Original Article

Polyamidoamine (PAMAM) dendrimers synthesis, characterization and adsorptive removal of nickel ions from aqueous solution

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ABSTRACT

Nickel is a toxic metal and present in the effluents of electroplating industries. Conventional methods to remove nickel are expensive and ineffective. Heavy metals can be easily adsorbed by dendrimers. Dendrimers are radially symmetric, nano-sized molecules with homogeneous, mono-dispersed and well-defined structures consisting of the tree-like branches, characterized by terminal poly functionality. The present study was focused on the synthesis of PAMAM dendrimers by divergent method and their use for the removal of nickel from aqueous solution. Characterization of synthesized dendrimers were carried out by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-visible spectroscopy and zeta sizer analysis. Different parameters such as contact time, concentration of dendrimers, pH and metal concentration have been optimized. Therefore, equilibrium isotherms and adsorption kinetics were determined. Estimation of extent of metal removal was carried out by Atomic Absorption Spectroscopy. Results have revealed that PAMAM dendrimers could possibly be used for the removal of nickel from industrial effluents.

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1. Introduction

Polymers have vast applications in the biomedical field due to their useful properties, such as: easy processing, lightweight and flexibility, high strength to weight ratio, availability and recyclability[1–7]. A dendrimer is generally reported as a macromolecule, which is distinguished by its extremely 3D branched structure that gives a high degree of versatility and surface functionality. Dendrimers have usually been referred to as “21st century Polymers”. The globular structure of dendrimers, exclusive architectural design, high degree of

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branching, precise molecular weight and multivalence clearly differentiates these as optimum and unique nanocarriers in the medical applications such as tumor therapy, drug delivery, diagnostics and gene transfection [8–16]. A dendrimer is extremely branched man-made polymer with a core where monomer unit is attached, leading to a tree-like, monodispersed, generational or star-shaped structure with well-defined molecular weights [17–20]. There are mainly two methods for dendrimer synthesis i.e. divergent and convergent [21]. PAMAM dendrimer was generally synthesized by the divergent method. Main disadvantage of convergent method is that we cannot synthesize a large molecule for drug loading due to crowding and steric effect. Hence divergent method of dendrimer synthesis was selected. In the divergent approach, the construction of the dendrimer takes place in a stepwise manner starting from the core and building up the molecule toward the periphery using two basic operations (1) coupling of the monomer and (2) de-protection or transformation of the monomer end-group to create a new reactive surface functionality and then coupling of a new monomer in a manner somewhat similar to that known from solid-phase synthesis of peptides or oligonucleotides [22]. Nitrogen acts as a starting atom to build the dendrimer, to which through reiterating series of chemical reactions, carbon and the other elements are attached that produces a spherical branching structure [23,24]. Dendrimers have three architectural components, namely (i) Generations (Interior layers) consists of the repeating units, attached radially to interior core, (ii) Terminal functionality (exterior) attached to the peripheral interior generations, (iii) An initiator core [25].

Dendrimers are also useful for the removal of heavy metals from industrial wastewater. The removal of metal ions from dendrimers can be quickly attained by the protonation of amine functional groups at low pH. The adsorbed ions can be recovered for reuse. This property makes PAMAM dendrimers mainly auspicious as recyclable chelating agents for the metal ion separation. Although dendrimers have benefits in water and wastewater treatment, preparation of these materials is a challenge [26–33].

The objectives of the present work were the application of synthesized full zero generation dendrimers to remove metal ions such as Ni from industrial wastewater [24]. Effect of factors such as pH, contact time, adsorbent concentration and concentration of adsorbate on metal ion uptake was studied. G0 dendrimers were characterized by FT-IR analysis, UV-Vis spectroscopy and zeta sizer analysis.

2. Material and methods

All the chemicals and reagents used in this study were of analytical grade and were purchased from Sigma–Aldrich (Ethylene diamine) and Dae-Jung Korea (Methyl acrylate, Methanol).

2.1. Method of preparation of PAMAM dendrimers

PAMAM dendrimers were synthesized by divergent method starting with a core initiator molecule which contains functional groups capable of acting as active sites in the initial reaction. Outward growth of PAMAM dendrimers was accomplished by alternating between two reactions: Michael addition of the amino-terminated surface onto methyl acrylate, resulting in an ester-terminated outer layer and coupling with ethylene diamine to achieve a new amino-terminated surface [35].

2.2. Synthesis of ester-terminated (half-generation) PAMAM dendrimers

Ethylene diamine (EDA) in the very first step was dissolved in methanol, cooling the mixture in an ice bath. Then methyl acrylate was added dropwise at stirring to the dendrimer solution. The mixture was kept at room temperature several days and at 45 °C a few days. Nearly pale amber colored syrup was obtained which leads to the formation of solid particles [36].

2.3. Synthesis of amino-terminated (full-generation) PAMAM dendrimers

EDA and multi-ester was dissolved in methanol separately and then cold multi-ester solution was gradually added to the EDA solution. After the addition was completed the mixture was allowed to warm at room temperature and the reaction continued for several days. As a result, nearly colorless viscous syrup was obtained [37].

2.4. Evaluation of PAMAM zero generation dendrimers

Zero generation PAMAM dendrimers were scanned in the range of 200 nm–400 nm against distilled water. The changes in \( \lambda_{\text{max}} \) values were noted [38–40]. Dendrimers were also subjected to FT-IR spectroscopy analysis (Bruker Optics, Germany), UV-Vis spectroscopy (CECIL, CE7200, 7000 Series), Scanning electron microscopy (SEM) and Particle size analysis [41].

2.5. Removal of Nickel from metal ion solution

Ni solution was formed by dissolving NiCl₂ in distilled water and zero generation dendrimer was dissolved in the above solution, mixed these solutions and kept at room temperature for 4 min. Extent of removal of Ni from solution was evaluated by AAS (Atomic Absorption Spectroscopy).

2.6. Optimization of Adsorption conditions (Adsorbent concentration, Adsorbate concentration, Contact time, pH)

Different concentrations 1, 2, 3, 4, 5, 6, 7, 8 mL of adsorbent were added to the fixed concentration of metal ion solution to check optimum concentration of adsorbent and extent of metal removal was evaluated by AAS [42]. Metal ion uptake experiment was performed with different concentrations of adsorbate like 100, 200, 300, 400, 500 ppm for fixed concentration of adsorbent and check the optimum concentration of adsorbate. Metal uptake through dendrimer was estimated by AAS [43].

To study the effect of contact time on the metal uptake by the dendrimer, the polymer was allowed to react with the metal ion solution in water at various time intervals i.e. 1, 2, 3,
PAMAM dendrimers were observed to be in nano scale. Surface morphology shows that -0.5 generation of PAMAM dendrimer have needle like structure while zero generation have spherical shape (Fig. 3) [49]. Particle size of zero generation dendrimer was found to be 827 nm (Fig. 4). It was determined by using the zeta sizer and confirmed to be in nanometer range [37]. A series of experiments were carried out with the various variables to remove nickel from industrial waste water [50–57].

3.2. Optimization of adsorption condition for the removal of nickel

3.2.1. Effect of dendrimer concentration

Dendrimers have certain capacity for adsorption and Fig. 5 exhibits that the removal of nickel is increased by increasing dendrimers concentration to certain level and then is declined. When concentration of dendrimers is increased, interaction between adsorbent molecules is high as compared to adsorbent and adsorbate molecules. Dendrimer optimum concentration for the removal of nickel was 6 mL. The effective removal of nickel increases due to accessibility of additional active surface sites in the high dendrimer concentration for the nickel adsorption [43]. Dendrimers are known as ligands soluble in water, which remove toxic metal ions from water [58].

3.2.2. Effect of adsorbate concentration

Fig. 5 showed that dendrimers active sites are reduced when concentration of nickel is increased. There is an equilibrium between adsorption and desorption process and when this equilibrium is achieved, interaction between adsorbent and adsorbate molecules is nearly constant. It was observed that 300 ppm was optimal concentration of adsorbate for the removal of nickel [59].

3.2.3. Effect of contact time

It was observed (Fig. 5) that 4 min was the optimum time for equilibrium for the zero generation dendrimers. After 4 min, uptake efficiency of dendrimer was nearly constant. So, further studies were carried out at seeing 4 min as optimum time for nickel metal ion uptake [60].

3.2.4. Effect of adsorption pH

Metal ion uptake by G0 dendrimer was studied at different pH (Fig. 5). It was observed that for zero generation dendrimer, metal ion uptake was increased with increase in pH. When pH of the solution was increased, number of the positively charged sites on surface of the dendrimers was reduced and negatively charged sites were increased and adsorption of nickel was also increased [42]. In elevated pH, dendrimers surface charges become negative and tendency to nickel adsorption by electrostatic process was increased. It was observed that, effect of metal ion uptake is independent to core and spacer length of dendrimer [26].

All the above optimized conditions were applied to treat the industrial waste water for the removal of nickel. Results exhibited that before treatment with dendrimers, Ni metal concentration in industrial wastewater was 0.4 ppm. While after treatment, Ni metal was captured by dendrimer and

4, 5 min. The metal uptake was estimated by AAS after fixed interval [44].

Metal ion uptake experiments were carried out at different pH 5, 6, 7, 8, 9, 10 for a fixed interval of time with the metal containing dendrimer and metal ions in water and from the amount of metal intake of the metal containing dendrimer the influence of these factors was generalized [45]. The mixture of 10 mL industrial waste water and 5 mL dendrimer was kept at 25 °C for 4 min. Upon completion extent of removal of nickel from aqueous solution was carried out by AAS.

3. Results and discussion

3.1. Characterization of PAMAM dendrimers

Dendrimers were kept in the beakers in the non-aqueous and aqueous solvents e.g. ethanol, water, n-butanol and methanol. Precisely weighed dendrimers were kept separately with all the solvents and then for twelve hours kept at room temperature to check the dendrimers solubility. The dendrimers are soluble in methanol and sparingly soluble in ethanol, butanol and distilled water. PAMAM dendrimers were characterized by the techniques like UV-Vis, SEM, FTIR and particle size analysis.

UV-Vis spectroscopy provides the evidence of formation as well as the conjugation (surface modification) on dendrimers due to characteristic shift in value of lambda max. UV-Vis spectroscopy is used to identify the functional groups attached on dendrimer molecules. Characteristic curves in UV-Vis spectrum shows the specific maximum absorption peaks at particular wavelength, which is assigned to the contribution of the conjugated part. Absorption maxima ($\lambda_{\text{max}}$) was recorded for G0 dendrimers. The $\lambda_{\text{max}}$ of G0 PAMAM dendrimers (Fig. 3) were at 278 nm [46,47].

The G0 dendrimers were analyzed by FT-IR spectroscopy. The FT-IR peaks provide the proof of modification of free amino group into amide group. The FT-IR spectra of G0 PAMAM dendrimers were in Fig. 2 [48]. The peaks are observed at 3352 cm$^{-1}$, 1596 cm$^{-1}$, 1453 cm$^{-1}$ are characteristics of NH stretch (primary amines), NH bending of N-substituted amide and CH bending respectively. On the other hand, CH stretch is observed with the peaks at 2865 cm$^{-1}$ and 2937 cm$^{-1}$.

![Fig. 1 – UV Spectra of G0 PAMAM dendrimers.](image-url)
decreased up to 0.15 ppm. The result showed that industrial wastewater was successfully treated for the removal of nickel by the dendrimer than any other adsorbent and results obtained in a very short time due to the effectiveness of dendrimer.

3.3. **Kinetic studies**

In the present study, the experimental data were analyzed using different kinetic models such as pseudo first order, pseudo second order and intra-particle diffusion equations.
3.3.2. Pseudo-second-order model
The second order model assumes that the adsorption process is of pseudo-second-order and the rate limiting step is chemisorption. The mechanism may involve sharing of valence forces or through the exchange of electrons between the adsorbent and the adsorbate [63].

The pseudo-second-order equation may be expressed in the following form:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

A plot of \( \frac{t}{q_t} \) versus \( t \) gives a straight line of slope \( \frac{1}{q_e} \). Values of \( k_2 \), \( q_e \) and \( R^2 \) were depicted in Table 1. The correlation coefficient of pseudo-second order was in the range of 0.961–0.997 which reveals that experimental data is also in good agreement with this kinetic model. Consequently, it can be inferred that chemical process controls the adsorption rate [42].

3.3.3. Intra-particle diffusion model
Intra particle diffusion is a process probably governs the adsorbate transport from the bulk of the solution into the solid-phase [64]. Adsorbate transportation from liquid to solid phase is often the main limiting step in adsorption processes.

The equation of intra-particle diffusion model is given below:

\[ q_t = K_{pi} t^{1/2} + C_i \]  

Here \( C_i \) is intercept that explain the thickness of the boundary and it rises with increase in concentration and \( K_{pi} \) (mg/g) is the rate constant for intra-particle diffusion. Regression correlation coefficient \( R^2 \) is in the range of 0.907–0.984. It was studied that the data was best explained by intra-particle diffusion model when the plot was linear and pass from the

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**Table 1 – Kinetic models and parameters.**

<table>
<thead>
<tr>
<th></th>
<th>( q_e )</th>
<th>( k )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>10</td>
<td>-0.5326</td>
<td>0.9305</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>113.63</td>
<td>0.086</td>
<td>0.9999</td>
</tr>
<tr>
<td>Intra particle diffusion</td>
<td>98.644</td>
<td>6.289</td>
<td>0.9425</td>
</tr>
</tbody>
</table>

Kinetic studies of adsorption of metal ions by adsorbent determined the reasonable length of time to attain the adsorption equilibrium and explain the process mechanism of metal ions adsorption onto the adsorbent.
3.4. Adsorption isotherm study

Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites and its degree of accumulation onto adsorbent surface at constant temperature. Adsorption isotherm describes the equilibrium relationship between the quantities of metal ions adsorbed onto the adsorbent (Qe) and the concentration of metal ions in solution (Ce) at a given experimental condition. Freundlich and Langmuir isotherm models were mostly used for the explanation of isotherm data [65].

3.4.1. Langmuir adsorption model

The Langmuir adsorption model [66] is based on the assumption that a maximum limiting uptake exists, corresponding to a saturated monolayer of adsorbate molecules at the adsorbent surface. In this model, all the adsorption sites have the same adsorption activation energy. The Langmuir equation can be written as

\[
\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q}
\]  

(4)

where \(q_e\) is the amount of metal adsorbed per unit mass of adsorbent, \(C_e\) is the concentration of adsorbate in the solution at equilibrium, the maximum capacity of adsorption is \(q_m\) that gives the explanation of adsorption on entire single layer and \(K_a\) is the Langmuir constant related to the adsorption energy. Fig. 7 revealed that Langmuir model could not explain the experimental data. A Low R² value indicates that there was no homogeneous distribution of active sites on the adsorbent surface.

3.4.2. Freundlich isotherm

The Freundlich adsorption isotherm [67] assumes that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism, and that the adsorbed amount increases with the concentration according to the following equation:

\[
q_e = K_f C_e^{1/n}
\]  

(5)

The energy of biosorption logarithmically decreases with the increase in active sites that are occupied. \(K_f\) and \(n\) are Freundlich isotherm incorporating adsorption capacity and intensity, respectively. Freundlich isotherm can properly estimate the adsorption intensity of adsorbent towards the adsorbate. The values of \(K\) and \(n\) can be determined from the slope and intercept of the linear plots of \(\ln(q_e)\) vs. \(\ln(C_e)\), respectively. Adsorption is considered as satisfactory when the Freundlich constant \(n\) takes values within the range 1–10. The R² value was very close to 1, indicating that the adsorption isotherm is very well modelled by the Freundlich equation. Since the adsorption of Ni from aqueous solution is suitable method with PAMAM dendrimers so these could possibly be used for removal of metals from industrial effluents [56,68–71].

4. Conclusions

Following conclusions have been drawn;

The study points out that dendrimers (PAMAM G3) have a high adsorption capacity for nickel removal from aque-
ous solutions. Characterization of synthesized dendrimers were carried out by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-visible spectroscopy and zeta sizer analysis. Adsorption kinetics was studied using intra-particle diffusion, pseudo first and pseudo second order equations. The effects of variables such as nickel concentration, concentration of dendrimers, contact time and pH were also investigated. Data have a good correlation with Freundlich isotherm. So, it can be concluded that adsorption of nickel with dendrimers is a suitable method with high efficacy for nickel removal from aqueous solutions. Higher generation dendrimers also have more exposed functional groups on the surface, which can later be used for customizing the dendrimer in a given application.

Conflict of interest

The authors declare that there is no conflict of interest.

References


