



## Review

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



Muhammad Sajid<sup>a,\*</sup>, Mazen Khaled Nazal<sup>a</sup>, Ihsanullah<sup>a</sup>, Nadeem Baig<sup>b</sup>,  
Abdalghaffar Mohammad Osman<sup>b</sup>

<sup>a</sup> Center for Environment and Water, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

<sup>b</sup> Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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## 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

\* Corresponding author.

E-mail addresses: [msajid@kfupm.edu.sa](mailto:msajid@kfupm.edu.sa), [analyticalchemist508@gmail.com](mailto:analyticalchemist508@gmail.com) (M. Sajid).

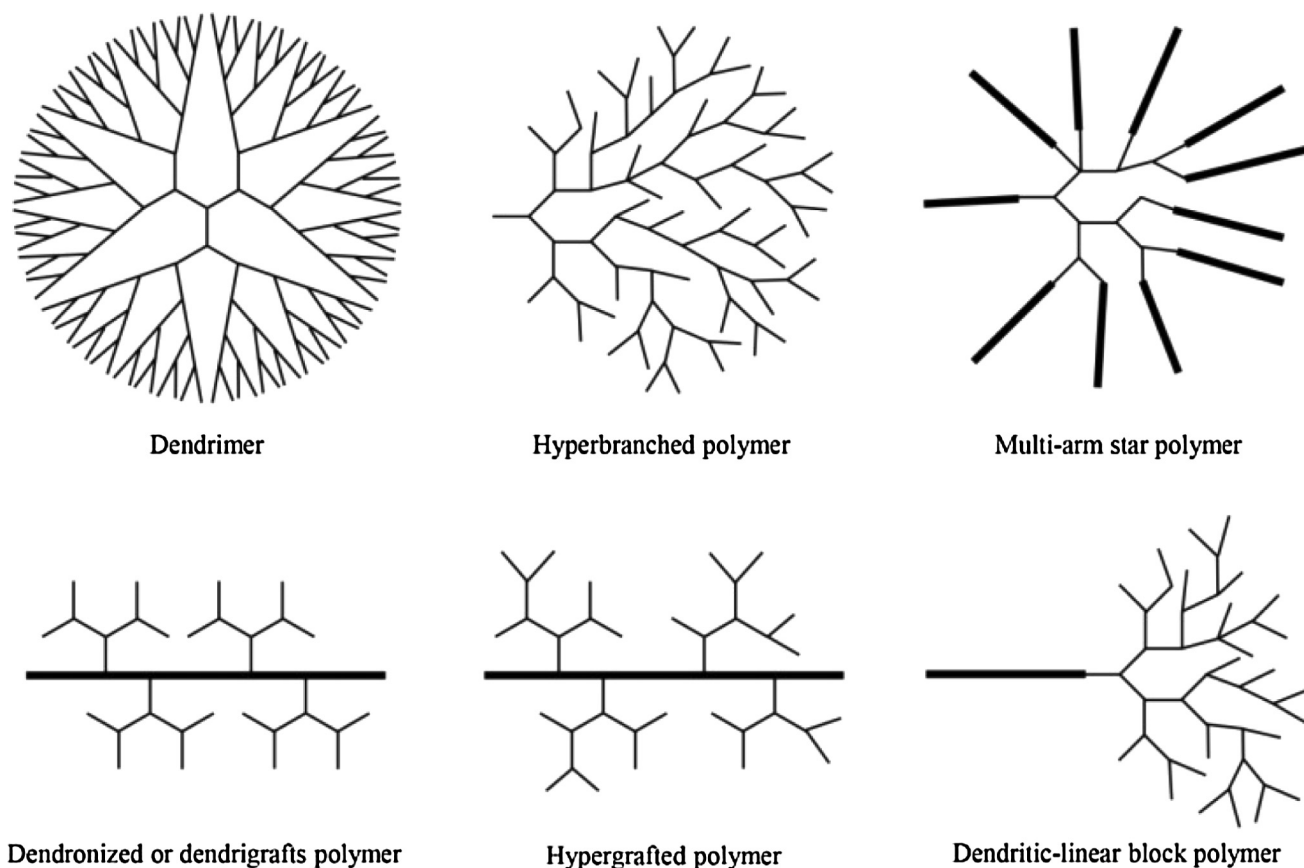


Fig. 1. Schematic description of six subclasses of dendritic polymers. Reproduced with permission from [11]. Copyright (2016) Ivyspring International Publisher.

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

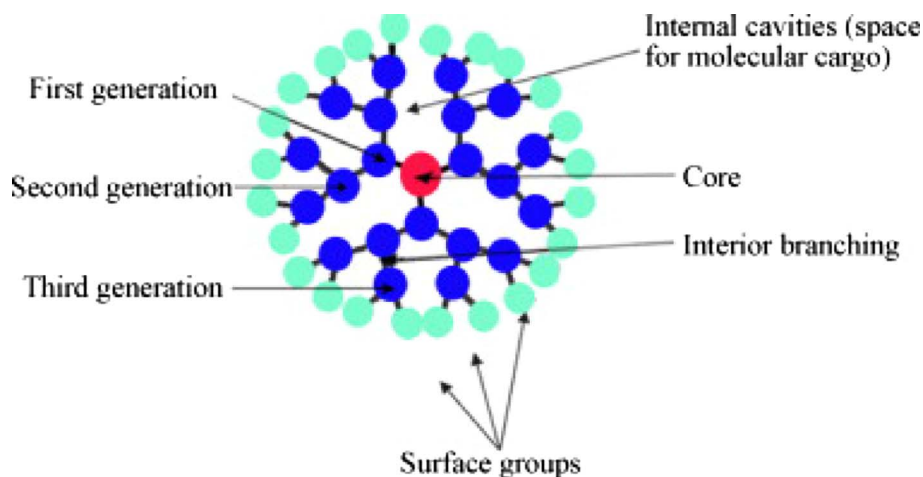


Fig. 2. The general structure of dendrimers. Reproduced with permission from [34]. Copyright (2010) Elsevier B.V.

adsorption parameters is critically reviewed and appraised. At the same time, we avoided establishing separate sections for the description of the toxicity of heavy metals and other pollutants, as it is already well-established and covered in detail in a number of the review articles.

## 2. Adsorption mechanism of various pollutants onto dendrimers

The sorption mechanism of heavy metals, dyes, and organic compounds onto dendrimers based adsorbents is complex. However, electrostatic attraction, chemical interaction and physical adsorption are the most common mechanisms reported in the literature.

### 2.1. Adsorption mechanism of heavy metals

The sorption of heavy metals onto dendrimer modified adsorbents is dependent on the pH. The pH of the solution, from which the metal is removed, plays a major role in the adsorption process and removal efficiency because of its impact on the functional groups on the molecular surfaces of dendrimers on the one hand. On the contrary, it mostly determines the form of metal ions, dye molecules or other pollutants.

Under acidic conditions, amine groups existing in most of the dendrimers could be protonated to form positively charged sites, e.g.  $-\text{NH}_3^+$  groups that adsorb negatively charged ions by electrostatic attraction. For example, hexavalent chromium in the form of  $\text{HCrO}_4^-$ , is efficiently removed by poly (amidoamine)-grafted cellulose nanofibril aerogel (PAMAM-g-CNF) at low pH (nearly 2). At higher pH, it becomes difficult for  $-\text{NH}_2$  to be protonated and the removal capability is declined, while when pH decreases (lower than 2),  $\text{H}_2\text{CrO}_4$  becomes the dominant species which cannot be electrostatically attracted by the  $-\text{NH}_3^+$  groups, leading to decrease of removal capability as shown in

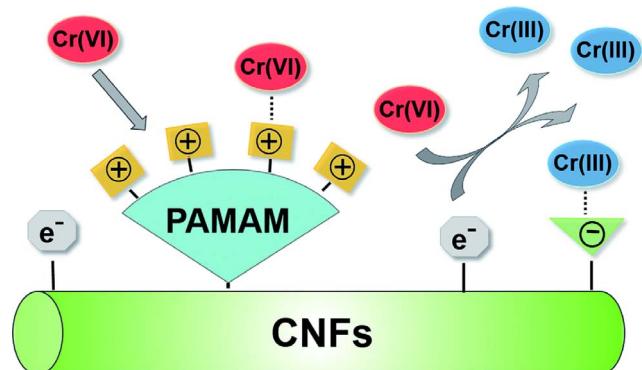


Fig. 3. Proposed mechanism of Cr(VI) removal by PAMAM-g-CNFs. Reproduced with permission from [37]. Copyright (2015) Royal Society of Chemistry.

Fig. 3 [37]. In contrast to Cr(VI), uptake of Pb(II) by chitosan-PAMAM dendrimer decreases at lower pH due to the increase of the overall positive charge on the sorbent surface, which inhibits the approach of positively charged metal cations [16].

The mechanism of metal ions (Cu(II), Ni(II), and Cr(III)) removal by the dendrimer/titania composites is demonstrated in Fig. 4 [36]. Sorption of metal ions ( $\text{M}^{n+}$ ) by generation 4 hydroxyl-terminated PAMAM (G4-OH) involves the transfer of electrons from the tertiary amine in dendrimer to the metal center that is referred as ligand-to-metal charge-transfer. Each metal is coordinated with dendrimer's 62 tertiary amine sites.

In another study, the authors reported that the adsorption Pb(II) ions on dendrimer/titania composites are attributed to the electrostatic interaction between the negative charge on the terminal hydroxyl groups of the PAMAM dendrimers with the positive charges on the metal ions [38]. Similarly, the removal of Zn(II) ions by using dendrimer-conjugated magnetic nanoparticles (Gn-MNPs) mainly involves electrostatic interactions [15].

The adsorption of precious metals (Au(III), Pd(IV), Pd(II) and Ag(I)) by third-generation dendrimers MNP-G3 is reported to a chemisorption process that occurs due to the complexation reaction. The adsorption

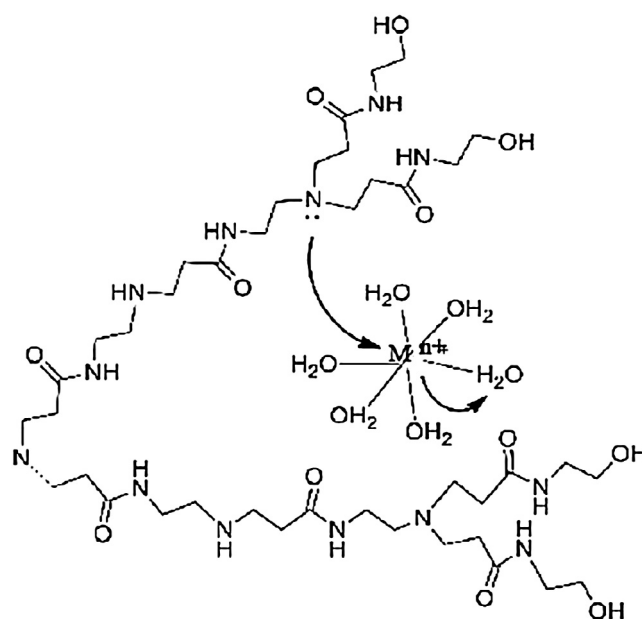


Fig. 4. The conceptual mechanism of metal cations removal by PAMAM dendrimers/titania composites. Reproduced with permission from [36]. Copyright (2013) Elsevier Ltd.

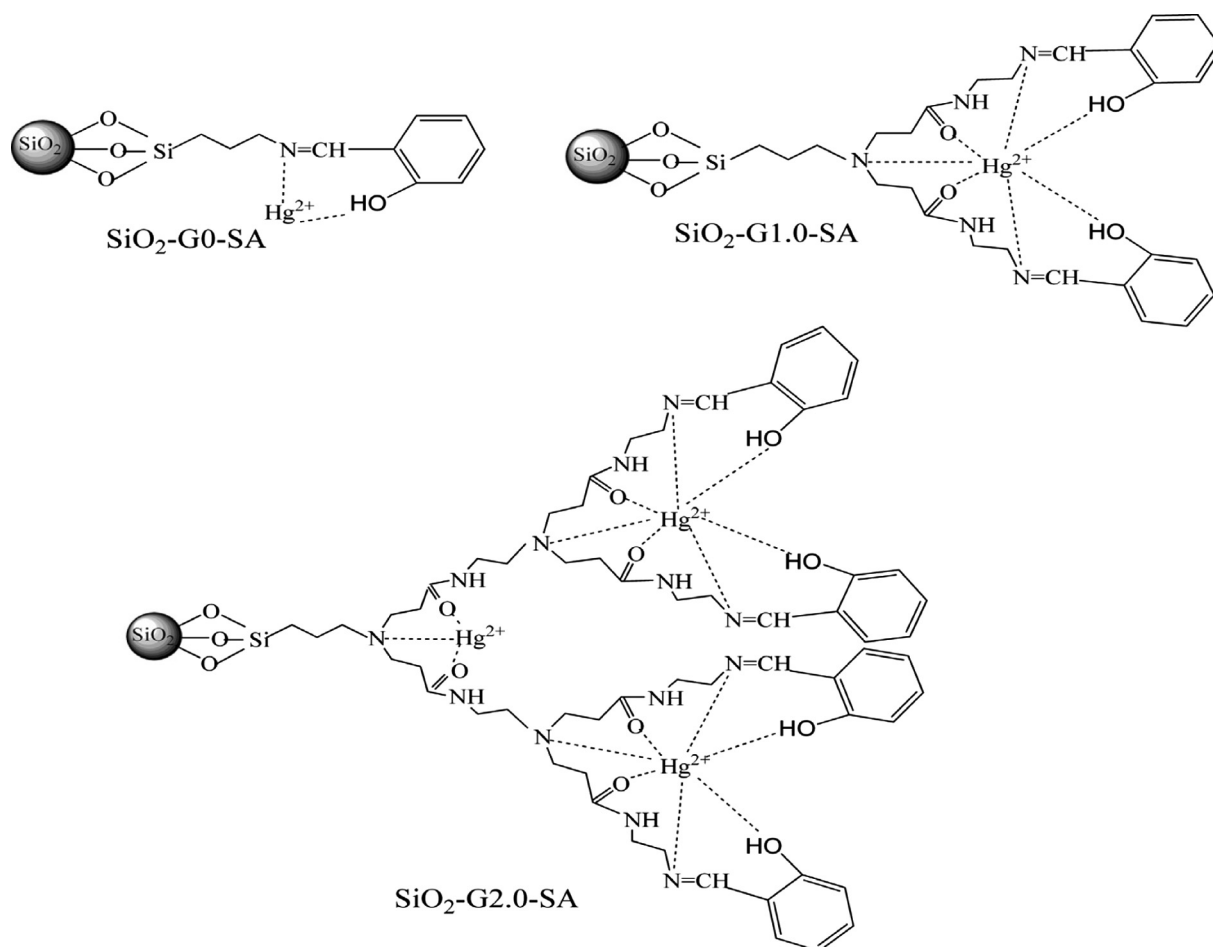


Fig. 5. Proposed chelating mechanism of Hg(II) adsorption onto SiO<sub>2</sub>-G0-SA ~ SiO<sub>2</sub>-G2.0-SA. Reproduced with permission from [40]. Copyright (2014) Elsevier B.V.

efficiency of the dendrimer was reported to enhance after modification with EDTA through the complexation reaction [35]. Adsorption of copper molecules onto poly(amidoamine) dendrimers is reported to involve a number of mechanisms including complexation with interior donor atoms and terminal donor atoms, electrostatic interactions with charged terminal groups, and physical encapsulation [39].

One study reported the application of density functional theory (DFT) method to explore the adsorption mechanism of Hg(II) ions removal by silica gel supported salicylaldehyde modified PAMAM dendrimers (SiO<sub>2</sub>-G0-SA ~ SiO<sub>2</sub>-G2.0-SA) [40]. According to the schematic shown in Fig. 5, mercury ions may interact with dendrimers by a chelating mechanism involving nitrogen and oxygen groups. In addition to the chelating interaction, it might also involve the weak Hg(II)- $\pi$  interaction. The values obtained from Dubinin-Radushkevich (D-R) isotherm model suggest that the removal of Hg(II) was carried out by a chemical mechanism. The thermodynamics studies confirmed that the adsorption endothermic and processes were spontaneous in nature.

## 2.2. Sorption mechanism of dyes

The sorption of dyes is strongly dependent on pH. In general, for anionic dyes, the maximum adsorption is reported at low pH, while for cationic dye, high pH is desirable for maximum uptake. The adsorption of the anionic dyes Direct red 23 (DR23) and Direct red 80 (DR80) on to cotton fabric grafted with PPI dendrimers increases when the pH of the solution decreases [41]. In contrast, the maximum adsorption of the cationic dye Basic Blue 9 (BB9) took place at high pH (around 11) [42].

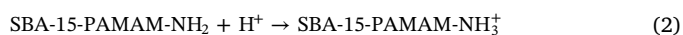
### 2.2.1. Anionic dyes

The adsorption of anionic dyes on dendrimers based adsorbents could be explained by the ionic interactions between the dye molecules and adsorbent surface.

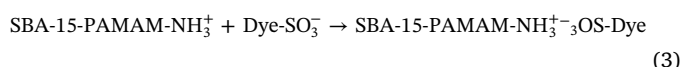
The adsorption of AB62 on the surface SBA-15 functionalized with PAMAM dendrimer is reported in a recent study [43]. It is reported that various mechanisms might involve in the adsorption AB62 onto the surface of SBA-15/PAMAM surface including ionic attraction between the dendrimer's cationic amino end groups and anionic sulfonate groups of dissolved AB62. The proposed mechanism of AB62 adsorption on SBA-15/PAMAM is illustrated in Fig. 6. The AB62 is dissolved and form sulfonate groups (D-SO<sub>3</sub>Na) according to the reaction.



On the other hand, the amino end groups of the dendrimer (PAMAM) on the silica surface (-NH<sub>2</sub>) are protonated.



Finally, the electrostatic interactions take place leading to the adsorption of dye molecules.



Beside electrostatic interactions, hydrogen bonding might also contribute to the adsorption of dye molecules on the dendrimer surface.

Similarly, the adsorption of anionic dye (Direct Red 80) on cotton fabric grafted poly(propylene imine) (PPI) dendrimers mainly involves electrostatic attraction [42]. In the acidic pH range, the attraction between the primary amine groups (-NH<sub>2</sub>) and the tertiary amine groups

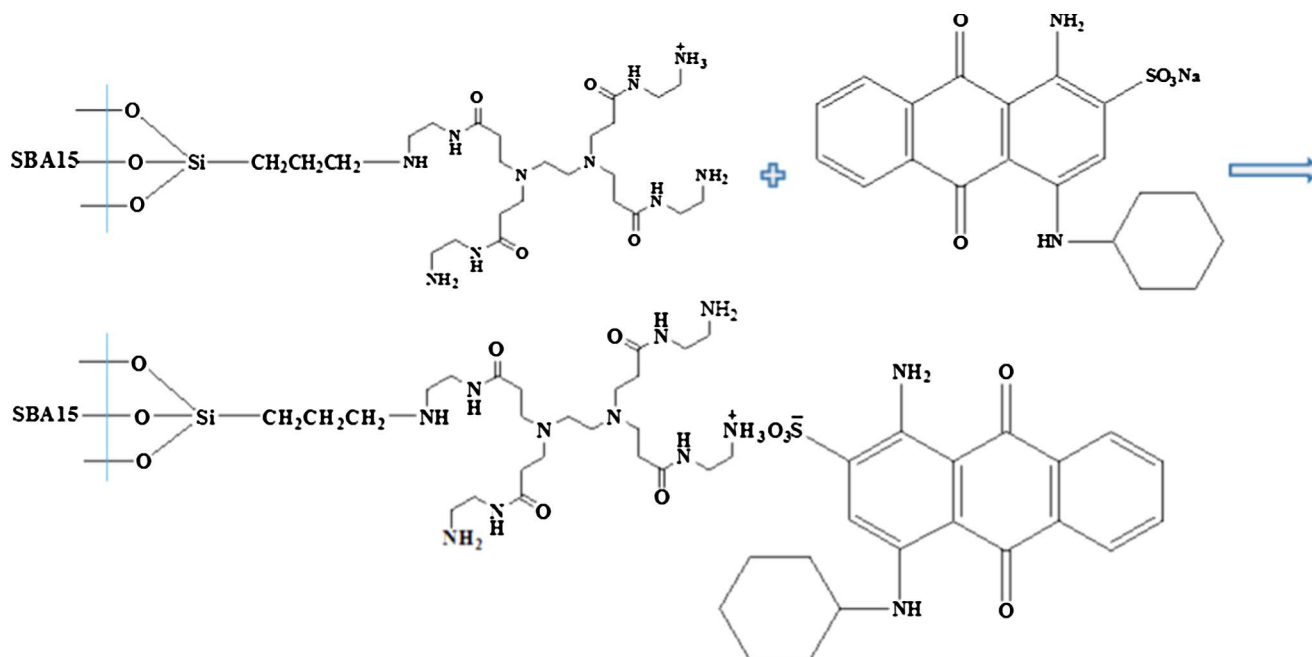


Fig. 6. Illustration of adsorption mechanism of AB26 on SBA-15/PAMAM. Reproduced with permission from [43]. Copyright (2017) American Chemical Society.

( $\text{N}^-$ ) of the dendrimers and the polar molecule ( $\text{R-SO}_3^-$ ) of the Direct Red 80) are mainly responsible for dye adsorption. Furthermore, the void cavities) among the branches dendrimers also capture some dye molecules. Hydrogen bonding between the PPI dendrimers and functional groups of the dyes might also play a role in dye adsorption of dye.

The adsorption of DB78 and AB26 dyes by PPI dendrimers are also explained by electrostatic attraction and encapsulation mechanism (dye molecules encapsulated by the PPI dendrimer) [44].

The adsorption of DB86 and DR23 by carbon nanotubes modified poly propyleneimine dendrimer (CNT-Den) is strongly pH dependent [45]. The maximum removal of both the dyes was reported at pH 3. Both DB86 and DR23 dyes are polar molecules. In aqueous solution, the sulfonate groups are dissociated and converted into anionic dye ions, according to the reaction.



On the other hand, the amino groups of CNT-Den were protonated under acidic condition according to the following reaction:



The protonation of  $-\text{NH}_2$  groups at pH 3 favors the adsorption of direct dyes. Above the optimum pH value, the lower protonation of amino groups existing in CNT-Den decreases the uptake values.

The mechanism of direct blue 78 (DB78) and direct red 80 (DR80) adsorption by Dendrimer–titania nanocomposite is investigated by the application of Dubinin–Radushkevich (D-R) isotherm model and thermodynamic data [46]. From the value of isotherm constant and thermodynamic parameters, it was postulated that physical mechanism is dominating the adsorption process. Removal of Reactive Blue 21 onto magnetic chitosan microparticles functionalized with polyamidoamine dendrimers mainly involves diffusion as a dominant mechanism during the adsorption process [47].

### 2.2.2. Cationic dyes

The adsorption of cationic dye (Basic Blue 9) on cotton fabric grafted poly(propylene imine) (PPI) dendrimers is reported [42]. The dye molecules were not adsorbed onto the dendrimers at acidic pH. This is due to electrostatic repulsions between the dye molecules and positively charged groups of the grafted cotton fabric ( $-\text{NH}_3^+$  or  $>\text{NH}^+-$ ). The adsorption was found to increase with increase in pH, and

maximum adsorption was recorded at pH 11, as shown in in Fig. 6. It was reported that in addition to the electrostatic interactions at high pH, hydrogen bonding and dye molecules trapped in the cavities of the PPI dendrimers also contribute to the adsorption of dye.

### 2.3. Sorption mechanism of organic compounds

It has been noticed that the removal of phenol from wastewater by PAMAM/titania nanohybrid dendrimers is not pH dependent and the removal efficiency is not affected significantly by varying the pH of solutions. This behavior is explained by the possible electrostatic interactions between negatively charged titania and the positively charged dendrimer and by the hydrogen bonding formed between phenolic hydroxyl groups adsorbed on titania surface and terminal amino groups of the polyamidoamine. These interactions prevent the interaction between amino and phenol molecules at varying pH values. The removal may be attributed to the encapsulation of phenol molecules in the internal cavities of dendrimer and Van der Waals attraction rather than adsorption [48].

## 3. Removal of heavy metals

This section reviews the applications of dendrimers based adsorbents for removal of the heavy metals. The dendrimers are classified based on the support material they were immobilized, and under the same classification, their removal applications are discussed.

### 3.1. A note on the support materials for dendrimers immobilization

The dendrimers have distinct properties in their symmetrical structures such as their branch flexibility and intermolecular interactions with ionic or neutral molecules. Therefore, they can be easily and more efficiently integrated/immobilized with other inorganic (i.e. Titania, ceramic, mesoporous silica and magnetic nanoparticles and silica gel) or organic materials (i.e. chitosan, polystyrene, poly-tetrafluoroethylene, carbon nanotubes and graphene oxide) to enhance the mechanical strength and surface area of the composite, which can be used for efficient removal of heavy metals.

The usefulness of any adsorbent can only be proved if it demonstrates cost-effectiveness in the overall process of removal. The

collection of the dispersed loaded adsorbent from the effluent is a challenge. The support sometimes facilitates the removal of the adsorbent from the effluent and makes it reusable. To achieve this target, sometimes magnetic properties are introduced into the adsorbent to make regeneration and separation process easy by facile removal of adsorbent. For this purpose, the iron based magnetic nanoparticles were frequently used to impart the magnetic properties to the adsorbent. Magnetic nanoparticles can be prepared in large quantities through simple preparation procedures. Amine-functionalized magnetic-cored dendrimer was used for removal of heavy metals. The adsorbent could be separated magnetically after removal of the metal and during regeneration [49]. Chih-Ming Chou and Hsing-Lung Lien introduced the dendrimer-conjugated magnetic nanoparticles for removal of Zn(II) from aqueous solutions. Due to magnetic nanoparticles support, the developed dendrimer was recovered and reused effortlessly [15].

The other support materials include silica gel and carbon. Silica support has high hydrophilicity due to the presence of silanol group which enhances the adsorption capacity [50]. For mercury removal, silica-gel-supported sulfur-capped PAMAM dendrimers were used [51]. Carbon based materials are useful adsorbents. Mesoporous carbon incorporated with nitrogen proved efficient material for removal. Further functionalization of the mesoporous carbon nitride with amine dendrimers enhanced its selectivity and adsorption capability [52]. The support materials are used to perform one or more of the following functions:

- (i) To provide surface for the attachment of the different functionalities.
- (ii) To remove/separate and recover loaded adsorbent from effluent.
- (iii) To regenerate the adsorbent in a facile way.
- (iv) To provide mechanical stability to the adsorbent.
- (v) Supports also act as adsorbents which enhance the adsorption process.
- (vi) Support enhances the surface area of the adsorbent.

### 3.2. Dendrimers supported on titania

An inorganic supporting material titanium oxide  $\text{TiO}_2$  was modified by generation 4 of polyamidoamine (PAMAM) dendrimers having ethylenediamine as cores (G4-OH) and used in the remediation of Cu(II), Ni(II), and Cr(III) from simulated wastewater [36]. The schematic of immobilization is shown in Fig. 7.

One interesting fact was noted related to the BET surface area of titania that remained same before and after modification with PAMAM, but the removal efficiency after the modification was much enhanced. This is attributed to the presence of ternary amine functional groups in

dendrimer structure; those can make an efficient complexation with metal cations. Another most interesting thing in PAMAM/titania composites is its ability to remediate Cu(II), Ni(II), and Cr(III) over a wide concentration range from a mixture, with high removal efficiency in shorter times at pH 7 and 9. Also, there was an improvement in the removal of  $\text{Ni}^{+2}$  from the mixture ions compared to its removal from a single system. This can be attributed to the enhancement of association of Ni complexes in the presence of other two metals cations (Cu(II) and Cr(III)).

Fig. 4 shows the suggested mechanism of the removal of metals cations using dendrimers/titania composite as an adsorbent.

Similarly, titania/PAMAM composite was used for removal of Pb(II) ions, and it showed an adsorption capacity of 400 mg/g [38].

Castillo et al. investigated the removal rate and oxidation state of Ni and Fe from model wastewater solution using generation 4 of PAMAM terminated with a hydroxyl group (G4-OH). They also studied the effect of immobilization of G4-OH on titania supporting materials and its chelating ability on the Ni(II) removal. It has been found the rate of complexation and interaction of tested cations follow the trend of Ni(II) > Fe(III) > Fe(II) which is attributed to the metal ions d-electron configuration and the charge density. Also, the ability of Ni(II) complexation to free PAMAM dendrimer is seven times better than its complexation to PAMAM dendrimer immobilized on a titania support. They explained that to two main reasons, the first one is due to the diffusional limitation within the titania's pores and the second is because of decreasing the flexibility of the PAMAM dendrimer which leads to increase the constrain to accommodate metals ions [53].

### 3.3. Dendrimers supported on silica

Ordered nanoporous silicas are materials well-known due to their large surface area, excellent physicochemical stability, uniform pore size distribution, long-range homogeneity of texture and ease of surface functionalization. Within these materials, SBA-15 has a larger uniform pore size that provides sufficient room for functionalization. In addition to that its thick silica walls exhibit enhanced hydrothermal stability compared to analogous materials. Owing to this, SBA-15 can be used as a reliable support for generation of selective adsorbents. Interestingly, metal cations in aqueous solutions can efficiently diffuse onto the pores of SBA-15 leading to physical and chemical interactions between sorbate and sorbent and play some role in heavy metal removal. The open-end pores in SBA-15 and its hydrophilic surface is somehow responsible for this. The performance of SBA-15 as an adsorbent can be improved through effective immobilization of desired functionalities over it. Shahbazi et al. employed the functionalized SBA-15 mesoporous silica by melamine-based dendrimer amines for the adsorption of Cd(II), Cu

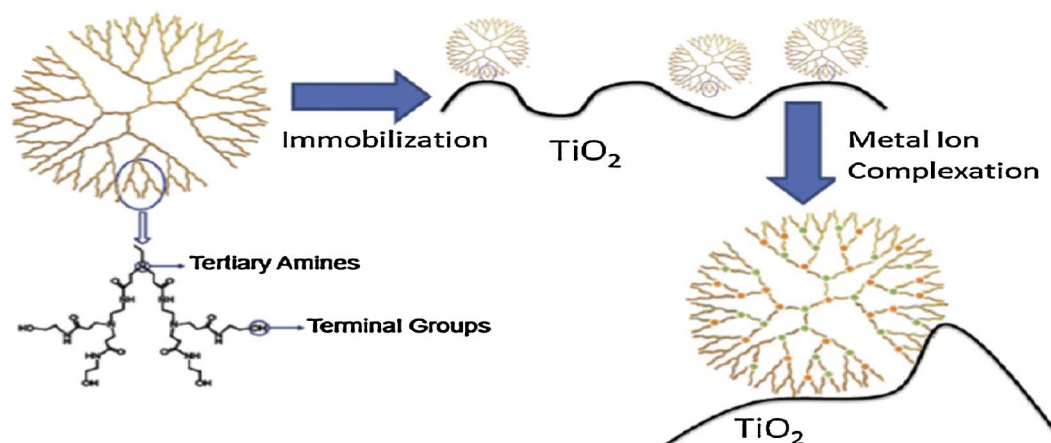


Fig. 7. The synthesis strategy to immobilize G4-OH dendrimers on titania to achieve dendrimer/titania composites. Reproduced with permission from [36]. Copyright (2013) Elsevier Ltd.

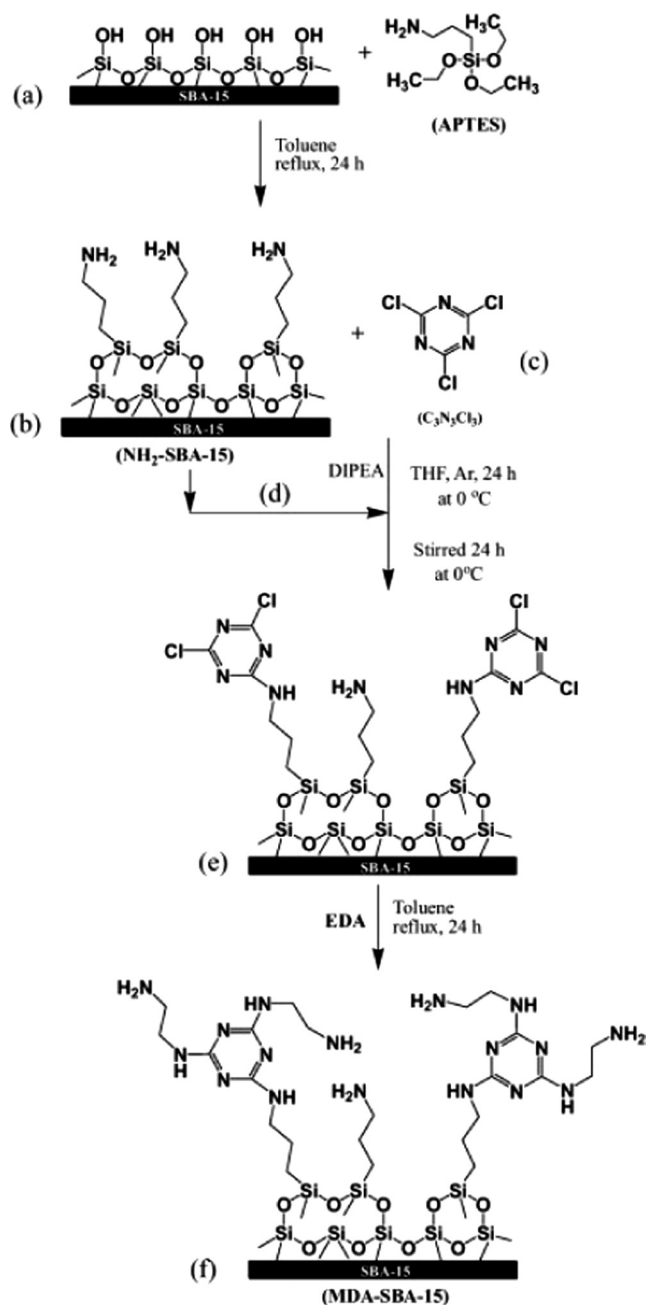


Fig. 8. Schematic representations of synthesis of melamine-based dendrimers amine-functionalized SBA-15 (MDA-SBA-15). Reproduced with permission from [14]. Copyright (2010) Elsevier B.V.

(II) and Pb(II) in fixed bed column and batch system. Fig. 8 shows the schematic illustration of melamine-based dendrons amine-functionalized SBA-15 (MDA-SBA-15) synthesis [14].

The removal experiments were performed at ambient temperature. The effect of metal ions concentration, solution pH, contact time and the adsorbent dose was studied on the removal of heavy metals in batch experiments. It was observed that the removal of metals increases while increasing the pH from 2 to 4, and decreases at the pH > 4. The nonlinear Langmuir and Freundlich adsorption isotherms were used to predict the absorption behavior. However, the correlation coefficient value was lower for Freundlich model than Langmuir model. The maximum adsorption capacity ( $q_m$ ) was determined as 98, 126 and 130 mg/g for Cd(II), Cu(II) and Pb(II), respectively. The results obtained from the experiments showed that bed height, flow rate, and initial metal ion concentration are critical parameters that affect the

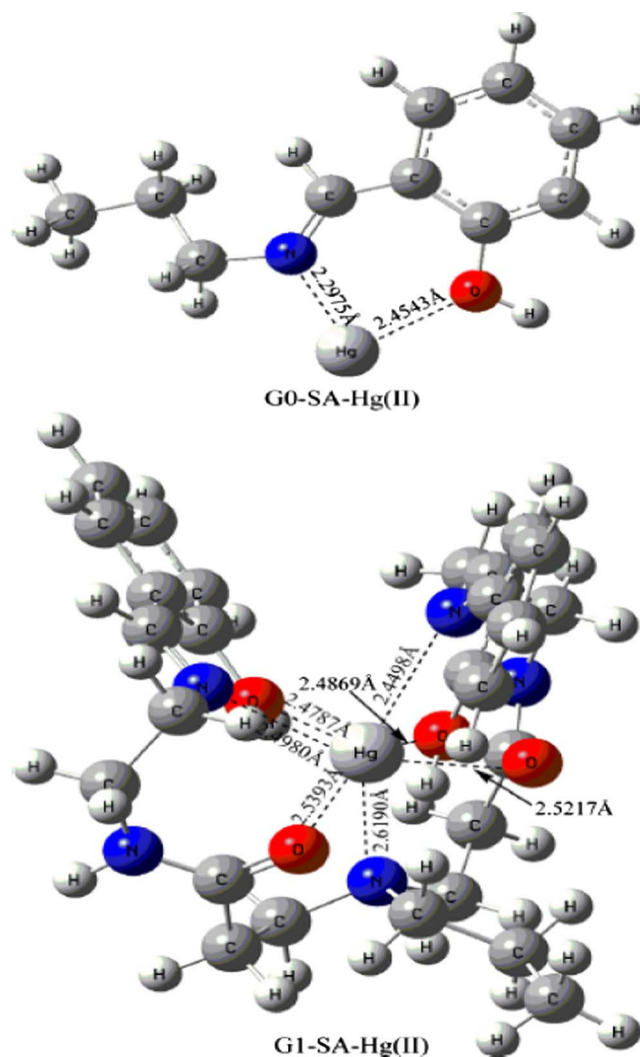


Fig. 9. The B3LYP/6-31 + G(d) (LANL2DZ for metal ion) optimized geometries of the complexes G0-SA-Hg(II) and G1-SA-Hg(II) with the atomic numbering. Reproduced with permission from [40]. Copyright (2014) Elsevier B.V.

removal of Cd(II), Cu(II) and Pb(II) ions.

Due to the simplicity of preparation, the mechanical, chemical and thermal stability as well as the rapid adsorption kinetics, silica gel is an excellent supporting material for immobilization of other adsorbents. PAMAM dendrimers adsorbent with salicylaldehyde modified silica gel (SiO<sub>2</sub>-G<sub>n</sub>(n=0,1 or 2)-SA) was synthesized for removal of Hg(II) [40]. The nitrogen and oxygen containing groups in PAMAM dendrimer and salicylaldehyde structures respectively, play the main role in the removal of Hg(II) by the chelating mechanism through its ionic interaction and  $\pi$  interaction with these functional groups. The surface area, a pore volume as well as the pore radius of silica gel decreased after the modification with PAMAM dendrimer, the same trend was observed with increasing PAMAM dendrimer's generation number, which could be attributed to the formation of dendrimers in the silica gel pores. In the same study, the coordination geometry of the formed complex between Hg(II) and the dendrimer was investigated further by computational DFT method. As shown in Fig. 9, the nitrogen and oxygen atoms in the G0-SA behave as a bidentate ligand forming a five-membered ring complex with Hg(II). The bond length between Hg and N was shorter than Hg and O which indicates the stronger interaction between Hg and N.

Niu et al. also removed Hg(II) using silica-gel-supported sulfur-capped PAMAM dendrons. The developed adsorbent was found 100% selective for Hg(II) in the presence of Fe(III), Cd(II), Ni(II), and Zn(II).

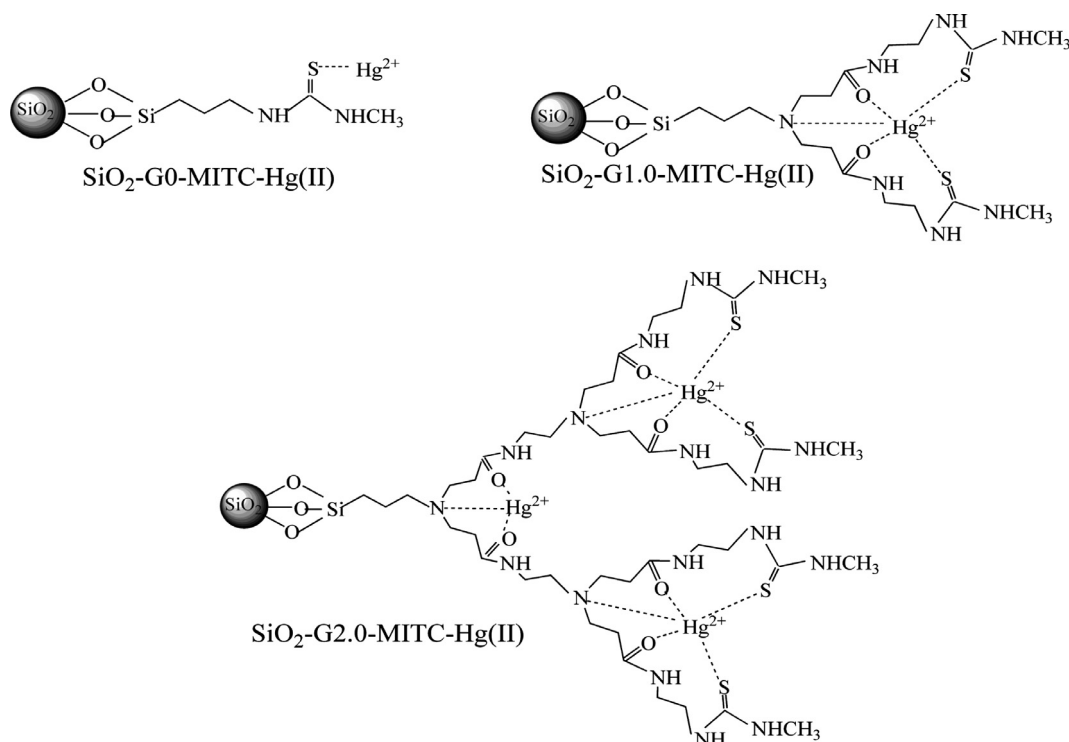


Fig. 10. Proposed chelating mechanism of SiO<sub>2</sub>-G0-MITC – SiO<sub>2</sub>-G2.0-MITC with Hg(II). Reproduced with permission from [51]. Copyright (2016) American Chemical Society.

The selectivity towards Hg(II) is well-interpreted by HSAB theory. This due to the excellent selectivity, affinity and the adsorption capability of sulfur containing ligands for Hg(II) in the presence of other ions. The Hg(II) with various generations of the synthesized dendrimers could be observed in Fig. 10 [51].

Arkas et al. reported the application of hyperbranched poly(ethylene imine) with silicic acid for the removal of metal ions Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Hg(II), Cd(II) and Pb(II) from water [54].

### 3.4. Dendrimers supported on magnetic supports

Magnetic supports have also been utilized for functionalization of dendrimers. Magnetic particles based separations provide better phase separation and avoid many steps like centrifugation or filtration for post-removal collection of adsorbent. The combination of magnetic nanoparticles not only facilitates the facile separation of the adsorbent but also significantly enhances the adsorption capability. It also avoids generation of secondary waste from used nanoparticles. Chou et al. reported the removal of Zn(II) from aqueous solutions in a batch system by using dendrimer-conjugated magnetic nanoparticles (G3-MNPs) as an adsorbent. The maximum adsorption capacity was 24.3 mg/g at pH 7 and 25 °C, as predicted by the Langmuir model. Interestingly, the adsorbent can be easily regenerated using an aqueous solution of 0.1 M HCl. It was found that the original removal capacity of Zn(II) by G3-MNPs was retained even after ten consecutive adsorption–desorption cycles [15].

In another report, third generation dendrimers were formed on the surface of magnetic nanoparticles (MNP-G3) and used for the adsorption of precious metals such as Pd(IV), Au(III), Pd(II) and Ag(I). The higher valence precious metals (Pd(IV) and Au(III)) demonstrated better adsorption compared lower valence metals (Pd(II) and Ag(I)). It is indicated that adsorption of precious metals on the MNP-G3 is dependent upon their valence. The regeneration of the adsorbent was attained using 1% HCl solution [35].

Similarly, PAMAM was used for the grafting of dendrimers on the surface of magnetic silica nanoparticles. It was applied for the removal of Hg(II) and MeHg(I). Hg(II) and MeHg(I) are considered highly toxic,

and exposure to them could cause neurological and immunological disorders. The surface activity of PAMAM grafted magnetic silica nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-PAMAMs) for the removal of Hg(II), and MeHg(I) was improved by immobilization of herring sperm DNA fragments using Coulomb attraction on the surface of the nanocomposite. Herring sperm DNA performed its function as mercury removal reagent. Due to the presence of some residual surface hydroxyl groups, Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> nanoparticles itself can adsorb Hg(II) or MeHg(I). The surface of the nanoparticles become positively charged due to their grafting with PAMAMs and higher generations of dendrimer further increase the density of the amine groups leading to further enhancement of the positive charge. In this case, the adsorbate removal capacity of adsorbent will decrease due to the amine groups which shield negatively charged surface hydroxyl group of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> nanoparticles, and moreover it displays coulombic repulsion to the adsorbate. As a result, the adsorbate moieties are exhibiting poor interaction with the interior tertiary nitrogen. Due to the reasons above, the Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-PAMAMs removal performance for Hg(II) and MeHg(I) was poor. The removal efficiencies were significantly improved by immobilization of DNA on the surface. The presence of primary amine groups in higher generation PAMAMs not only enhances immobilization of DNA but overall removal efficiency of the adsorbent [55].

Magnetic core dendrimers were also used for the removal of other heavy metals such as Pb(II) and Cd(II). The dendrimers on the surface of magnetic nanoparticles were terminated using amine group (MD). The pH has shown significant effect on the adsorption of the heavy metals and the regeneration of the adsorbent. The Pb(II) and Cd(II) adsorption on the MD increased as the pH increased. It is due to the competition between the metal and the H<sup>+</sup> ions. With increase in pH, this competition decreases due to lesser H<sup>+</sup> ions. Although, high pH facilitates the better adsorption of the metal ions, but at pH above than 5 the Pb(II) and Cd(II) precipitate as their respective hydroxides. The adsorption and desorption process is explained in Fig. 11. The affinity of the Pb(II) toward the sorbent was greater compared to Cd(II) just because Pb(II) is exhibiting higher Pauling electronegativity than Cd(II) and showing higher affinity towards lone pair of the nitrogen of the dendrimer amine group. The adsorbent can be regenerated using HCl as



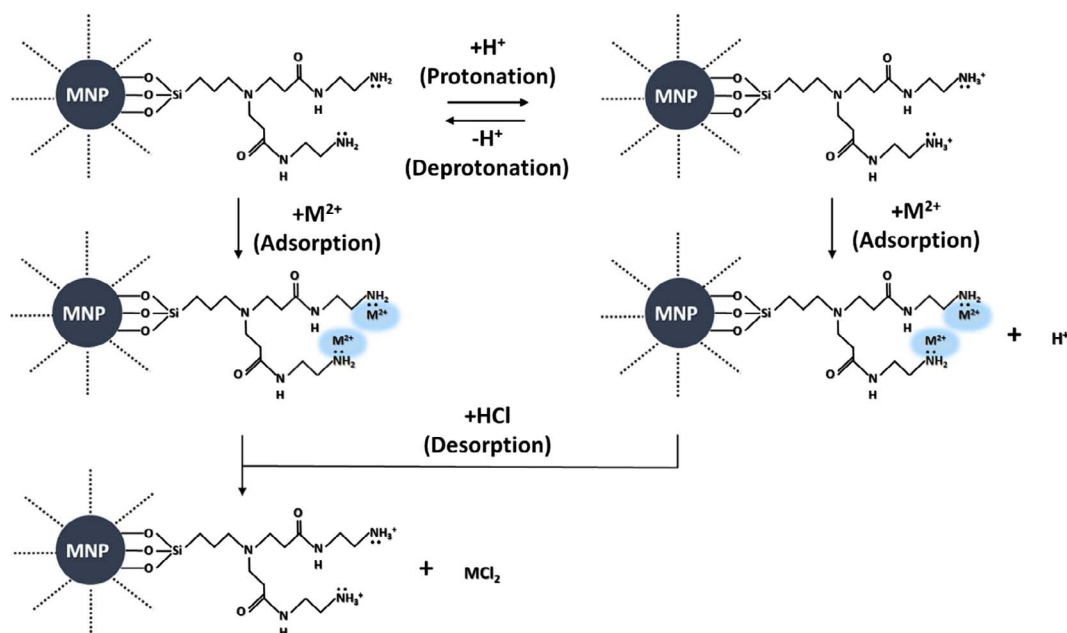


Fig. 11. Schematic diagram of metal ion adsorption to MDs. Reproduced with permission from [49]. Copyright (2016) Springer Science + Business Media New York.

an extracting reagent. Approximately, 80% adsorption capability of the adsorbent retained after 7 regeneration cycles. In acidic medium, the leaching of iron from the magnetic core and the impairment of the dendrimer branches actually affect the adsorption capability and the stability of the adsorbent [49].

Likewise, Pourjavadi et al. synthesized magnetic nanocomposite dendrimer, which was applied for the removal of lead ions in aqueous solution. For this purpose, PAMAM graft-poly(methyl acrylate) magnetic nanocomposite was produced. The dendrimer magnetic nanocomposite was synthesized using radical methyl acrylate polymerization and later the methyl ester group was functionalized with PAMAM dendrimer. The synthesized adsorbent has great tendency to adsorb lead ions and it can adsorb 310 mg/g of lead ions. The strong interaction between the metal ions and PAMAM-graft-poly(methyl acrylate) magnetic nanocomposite was observed. At lower pH, it has less adsorption tendency due to protonation of the surface, in other words, the competing behavior between  $H^+$  and the  $Pb(II)$ . The optimum pH range was found 5–6, as above that lead ions precipitated as hydroxide. The synthesized dendrimer exhibited good reusability for the three cycles after that the adsorption capability reduced [56].

Zhou et al. tested the performance of modified magnetic nanoparticles with PAMAM dendrimer ( $MNP-G_n$ ) for adsorptive removal of reactive black 5 (RBk5) dye from solution. The highest adsorption capacity was 70.423 mg of RBk5/g of  $MNP-G_3$ . Moreover, they found the rate of adsorption decreases with the increase of the initial concentration of RBk5. They attributed that to the larger availability of vacant adsorption sites when the concentration of RBk5 adsorbate is low [57].

### 3.5. Dendrimers supported on carbon based materials

Due to large surface area and presence of oxidized functional groups, graphene oxide (GO) has exhibited excellent adsorption properties for organic and inorganic pollutants. Recently, research has focused on functionalization of GO to further enhance its adsorption capacity and selectivity toward certain target pollutants.

Selenium is a trace nutritional element. It can be toxic if consumed in excess. The toxicity of the elemental and the metallic selenides are relatively low whereas the selenite and selenate are highly toxic. Various adsorbents are being applied to remove  $Se(IV)$  and  $Se(VI)$ . The removal of  $Se(VI)$  is more challenging, and low adsorbent capability is shown by some adsorbents. Xiao et al. synthesized the dendrimer

functionalized graphene oxide which was found good for removal of  $Se(VI)$ . The facile functionalization of the graphene oxide is due to the presence of numerous functional groups on the basal plan. Functionalized graphene oxide can be used for efficient contaminant removal due to the huge surface area and the presence of functional groups. The different generation dendrimers were synthesized by functionalizing the graphene oxide with PAMAM. These adsorbents were added into the solution containing  $Se(IV)$  or  $Se(VI)$ . The supernatant was collected after 24 h, and the concentration of the Se ions was analyzed by ICP-MS. The maximum adsorption capability was observed for  $Se(IV)$  and  $Se(VI)$  by adsorbent GO-G3 and GO-G4, respectively. It was observed that  $Se(VI)$  adsorption more depends upon the presence of the amine group. The simulated waste water results revealed the removal capability of the synthesized adsorbent was improved as the dendrimer generation increased. PAMAM-GO was exhibiting greater selectivity towards  $Se(VI)$ . Interaction of the selenite and selenate ions with GO-G4 is electrostatic in nature and mainly depends upon the initial pH. At lower pH, the primary and tertiary amine group remain protonated and provides more active sites for the binding of the negative charge selenium ions while higher pH the amine group deprotonated. The adsorption capability of the GO-G4 was more than magnetic graphene oxide and the graphene oxide itself. The removal capacity for  $Se(IV)$  and  $Se(VI)$  was found 60.9 mg/g and 77.9 mg/g, respectively at pH 6 [58].

GO-PAMAMs have been synthesized both by “grafting from” [59] and “grafting to” [60] methods and utilized for adsorption of heavy metals. GO-PAMAM prepared by “grafting from” method showed superior adsorption properties compared to GO and it was attributed to additional complexation between the amines of the PAMAM and heavy metal ions [59]. Authors claimed that GO-PAMAM was easily and more efficiently prepared by grafting to method. GO/PAMAMs was reported to have much superior adsorption ability and higher affinity for  $Pb(II)$  than  $Cd(II)$ ,  $Cu(II)$ , or  $Mn(II)$  [60].

The other well-known carbon material is carbon nanotubes (CNTs). CNTs are of great importance for adsorption applications due to their high capacities and shorter contact times. CNTs have been widely applied for removal of both organic and inorganic contaminants in liquid media. CNTs may interact effectively with target pollutants because of their high specific surface areas, and ability to develop electrostatic interactions and van der Waals forces. CNTs suspensions may agglomerate leading to reduced adsorption performance. CNTs can be modified

with various functionalities to avoid the problem of agglomeration [61].

Iannazzo et al. functionalized the multiwall carbon nanotubes (MWCNTs) using triazol to develop the dendrimer on their surface, and it was applied for the adsorption of the heavy metals. The  $\alpha$ -amino-phosphonate nanosystem (MWCNT-TD2P) was generated by carrying the Moedritzer-Irani reaction on the amino group of MWCNT-TD2. The developed adsorbent exhibited the chelating behaviors towards heavy metals such as Pb(II), Ni(II), and Hg(II). However, the MWCNT-TD2P demonstrated excellent chelating activity towards Hg(II) and in Hg(II) chelating; the 2 oxygen of the phosphate group is participating [62]. Interestingly, very high adsorption capacities of 3333 and 4870 mg/g have been reported for Cu(II) and Pb(II) ions respectively by employing PAMAM/CNT nanocomposite as an adsorbent [61].

### 3.6. Natural materials supported dendrimers

Being cheap, abundant, and environmentally benign, biosorbents based dendrimers have received increasing attention for the removal water pollutants such as heavy metals and dyes in recent years. Cellulose and chitin are the most abundant natural biopolymers available worldwide. Cellulose and chitosan produced from chitin, have been used as biosorbents because of their biocompatibility, biodegradability, non-toxicity and adsorption properties. Dendrimers based on cellulose and chitosan have been used for adsorptive removal of heavy metals and dyes [16,37]. Fig. 12 shows the poly(amidoamine)-grafted cellulose nanofibers which were used for removal of Cr(VI) in the aqueous system. The bioadsorbent had very low density, high porosity and it was multi-functionalized with amine groups that can be easily protonated at low pH. The characterization of PAMAM-g-CNF aerogel revealed that it had an open-cell geometry with pore sizes in the range of 5–3 mm, and these cells were an interconnected network of cells having sheet-like “walls”. On each wall, there were numerous minor pores with sizes of 50–200 nm. Both types of pores have a positive effect on adsorption. The adsorbent exhibited internal cavities and high specific area. The maximum Cr(VI) removal capacity by this super biosorbent was  $377.36 \text{ mg g}^{-1}$ , the highest for any biosorbent reported so far [37].

Chitosan is a nitrogenous polysaccharide composed mainly of poly ( $\beta$ -1-4)-2-amino-2-deoxy-d-glucopyranose and is produced by the

deacetylation of chitin, which is widely found in marine and terrestrial invertebrates and in lower forms of the plant kingdom. Chitosan is naturally occurring support, and it can be modified with selective chemical moieties to adsorb inorganic and organic pollutants [63]. Amine groups of chitosan are easily functionalized and converted to Chitosan/poly(amidoamine) dendrimers which in turn used in the removal of heavy metals [16] and dyes [47] from aqueous solutions. Chitosan microparticles may be converted to magnetic microparticles functionalized with polyamidoamine dendrimers. Such biosorbents have a magnetic property, which is effective for solid–liquid phase separation, in addition to other advantages [47]. PAMAM modified chitosan was used for removal of  $\text{Pb}^{2+}$  [16].

To Incorporate the biocompatibility, high surface area, high hydrophilicity, good resistivity for chemical and solvent as excellent properties of regenerated cellulose membrane with the unique molecular structure of dendrimer and their easily functionalization and manipulation of their terminal groups, a Diaminobutane based poly (propyleneimine) functionalized with sixteen thiol active group (DAB-3-(SH)<sub>16</sub>) was embedded in a cellulose membrane for toxic heavy metals (i.e., Cd(II), Hg(II) and Pb(II)) removal as shown in Fig. 13 [64]. The unembedded and embedded cellulose membrane with DAB-3-(SH)<sub>16</sub> dendrimer was characterized using electrochemical impedance spectroscopy (EIS). The bode plots in Fig. 14 for membranes before and after modification and immersing in target metals solution show decreasing in the  $Z_{\text{real}}$  values which indicate entrapment the heavy metals in the membrane, and this leads to increase the number of charges.

### 3.7. Dendrimer grafted micro-filters or membranes

Incorporation of dendrimers with the microfiltration technology is a good choice for water treatment because of its high-water permeability and low operation pressure, as a result, reducing the operation cost and energy consumption. As a good example for a membrane material used in this technology is poly(tetrafluoroethylene (PTFE)). PTFE has excellent mechanical strength, high insulation performance, strong chemical inertness and thermal stability [65]. In 2013, the PTFE membrane has been grafted with hyperbranched poly amidoamine (HPAMAM) by Hyonggoo Yoo et al. for the removal of Cu(II) cations from aqueous media. Fig. 15 illustrates the steps of grafting the PAMAM on the PTFE microfiltration membrane. Briefly, the PTFE membrane was aminated

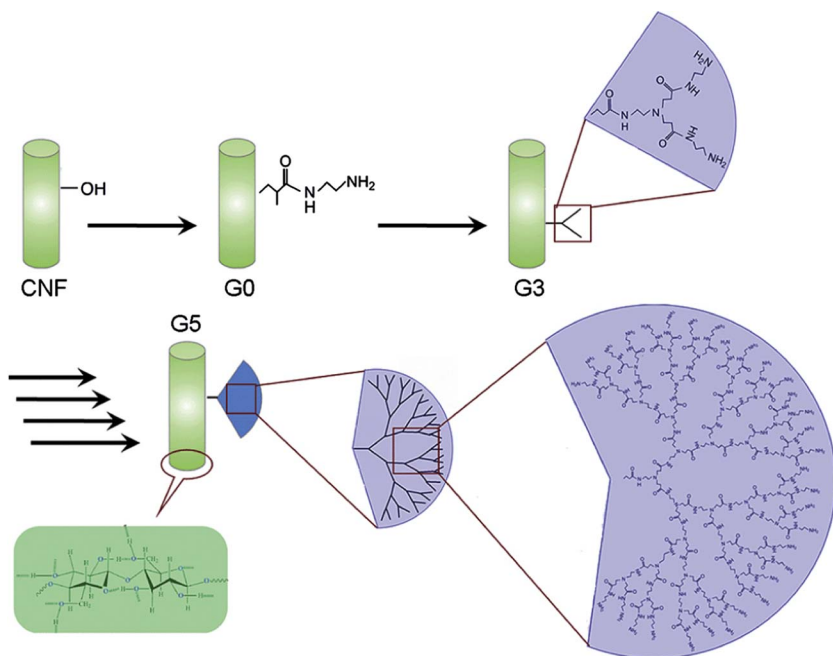


Fig. 12. The schematic of the synthesis of poly(amidoamine)-grafted cellulose nanofibers, PAMAM-g-CNFs. Reproduced with permission from [37]. Copyright (2015) Royal Society of Chemistry.

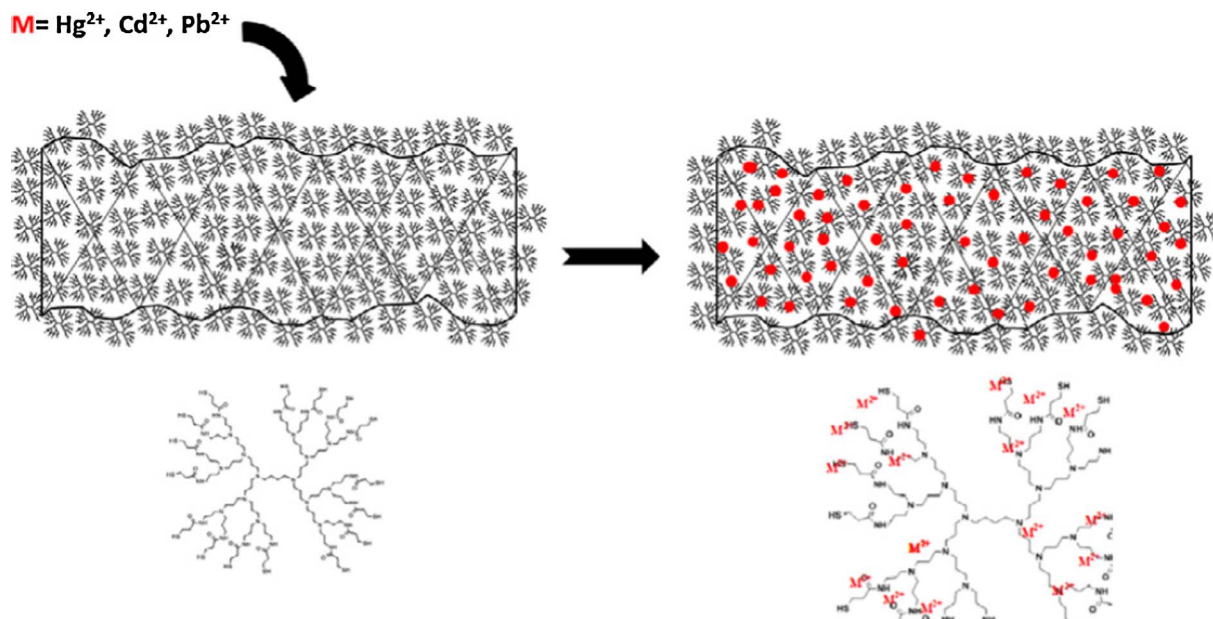


Fig. 13. Schematic of heavy metal removal by using cellulose membrane embedded with DAB-3-(SH)<sub>16</sub> dendrimer. Reproduced with permission from [64]. Copyright (2014) Elsevier B.V.

in the presence of hydrazine vapor by UV radiation and then was immersed in 2,4,6-trichlorotriazine in chloroform solution. The resulted functionalized membrane was washed and dried before incubation in an aqueous solution of HPAMAM for 12 h [66].

Relatively at low operation pressure (25 kPa), the water flux through grafted PTFE membrane was higher than PTFE membrane before modification due to the increase in its hydrophilicity. The grafted membrane was able to adsorb 1.42 g Cu<sup>2+</sup>/m<sup>2</sup>.

Han et al. reported the removal of cadmium ions in a dead end ultrafiltration unit using composite membrane composed of polysulfone (PSf) and hyperbranched poly(amidoamine) (HYPAM). The HYPAM/PSf was prepared using a phase inversion process with different weight percentages (1, 3, 5 wt%) of HYPAM to PSf solution. Fig. 16 shows the schematic representation of the preparation of HYPAM. Fig. 17 displayed the SEM images of the membranes. It can be seen that HYPAM content has significantly affected the morphology of membrane surfaces. Increase in HYPAM has converted the membrane surface to a more sponge-like structure. The accumulated uptake of Cd(II) ions by various membranes at different time intervals was recorded, and HYP5-F showed the highest uptake of cadmium ions after 2 h of operation [13].

Dendrimers have a broad range of physicochemical properties that make them particularly attractive for water purification [67]. Diallo et al. [68], performed some pioneer works describing the use of dendritic polymers as chelating agents for metal ions. They reported the

binding of Cu(II) ions to PAMAM dendrimers. PAMAM dendrimers (EDA core with NH<sub>2</sub> terminal groups) of generation G3, G4, G5, G6, G7, and G8 were used. Batch experiments were performed and the extent of binding (EOB) i.e. number of molecules of Cu(II) bound per mol of the dendrimer, are reported. Maximum EOB of 153 ± 20 mol of Cu(II) ions per molecule of dendrimer was reported in the pH range 5.9–6.1 by G8 PAMAM dendrimers at room temperature. Conventional chelating agents (e.g., triethylene tetramine) and macrocycles (e.g., cyclams) with nitrogen donors, can bind only one Cu(II) ion per molecule while a generation eight (G8) PAMAM dendrimer can bind up to 153 ± 20 Cu(II) ions per molecule [68].

Likewise, Diallo et al. reported the removal of Cu(II) ions using PAMAM dendrimers with ethylenediamine (EDA) core and terminal NH<sub>2</sub> groups in dead-end ultrafiltration (UF) system using polymeric membranes. UF experiments were conducted to recover Cu(II) efficiently from aqueous solutions by model UF membranes such as regenerated cellulose (RC) and polyethersulfone (PES). A feed solution containing a molar ratio of 0.2 of Cu(II) to dendrimer NH<sub>2</sub> groups was used in all experiments [69].

It was observed that at pH 7.0 the G<sub>x</sub>-NH<sub>2</sub> EDA cores PAMAM have much less tendency to pass through the pores of UF membranes. They also have low affinity to foul the RC membranes.

Likewise, the RC and PES membranes could retain above 92% of Cu(II)-dendrimer complexes at pH 7.0. The Cu(II)-dendrimer complexes can be easily separated by ultrafiltration.

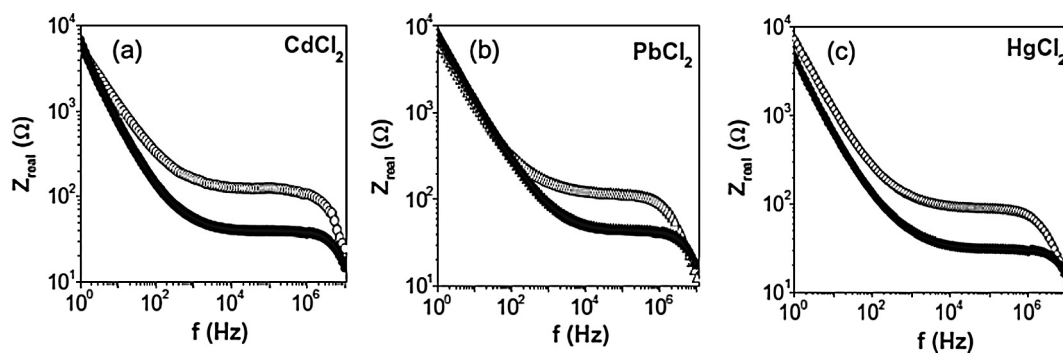


Fig. 14. Comparison of Bode plots for RC/4 membrane (open symbols) and RC/4+dendrimer membrane (dense symbols) after 24 h immersion in (a) CdCl<sub>2</sub>, (b) HgCl<sub>2</sub> and (c) PbCl<sub>2</sub>. Reproduced with permission from [64]. Copyright (2014) Elsevier B.V.

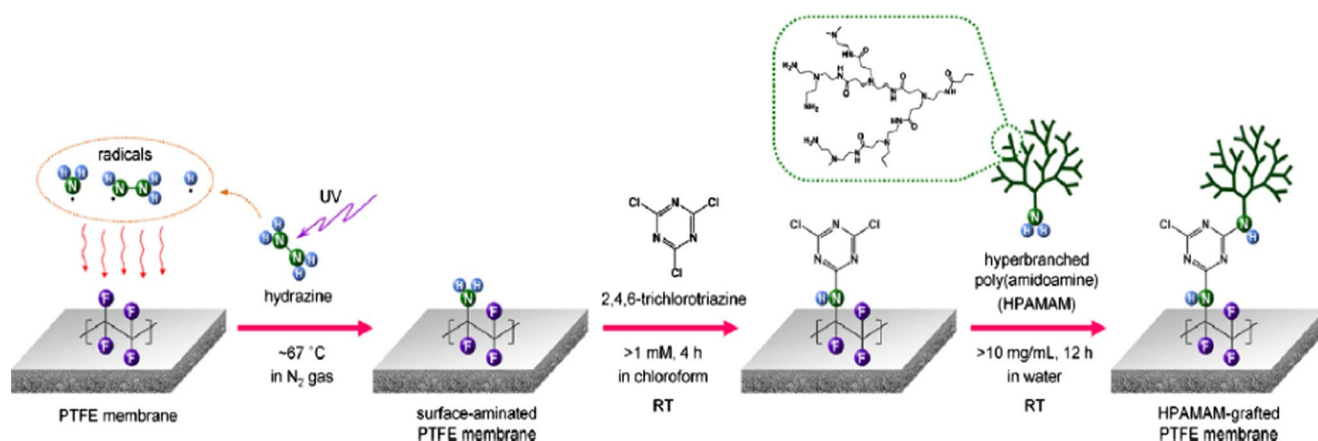


Fig. 15. Schematic illustration of the procedure used for the preparation of HPAMAM grafted PTFE microfiltration membrane. Reproduced with permission from [66]. Copyright (2013) Elsevier B.V.

The possible mechanism of Cu(II) ions with G<sub>x</sub>-NH<sub>2</sub> EDA PAMAM dendrimer is the formation of octahedral complexes in which a Cu(II) central metal ion is coordinated to four dendrimer tertiary amine groups and two axial water molecules inside the dendrimers. The dendrimers can be regenerated by reducing the solution pH to 4.0.

In another study, they reported that PAMAM dendrimers with EDA core were capable of removing Cu(II) ions. Maximum EOB of 92 mol of Cu(II) per mol of dendrimer was reported for glycidyl terminal groups (G<sub>4</sub>-Gly). It was found that dendrimer generation/terminal group chemistry, solution pH and metal ion-dendrimer loading are critical parameters that affect the extent of binding of Cu(II) ions [70].

Dendrimer filtration could provide a viable alternative to ion exchange for the treatment of ClO<sub>4</sub><sup>-</sup> contaminated water. G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer with a diaminobutane core has shown a clear superiority over ion exchange resin in removing perchlorate from aqueous solutions. At room temperature and pH 4, 99% of the tertiary amine groups of G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer are protonated and allow high electrostatic interactions with ClO<sub>4</sub><sup>-</sup> anions. The EOB of ClO<sub>4</sub><sup>-</sup> to G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer at these conditions corresponds to a binding capacity of 125 mg of ClO<sub>4</sub><sup>-</sup> per g of the dendrimer, which is comparable to 75 mg/g achieved by selective bifunctional polystyrene ion exchange resin with ethyl/hexyl ammonium groups. G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer selectively binds ClO<sub>4</sub><sup>-</sup> over more hydrophilic anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> [71]. Addition of G<sub>4</sub>-NH<sub>2</sub> PAMAM suppresses the

interference of SO<sub>4</sub><sup>2-</sup> ions and allows selective binding of ClO<sub>4</sub><sup>-</sup>. Binding of ClO<sub>4</sub><sup>-</sup> to G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer reaches the equilibrium in ~1 h compare to 24 h in most cases for ion exchangers. The relatively fast kinetics of perchlorate uptake by the dendrimer is due to the homogeneous medium. In addition to the aforementioned advantages of dendrimers over ion exchange resins, only a high pH (~10–11.0) aqueous solution is needed to regenerate more than 90% of the G<sub>5</sub>-NH<sub>2</sub> PPI dendrimer while most perchlorate-selective resins cannot be regenerated by a simple change of solution pH.

The process of combining functionalized dendritic nanoparticles with membrane-based ultrafiltration provides an efficient technology to recover U(VI) in aqueous solutions. Diallo et al. reported the PAMAM and PPI dendrimers as a high capacity and selective chelating ligands for U(VI) in aqueous solutions [72]. A Millipore Centricron filter with a molecular weight cutoff of 5 kDa was used to separate the uranyl-laden dendrimers from the aqueous solutions. The extent of binding, EOB, of G<sub>4</sub>-NH<sub>2</sub> PAMAM dendrimer at pH 7 and 9 was 227 UO<sub>2</sub><sup>2+</sup> ions per dendrimer molecule, which is on a mass basis, equivalent to ~4200–4300 mg of U(VI) ions per g of the dendrimer. This binding value is very large compared to ~100 mg/g for uranyl binding capacity of typical ion exchange chelating resins with NH<sub>2</sub> groups. Moreover, kinetics of uranyl uptake by dendrimers is faster, and dendrimers recycling is simpler.

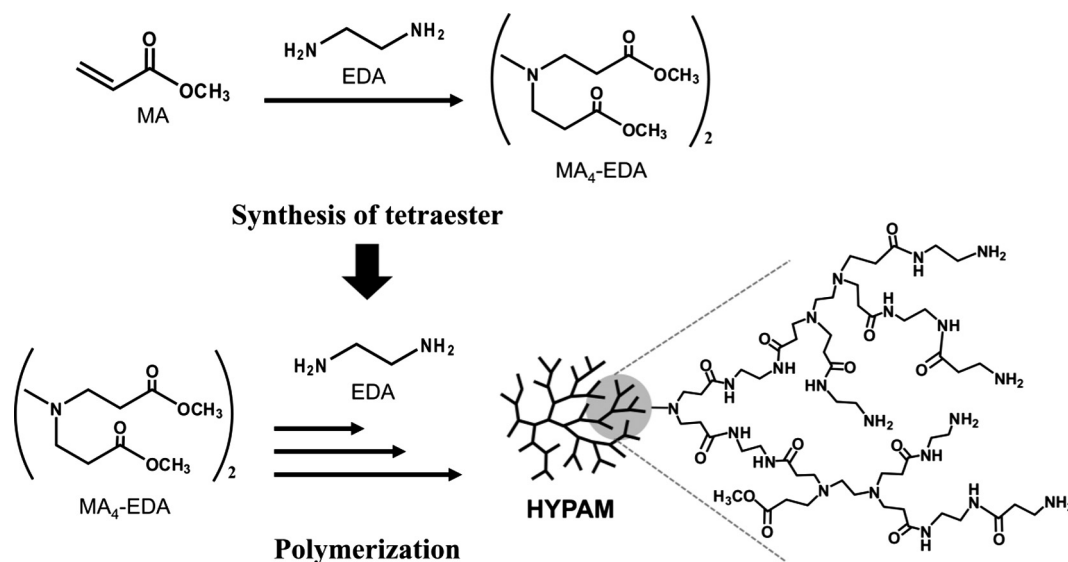


Fig. 16. Schematic representation of the preparation of HYPAM. Reproduced with permission from [13]. Copyright (2012) Elsevier B.V.

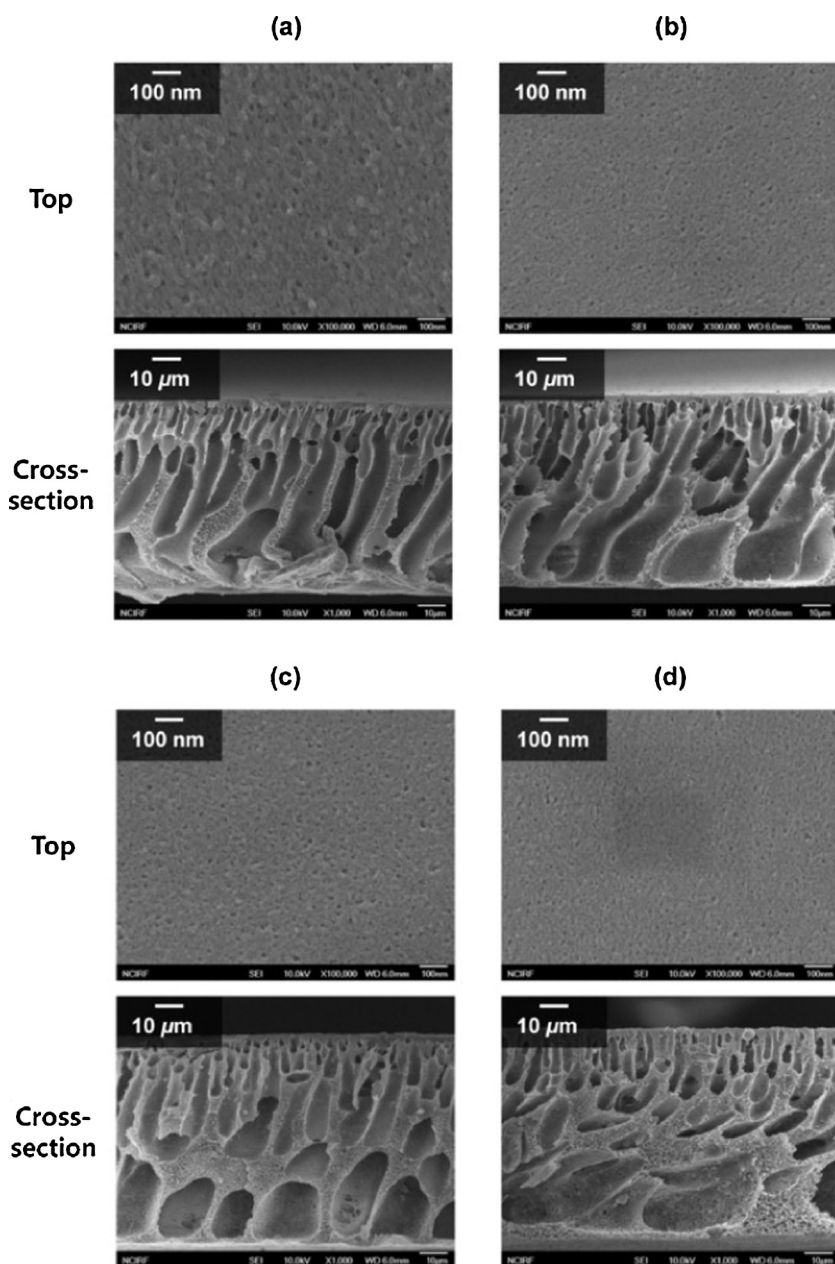


Fig. 17. SEM images of (a) neat-F, (b) HYP1-F, (c) HYP3-F, and (d) HYP5-F. Reproduced with permission from [13]. Copyright (2012) Elsevier B.V.

### 3.8. Miscellaneous dendrimer adsorbents

Taleb et al. synthesized the poly(methacrylic acid-g-poly-amidoamine dendrimer) with different loads of nickel salt by gamma radiation-induced copolymerization of polyamidoamine dendrimer and methacrylic acid (MAA). The adsorption potential of the dendrimer was studied in batch experiments for Cr(III), Co(II) and Cu(II) metal ions. It was found that the presence of nickel has improved the adsorption capacity of the dendrimer for the adsorption of Co(II) and Cu(II) ions. This is due to the similar structure of nickel to those of Co(II) and Cu(II). However, since Cr(III) has a different structure than nickel, therefore, the addition of nickel to the dendrimer has an adverse effect on the removal of Cr(III) ions. Metal uptake (mg/g) of 16.37, 17.2 and 9.7 was observed for Cr(III), Co(II) and Cu(II) metal ions by dendrimer with 25 mg Ni(II) ions at pH 6. Cu(II) ions can also be removed efficiently from contaminated soil by PAMAM dendrimers [73].

Xu et al. reported the applications of five dendrimers, G1.0-NH<sub>2</sub>, G1.5-COOH, G4.0-OH, G4.0-NH<sub>2</sub> and G4.5-COOH (G indicates generation number; -COOH, -NH<sub>2</sub>, and -OH refer to respective terminal

groups). The experiments were performed in fixed bed column. Over 90% of copper initially sorbed by G4.5-COOH at pH 6. The dendrimer was then regenerated with 100 mL of 2 N HCl for 24 h [39].

PAMAM dendrimers are also reported as potential adsorbents for the removal of lead from contaminated soils in fixed-bed column [74]. The spent dendrimers can be regenerated efficiently using 2 N HCl and 94% of the dendrimer-bound Pb<sup>2+</sup> species were desorbed from the dendrimers upon acid regeneration.

Cr is another toxic metal and Cr(VI)-based salts are being used for metal surface treatment and in the leather industry. The effluent from these industries are generally loaded with Cr(VI). The first and second generation phosphorous based cationic dendrimers and Na-saturated montmorillonite were used for the removal of Cr(VI). The amount of Cr (VI) retained by Na-montmorillonite, GC1-montmorillonite, GC2-montmorillonite was found 6.2, 10.2, and 7.15 mg/g, respectively [75].

Gajjar et al. synthesized a triazine dendrimer with hydroxyl terminals and without any supporting materials using a divergent method. They synthesized a group of triazine dendrimers generations (i.e. G0, G0.5, G1.0, G1.5, G2.0, G2.5 and G3.0) and found the core and half

**Table 1**  
Applications of dendrimer based adsorbents for removal of heavy metals.

Name of dendrimer or dendrimer modified material	BET Surface Area (m <sup>2</sup> /g)	Name of target pollutant	Mode of adsorption experiment	Adsorption conditions			Flow rate (in case of dynamic or column)	Adsorption capacity (mg g <sup>-1</sup> )	Isotherms/kinetics	Regeneration (condition/cycles)	Ref.
				pH	Time	T (°C)					
Graphene oxide/PAMAM dendrimers	25	Pb(II)	Batch	4.5,	60 min	25	-	568.18	Langmuir isotherm /pseudo-second-order	-	[60]
		Cd(II)	Batch	5.0	60 min	25		253.81			
PAMAM, functionalized graphene oxide Dendrimer-functionalized multi-walled carbon nanotubes Dendrimers-clay nanocomposites Polystyrene PAMAM iminodiacetic acid PAMAM-grafted cellulose nanofibril, aerogels, G5 Porphyrin-PAMAM modified nylon membranes Hyperbranched PAMAM (HYPAM)/polysulfone (PSf) membrane PPI G2-grafted thin film composite nanofiltration polyethersulfone membranes PPI-grafted chitosan, CS-G3 Dendrimer/titania	-	Cu(II)	Batch	4.5	-	-	-	68.68	Langmuir	-	[58]
		Mn(II)	Batch	4.0	-	-		18.29			
		Se(IV)	Batch	6	-	25		60.9			
		Se(VI)	Batch	7.0	24 h	25		77.9			
G-4 PAMAM dendrimers with ethylenediamine cores (G4-OH) immobilized on titania (TiO <sub>2</sub> )	2.7	Pb(II), Hg(II), Ni(II)	Batch	7.0	-	-	-	-	-	-	[62]
		Pb(II), Cr(III), Ni(II)	Batch	7.0	24 h	25		-			
Functionalized SBA-15 mesoporous silica with amine (-NH <sub>2</sub> )/melamine-based dendrimer amines (MDA)	293	Pb(II)	Batch	4	2 h	25	-	130.1	Langmuir/Pseudo-first-order	With 0.3 M HCl/4 cycles	[14]
		Cu(II)	Batch	4	2 h	25		126.2			
Functionalized SBA-15 mesoporous silica with amine (-NH <sub>2</sub> )/melamine-based dendrimer amines (MDA)	293	Cd(II)	Fixed bed column	4	-	25	0.6 mL/min	39.6	Thomas model	Three adsorption-desorption cycles	[54]
		Cu(II)	Batch	6.2	24 h	25		37.6			
Poly(ethylene imine) hyperbranched polymer with silicic acid	20.6	Pb(II)	Batch	6.2	24 h	25	-	632.91	Langmuir	-	[40]
		Cd(II)	Batch	6.2	24 h	25		595.24			
Silica gel supported salicylaldehyde modified PAMAM dendrimers	211.32	Hg(II)	Batch	6.2	12 h	25	-	0.91	Langmuir isotherm /pseudo-second-order	-	[40]
		Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	Batch	6.2	12 h	25		-			
SiO <sub>2</sub> -G0-SA SiO <sub>2</sub> -G1.0-SA SiO <sub>2</sub> -G2.0-SA silica-gel supported	159.90	Pb(II)	Batch	5	10 h	25	-	1.52	Langmuir isotherm	-	[88]
		Pb(II)	Batch	5	10 h	25		1.81			
SiO <sub>2</sub> -G0-SA SiO <sub>2</sub> -G2.0-SA silica-gel supported	101.21	Pb(II)	Batch	5	10 h	25	-	0.80 mmol g <sup>-1</sup>	Langmuir isotherm	-	(continued on next page)
		Pb(II)	Batch	5	10 h	25		-			

Table 1 (continued)

Name of dendrimer or dendrimer modified material	BET Surface Area (m <sup>2</sup> /g)	Name of target pollutant	Adsorption conditions			Mode of adsorption experiment	pH	Adsorption conditions		Flow rate (in case of dynamic or column)	Adsorption capacity (mg g <sup>-1</sup> )	Isotherms/kinetics	Regeneration (condition/cycles)	Ref.
			Time	T (°C)	Time			T (°C)						
hyperbranched PAMAM dendrimers (amino-terminated) (ester-terminated)	-	Hg(II)	5 s	Ambient	-	Batch	7.5	-	-	-	Langmuir, Freundlich models/Pseudo 2nd order	For MeHg(I), MeHg(II)-loaded adsorbents dispersed in EDTA solution and stirred 30 min. Collected by magnet and re-dispersed. For regeneration, added into DNA solution for 20 min.	[55]	
PAMAM-grafted core-shell magnetic silica nanoparticles	-	MeHg(I)	5 s	Ambient	-	Batch	7.5	-	-	134.6	Langmuir, Freundlich models/Pseudo 2nd order	For MeHg(I), MeHg(II)-loaded adsorbents dispersed in EDTA solution and stirred 30 min. Collected by magnet and re-dispersed. For regeneration, added into DNA solution for 20 min.	[55]	
DNA fragments assembled-PAMAM-grafted core-shell magnetic silica nanoparticles	-	MeHg(I)	5 s	Ambient	-	Batch	7.5	-	-	39.49	Langmuir, Freundlich models/Pseudo 2nd order	For MeHg(I), MeHg(II)-loaded adsorbents dispersed in EDTA solution and stirred 30 min. Collected by magnet and re-dispersed. For regeneration, added into DNA solution for 20 min.	[55]	
Hydroxyl terminated Triazine, G3(OH)128	-	Cu(II)	24 h	25 °C	-	Batch	10	-	-	5.19 mmol g <sup>-1</sup>	-	-	[89]	
		Ni(II)								4.95 mmol g <sup>-1</sup>				
		Zn(II)								4.75 mmol g <sup>-1</sup>				
Poly(methacrylic acid-g-PAMAM dendrimer) with Ni <sup>2+</sup>	-	Cu(II)	6 h	25–60	-	Batch	6	-	-	16.37	-	-	[73]	
		Co(II)								17.2				
		Cr(II)								9.7				
PAMAM dendrimers	-	Cu(II)	-	-	-	Fixed-bed column	6	-	-	-	-	-	[39]	
PAMAM dendrimers with ethylenediamine (EDA) core and terminal NH <sub>2</sub> groups	-	Cu(II)	4.5 h	25	-	Dead-end ultrafiltration	9	-	-	451	Two-site thermodynamic model	Regeneration with 100 mL of 2 N HCl for 24 h	[69]	
PAMAM Dendrimers	-	Pb(II)	-	-	-	Fixed-bed column	6	-	0.06 mL/min	-	Freundlich	Regeneration with 50 mL of 2 N HCl for 24 h	[74]	
Hydroxyl terminated triazine based dendrimer G1	-	Cu(II)	24 h	25	-	Batch	10	-	-	2.30	-	-	[76]	
		Ni(II)								2.10				
		Zn(II)								2.06				
Hydroxyl terminated triazine based dendrimer G2	-	Cu(II)	-	-	-	Batch	6	-	-	3.61	-	-	[39]	
		Ni(II)								3.46				
		Zn(II)								3.33				
Hydroxyl terminated triazine based dendrimer G3	-	Cu(II)	-	-	-	Batch	6	-	-	5.20	-	-	[64]	
		Ni(II)								4.97				
		Zn(II)								4.71				
Diaminobutane based PPI dendrimer functionalized with sixteen thiol groups	-	Cd(II), Hg(II) and Pb(II)	5.8 ± 0.3	-	-	Used as a membrane and the permeability was tested	5.8 ± 0.3	-	-	-	-	-	[64]	
G-4 dendrimers with external hydroxyl functional groups	-	Ni(II), Fe(II), Fe(III)	-	25	-	Batch	7	-	-	-	-	-	[53]	
Dendrimer-conjugated magnetic nanoparticles (Ch-MNPs)	56.9	Zn(II)	8 h	25	-	Batch	7	-	-	24.3	Langmuir	At pH < 3, 10 adsorption-desorption cycles with 0.1 M HCl	[15]	
Third-generation dendrimers modified magnetic nanoparticles	60.0	Pd(IV)	-	25	-	Batch	6.5	-	-	3.60	DR, Langmuir, Freundlich isotherm/Pseudo 2nd order	1.0% HCl solution used as desorbent solution.	[35]	
		Au(III)								3.58				
		Pd(II)								2.75				
		Ag(I)								2.84				
Amine terminated-Magnetic cored dendrimers	84.14	Pb(II)	6 h	25	-	Batch	5	-	-	170.42	Langmuir, Freundlich models/pseudo-2nd order	HCl used as extracting agent and the adsorbent mixed for 3 h, removed, washed and reused	[49]	
		Cd(II)								75.15				

(continued on next page)

Table 1 (continued)

Name of dendrimer or dendrimer modified material	BET Surface Area (m <sup>2</sup> /g)	Name of target pollutant	Mode of adsorption experiment	Adsorption conditions			Flow rate (in case of dynamic or column)	Adsorption capacity (mg g <sup>-1</sup> )	Isotherms/Kinetics	Regeneration (condition/cycles)	Ref.
				pH	Time	T (°C)					
PAMAM-graft-poly(methyl acrylate) magnetic nanocomposite	-	Pb(II)	Batch	5–6	30 min	25	-	310	Langmuir Isotherm model/ Pseudo-2nd order kinetic model	Pb(II)-loaded adsorbent was put into 0.1 M HCl for 10 min. and separated magnetically for reuse.	[56]
PAMAM/CNT	-	Cu(II) single system Pb(II) single system Cu(II) binary system Pb(II) binary system	Batch	8, 7	-	298 K	-	3677 4080 3333 4320	Single systems fit the Langmuir and binary component fit the extended Langmuir models Pseudo-2nd order kinetic model	Aqueous solution at pH 2	[61]

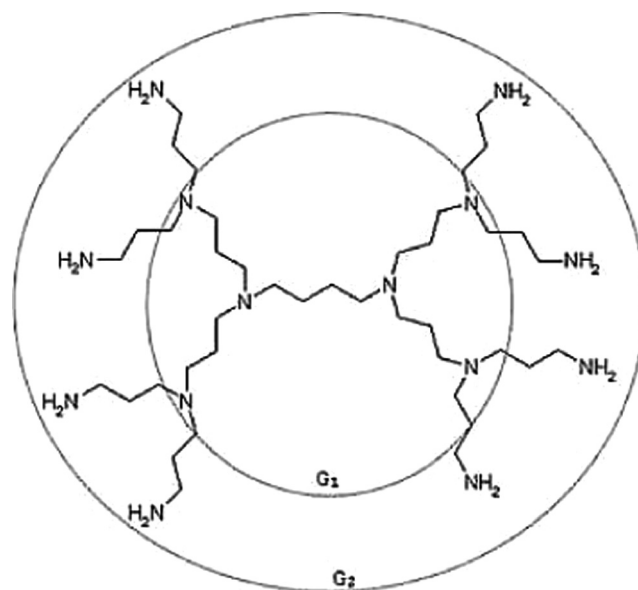


Fig. 18. Chemical structure of PPI dendrimer (G2). Reproduced with permission from [77]. Copyright (2011) Wiley Publishers.

generation dendrimers are white colored and insoluble in water because they were chlorine terminated. In contrast, the hydroxyl terminated dendrimers generation were brown colored and water soluble. Also, it was found that the adsorption capacities of the prepared dendrimers for Cu, Ni and Zn increased with increasing the generation number which is attributed to the increasing in the number of terminal hydroxyl groups in dendrimer [76]. Table 1 summarizes the applications of different dendrimers in the removal of heavy metals.

#### 4. Removal of dyes

Dyes typically acid dyes are widely used in the textile sector. Acid dyes are toxic and can cause nausea, drowsiness, diarrhea, blood clot and breathing problems. Poly (propylene imine) dendrimer (PPI) has been employed for the removal of various dyes from aqueous solutions. Hayati et al. reported the application of PPI dendrimer for the removal of Direct Red 23 (DR23), Acid Blue 7 (AB7), Acid Green 25 (AG25), and Direct red 80 (DR80) from water [77]. Fig. 18 shows the chemical structure of PPI dendrimer (G2).

The adsorption measurements were conducted in the batch system at pH (2–10) by using 50–100 mg/L of dye concentration and dendrimer amount of 1.8 mg/L. It was found that pH, dye concentration, and dendrimer concentration affect the adsorption process. Langmuir isotherm model was found to best describe the adsorption process of all the dyes by PPI dendrimers. It was found the dye removal decreases with an increase in pH, and the maximum dye adsorption occurred at pH 2. This is due to strong electrostatic attraction between the anionic dye and positively charged surface of the dendrimer at pH 2. With the increase in pH, adsorption of dye anions decreases due to decrease in the number of positively charged sites. Desorption experiments indicated that maximum dye releasing of 93% for DR23, 87% for AB7, 84.5% for AG25 and 76.5% for DR80 were achieved at pH 12. The number of positively charged sites reduced with an increase in pH of the system which favors desorption process.

PPI dendrimer was also employed for the adsorption of Direct Blue 78 (DB78) and Acid Black 26 (AB26) in a binary system [44]. Experiments were performed at pH 2 and 25 °C for 30 min using 1.8 mg L<sup>-1</sup> of dendrimer and different concentrations of AB26 and DB78 in single and binary systems. Again, the maximum removal of both dyes was found at pH 2 and dyes can be desorbed at pH 12.

A. Ghasempour introduced a method for removal of the acid dye



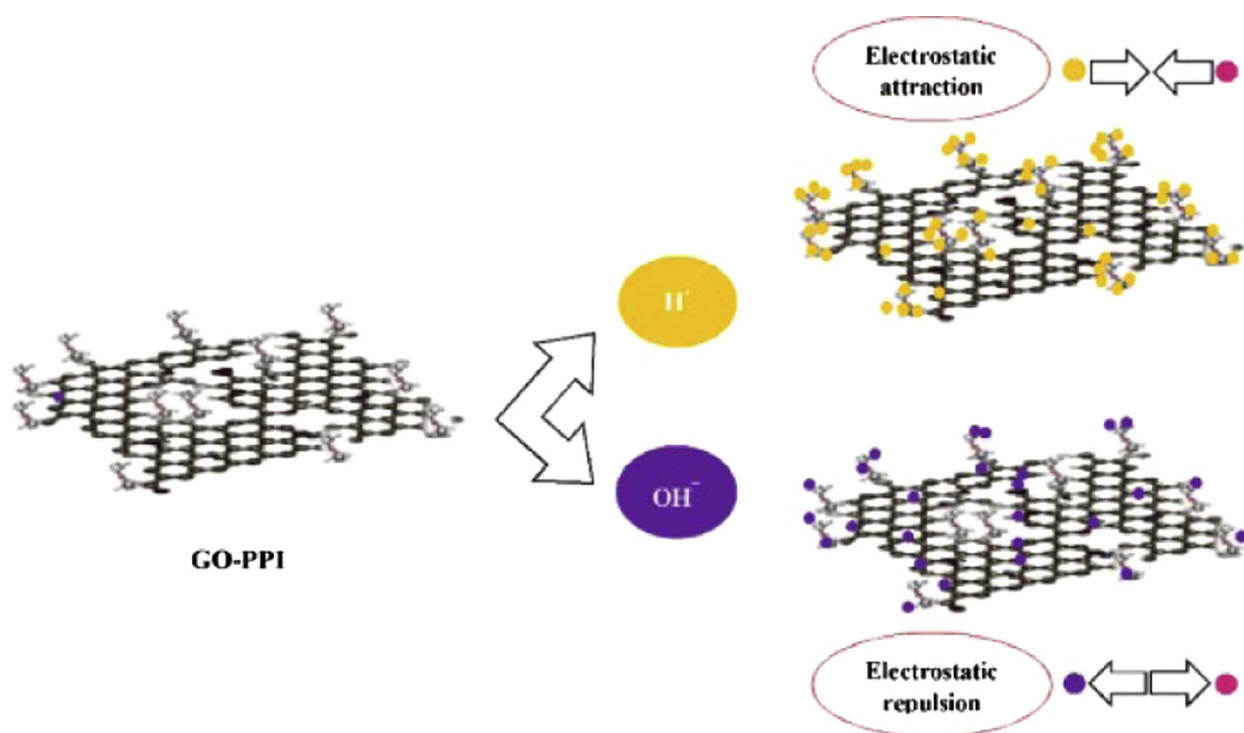


Fig. 19. Schematic behavior of GO-PPI in acidic and alkaline media. Reproduced with permission from [78]. Copyright (2016) Taiwan Institute of Chemical Engineers. Published by Elsevier.

contaminants by the generation of dendrimers on the graphene oxide surface. The dendrimer was generated using PPI on graphene oxide surface (GO-PPI). The removal capabilities of the graphene oxide are poor towards anionic dyes due to negatively charged functionalities which cause electrostatic repulsion. GO-PPI has highly branched structure containing eight amine functionalities at the terminal end. The amine group can be protonated to have a positive charge. Thus, the GO-PPI attained the electrostatic attraction for the anionic dyes and the adsorption capability for the dye significantly improved compared to graphene oxide alone. In the removal of dyes AB92 and AR 14, pH played a significant role. The adsorbent and adsorbate attraction or repulsion forces are being changed with pH change. At lower pH, the adsorbent surface is protonated and exhibiting great attraction and removal capabilities for the dyes. At higher pH, surface deprotonated and adsorption capabilities sharply decreased (Fig. 19). At pH 3, the removal for AB92 and AR14 were attained about 86 and 94.4%, respectively. Moreover, the adsorption was following the Langmuir isotherm and pseudo-second-order kinetic model [78].

On the other hand, Ladan Eskandarian, et. al., modified a functionalized multiwall carbon nanotube (CNT-COOH) with PPI dendrimers and used it as an adsorbent for removal of trace anionic organic direct dyes (C.I. Direct Blue 86 (DB86) and C.I. Direct Red 23 (DR23)).

The performance of the modified adsorbent was evaluated, and it was found that the adsorption capacity and removal efficiency for DB86 and DR23 from both systems (single or binary) were greatly improved. In both systems, the adsorption isotherms of DB86 and DR23 followed Langmuir model and the adsorption kinetics fitted by pseudo second order kinetics. In case of single dye system, the maximum adsorption capacities at room temperature were around 666 and 1000 mg/g for DB86 and DR23 respectively, and in case of the binary system, they were 370 and 555 mg/g [45].

Dendrimer modified magnetic nanoparticles were used for removal of reactive black 5 dye from the water, and the adsorption was found dependent on dendrimer generation and pH [57].

Polyacrylonitrile (PAN) is a general, cost-effective and environmental stable polymer, and it can be easily electrospun into nanofibers.

Electrospun PAN/PAMAM dendrimer composite was used to remove Direct red 80 (DR80) and Direct red 23 (DR23). The viscosity of the spinning solution is altered by the addition of PAMAM in PAN matrix. Likewise, the number of converted nitrile group to N–C=N linkage increases through this combination. The maximum adsorption capacity was recorded as 1666.66 and 2000 mg/g for DR80 and DR23, respectively [41]. Table 2 summarizes the applications of different dendrimers for removal of dyes.

## 5. Removal of polycyclic aromatic hydrocarbons

Polyaromatic hydrocarbons (PAHs) are hydrocarbons with two or more fused aromatic rings, and they are hundreds in number. They are produced from incomplete combustion or pyrolysis of carbonaceous and organic matter PAHs. They are highly toxic and may induce endocrine disrupting disorders like famous persistent organic pollutants [79]. They are suspected carcinogens and mutagens [80]. It is therefore highly important to remove them from water sources.

Arkas et al. reported the application of hyperbranched poly(ethylene imine) with silicic acid for the removal of polycyclic aromatic hydrocarbons (pyrene and phenanthrene) from the water. The dendrimer was prepared via sol-gel reactions. PEI was supported on silica nanoparticles. It was found that the presence of PEI into the silica nanoparticles enhanced the sorption of polycyclic aromatic hydrocarbons. The higher removal of these hydrocarbons by PEI-silica nanoparticles is due to the formation of charge-transfer complexes between the tertiary amino groups of the hyperbranched polymer and polyaromatics [54].

For dendritic materials, Michael Arkas et. al., studied the performance of organosilicon dendritic polymers modified ceramic and alumina filters [81] Diaminobutane poly(propylene imine) dendrimer (DAB), Polyethylene imine (PEI), b-Cyclodextrine (CD) [82] and poly(ethylene imine) hyperbranched polymer functionalized with octyl aliphatic chains [83] for removal of poly aromatic hydrocarbons (PAH) from aqueous media. They found that, impregnation procedure for ceramic filters must be clearly and experimentally defined based on its pore surface area, mean pore diameters, pore size distribution as well as

**Table 2**  
Applications of dendrimer based adsorbents for removal of dyes.

Name of dendrimer or dendrimer modified material	BET Surface Area (m <sup>2</sup> /g)	Name of target pollutant	Mode of adsorption experiment	Adsorption conditions			Flow rate (in case of dynamic or column)	Adsorption capacity (mg g <sup>-1</sup> )	Isotherms/kinetics	Regeneration (condition/cycles)	Ref.
				pH	Time	T (°C)					
Dyes polyacrylonitrile/PAMAM composite nanofibers, PAN-20%/w PAMAM	18.5	Direct red 80	Batch	2.1	1 h	25	-	2000	Langmuir/pseudo 2nd order	-	[41]
		Direct red 23	Batch	6	12 h	30	-	2000	Langmuir/pseudo 2nd order	0.5 M NaOH followed by 0.5 M HCl/6 cycles	[47]
Magnetic Chitosan/PAMAM	-	Reactive Blue 21	Batch	8	6 h	25	-	555.56	Langmuir isotherm	-	[57]
Dendrimer Modified Magnetic Nanoparticles	59.4	Reactive black 5 (RBK5)	Batch	3	30 min	25	-	70.423	Langmuir isotherm /pseudo-second-order	At pH 11	[45]
Carbon nanotubes were modified using PPI dendrimer	-	Direct Blue 86 (DB86)	Batch	3	30 min	25	-	666.67	Langmuir isotherm	-	
		C.I. Direct Red 23 (DR23)						1000			
								Binary system			
								370.370			
								555.55			
PPI – grafted cotton fabrics, G5-PPI	-	Direct Red 80	Batch	3	20 min	25	-	143.3	Langmuir/pseudo 2nd order	-	[42]
		Disperse Yellow 42						104.8			
		Basic Blue 9						105.8			
Chitosan-PPI	-	Reactive black 5 (RB5)	Batch	2	30 min	40	-	6250	Langmuir isotherm/pseudo-second-order	-	[90]
		Reactive red 198 (RR198)						for RB5 and 5882.35 for RR198			
PAMAM – titania nanocomposite, G4	-	Direct Blue 78	Batch	2	25 min	25	-	1250	Langmuir/pseudo 2nd order	-	[87]
		Direct Red 80						990		-	
PPI hyperbranched polymer with silicic acid	20.6	Direct Red 23 (DR23)	Batch	-	24 h	25	-	33,333	Langmuir	-	[54]
PPI dendrimer	-	Direct red 80 (DR80)	Batch	2	0.5 h	25	-	33,333	Langmuir	Desorption with water at different pH	[77]
		Acid Green 25 (AG25)						33,333	Langmuir		
		Acid Blue 7 (AB7)						50,000	Freundlich		
		Direct Red 23 (DR23)						33,333	Langmuir		
PPI dendrimer	-	Direct Blue 78 (DB78)	Batch	2	0.5 h	25	-	33,333	Langmuir/Pseudo-second order	Desorption with water at different pH	[44]
		Acid Black 26 (AB26)						50,000			
Graphene oxide-PPI dendrimer	-	Acid Red 14	Batch	3	-	25	-	434.78	Langmuir isotherm/pseudo-2nd order	-	[78]
		Acid Blue 92						196.08			

the used impregnation percentage in order to get optimum removal capacity. Whereas, increasing the polymer concentration in chloroform leads to increase the impregnation percentage subsequently decrease the pore surface and mean pore size.

Allabashi et al. synthesized the ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers such as  $\beta$ -cyclodextrin, polyglycerol hyperbranched polymers, polyethylene imine and triethoxysilylated derivatives of poly(propylene imine) dendrimer. These compounds were impregnated via sol–gel reaction on different ceramic substrates ( $\text{TiO}_2$ , SiC, and  $\text{Al}_2\text{O}_3$ ) that led to the chemical bond formation with the ceramic substrates. The ceramic membranes were employed in a continuous filtration system for the removal of some organic pollutants from water. The impregnation has significantly improved the performance of ceramic membranes for sorption of selected organic pollutants. The empty ceramic substrate exhibited lower removal for the selected organic compounds. These membranes could remove methyl-tert-butyl ether (up to 46%), pesticides (up to 43%), trihalogen methanes (up to 81%), monocyclic aromatic hydrocarbons (up to 93%) and polycyclic aromatic hydrocarbons (up to 99%) [84].

PPI dendrimers functionalized with long aliphatic chains were effectively employed for the removal of fluoranthene, phenanthrene, and pyrene from water [85]. PPI dendrimers with 32 and 64 primary amino groups were used in the study. The maximum loading capacities of the dendrimers were found to be 67, 57 and 19 mg/g for pyrene, phenanthrene and fluoanthren, respectively. The higher sorption performance of PPI dendrimers towards the polyaromatic hydrocarbons is mainly due to the easy solubility of these hydrocarbons in the dendrimers environment. The polycyclic aromatic hydrocarbons (PAHs) are insoluble in water and soluble inside dendrimers. Therefore, the inclusion of these PAHs in dendrimers is a thermodynamically favorable process. Also, the formation of charge-transfer complexes between the tertiary amino groups and polyaromatics has amplified the solubilizing of PAHs. The dendrimers are reported to be easily regenerated with appropriate nonpolar solvent.

A molecular dynamics simulation for removing polycyclic aromatic hydrocarbons (PAHs) from water by PAMAM dendrimers and graphene oxides revealed that not only the surface area of the sorbent determines the amount removed of PAHs, but also the interaction between PAHs molecules [86]. This highlights that for developing materials for removal of polycyclic aromatic contaminants from water the interactions between the contaminants themselves should be considered. Table 3 summarizes the applications of different dendrimers for removal of organic compounds.

## 6. The factors affecting adsorption parameters

### 6.1. The pH of the solution

As mentioned in many examples above, the pH of the solution plays a major role in determining the adsorption efficiency of the dendrimer based adsorbents [49,77]. The pH considerably affects the chemistry of the surface and inner cores. It also affects the form of the metal ions, dyes, and other organic molecules. Especially in case of functional groups containing adsorbents, like amines in most of the dendrimers, pH change can protonate or deprotonate these groups. It can be noted that the maximum adsorption by the metal ions such as Pb(II), Cd(II), Cu(II), and Cr(II) on different dendrimer based adsorbents has been recorded in the pH range of 4.0–7.0, 4.0–6.2, 4.0–6.0 (with few exceptions), and 6.0–7.0 respectively. With the PAMAM dendrimers where the end groups are amines, increase in pH (from 2 to 7) leads to better adsorption of divalent metal ions. Actually, in all this pH range, there is a competition between divalent metal ions and hydrogen ions to adsorb on the surface, but with the increase in the pH, the hydrogen ions concentration decreases. At the pH higher than 7, metal ions precipitate into their hydroxides leading to low adsorption. Keeping all

the affecting parameters in view, optimum pH is selected. Fig. 20 shows the effect of solution pH on the adsorption of  $\text{SiO}_2$ -G0– $\text{SiO}_2$ -G4.0 for Pb(II), the optimal pH was found to be about 5. However, in case of anionic dyes, the role of the pH will be opposite. As the pH increases, the adsorption of anionic dyes will decrease. With the increase in pH the overall positive charge on the dendrimer surface decreases and thus the electrostatic interactions between adsorbent and anionic dyes. The optimum adsorption for dyes was observed in the pH range of 2.0–3.0 [42,44,77,87] (with few exceptions).

### 6.2. The effect of dendrimer generation

It has been reported that increase in dendrimer generation affects removal process positively [89]. For example, the adsorption capacity of CS-G3 was almost 18 times higher than bare chitosan (CS) [16]. The same finding has been reported by using the 4th generation of PAMAM-GO for the removal of selenium from wastewater [58]. The reason for increase in adsorption capacity with generation number is very obvious and it is related to increase in binding sites and reactive functional groups on the adsorbent surface and availability of higher number of internal cavities.

### 6.3. The contact time

The contact time is an important parameter in adsorption applications. Generally, with increase in contact time, the removal of pollutants increases, until an equilibrium state is achieved. The equilibrium time is dependent on pollutant concentration in the solution. The equilibrium may establish quickly with low pollutant concentration. Although the contact times ranging from 5 min [55] to 24 h [89] have been reported for removal of heavy metals by dendrimers, these times show some extreme values. With 100 mg/L of the initial concentration of MeHg(I), the adsorption capacity was reached/diminished significantly after 5 min. It was also observed that the percentage removal of MeHg(I) considerably improved with a decrease in initial concentration, 90% at 6 mg/L [55]. The reason for selecting 24 h as a contact time was not given, probably the time was not optimized and approximately maximum time was selected [89]. However, in most of the cases, for the removal of heavy metals, optimum contact time was in the range of 0.5–12 h.

The contact time for adsorption of Pb(II) by PAMAM-MNC was investigated in a range of 30–120 min at initial concentration 600 mg/L and pH 5.5. The maximum adsorption was observed at 30 min, and it was attributed to the fact that removal process was faster at the start due to the availability and abundance of active sites on the adsorbent surface which was gradually decreased [56]. Almost, similar trends have been observed for adsorption of organic pollutants and dyes.

### 6.4. Adsorption temperature

In most of the reports, the room temperature was used for adsorption of pollutants on dendrimer based adsorbents [14,16,41,42,48,89]. It might be attributed to the fact that good removal capacity by the adsorbents is desired at room temperature in real world applications.

However, a higher temperature of 40 °C was selected as optimum for the adsorption of some dyes on chitosan-polypropylene imine (CS-PPI). The results showed increased adsorption with the temperature due to the mobility of the large dye ion and swelling effect within the internal structure of the chitosan that allows the large dye molecule to penetrate further. The temperature was also found to influence the adsorption rate by affecting the molecular interactions and the solubility and a chemical reaction that may take place among the functional groups of the adsorbate/adsorbent and the dye [90].

**Table 3**  
Applications of dendrimer based adsorbents for removal of organic pollutants.

Name of dendrimer or dendrimer modified material	BET Surface Area (m <sup>2</sup> /g)	Name of target pollutant	Mode of adsorption experiment	Adsorption conditions				Adsorption capacity (mg g <sup>-1</sup> )	Isotherms/kinetics	Regeneration (condition/cycles)	Ref.
				pH	Time	T (°C)	Flow rate (in case of dynamic or column)				
Ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers	–	Polycyclic aromatic hydrocarbons Monocyclic aromatic hydrocarbons Trihalogen methanes Pesticides Methyl-tert-butyl ether	Continuous filtration	–	–	–	9, 3 and 1.7 mL/min	–	–	Using acetonitrile and gentle heating	[84]
PAMAM – titania nanohybrid, G4	–	Phenol	Batch	7	70 min	25	–	77	Langmuir/pseudo 2nd order	–	[48]
PPI hyperbranched polymer with silicic acid	20.6	Pyrene Phenanthrene	Batch	6.2	24 h	25	–	–	Langmuir	–	[54]
PPI dendrimers functionalized with long aliphatic chains	–	Fluoranthene Phenanthrene Pyrene	Batch	–	2 h 2.15 h 1.0 h	–	–	19 67 57	–	Regeneration is possible with appropriate nonpolar solvent	[85]
Organosilicon dendritic polymers impregnated the ceramic surface filter	–	Pyrene Phenanthrene β-naphthol	Dynamic	–	2 h	–	2–7 mL/min	–	–	Treatment with acetonitrile and gentle heating (< 50 °C)	[81]
PEI5-12 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	Batch	–	2 h	25	–	31 44 20	–	With acetonitrile	[96]
PEI5-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	21 44 11	–	–	–
PG5-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	6 15 8	–	–	–
PS2550-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	24 54 35	–	–	–
SL1520-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	21 35 19	–	–	–
S1200-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	11 14 6	–	–	–
H1500-18 <sup>1</sup>	–	Fluoranthene Phenanthrene Pyrene	–	–	–	–	–	12 15 20	–	–	–
Diaminobutane poly (propylene imine) dendrimer (DAB) Polyethylene imine (PEI) b-Cyclodextrine (CD)	–	Anthracene MTBE BTX Fluoranthene Atrazine Simazine Bromodichloromethane Dibromochloromethane	Dynamic	–	–	–	0.1–9.9 mL/min	–	–	–	[82]
Alumina filter impregnated with poly(ethylene imine) hyperbranched polymer functionalized with octyl aliphatic chains (PEI5-C8)	3.48 2.75 2.24	Phenanthrene and β-naphthol	Dynamic	–	–	–	2 mL/min	–	–	–	[83]

### 6.5. The adsorption isotherm models

Adsorption isotherms are imperative as they offer information about the adsorption capacity and how adsorbate interacts with an adsorbent, which is critical in optimizing the application of an adsorbent. Two commonly used isotherm models are the Langmuir and Freundlich models.

The Langmuir model assumes the uptake of pollutants occurs on a

homogenous surface by monolayer adsorption without any interaction between adsorbed ions while the Freundlich model provides an empirical relationship that explains the uptake of pollutants on a heterogeneous surface by multilayer adsorption, and also assumes that different sites with several adsorption energies are involved [88]. Generally, one of these isotherms models can best describe the adsorption process. The adsorption of heavy metals and organic pollutants on dendrimer based adsorbents was best described by Langmuir

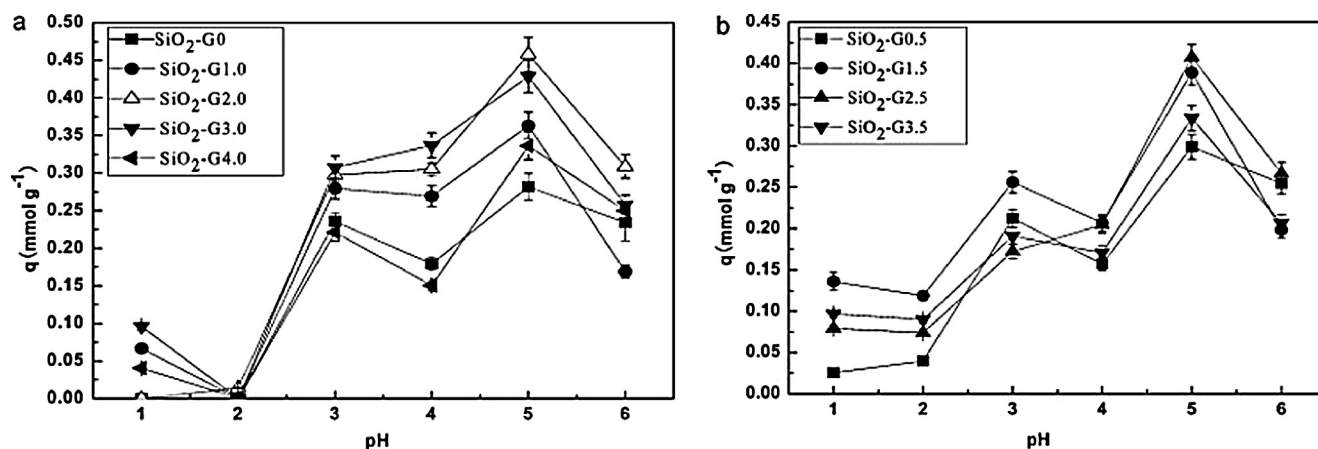


Fig. 20. Effect of pH on the adsorption of SiO<sub>2</sub>-G0–SiO<sub>2</sub>-G4.0 for Pb(II) (a) for amino-terminated products and (b) for ester-terminated products. Reproduced with permission from [88]. Copyright (2013) Elsevier B.V.

equation [16,37,40,48,54,57,58,60,62,88]. However, in some cases, Freundlich equation can correlate adsorption process in the best way [35,36]. There are few reports where authors have employed models other than these two [75].

#### 6.6. Regeneration of dendrimer adsorbents

Regeneration of the adsorbent is not only necessary for the repeated use in practical applications but it also reduces the amount of adsorbent materials, thereby lowering the costs of the adsorbent. Studies have confirmed that dendrimer based adsorbents can be reused for several cycles without noticeable loss in the adsorption capacity.

Functionalized SBA-15 mesoporous silica with amine (–NH<sub>2</sub>)/melamine-based dendrimer amines (MDA) employed for the removal of Cd(II), Cu(II) and Pb(II) was successfully regenerated by using different acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl [14]. However, 0.3 M HCl was found to be more effective than other concentrations as well as other acid types. It was found that a minor loss in the adsorption capacity of only 5.7% for Cd(II), 6.3% for Cu(II) and 4.7% for Pb(II) occurs compared to the initial value after four cycle.

Xiao et al. reported 90% and 80% removal of 20 mg/L Hg(II) and MeHg(I) respectively by DNA fragments assembled-Polyamidoamine grafted core-shell magnetic silica nanoparticles after five consecutive regeneration cycles [55]. For regeneration, MeHg(I), MeHg(I)-loaded adsorbents were dispersed in 2 mL of 0.2 mol/L EDTA solution and stirred for 30 min, then collected by magnet and re-dispersed, and finally added into 2 mL of 20 mg/mL herring sperm DNA solution. The nanoparticle assemblies were collected after 20 min, washed three times and stored at 4 °C before next run.

Similarly, G3-MNPs retain their original removal capacity for removal Zn(II) even after 10 consecutive adsorption–desorption cycles [15]. Regeneration of the adsorbent was carried out by mixing the Zn(II)-laden G3-MNPs with 10 mL of 0.1 M HCl solution where Zn(II) was recovered in a concentrated form. As shown in Fig. 21, more than 90% of Zn(II) was recovered in 10 cycles except cycle 6. This suggest that G3-MNPs can be used repeatedly for the adsorption of Zn(II) ions. Similarly, poly(amidoamine) (PAMAM) dendrimers were regenerated after Cu<sup>2+</sup> and Pb<sup>2+</sup> ions adsorption by 2 N HCl solution [39,74]. It was found that HCl is also efficient in regenerating amine terminated-magnetic cored dendrimers [49] and poly(amidoamine)-graft-poly(methyl acrylate) magnetic nanocomposite [56].

Besides, applications of solvents for the regeneration of adsorbents, some adsorbents can be regenerated easily by decreasing the solution pH. PAMAM dendrimers with ethylenediamine (EDA) core and terminal NH<sub>2</sub> groups was regenerated after Cu(II) ions adsorption by decreasing the solution pH to 4 [69]. Similarly, carbon nanotubes modified poly-

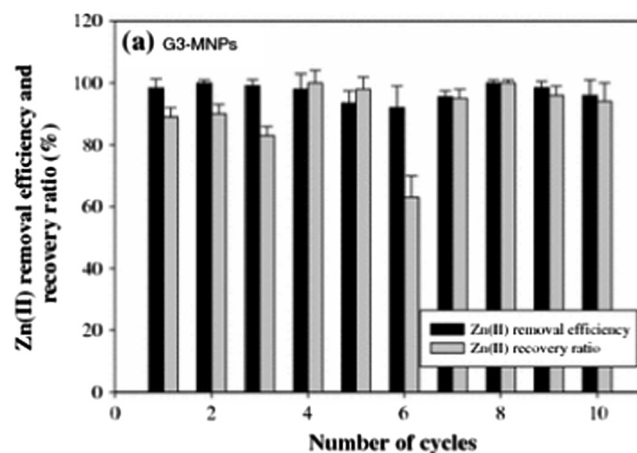


Fig. 21. Adsorption and desorption of Zn(II) by G3-MNPs at pH 7. Reproduced with permission from [15]. Copyright (2010), Springer Science + Business Media B.V.

amidoamine dendrimer was regenerated after heavy metals (Cu(II) and Pb(II)) adsorption by using aqueous solution at pH 2 [61].

Magnetic chitosan/poly(amidoamine) dendrimers was regenerated after adsorption of Reactive Blue 21 by using 0.5 M NaOH [47]. The adsorbent was washed with 0.5 M HCl and deionized water before using it for the next run.

Fig. 22 shows reusability of the adsorbents after six cycles. The reusability of the adsorbent decreased rapidly before the first cycle. However, a recovery rate of 41.64% was noticed after three cycles. Regeneration of the dendrimers based adsorbents after adsorption of organic pollutants is possible appropriate nonpolar solvent [85].

#### 7. Toxicity of dendrimers based adsorbents

For the remediation of heavy metals in aqueous media, a wide variety of adsorbents has been employed. The toxicity of the adsorbent itself is a major concern when it is used for water purification. If we talk about carbon based adsorbents, they have been extensively used for water purification due to their exceptionally high surface areas and ability to form a different kind of interactions with target pollutants. Moreover, they have shown excellent adsorption potential both for inorganic and organic pollutants. However, their toxicity is a big issue. Carbon nanotubes and graphene have shown severe toxicity to human health, and it has been suggested to remove these materials from the water [92].

As they can dissolve poorly soluble drugs and improve their bio-availability, dendrimers have been extensively employed as carriers for

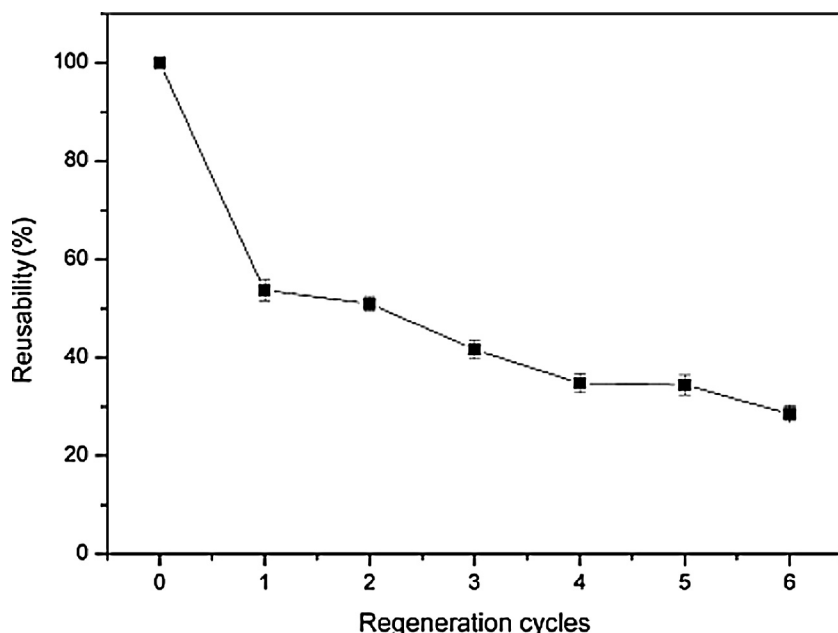


Fig. 22. Reusability of the chitosan/poly(amidoamine) dendrimers after Reactive Blue 21 adsorption. Reproduced with permission from [47]. Copyright (2016) Taylor & Francis.

delivery of anticancer, anti-viral, anti-bacterial, antitubercular drugs. Dendrimers have been reported less or non-toxic but overall data in this direction is scarce as the field of synthesis of dendrimers is still in its infancy stage. However, safe and efficacious dendrimers can only emerge from the rational chemical design supported by a clear understanding of biological rationale [93]. In most of the studies, dendrimers are used in combination with other materials such as CNTs, graphene oxide, and magnetic nanoparticles, so it encourages to investigate the toxicity of the whole system instead of dendrimers alone. There is a perception that carbon based supports are toxic only in pure form due to the presence of metallic impurities and their functionalization leads to a reduction in toxicity. However, such claims should be supported by experimental evidence.

## 8. Outlook

The dendritic polymers based adsorbents are getting the attention of the researchers due to their tunable structures and properties. The dendritic polymers can be synthesized per nature of the pollutants by using suitable functional moieties. In addition to external surface areas, they provide higher inner surface areas for capturing target pollutants. They can be used in combination with different supports and other materials. As it can be noted from the published literature, the dendritic polymers have not been much explored in the area of removal. The one possible reason can be their multistep synthesis which requires a lot of expertise. This difficulty can be overcome by research collaboration between the organic synthetic chemists and experts of separation science. Such collaboration can help in designing more selective, application-oriented, and cost-effective dendritic polymers. Dendrimers are the one widely investigated, but it also needs to evaluate the potential of other dendritic structures besides dendrimers for removal applications such as dendrons, dendrigrafts, hyperbranched polymers, and dendronized polymers. Instead of a general description of dendritic features, researchers need to more often demonstrate dendrimer features for pollutant removal applications to the separation science communities. Prominently, these demonstrations have to focus on a precise removal application that requires improvement and describe how dendrimers can serve in that particular problem. The newly developed dendrimers should be benchmarked against existing adsorbents. Also, any new dendrimer has to improve removal efficiency compared to other adsorbents, just demonstrating a new kind or

addition will be not enough. In summary, the scope of dendrimers in removal application should be further investigated in different possible directions.

## 9. Conclusion

The performance of adsorption based removal depends on the nature and physicochemical properties of the adsorbent. Specific surface area and amount of functionalization are critical in determining the efficiency of a newly synthesized adsorbent. Dendrimers are an excellent addition to the world of adsorbents as they are hyperbranched macromolecules with unique three-dimensional structures and extensively functionalized with reactive end groups. They have high internal and external specific areas. Both surface and internal cavities can entrap and bind with target pollutants through a wide variety of interactions. They have shown extra-ordinary potential in water remediation. Dendrimers can be used alone or supported on different materials. They can be immobilized over the membranes in dynamic systems. Their performance is affected by dendrimer generation, solution pH, contact time, etc. Dendrimers can be tailored and fine-tuned as per nature of the target pollutants. They are relatively less-toxic and biocompatible which is a positive indicator for their future applications in water treatment and commercialization.

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