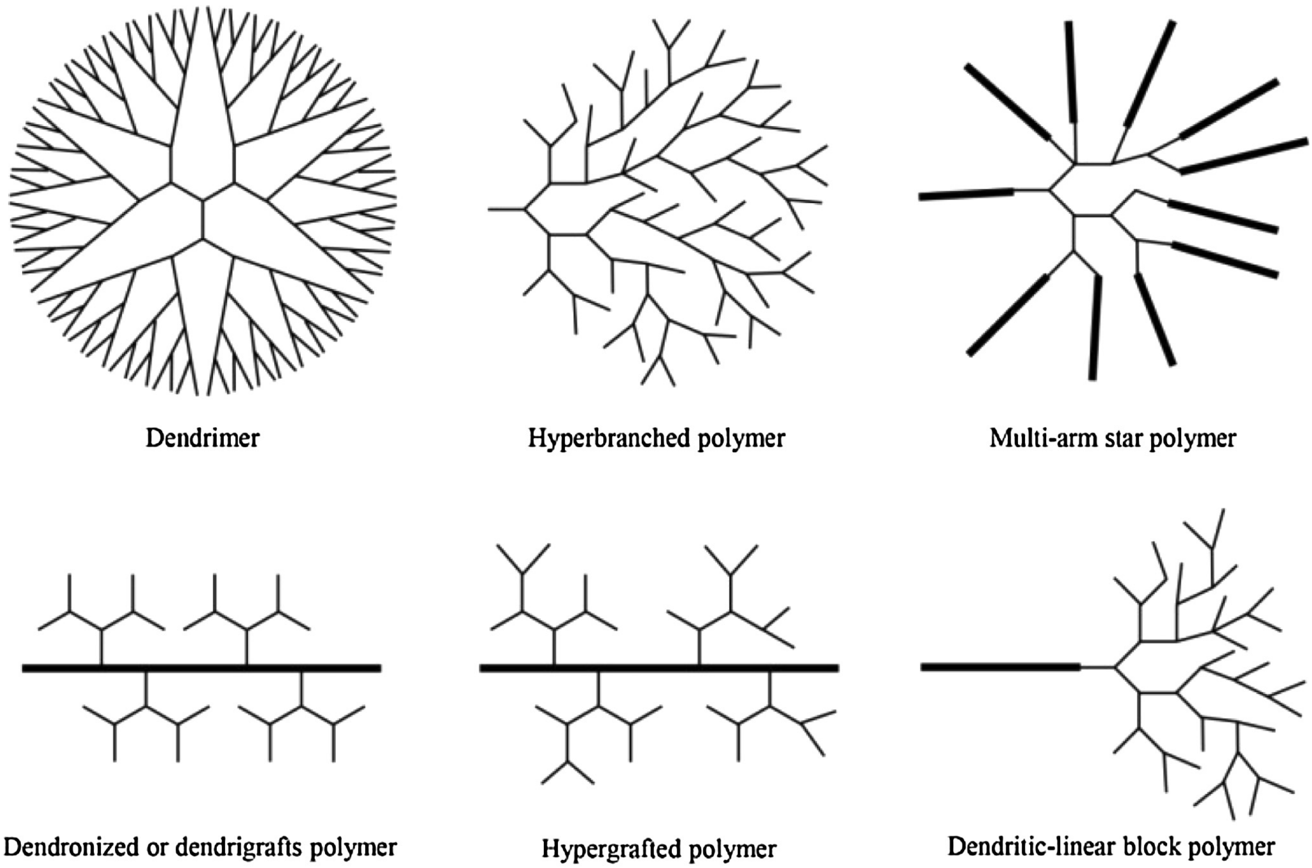

Fig. 1. Schematic description of six subclasses of dendritic polymers. Reproduced with permission from [11]. Copyright (2016) Ivyspring International Publisher.

distribution, and flexibility [16].

Exploration of different applications of dendrimers is still a growing field of research in supramolecular chemistry. They exhibited promising potential to be used in drug delivery [17], tissue engineering [18], bio-imaging [19], catalysis [20], cancer therapy [21], and in many other areas. They have been anticipated as promising adsorbents for the removal and analytical extraction of different pollutants from water. It is their ease of functionalization with different chemical groups and presence of numerous internal cavities that enable them to selectively adsorb the target pollutants. They have a wide range of applications in water treatment particularly as an adsorbent for the removal and extraction of different heavy metals, dyes, and organic pollutants. As analytical extractions and removal rely on the same concept [22], dendrimers have shown some exciting applications in analytical extractions [23–32], but the core of this article is to focus and highlight their applications in the adsorption based removal of pollutants.

The structure of dendrimers is fundamental in understanding their role as adsorbents. Dendrimers basically consist of three major parts (i) interior core (ii) interior branched cells composed of repeating units (generations) (iii) exterior branched cells (the surface functional groups). Among the branches of dendrimers, there are a large number of empty cavities (voids) which can trap or encapsulate pollutants [33]. The presence of such cavities makes dendrimers ideal materials for host-guest chemistry. A general dendrimer structure is given in Fig. 2.

Dendrimers can be considered as excellent adsorbents for removal of inorganic and organic pollutants due to following reasons:

(i) They are highly branched exceptional type of macromolecules, with modifiable surfaces, accessible internal cavities, three-dimensional architecture with highly functionalized exterior.
(ii) They can show high capacities for capturing pollutants due to high external and internal areas and extended network of peripheral functional moieties.
(iii) The excellent selectivity can be expected due to the presence of a large number of desired peripheral functional groups. More interestingly, these functional groups can be tailored per the nature of the target pollutants.
(iv) Controlled modification of core, interior cells, and outer end groups can have a huge impact on their physicochemical properties and thus applications as adsorbents.
(v) Dendrimers can be grafted over high area supports resulting in high selectivity and capacity as well.

Among the dendrimers, poly(amidoamine) (PAMAM) dendrimers are most widely used as adsorbents in water purification. They consist of three basic units including an ethylenediamine core, repeating units, and terminal units. Their synthesis is accomplished by a serial repetition of two reactions: Michael addition reaction of amino groups to the double bond of methyl acrylate, followed by amidation of the resulting methyl ester with ethylene diamine. Notably, each complete reaction sequence outcomes in a new dendrimer generation. By increasing the repeating units, the addition-amidation reaction increases the diameter of PAMAM dendrimers. This increase is roughly 1 nm per generation [35]. PAMAM dendrimers are known as outstanding candidates for different applications of catalysis reactions, molecular recognition, drug delivery and purification. The advantages of using PAMAM dendrimers in removal applications include their non-toxic nature, cost-effectiveness, synthesis from readily available materials and high affinities to interact with target pollutants through a range of phenomenon [36].

This article is focused on applications of dendrimer based adsorbents in the removal of inorganic and organic pollutants from water. The mechanism of adsorption, the role of support and dendrimer structure on adsorption process, and the influence of the main