



Computational calculation identified optimal binding sites in nano-sized magnetic-cored dendrimer

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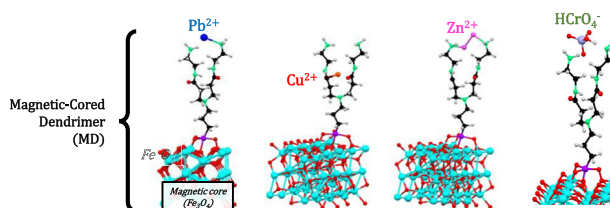
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HIGHLIGHTS

- Binding of four metal ions to magnetic-cored dendrimer was examined.
- Binding configuration and energies were calculated using density functional theory.
- Stable configuration between each ion and the dendrimer was identified.
- Pb^{2+} was preferably adsorbed in the mixed solution of Pb^{2+} , Cu^{2+} , and Zn^{2+} .

GRAPHICAL ABSTRACT

Optimal configuration between each metal ion and magnetic-cored dendrimer was identified through density functional theory



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ABSTRACT

Magnetic-cored dendrimers (MDs) with amino groups were prepared with the formation of poly(-amidoamine) dendrimer on the surface of magnetite nanoparticles (MNPs). The experiment involved the binding of four different heavy metal ions including Pb (II), Cu (II), Zn (II), and Cr (VI). Density functional theory (DFT) calculation was applied to the experimental results to determine the optimal configurations between the heavy metal species and generation 1 amino ($-\text{NH}_2$) functionalized MD (G1- NH_2 -MD). Different binding configurations among the possible binding positions of inner and outer G1- NH_2 -MD were determined with the ionic radius and coordination number of each heavy metal ion. Although Pb^{2+} and Zn^{2+} were stable in the terminal positions, Cu^{2+} was the most stable in the internal position. The oxygen and hydrogen atoms of HCrO_4^- formed a hydrogen bond with the $-\text{NH}_2$ groups, and thus dipole-nonpolar molecular interaction occurred with the $-\text{CH}_2$ groups of G1- NH_2 -MD. Specific binding positions and energies of different heavy metal species were identified through the DFT calculation in the study. The DFT calculation results also contributed to an understanding of the binding priority of each metal ions in the mixed solution. Furthermore, Pb^{2+} was preferably adsorbed in the mixed solution of Pb^{2+} , Cu^{2+} , and Zn^{2+} .

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1. Introduction

Dendrimers with tree-like molecular structures are used for various applications such as drug delivery and light harvesting

(Crooks and Zhao, 1999; Diallo et al., 1999; Trinchì and Muster, 2007). Different methodologies were developed to synthesize different types of dendritic structures (Tomalia et al., 1985; Bryszewska, 2001; Abbasi et al., 2014). The poly(amidoamine) (PAMAM) dendrimer is one of the most frequently examined dendrimers (Liu et al., 2005). Recently, applications of dendrimers to environmental decontamination were actively performed owing

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to an increase in the interest to utilize nanomaterials (Inoue, 2000; Quintana et al., 2002). Terminal groups were modified with various moieties including simple functional groups, macromolecules, and inorganic materials to expand the applicability of dendrimers to different types of target compounds. Combinations with templates, such as insoluble organic, inorganic, or hybrid supports, were also suggested to enhance the surface area and obtain unique properties (Huang et al., 2014; Sun et al., 2016).

Dissolved ions as target compounds are attached to the periphery of the branches or encapsulated in the interior voids of dendrimers. The suggested possible binding sites of PAMAM dendrimers included core tertiary amine, interior amide, and terminal primary amines (Tarazona-Vasquez and Balbuena, 2004). The density functional theory (DFT) is used to understand the structural and dynamical characteristics between dendrimers and target ions. The optimal molecular geometry and vibrational frequencies of different dendrimers were also investigated using DFT calculations (Furer et al., 2017; Gao et al., 2017). The DFT calculation revealed a stable configuration between generation 0 PAMAM dendrimers and metal ions (Camarada, 2016, 2017). The DFT calculation was utilized to interpret the experimental results from metal ion binding onto dendrimers with various terminal groups such as hydroxyl, sulfur capped, and salicylaldehyde (Tarazona-Vasquez and Balbuena, 2005; Niu et al., 2014, 2016). This enabled the interpretation of experimental results and prediction of the molecular-level structural properties and relationships (Mason et al., 2015).

Magnetic-cored dendrimers (MDs) exhibit dendritic branches developed on the surface of magnetic nanoparticles (MNPs) (Jung et al., 2016; Kim et al., 2016; Kim and Park, 2017). With the magnetic core, the chemistry around MDs is significantly different from that of the PAMAM dendrimer. Although extant studies extensively examined the PAMAM dendrimer, there is a paucity of information on the structural configuration of MDs. Metal ions may interact with both the interior and terminal amino groups of the PAMAM dendrimer (Diallo et al., 2005; Jiang et al., 2007). Rigid terminal groups prevent the diffusion of metal ions into the inner space of the PAMAM dendrimer as the outer functional groups form a positive shell at the surface of dendrimers. It is necessary to identify the positions of MDs that are responsible for the binding of different metal ions such that we understand the microscopic behavior of the MDs and target material in environmental interfaces.

The objective of the present study involved applying DFT calculations to the MDs such that it is possible to obtain a better understanding of the binding between the MDs and dissolved ions. Previous studies reported on applications of DFT to PAMAM grafted magnetic nanocomposite although they only included the PAMAM dendrimer segment in the calculation (Pourjavadi et al., 2016). Extant studies did not focus on the theoretical interpretation of the interaction between heavy metals and MDs with an amine terminal group. In the present study, four different heavy metal ions of Pb (II), Cu (II), Zn (II), and Cr (VI) were experimentally bound to generation 1 amino ($-NH_2$) functionalized MD (G1- NH_2 -MD). The experimental results were interpreted via DFT calculations. Different configurations between the G1- NH_2 -MD and the metal ions were calculated using the DFT. The DFT calculations in the study aid in understanding intermolecular bonds formed between the functional groups of the dendrimer and metal ions.

2. Experimental section

2.1. Materials

Iron (II) sulfate heptahydrate (>99%), 3-aminopropyl trimethoxysilane (APTS, 97%), zinc chloride (>97%), potassium dichromate (>99%), copper (II) sulfate pentahydrate (99.9%), and lead (II)

nitrate (>99%) were purchased from Sigma-Aldrich (USA). Iron (III) chloride hexahydrate (97–101%), methyl acrylate (MA, 99%), and hydrochloric acid (35%) were from Junsei Chemical Co (Japan). Ethylenediamine anhydrous (EDA, 97%) and ammonium hydroxide (25–28%) were obtained from Daejung Chemicals & Metals Co (Korea). Sodium hydroxide (93%) was purchased from Showa Co (Japan). Cadmium nitrate tetrahydrate (99.9%) was supplied by Alfa Aesar (USA). Methyl alcohol (99.5%) was purchased from Samchun Pure Chemical Co (Korea). The quality control standard 21 at $100 \mu\text{g ml}^{-1}$ (PerkinElmer, USA) was used for calibration in inductively coupled plasma-optical emission spectrometry (ICP-OES). All reagents were used without further purification. Deionized water purified to $18.2 \text{ m}\Omega\text{-cm}$ was used in all the experiments.

2.2. Preparation of MNP, G0-MD, and G1- NH_2 -MD

In the experiment, MNPs, generation 0 MD (G0-MD), and G1- NH_2 -MD were synthesized by following procedures used in previous studies as shown in Fig. 1(a) (Jung et al., 2016; Kim et al., 2016; Kim and Park, 2017). Bare MNPs were formed when ammonium hydroxide solution was added to the mixed solution of iron (II) sulfate heptahydrate and iron (III) chloride hexahydrate. The molar ratio of Fe (III) and Fe (II) was 1:2, and the pH was set to 10 (Chou and Lien, 2011). The solution was stirred at 80°C for 30 min and washed with deionized water and methanol five times after magnetic separation following the reaction. Subsequently, the surface dendritic structure was grown in three steps. The MNPs were dispersed in 400 ml methanol, and 25 ml APTS was added to the solution. The solution was agitated at 60°C for 7 h to form G0-MD. The G0-MD was dispersed again in 100 ml methanol, and 50 ml MA was added and stirred at room temperature for 7 h. Subsequently, 10 ml EDA was added and agitated at room temperature for another 3 h to form G1- NH_2 -MD. The synthesized G1- NH_2 -MD was washed with methanol five times. The products were dried at 60°C and stored as powders in a dark container (Kim and Park, 2017).

2.3. Characterization

The morphology of the final products was observed via a transmission electron microscope (TEM, JEM-2010, JEOL, Japan) and scanning electron microscope (SEM, JSM-6340F, JEOL, Japan) with an acceleration voltage of 15.0 kV. Portions of the final products were dispersed in methanol and subsequently dropped on the carbon-copper grids for TEM analysis. Thermogravimetric analysis (TGA) was performed with a simultaneous TGA/DTA/DSC (SDT Q600, TA Instruments, USA) at a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 800°C under N_2 . Fourier transform-infrared (FT-IR) spectra were obtained on a Spectrum Two IR Spectrophotometer (L160000A, Perkin Elmer, USA) with a range of 4000 to 400 cm^{-1} . X-ray diffraction (XRD) patterns of the samples were obtained by using an X-ray diffractometer (Rigaku D/MAX RINT 2000, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418740 \text{ \AA}$) in the range of $2\theta = 20$ – 80° . The specific surface area and pore size distribution were measured with a surface area analyzer (Autosorb-iQ 2ST/MP, Quantachrome, USA) using the Brunauer–Emmett–Teller (BET) N_2 method. All samples were degassed at 100°C for 3 h under N_2 gas flow prior to the analysis. Zeta potential of the particles was characterized with a zeta-sizer (ZS-90, Malvern, UK). Aqueous heavy metal ions were analyzed with an ICP-OES (Optima ICP-OES 8000, Perkin Elmer, USA).

2.4. Binding of the metal ions to MD

Sorption experiments were performed in a batch mode at ambient temperature. Specifically, G1- NH_2 -MD (0.05 g) was added

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