DENDRIMER MODIFIED MAGNETITE PARTICLES
FOR HEAVY METAL (COPPER(II), COBALT(II), ZINC(II), NICKEL(II))
REMOVAL FROM WATER

by

Xuesong Liu

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Civil Engineering

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ABSTRACT

In this study, magnetite particles were synthesized and functionalized with (3-aminopropyl)trimethoxysilane (APTS) to obtain Generation 0 Poly(amidoamine) (PAMAM) dendrimer modified magnetite particles. Particles were tested for the adsorption of Cu(II), Co(II), Zn(II), and Ni(II) from aqueous system. Magnetite particles were synthesized by coprecipitation under optimized reaction condition. Various parameters that may affect particle size, such as iron ratio, temperature, heating time, and mixing speed were tested. X-ray Diffraction (XRD), Vibrating Sample Magnetometer (VSM), Dynamic Light Scattering (DLS), and Zeta-potential were used to characterize magnetite particles. XRD shows particles were in the form of Fe$_3$O$_4$; VSM shows that the saturate magnetic moment of magnetite was 60.8 emu/g; DLS shows that the diameter of particle was 158 ± 8 nm; pH$_{zpc}$ was 4.4. To modify the magnetite, APTS was introduced to form G0 (1st generation) dendrimer on the surface of magnetite particle. Zeta-potential was used to characterize the particle and it showed that the pH$_{zpc}$ of dendrimer modified particle was 9.6. Four heavy metal, Cu(II), Co(II), Zn(II), and Ni(II), were used as adsorbate to test the metal adsorption capacity of this material. Cu(II), Ni(II), Zn(II), and Co(II) was totally removed at pH 6.7, 7.3, 7.5, and 9.3, respectively. Cu(II) was easily removed and Co(II) was the most difficult one to be removed by following the
decreasing order: Cu(II) > Ni(II) > Zn(II) > Co(II). The highest net removal efficiency of Ni(II), Cu(II), Zn(II), and Co(II) was 85, 65, 55, and 42%, respectively. The adsorption behavior of the above four heavy metals can be described by the Langmuir model.

Key word: magnetite, PAMAM dendrimer, heavy metal, adsorption
Chapter 1
MAGNETITE SYNTHESIS

1.1 Literature Review

In recent decades, the environmental challenge has attracted human more and more attention. Iron oxide complexes, especially the materials with magnetic properties, have been widely used in environmental treatment with significant performance in pollution control[1]. In recent years, magnetite(Fe₃O₄), one kind of iron oxide magnetic material, has attracted great public attention. Magnetite has unique magnetic properties due to its cubic inverse spinel structure and electron transfer between Fe³⁺ and Fe²⁺ ions[2]. Fig. 1.1 shows the structure of magnetite. It contains both Fe³⁺ and Fe²⁺ ions and its composition can be seen as FeO ·Fe₂O₃. In the cubic inverse spinel structure, Fe₃O₄ is consisted of a cubic close packed array of oxide ions and Fe²⁺ ions occupy half of the octahedral sites, the remaining octahedral sites and the tetrahedral sites are across split evenly by Fe³⁺ ions[3]. The ferrimagnetism of Fe₃O₄ are caused by electron spins of the Fe²⁺ ions and Fe³⁺ ions which are coupled in the octahedral sites and the spins of the Fe³⁺ ions in the tetrahedral sites are anti-parallel to the former although they are coupled. The net effect is that the magnetic contributions of both sets are not balanced and there is a permanent magnetism[4]. Besides the unique magnetic property, Fe₃O₄ also shows high magnetic saturation, low cytotoxicity, good bio-compatibility and stability under various physiological conditions[5]. The magnetic property makes magnetite easy to recycle from aqueous system. This property makes magnetite as a good and effective reused carrier in environment, especially after the functionalization and modification on the surface of magnetite[6].
There are several methods to synthesis magnetite particles. The commonly used is sonochemical synthesis, which uses ultrasonic to generate hydrogen peroxide to oxide ferrous ion to obtain magnetite particle[7]; microwave synthesis is using microwave to age reaction solution [8]; hydrothermal process is heating reaction solution to get precipitation[9]; hydrolysis method is hydrolysis iron salt with alkaline[10]; thermal decomposition[11]; electron irradiation[12]; and coprecipitation[13].

1.1.1 Sonochemical Synthesis

In sonochemical synthesis, Fe$_3$O$_4$ nanoparticles were synthesized through iron (II) acetate and double distilled de-oxygenated water[7].

Iron (II) acetate was dissolved in double distilled de-oxygenated water and irradiated with a high-intensity ultrasonic horn under the condition of 1.5 atm of Ar at 298 K for 3 h. After this process, the product is washed thoroughly with double distilled
deoxygenated water and finally dried in pentane in an inert glove box, which the concentration of O₂ is less than 1 ppm. Then, it is dried in a vacuum[7].

In sonochemical synthesis, the amount of contaminants in Fe₃O₄ depends on the irradiation time. The shorter the sonication, the fewer amounts of contaminants is needed.

The sonochemical formation of Fe₃O₄ nanoparticles is driven by the H and OH radicals that produce by water molecules due to the absorption of ultrasound. The likely reaction steps for the sonochemical oxidation process are as follows:

\[ H₂O \rightarrow H⁺ + OH⁻ \] (1.1)
\[ H⁺ + H⁺ \rightarrow H₂O \] (1.2)
\[ OH⁺ + OH⁺ \rightarrow H₂O₂ \] (1.3)
\[ \text{Fe(CH}_3\text{COO)}_2 \rightarrow \text{Fe}^{2⁺} + 2(\text{CH}_3\text{COO})⁻ \] (1.4)

Since the oxidant H₂O₂ generated, it can initiate the oxidation of Fe(II) :

\[ 2\text{Fe(II)} + H₂O₂ \rightarrow 2\text{Fe(III)} + 2OH⁻ \] (1.5)

1.1.2 Microwave Irradiation

Microwave irradiation is a promising method in material synthesis, because it has thermal and non-thermal effects. Compared to traditional methods, microwave synthesis has shorter reaction time, smaller particle size, and narrower size distribution[8].

To synthesize Fe₃O₄ nanoparticles, analytical grade ferric chloride (FeCl₃ • 6H₂O), ferrous sulfate (FeSO₄ • 7H₂O), aqueous ammonia, methyl alcohol, ethyl alcohol absolute, acetone and toluene are used, so is the stearic acid and paraffin liquid in chemical grade [8].

In the synthesis process, 0.5 M FeCl₃ and 0.5 M FeSO₄ are mixed with a molar ratio of 1.75 : 1 under Ar protection. Then, 10 ml ammonia aqueous solution is quickly introduced in the mixture solution with vigorously stirring. In the following step, more
ammonia solution is dropped into mixture solution slowly with stirring until pH reach 9. After that, the solution is kept stirring for another 30 min under Ar protection, and then the resulted black mixture is aged under microwave irradiation in water bath for 2 h with the frequency of 2.45 GHz. The final precipitate is collected and wash three times with deionized water and ethyl alcohol, respectively, and then dried under vacuum for 12 h[8].

1.1.3 Hydrothermal Process

Compared to other methods of Fe₃O₄ synthesis, hydrothermal process is a simple method. This method is sing-step and template-free, besides, it is cheap and facile[9]. In the preparation of Fe₃O₄ nanoparticles, 0.2 g of FeSO₄ and 0.1 g of glycine are dissolved in 35 mL of deionized water, and then, 1.0 g of NaOH is introduced into the mixture solution under a continuous stirring for 2 h. The resulting mixture is put into a Teflon-lined stainless steel autoclave with a capacity of 50 mL, and then maintained at 443 K for 50 h in an electron oven. After the 50 h, the autoclave is cooled to room temperature naturally. It will obtain some black products after centrifugation. Then wash it several times with distilled water and absolute ethanol and then dried at vacuum condition for 24 h[9].

1.1.4 Hydrolysis

In the hydrolysis method, nanoparticles of Fe₃O₄ can be synthesized by hydrolysis of ferrous and ferric salts and with a base of 1,6-hexanediamine. It has been found that the size of Fe₃O₄ nanoparticles can be adjusted by the ratio of ferrous to ferric[10]. If the ratio of ferrous to ferric is increased, the precursor of Fe₃O₄, such as large hydroxide particles, will be promoted. It causes an increase in the size of Fe₃O₄ nanoparticles. In addition, the magnetic properties of Fe₃O₄ can be also influenced by the ratio of ferrous to ferric[10].
The nanosized Fe$_3$O$_4$ is synthesized by hydrolysis of an aqueous solution, which containing iron salts and a base at room temperature in ambient atmosphere. In the process, ferrous sulfate (FeSO$_4$•7H$_2$O), ferric sulfate (Fe$_2$(SO$_4$)$_3$• n H$_2$O), ferrous chloride (FeCl$_2$• 4H$_2$O), and ferric chloride (FeCl$_3$• 6H$_2$O) are used as iron salts, and 1,6-hexanediamine (H$_2$N(CH$_2$)$_6$NH$_2$) is used as the base. First, two solutions, one solution containing 0.05 mol dm$^{-3}$ of one kind of iron salts and the other solution containing 0.025 mol dm$^{-3}$ of 1,6-hexanediamine (pH = 12.1), are prepared separately. The kind of iron salt and the molar ratio of ferrous to ferric ions are varied, but the total molar concentration of iron is 0.05 mol dm$^{-3}$ constantly. In most experiments, the metal salt solution contain (a) ferrous sulfate, (b) ferrous and ferric sulfate, (c) ferrous chloride, or (d) ferrous and ferric chloride. The composition and concentration of the solution as follow[10]:

(a).FeSO$_4$ 0.05 M
(b).FeSO$_4$ 0.017 M + Fe$_2$(SO$_4$)$_3$ 0.033 M
(c).FeCl$_2$ 0.05 M
(d).FeCl$_2$ 0.017 M + FeCl$_3$ 0.033 M

In some cases, the ratio of ferrous to ferric ions in iron salt solution is varied by changing the molar percentage of ferrous ions with respect to the total amount of iron chloride (0.05 mol dm$^{-3}$ ) from 33% to 100%. When an iron salt solution is mixed with an aqueous solution of 1,6-hexanediamine, there will be a precipitate formed immediately. After a vigorous stirring for 24 h, the precipitate is filtered off by a porous membrane. The pH value of the filtrate is from 11.1 to 11.3. The filtered precipitate is washed with ultra pure water several times for the remove of excess amine molecules. The Fe$_3$O$_4$ nanoparticles is a black powder, it can be collected after drying at room temperature[10].
1.1.5 Thermal Decomposition

In the thermal decomposition method, a biocompatible magnetite nanocrystals with surface reactive moieties can be prepared. Fe(acac)$_3$ in 2-pyrrolidone undergoes the thermal decomposition in the synthesis process[11].

9-A.A•HCl (9-Amino acridine chloride), EDC• HCl
(1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide hydrochloride), Sulfo-NHS
(N-hydroxy-sulfosuccimimide sodium salt) and ferric acetylacetonate (Fe(acac)$_3$) are used. 9-A.A can be obtained by dropping ammonia solution (25%) into an aqueous solution of 9-AA•HCl. The obtained precipitate is collected by centrifugation and then washed with double distilled water for several times. There are three α,ω-dicarboxyterminated PEG (HOOC–PEG–COOH) with different molecular weight (2000, 4000 and 6000) [11].

The 12 nm magnetite nanocrystals is prepared as follows: 0.9 mmol Fe(acac)$_3$ and 1.1 mmol HOOC–PEG–COOH (Molecular weight = 2000) are dissolved in 90 mL 2-pyrrolidone. The obtained mixture is purged with nitrogen for 30 min to remove oxygen and then boiled for 70 min at 240 °C after the purification, the reaction mixture is cooled to room temperature followed by addition of a mixture of acetone and ether. As a result, a black and sticky precipitate was obtained. The precipitate is re-dissolved in double distilled water and then under a 2-day dialysis to remove species which molecular weight smaller than 12000. After that, the nanocrystals are settled from the aqueous solution by the mixture of acetone and ether, and collected with a permanent magnet (0.5 T)[11].

The 27 nm magnetite nanocrystals are prepared as similar as the 12 nm magnetite nanocrystals. The specific process is as follow: 20 mL of purified 2-pyrrolidone solution containing 2.0 mmol Fe(acac)$_3$ and 1.5 mmol HOOC–PEG–COOH (Molecular weight = 4000) is prepared and purged with nitrogen for 30 min to remove oxygen. Then it is
exposed to a reflux of 10 h. After the steps, the reaction mixture is treated the same way as that for the 12 nm sample[11].

1.1.6 Electron Irradiation

In electron irradiation, Fe₄N crystals are exposed to intense electron beam and the effect of irradiation of Fe₄N along [0 0 1], [0 1 1], [1 1 1] and [2 1 1] orientations are investigated. The transformation from Fe₄N to Fe₃O₄ is electron-irradiation dependent. It suggests that the electron irradiation method is a standard method to prepare Fe₃O₄ crystals[12].

In the process, the polycrystalline pure iron sample (<400 ppm impurities) is nitrided at 823 K for 4 h in a gas mixture of NH₃ and 10% of CH₃COCH₃ under a pressure of 800-930 Pa. From the top surface of the sample, a nitrided layer that four kinds of Fe₄N nitrides with different morphologies can be obtained.

1.1.7 Coprecipitation

Coprecipitation is done by mixing two or more cations in the solution, after adding precipitant, it can get uniform particle[13]. The advantage of this method is that it can produce particles directly from chemical reaction and the particles have uniform composition and size distribution[13]. Eq.1.6 show the chemical reaction occurs during coprecipitation.

There are two types of coprecipitation, normal coprecipitation and reverse coprecipitation[14]. Normal coprecipitation use alkaline solution to titrate iron mixture solution, which contain Fe(III) and Fe(II) in a specific ratio. Reverse coprecipitation is adding Fe(III) and Fe(II) mixture solution, which is in a specific ratio to solution of high alkaline concentration[14].

In normal coprecipitation, by adding alkaline solution, pH goes up slowly until
the amount of hydroxide ion is sufficient and then pH is increased rapidly, and the final pH is from 10 to 11[14]. Compared to normal coprecipitation method, reverse coprecipitation is adding iron source to high concentration of alkaline solution that will not change the pH environment significantly and provide a stable pH condition[14].

Compared to common magnetite synthesis method, reverse coprecipitation has the simplest reaction procedure and condition. In this study, we use reverse coprecipitation as magnetite synthesis method.

In addition, when reaction occurs in real environment, Fe(II) is easily oxidized to Fe(III) and the synthesized magnetite is also oxidized to Iron(III) hydroxide (Fe(OH)_3), especially at high temperature[14]. Eq. 1.7 and Eq. 1.8 show the reaction. So, all reaction solutions, which is alkaline solution and iron mixture solution, should be bubbled with nitrogen gas to get rid of the oxygen before it is used in reaction and the synthesis reaction must under nitrogen gas atmosphere.

\[
2\text{Fe}^{3+} + \text{Fe}^{2+} + 8\text{OH}^{-} = \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O} \tag{1.6}
\]

\[
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ = 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \tag{1.7}
\]

\[
4\text{Fe}_3\text{O}_4(s) + \text{O}_2 + 18\text{H}_2\text{O} = 12\text{Fe(OH)}_3(s) \tag{1.8}
\]

There is also a green synthesis of Fe_3O_4 by using coprecipitation. It uses glucose solution to which containing Fe^{3+} under mechanical stirring at 80 °C. Then, the mixture solution is added into NH_3⋅H_2O solution which pH is 10 by adding NaOH drop by drop under vigorous stirring for 30 min at 60 °C. The color of suspension turns into black, and the precipitated powders are collected and washed with double distilled water for three times and with ethanol for several times. Finally, the precipitate is dried in vacuum oven at 60 °C for 12 h[3].
1.2 Materials

FeCl$_3$·6H$_2$O, FeCl$_2$·4H$_2$O and NaOH were of analytical grade and used without further purification. All chemicals were purchased from Sigma-Aldrich.

1.3 Experiment

There are several parameters that can influence the particle size of the magnetite particle. In this chapter, we investigated the influence of molar ratio of Fe(III) and Fe(II), reaction temperature, heating time and mixing speed on the magnetite particle size. In this study, we optimized the reaction conditions to make magnetite particle in suitable size for further use.

1.3.1 Experiment Design

Fig. 1.2 shows the experimental design. Beaker with sodium hydroxide solution was put on hot plate with mechanical stirring at control mixing speed. Pump was used to make dosing rate at a constant speed. Erlenmeyer flask containing 25 mL Fe(III) and Fe(II) mixture solution is added into the beaker at a constant speed.
1.3.2 Experiment Method

In this chapter, reaction was set in different reaction condition to compare particle size. Experiment (1) (2) (3) and (4) used same dosing rate at $2.34 \times 10^{-3}$ mmol/L of Fe(III) and Fe(II) mixture solution and the concentration of sodium hydroxide was 1.5 mol/L. Experiments (1) (2) and (3) used same mixing speed at 1700 rpm. After reaction, all particles were collected by adding external magnetic field. Then particles were washed by DI water to remove residual sodium hydroxide and separate by centrifugation at 5000 rpm for 10 min. Repeat this washing process until the solution pH is neutral. After washing, magnetite particles were collected by permanent magnet. The resulting particles were dried at room temperature for 24 h.

(1) Molar ratio: Reaction was conducted at $298 \pm 1$ K with different Fe(III) to
Fe(II) ratio in iron mixture solution, at 3:2 and 2:1, respectively. To prepare the Fe(III) to Fe(II) solution at 3:2 molar ratio, dissolve 6.49 g of FeCl$_3$·6H$_2$O and 3.18 g of FeCl$_2$·4H$_2$O in 25 mL of DI water. The concentration of Fe(III) was 0.96 mol/L and Fe(II) was 0.64 mol/L. For the preparation of Fe(III) to Fe(II) at the ratio of 2:1, 8.65 g of FeCl$_3$·6H$_2$O and 3.18 g of FeCl$_2$·4H$_2$O were dissolved in 25 mL of DI water to reach the concentration of Fe(III) of 1.28 mol/L and Fe(II) of 0.64 mol/L.

(2) Reaction temperature: Reaction used specific Fe(III) to Fe(II) ratio determined by experiment (1) was conducted at 298 ± 1 K and 313 ± 1 K, respectively.

(3) Heating time: Reaction was carried out based on the Fe(III) to Fe(II) ratio and reaction temperature obtained from experiments (1) and (2), but with different heating time of 1 and 2 hours, respectively. For 1 hour heating time, use hot plate to keep the reaction in specific temperature for 1 hour; for 2 hours heating time, use hot plate to control the reaction temperature as the same above (1 hour heating time) but extend the heating time to 2 hours even reaction was finished.

(4) Mixing speed: Reaction was conducted in fixed Fe(III) to Fe(II) ratio, temperature and heating time which were obtained from experiments (1), (2) and (3). To investigate the impact of mixing speed on the particle size, mixing speed were varied from 400 to 2200 rpm.

Table 1.1 is a summary of the parameter and variable in the experiment.
Table 1.1 Experimental condition

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{NaOH} = 1.5 \text{ M}$</td>
<td>$\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ ratio: 3:2 or 2:1</td>
</tr>
<tr>
<td>Viron : Vsalt = 1:10</td>
<td>Temperature: 298 K or 313 K</td>
</tr>
<tr>
<td></td>
<td>Heating time: 1 hour or 2 hours</td>
</tr>
<tr>
<td>Dosing rate = $2.34 \times 10^{-3}$ mmol/L</td>
<td>Mixing speed: 400 to 2200 rpm</td>
</tr>
</tbody>
</table>

1.3.3 Analysis Equipment and Method

X-Ray Diffraction (XRD), Rigaku Corporation model Ultima IV, was used to characterize magnetite particles.

Vibrating Sample Magnetometers (VSM), LakeShore Cryotronics, Inc., model 7404, was used to measure magnetic moment of magnetite particles.

Motomatic motor generator and speed control were used to stir and control speed during the synthesis procedure.

MasterFlex C/L pump, model 77120-62, was used to control mixing speed.

Fisher Scientific hot plate was used to control reaction temperature during the synthesis procedure.

Zeta-sizer, Nano-ZS, Malvern Instrument, model ZEN 3600 with MPT-2 multipurpose titrator was used to measure Zeta potential of magnetite particles.
1.4 Results and Discussions

**Figure 1.3** Particle size under different reaction condition. A: $\text{Fe}^{3+}:\text{Fe}^{2+} = 3:2$, $T = 298$ K, heating time = 1 h; B: $\text{Fe}^{3+}:\text{Fe}^{2+} = 2:1$, $T = 298$ K, heating time = 1 h; C: $\text{Fe}^{3+}:\text{Fe}^{2+} = 2:1$, $T = 313$ K, heating time = 1 h; D: $\text{Fe}^{3+}:\text{Fe}^{2+} = 2:1$, $T = 313$ K, heating time = 2 h. Experiment condition: mixing speed 1700 rpm; $C(\text{NaOH}) = 1.5$ M, dosing rate = $2.34 \times 10^{-3}$ mmol/L.

Fig. 1.3 shows the magnetite particle size synthesized under different reaction condition. Result showed that when the molar ratio of Fe(III) to Fe(II) was 2:1, the particle size was 193 nm, which was smaller than 226 nm the particle synthesized at the ratio of 3:2. In the reaction system, the synthesis reaction was carried out under nitrogen gas, which made the system oxygen free. In the oxygen free system, Fe(II) cannot be oxidized to Fe(III) and Reaction (6) can occur at theoretical Fe(III) to Fe(II) molar ratio of 2:1. When the Fe(III) to Fe(II) ratio was adjusted to 3:2, in the oxygen free system, there would be exceed Fe(II), which may precipitate with NaOH with the formation of
Fe(OH)$_2$ (s). The precipitation of Fe(II) may compromise of particles uniform distribution and composition of the magnetite particle. To achieve a smaller particle and homogeneous composition, the Fe(III) to Fe(II) ratio was 2:1 adjusted to following experiment. To investigate the thermal impact to the particle size, the Fe(III) to Fe(II) ratio was adjusted to 2:1 and the reaction temperature was increased from 298 ± 1 K to 313 ± 1 K in experiment (2). Results showed in Fig. 1.3 indicated that the magnetite particle size was decreased from 193 nm to 167 nm. When reaction was carried out at high temperature, the reaction was faster with the formation of crystals and the particle became smaller. So when the reaction temperature was increased to 313 ± 1 K, the particle size became smaller compared with reaction was carried out at 298 ± 1 K. Higher reaction temperature would facilitate the reaction and the formation of crystal structure. When the reaction underwent a longer heating time, beyond the critical time, the crystal structure started to grow, while particles became aggregates and particle size was increased. Result of experiment (3) that when heating time was increased from 1 to 2 hours, the particle size was increased significantly that from 167 to 225 are shown in Fig. 1.3. The 2 hours of heating exceeded the critical time when crystal growth started. Therefore 1 hour of heating time was used in following experiment. Results in Fig. 1.3 show the optimal reaction condition: molar ratio of Fe(III) to Fe(II) = 2:1, reaction temperature = 313 ± 1 K and heating time = 1 hour.
Figure 1.4 Particle size under different mixing speed. Experiment condition: Fe(III) : Fe(II) = 2 : 1; heating time = 1 h; T = 313 ± 1 K; C(NaOH) = 1.5 M, dosing rate = 2.34 \times 10^{-3} \text{ mmol/L}.

Attempt was made to optimize the reaction condition in the following experiment as to find out the influence of mixing speed on particle size. Fig. 1.4 shows the particle size with different mixing speed. From Fig. 1.4, it is seen that when the mixing speed was increased from 400 to 2200 rpm, the particle size were: 235±15 nm (400 rpm), 195±10 nm (700 rpm), 180±18 nm (900 rpm), 167±5 nm (1700 rpm) and 158±8 nm (2200 rpm), respectively. Increasing the mixing speed, the particle size became small. High mixing speed facilitated the particle dispersion. At high mixing speed, particles were better dispersed than at low speed. Therefore the high mixing speed prohibited particle agglomeration during particle synthesis.
Fig. 1.5 is the XRD pattern of magnetite particle synthesized in this study. The specific peak shows that the product synthesized was magnetite.

Fig. 1.6 is the VSM of magnetite particle synthesized in this study. Result show
the magnetic properties of the magnetite particle. From the pattern shown in Fig. 1.6, it can be concluded that the magnetite particle is soft magnet material which means that it is easy to reach the maximum magnetic strength in a weak external magnetic field. From Fig. 1.6, the saturate magnetic moment of magnetite can be calculated. The sample weight used in test was 2.96 mg and from Fig. 1.6, it is seen that the maximum magnetic moment was 0.18 emu and the saturate moment was 60.8 emu/g.

![Zeta potential of magnetite](image)

**Figure 1.7** Zeta potential of magnetite

Fig. 1.7 shows the zeta potential of magnetite particle in different ionic strength. Zeta potential is the electric potential in the interfacial double layer. Zeta potential represents the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. In zeta potential curve, it is seen that at zero point of charge (ZPC), the net surface charge of particles is zero at the specific pH
value. Fig. 1.7 shows the zeta potential of the magnetite particle in three different ionic strength. The ZPC was 4.4, under which the magnetite particle, aggregates easily since there is no repulsive force to counter the magnetic force. At pH > ZPC, the particle became negatively charged, thereby the repulsive force tend the dispersion of magnetite particles. In Fig. 1.7, it is seen that zeta potential of magnetite decreases with increase in ionic strength. In higher ionic strength, there are more sodium ion in solution, they has more opportunity to reach and occupy the surface site of magnetite particles than low ionic strength. Compare with the size of hydrogen ion, sodium ion is much larger and would occupy more space than hydrogen ion. This made the finite surface of magnetite attach some large sodium ion instead of small hydrogen ion when sodium ion present in the solution, therefore the surface charge is decreased.

1.5 Conclusion

It can be concluded that the optimal reaction conditions were: (1) Molar ratio of Fe(III) to Fe(II) = 2:1, (2) Reaction temperature = 313 ± 1 K, (3) Heating time = 1 hour, (4) Mixing speed = 2200 rpm. The particle size was 158 ± 8 nm. The magnetite saturate moment was 60.8 emu/g magnetic. The pH_{ZPC} was 4.4.
Chapter 2
SURFACE MODIFICATION

2.1 Literature Review

Polyamidoamine (PAMAM) dendrimer is a new class of macromolecular [15]. It is composed of ethylenediamine and methacrylate. Dendrimer has hyper-branching structure, repetitively functional group [16] and introduce an outer functional group shell[17]. Dendrimer has some significant advantages compared with other classic polymers, it has a high degree of molecular uniformity, narrow molecular weight distribution, specific size and shape characteristics, and a highly functionalized terminal surface[18]. PAMAM dendrimer has a sphere-like shape and tree-like structure. In the chain of each branch, it also has carbonyl group, which can be the adsorption site. The PAMAM dendrimer has high density of surface functional group, primary amine, which can also be the adsorption site. PAMAM dendrimer can be classified by generation and its initial core, the central area, is a molecule ethylene diamine. Ethylene diamine and methyl acrylate have been used to synthesize PAMAM dendrimer[19]. Fig. 2.1 and Fig. 2.2 show the structure of ethylene diamine and methyl acrylate, respectively.
The following Eq. 2.1 is the PAMAM dendrimer growth process:

\[ \text{Ethylene diamine} + \text{Methyl acrylate} \rightarrow \text{PAMAM} + 4\text{CH}_3\text{OH} \]  (2.1)

In the synthesis process, ethylene diamine is used as a core initiator, each hydrogen ion in the amine group of ethylene diamine is replaced by one molecule methyl acrylate. In Eq. 2.1, the blue highlighted area is the central area of PAMAM dendrimer, which is ethylene diamine. In the next step, the product of Eq. 2.1 will react with ethylene diamine in each branch. So the total reaction for one generation will be as follow:

\[ 5 \text{C}_2\text{H}_4(\text{NH}_2)_2 + 4 \text{CH}_2\text{CHCO}_2\text{CH}_3 \rightarrow \text{PAMAM} + 4\text{CH}_3\text{OH} \]  (2.2)

To grow higher generation, it is a repetitive step by repeatedly adding ethylene diamine and methyl acrylate[20]. Fig. 2.3 shows the structure of generation two of PAMAM dendrimer. From Fig. 2.3, we can find that in generation zero the surface group number is four, when reach the next generation, i.e., generation one, this number becomes eight and in generation two the amine group on the surface is sixteen. Table 2.1 shows some theoretical parameter of PAMAM dendrimer in different generation.
Table 2.1  PAMAM dendrimer theoretical properties by generation[22]

<table>
<thead>
<tr>
<th>Generation</th>
<th>Molecular weight</th>
<th>Measured diameter(Å)</th>
<th>Surface group</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>517</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1430</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>3256</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>6909</td>
<td>36</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>14215</td>
<td>45</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>28826</td>
<td>54</td>
<td>128</td>
</tr>
<tr>
<td>6</td>
<td>58048</td>
<td>67</td>
<td>256</td>
</tr>
<tr>
<td>7</td>
<td>116493</td>
<td>81</td>
<td>512</td>
</tr>
</tbody>
</table>

From table (2.1), it can be seen that when generation grow, the molecular weight of dendrimer roughly becomes two times than previous generation; the diameter is increased about 10 Å for each generation, and the surface amine group number is twice than previous generation. When PAMAM dendrimer reaches high generation, e.g., generation eight or generation nine, there will be a significant amount of amine group being exposed on the surface[17].
Lower generations can be thought as flexible molecules which do not have appreciable inner regions; medium generation such as G3 or G4 has internal space that is basically separated from the outer shell of the dendrimer and high generation dendrimers like G7 or higher can be solid-like particles with very dense surfaces due to the structure of outer shell[23].

Magnetite has an important magnetism property, which is useful for water treatment[15]. Magnetite particles can be easy for separation from aqueous system and for materials recycle and reuse[24]. This will make it more cost effective than convenient treatment method. In recent year, it has been reported that PAMAM dendrimer can be attached onto the surface of magnetite[25]. A material made of magnetite particle and PAMAM dendrimer has been widely used in various situation. After surface silanization the of magnetite, PAMAM dendrimer can be grown on magnetite particles by the Micheal reaction[25] and use step growth reaction to achieve higher generation[26].
The method to grow PAMAM dendrimer on the surface of magnetite can be defined as two steps: surface silanization and dendrimer growth[25]. The first step was aminosilane to modify the magnetite surface. After this step, the outer shell functional groups of magnetite are changed to amine group, which can be the core initiator to grow dendrimer on it. The second step is the same as its first that enables more dendrimer synthesis by repetitively adding methyl acrylate and ethylenediamine to achieve higher generation. The synthesis process is shown in Fig. 2.4 below:

Figure 2.4 Magnetite particle modified by PAMAM dendrimer [25]

This material is can be used as absorbent in wastewater treatment. High generation PAMAM dendrimer has significant amount of reactive functional group. The magnetic properties of magnetite can be used as carrier in the environment and is easy to separate by magnetic field. So the significant amount of reactive surface groups in
dendrimer modified magnetite particles can help to absorb or remove pollutant and the magnetite core can help the recycling and reusing.

In this research, the G0 dendrimer modified magnetite particles was synthesized and characterized.

### 2.2 Materials and Methods

3-Aminopropyltrimethoxysilane (NH₂(CH₂)₃–Si–(OCH₃)₃, APTS), ethylenediamine, methacrylate, methanol, and ethanol were purchased from Sigma-Aldrich and used without further purification. Magnetite particles (Fe₃O₄) were synthesized according to the following procedures:

\[
2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NaOH} = \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2\text{O} + 8\text{NaCl}
\]  

(2.3)

### 2.3 Experiments

Aminosilane coated magnetite were made according to the method of Pan[25]. Typically, 2 gram magnetite particles, synthesized according to the method in above, were dissolved in 150 mL of methanol solution I. This solution was immersed in an ultrasonating water bath for 30 min to have a better dispersion. Then 10 mL of 3-Aminopropyltrimethoxysilane (NH₂(CH₂)₃–Si–(OCH₃)₃, APTS) solution were added solution I under a vigorous magnetic stirring for 7 hours. The resulting solution was washed with methanol five times and particles were separated and collected by an external magnetic field. APTS-coated magnetite particles were then dispersed in methanol solution and store for further use. G0 represent the magnetite particles which is only modified with APTS. Fig. 2.5 shows the synthesis process and structure change. Fig. 2.6 shows the experimental procedure.
2.4 Analysis Equipment and Methods

Water bath sonicator, BRANSON ultrasonic cleaner (model B-220), was used to sonicate magnetite particles.

Magnetic stirring, Cole Parmer, spin master (model 4802) was used to stir during the synthesis procedure.

Zeta-sizer Nano-ZS, Malvern Instrument (model ZEN 3600) with MPT-2 multipurpose titrator was used to measure Zeta potential of G0 dendrimer modified magnetite particles.
2.5 Result and Discussion

Fig. 2.7 shows the zeta potential of G0 dendrimer and the zero point of charge of dendrimer modified magnetite particle, G0, was 9.6. That means in acid or neutral condition, the surface of G0 dendrimer has positive charge. From Fig. 2.7, it is seen that the zeta potential of G0 dendrimer is greater in smaller ionic strength, which means that an increasing ionic strength decreased the zeta potential of G0 dendrimer.

![Zeta potential of G0 dendrimer](image)

The reason of this phenomenon can be explained by the concentration of NaCl and the size of Na$^+$ and H$^+$. In strong ionic strength, the Na$^+$ has more opportunity to reach and occupy the surface site of G0 dendrimer than in weak ionic strength, and Na$^+$ has a larger size compared with H$^+$, which has more opportunity and site to occupy the surface of G0 dendrimer when sodium chloride concentration is low.
Fig. 2.8 shows the zeta potential of row magnetite particle and G0 dendrimer. From Fig. 2.8, it is seen that the ZPC changed from 4.7 to 9.6. The reason is that after silanization the surface group was changed from –OH to –NH$_2$. From Fig. 2.8, it is seen that the G0 dendrimer is more positive than row magnetite particles below zero point of charge and above zero point of charge rough magnetite particles is more negative than G0 dendrimer. The two zeta potential curve, in three different ionic strength, respectively, show the same tendency that the absolute value of zeta potential decreased with increasing ionic strength.

2.6 Conclusion

After silanization reaction, APTS were attached to the surface of magnetite particles. The new surface groups were introduced to magnetite particles and magnetite
surface groups, –OH, were coated inside. The surface groups of new material were changed from –OH to –NH₂. The zero point of charge was also changed due to the introduced surface group. The zero point of charge of G0 dendrimer was 9.6, which was significant changed from, 4.7, the ZPC of magnetite. The ionic strength impact on zeta potential of G0 dendrimer showed same tendency with magnetite particles, that is with increasing ionic strength, the zeta potential of G0 dendrimer decreased.
Chapter 3

ADSORPTION

3.1 Literature Review

In recent decades, the content of heavy metal in aqueous environment increased rapidly due to various anthropogenic activities, such as industrialization, automobile emissions, agricultural activity and mining activity [27]. The problem of heavy metal contamination in the environment becomes more and more serious. Heavy metal shows negative effects, especially toxic effect, on environmental condition, it can jeopardize environmental quality [27].

The mining activity lead to aqueous system contaminated by heavy metals and also leave sediments which is enriched of those heavy metals[27]. Some industrial sources are also resulted in heavy metal contamination.

There are many different definitions of heavy metal, some based on density, some based on atom weight and some based on chemical properties or toxicity[28]. In the field of environmental pollution, heavy metal mainly refers to metal or metalloid that shows significant toxicity to living being, such as mercury, cadmium, lead, chromium, zinc, copper, cobalt, nickel, tin, and arsenic. Those kinds of pollution are hard to degrade by microorganism[28].

But in recent years, human activities have continuously increased the content of heavy metal in soil. Some heavy metals will jeopardize health or environment, such as mercury, cadmium, lead and chromium, some can lead to corrosion, such as zinc[28].

The biggest harm of heavy metal to environment is caused by the toxicity. After
entering into the environment, heavy metal can be present in different forms due to the reaction of dissolution, precipitation, agglomeration, complexation, and absorption and heavy metal in their free ionic forms is more toxicity[29].

Heavy metal can also accumulate in bio-system and be introduced to the food chain [30]. In agricultural area, it can also enter agricultural products. So, heavy metal pollution can not only compromise the environmental quality but also threaten the safety of human life [30].

In this chapter, our study focus on the removal of four kind of heavy metal, i.e., copper (Cu), nickel (Ni), cobalt (Co) and zinc (Zn).

It is a fact that a lot of chemical pollutions has discharged into our environment, both transiently and through one medium of environmental or another like water, atmosphere, or land. Hazardous heavy metals – Copper (Cu) from many anthropogenic activities, for examples, agricultural production, industrial wastes, and mining activity were usually discharged into our environment[31]. The impact of heavy metals on our environment must be concerned since we need to decrease their menace to soil and water system. Water plays an important function in our society, particularly for our body and agriculture production. Therefore it is an extreme important to protect water resource and ensure its sustainability[31].

Copper toxicity. Excess copper accumulated in the body, caused by ingest excess copper in drinking water or food and also by exposure to copper-rich environment. Free copper shows toxicity property; it generates reactive oxygen species such as hydrogen peroxide and hydroxyl radical, which would damage proteins, lipids and DNA[28]. Long term effects of copper exposure can damage liver and kidneys. Acute symptoms of copper poisoning can cause vomiting, hematemesis, hypotension, coma, and jaundice (yellowish pigmentation of the skin). The U.S. Environmental Protection Agency (EPA)’s Maximum Contaminant Level (MCL) in drinking water is 1.3 mg/L and LD$_{50}$ of 30
mg/kg in rats[32].

Nickel (Ni) is an element with an atomic number of 28 and molecule weight of 58.69. Nickel metal belongs to the transition metal. It is magnetic at or near room temperature[28]. Nickel exist in nature in the formation of nickel ore silicate or nickel compound combine with sulfate. The major sources of nickel contamination in aqueous system are from nickel plating, machine manufacturing and metal processing industry[33]. Those particulate matter can cause serious health and environmental problem.

Nickel is used for various applications, such as making nickel steels, alloys and super alloy, coinage, electroplating, and some other uses[34]. In the United State, the minimal risk level of nickel and its compound is 0.2 μg/m³ for inhalation during 15-364 days[35]. Nickel sulfide fume and dust are believed to be carcinogenic and various other nickel compounds also believed to be carcinogenic[36]. One of the nickel compounds, nickel carbonyl [Ni(CO)₄], is an extremely toxicity gas. In the United State, the tolerable upper limit of dietary nickel is 1000 μg/day and estimated average ingestion is 69 – 162 μg/day[37]. One pathway of nickel leaching is food cooked in stainless steel, for example, the amount of nickel leached after 10 cooking cycles into one serving of tomato sauce averages 88 μg[38]. Nickel is also an important cause of contact allergy, partly due to the jewelry usage intend for pierced ears[39]. Nickel allergies are often marked by itchy, red skin and many earrings are nickel free due to the allergy problem.

The most common ionic state of nickel is +2, but compounds of Ni⁰, Ni⁺, Ni³⁺ and Ni⁴⁺ are also well known[33]. Ni(II) can form compounds with all common anions. The most common compound used in electroplating nickel is Nickel(II) sulfate. Nickel(III) oxide is used as the cathode in many recharged batteries and some Li-ion batteries[33]. These are the most common nickel contamination sources in environment. In aqueous system, soluble nickel ion combining with water will form hydrated ion. The hydrated
ion will be adsorbed by ferric hydroxide, clay or flocculent organic compounds and it can precipitated with sulfate ion also[33]. In electroplating nickel industry, nickel contained in wastewater is soluble and stable in acidic condition, but it will produce precipitation in alkaline condition.

Cobalt is a chemical element with symbol Co and its atomic number is 27. Like nickel, cobalt belongs to the transition metal. The free cobalt element is a hard, lustrous, silver-grey metal. Cobalt has various applications in a wide field, it is primarily used as metal, wear-resistant and high-strength alloys[40]. One of the cobalt compounds, lithium cobalt oxide (LiCoO$_2$), is widely used in lithium ion battery as cathode[41]. Cobalt also can be used in electroplating due to its hardness and resistance to oxidation[42].

Cobalt is essential element to all animals. It is a key constituent of vitamin B$_{12}$ which is also the major reservoir of cobalt in organism[43]. But excess cobalt ingestion or exposure will also cause health problem. The LD$_{50}$ value of soluble cobalt salts has been estimated to be between 150 and 500 mg/kg[44]. The most serious damage to human health by cobalt is chronic cobalt ingestion. It is at doses far less than the lethal dose. As nickel, cobalt is also a major cause of contact dermatitis[45]. Charred pig bones are good absorbent which can effectively remove cobalt, however this adsorption process is compromised by copper and zinc due to their greater affinities to the bone char[46].

Zinc is a chemical element with symbol Zn and its atomic number is 30. Zinc is a bluish-white, lustrous, diamagnetic metal and it has a hexagonal crystal structure. Like nickel and cobalt, many alloys contain zinc and zinc is also a fair conductor of electricity[47]. The major application of zinc is galvanizing, alloy, and battery. Zinc is the most commonly used anti-corrosion agent, because zinc is more reactive than iron or steel and it will attract most local oxidation until it completely corrodes away[48]. This ability also make zinc an efficient sacrificial anode in cathodic protection and it is also used to cathodically protect metals which were exposed to sea water from corrosion[49].
The standard electrode potential (SEP) of zinc is -0.76 volts and it can be used as an anode material for batteries. Powered zinc is used in alkaline batteries and sheets of zinc is used as anode in zinc-carbon batteries[50].

Like cobalt, zinc is an essential trace element for human and it is the only metal, which appears in all enzyme classes[51]. There are 2-4 grams of zinc distributed throughout the human body, most of them is in the brain, muscle, bones, kidney, and liver[52].

Although zinc is an essential element for human health, excess zinc can be harmful. The free zinc ion in the aqueous system is highly toxic to plants, invertebrates, and vertebrate fish[53]. It is a powerful Lewis acid up to the point of being corrosive, people swallowing zinc product, like American one-cent piece which contains 97.5% zinc, will cause damage to stomach lining[54]. The reason is stomach acid contains hydrochloric acid and metallic zinc dissolves readily and produce zinc chloride, which is corrosive[54]. The U.S. Food and Drug Administration (FDA) also states that zinc can cause damage to the nerve receptor in nose, which will lead to anosmia[55].

The G0 dendrimer modified magnetite particle is a novel material, the amine group exposed on the surface is effective to react or absorb heavy metal. The prospect of this material is that it can be used as an absorbent in wastewater treatment. The magnetic properties of magnetite can be used as carrier in the environment and easy to separate by magnetic field.

In this chapter, we used G0 dendrimer modified magnetite particle to absorb four heavy metal, Cu(II), Co(II), Zn(II), and Ni(II), respectively. We investigated the adsorption efficiency, isotherm, mechanism, and reaction constants.

3.2 Materials

\[ \text{Cu(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}, \text{Ni(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}, \text{Zn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}, \text{Co(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}, \]
NaClO₄, HClO₄, NaOH, HNO₃ were of analytical grade and used without purification. All chemicals were purchased from sigma.

### 3.3 Experiments

13.60 g Cu(ClO₄)₂ · 6H₂O was dissolved in 1000 mL DI water (3.67 × 10⁻² M) as stock solution for further use. 15.40 g Co(ClO₄)₂ · 6H₂O was dissolved in 1000 mL DI water (4.21 × 10⁻² M) as stock solution for further use. 12.90 g Zn(ClO₄)₂ · 6H₂O was dissolved in 1000 mL DI water (3.46 × 10⁻² M) as stock solution for further use. 15.50 g Ni(ClO₄)₂ · 6H₂O was dissolved in 1000 mL DI water (4.24 × 10⁻² M) as stock solution for further use.

In adsorption experiments, Cu(II) stock solution (3.67 × 10⁻² M) was diluted to 3.67 × 10⁻³ M. 50 mL Cu(II) stock solution was added to 500 mL volumetric flask. To simulate real aqueous system, 5 mL of 1 M NaClO₄ solution was also added to the 500 mL volumetric flask to adjust ionic strength. The reaction solution contained 3.67 × 10⁻³ M Cu(II) with 0.01 M ionic strength.

Co(II) stock solution (4.21 × 10⁻² M) was diluted to 4.21 × 10⁻³ M. 50 mL Co(II) stock solution was added to 500 mL volumetric flask. To simulate the aqueous system, 5 mL of 1 M NaClO₄ solution was also added to the 500 mL volumetric flask to adjust ionic strength. The reaction solution contained 4.21 × 10⁻³ M Co(II) with 0.01 M ionic strength.

Zn(II) stock solution (3.46 × 10⁻² M) was diluted to 3.46 × 10⁻³ M. 50 mL Zn(II) stock solution was added to 500 mL volumetric flask. To simulate the aqueous system, 5 mL of 1 M NaClO₄ solution was also added to the 500 mL volumetric flask to adjust ionic strength. The reaction solution contained 3.46 × 10⁻³ M Zn(II) with 0.01 M ionic strength.

Ni(II) stock solution (4.24 × 10⁻² M) was diluted to 4.24 × 10⁻³ M. 50 mL Ni(II)
stock solution was added to 500 mL volumetric flask. To simulate the aqueous system, 5 mL of 1 M NaClO₄ solution was also added to the 500 mL volumetric flask to adjust ionic strength. The reaction solution contained $4.24 \times 10^{-3}$ M Ni(II) with 0.01M ionic strength.

### 3.3.1 Effect of pH on Adsorption

To investigate the pH influence on adsorption, the solution pH was adjusted by 1 M HClO₄ or NaOH at the beginning of the reaction. The initial pH was adjusted to 3, 4, 5, 6, 7, 8, 9, and 10, respectively. The concentration of Cu(II), Co(II), Zn(II) and Ni(II) was $3.67 \times 10^{-3}$, $4.21 \times 10^{-3}$, $3.46 \times 10^{-3}$, and $4.24 \times 10^{-3}$ M, respectively. The adsorbent load was 5 g/L. Centrifuge tubes were shaken for 24 h at 298 ± 1 K.

To eliminate the precipitation influence on heavy metal, blank reactions were also conducted. The concentration of Cu(II), Co(II), Zn(II) and Ni(II) was $3.67 \times 10^{-3}$, $4.21 \times 10^{-3}$, $3.46 \times 10^{-3}$, and $4.24 \times 10^{-3}$ M, respectively. The adsorbent load was zero. Centrifuge tubes were shaken for 24 h at 298 ± 1 K.

### 3.3.2 Adsorption Isotherm

The reaction pH was obtained by previous experiments. Adsorption isotherm experiment was conducted at 298 ± 1 K.

In batch reaction, 0.2 g G0 dendrimer and 40 mL of heavy metal solution at different concentration with 0.01M ionic strength were added to 50 mL centrifuge tubes and the initial concentration of heavy metals were show in Table 3.1. Using NaOH or HClO₄ to adjust solution to specific pH value. Centrifuge tubes were shaken in shaker continuously for 24 h.
Table 3.1  Initial concentration of Cu(II), Co(II), Zn(II), and Ni(II) in adsorption isotherm

<table>
<thead>
<tr>
<th></th>
<th>Cu(II) mmol/L</th>
<th>Co(II) mmol/L</th>
<th>Zn(II) mmol/L</th>
<th>Ni(II) mmol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>1.06</td>
<td>1.05</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>1.84</td>
<td>2.12</td>
<td>2.10</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>2.76</td>
<td>3.18</td>
<td>3.15</td>
<td>2.61</td>
<td></td>
</tr>
<tr>
<td>3.68</td>
<td>4.24</td>
<td>4.20</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>4.60</td>
<td>5.30</td>
<td>5.25</td>
<td>4.35</td>
<td></td>
</tr>
<tr>
<td>5.52</td>
<td>6.36</td>
<td>6.30</td>
<td>5.22</td>
<td></td>
</tr>
<tr>
<td>6.44</td>
<td>7.42</td>
<td>7.35</td>
<td>6.09</td>
<td></td>
</tr>
<tr>
<td>7.36</td>
<td>8.48</td>
<td>8.40</td>
<td>6.96</td>
<td></td>
</tr>
<tr>
<td>8.28</td>
<td>9.54</td>
<td>9.45</td>
<td>7.83</td>
<td></td>
</tr>
<tr>
<td>9.20</td>
<td>10.60</td>
<td>10.50</td>
<td>8.70</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Analysis Equipment and Methods

Atomic Absorption spectrometer, PerkinElmer (model AAnalyst 800), was used in quantitative analysis of heavy metals.

3.5 Results and Discussions

3.5.1 Removal Efficiency

Fig. 3.1, 3.2, 3.3, and 3.4 show the results of Cu(II), Co(II), Zn(II), and Ni(II) removal efficiency with G0 dendrimer and blank experiment, respectively.

In Fig. 3.1, the final pH for Cu(II) removal was 3.7, 4.5, 5, 5.5, 6.3, 6.7, 8.2, and 9.3, respectively. The corresponding removal efficiency was 4.0, 9.7, 17.3, 46.4, 95.1, 100, 100, and 100%, respectively.

In Fig. 3.2, the final pH for Co removal was 4.9, 6.1, 6.4, 6.8, 7.2, 7.6, 8.3, and
9.3, respectively. The corresponding removal efficiency was 7.4, 21.1, 26.7, 38.2, 56.8, 74.9, 92.6, and 100%, respectively.

In Fig. 3.3, the final pH for Zn removal was 4.5, 5.8, 6.1, 6.7, 7.5, and 8.5, respectively. The corresponding removal efficiency was 24.7, 31.8, 44.6, 95.0, 100, and 100%, respectively.

In Fig. 3.4, the final pH for Ni removal was 3.7, 5.8, 6.3, 6.6, 6.7, 7.1, 7.3, and 8.3, respectively. The corresponding removal efficiency was 19.7, 29.8, 35.8, 49.9, 57.6, 88.3, 100, and 100%, respectively.

Figure 3.1 Cu(II) removal efficiency. Experiment condition: Cu(II) = 3.67×10⁻³ M; C(NaClO₄) = 0.01 M; G₀ = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.
Figure 3.2  Co(II) removal efficiency. Experiment condition: Co(II) = 4.21 × 10^{-3} M; C(NaClO_4) = 0.01 M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.

Figure 3.3  Zn(II) removal efficiency. Experiment condition: Zn(II) = 3.46 × 10^{-3} M; C(NaClO_4) = 0.01 M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.
Figure 3.4 Ni(II) removal efficiency. Experiment condition: Ni(II) = 4.24 × 10⁻³ M; C(NaClO₄) = 0.01 M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.

Fig. 3.5 shows the removal efficiency of four metals studied.

We compared the removal efficiency among the Cu(II), Ni(II), Co(II), and Zn(II) by G0 dendrimer. It is seen that Cu(II) can reach 100% removal efficiency at pH 6.7; Ni(II) was totally removed at pH 7.3; Zn(II) reached 100% removal at pH 7.5; Co(II) was not totally remove from aqueous system until pH reach 9.3. Copper was the easiest to be removed by G0 dendrimer, Nickel and Zinc were the second and third, respectively. Cobalt was the hardest to be removed among all four heavy metals.
Figures 3.6, 3.7, 3.8, and 3.9 show the net removal efficiency of Cu(II), Co(II), Zn(II), and Ni(II) with G0 dendrimer, respectively. The experimental removal efficiency was subtracted the blank to obtain the net efficiency of G0 dendrimer for each heavy metal. Compared with four heavy metals, it is seen that the highest net removal efficiency of Ni(II) by G0 dendrimer was near 85%, which is the highest among four heavy metals. The second one was Cu(II) which was around 65%. The third one was Zn(II), 55% Zn(II) was removed by G0 dendrimer. The forth one was Co(II), only 42% Co(II) was removed by G0 dendrimer. Cu(II), Co(II), Zn(II), and Ni(II) reached their highest net removal efficiency by G0 dendrimer at pH 5.9, 7.2, 6.6, and 7.3, respectively.
Figure 3.6  Cu(II) net removal efficiency. Experiment condition: Cu(II) = \(3.67 \times 10^{-3}\) M; C(NaClO\(_4\)) = 0.01M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.

Figure 3.7  Co(II) net removal efficiency. Experiment condition: Co(II) = \(4.21 \times 10^{-3}\) M; C(NaClO\(_4\)) = 0.01M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.
Figure 3.8  Zn(II) net removal efficiency. Experiment condition: Zn(II) = $3.46 \times 10^{-3}$ M; C(NaClO$_4$) = 0.01M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.

Figure 3.9  Ni(II) net removal efficiency. Experiment condition: Ni(II) = $4.24 \times 10^{-3}$ M; C(NaClO$_4$) = 0.01M; G0 = 5 g/L; reaction time = 24 h; T = 298 ± 1 K.
3.5.2 Adsorption Isotherm

Fig. 3.10, 3.11, 3.12, and 3.13 show the adsorption isotherm of Cu(II), Co(II), Zn(II), and Ni(II), respectively.

Figure 3.10   Adsorption isotherm of Cu(II) by G0 dendrimer fitted with Langmuir equation at pH 5.9
Figure 3.11  Adsorption isotherm of Co(II) by G0 dendrimer fitted with Langmuir equation at pH 7.2

Figure 3.12  Adsorption isotherm of Zn(II) by G0 dendrimer fitted with Langmuir equation at pH 6.6
Figure 3.13  Adsorption isotherm of Ni(II) by G0 dendrimer fitted with Langmuir equation at pH 7.3

The adsorption data were fitted both the Langmuir and the Freundlich adsorption models. Langmuir model as shown in Fig. 3.10, 3.11, 3.12, and 3.13. Result shown that Langmuir isotherm model is better to describe to the adsorption behavior of Cu(II), Co(II), Ni(II), and Zn(II) on G0 dendrimer. The Langmuir isotherm is described as the following Eq. 3.1:

\[ \Gamma_e = \frac{\Gamma_m K_L C_e}{1 + K_L C_e} \]  

(3.1)

Convert it to linear equation to get Eq. 3.2:

\[ \frac{C_e}{\Gamma_e} = \frac{C_e}{\Gamma_m} + \frac{1}{\Gamma_m K_L} \]

(3.2)

Where \( \Gamma_e \) (mg/g) is the amount of adsorbate adsorbed on the sorbent at
equilibrium; \( C_e \) (mg/L) is the equilibrium adsorbate concentration; \( \Gamma_m \) (mg/g) is the maximum adsorption capacity of the sorbent; \( K_L \) is the Langmuir constant.

Plot \( \frac{C_e}{\Gamma_e} \) vs \( C_e \) to get the Langmuir in linear form.

In the linear equation, the slope is \( \frac{1}{\Gamma_m} \) and the intercept is \( \frac{1}{\Gamma_m K_L} \).

Table 3.2 shows \( R^2 \) of Cu(II), Co(II), Zn(II), and Ni(II) adsorption fit with the Langmuir isotherm model.

**Table 3.2**  
Linear regression of Cu(II), Co(II), Zn(II), and Ni(II) for Langmuir adsorption isotherm

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (II)</td>
<td>0.9985</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>0.9974</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>0.9834</td>
</tr>
<tr>
<td>Nickel(II)</td>
<td>0.9946</td>
</tr>
</tbody>
</table>

Table 3.3 shows the parameter of Cu(II), Co(II), Ni(II), and Zn(II) adsorption fit with Langmuir isotherm model.
Table 3.3  Langmuir isotherm model parameter of Cu(II), Co(II), Zn(II), and Ni(II)

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>$K_L$ (L/mg)</th>
<th>$\Gamma_m$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (II)</td>
<td>0.77</td>
<td>49.02</td>
<td>0.9985</td>
</tr>
<tr>
<td>Co (II)</td>
<td>0.45</td>
<td>21.69</td>
<td>0.9974</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>0.24</td>
<td>28.17</td>
<td>0.9834</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>0.21</td>
<td>22.73</td>
<td>0.9946</td>
</tr>
</tbody>
</table>

3.5.3 Metal Speciation

All metal ions in aqueous system are hydrated and they form aqueous complexes. Table 3.4 shows the hydrolysis reaction of Cu(II) and stability constant.

Table 3.4  Cu(II) hydrolysis reaction and stability constant

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant ($298,\text{K},, I = 0$) [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{CuOH}^+ + \text{H}^+$</td>
<td>$\log_{10}^* K_1 = -8.0$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_2 + 2\text{H}^+$</td>
<td>$\log_{10}^* \beta_2 = -16.2$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_3^+ + 3\text{H}^+$</td>
<td>$\log_{10}^* \beta_3 = -26.8$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_4^{2-} + 4\text{H}^+$</td>
<td>$\log_{10}^* \beta_4 = -39.9$</td>
</tr>
</tbody>
</table>
The total copper concentration, \([Cu]_T\), is the amount of five copper speciation, \([Cu^{2+}\], [CuOH\(^+\)], [Cu(OH)\(_2\)], [Cu(OH)\(_3\)], and [Cu(OH)\(_4\)]\(^2-\)], in aqueous system. Eq. 3.3 shows the relation of the copper species.

\[
[Cu]_T = [Cu^{2+}] + [CuOH^+] + [Cu(OH)]_2 + [Cu(OH)]_3^- + [Cu(OH)]_4^{2-} \\
= [\text{Cu}^{2+}] (1 + \ast K_1[H^+]^{-1} + \ast \beta_2[H^+]^{-2} + \ast \beta_3[H^+]^{-3} + \ast \beta_4[H^+]^{-4})
\] (3.3)

In the adsorption experiments, 0.01 M NaClO\(_4\) was added to adjust the ionic strength. The relation between ionic strength \((I)\) and salt concentration was shown below:

\[
I = \frac{1}{2} \Sigma C_i z_i^2
\] (3.4)

Where \(C_i\) and \(z_i\) represent the concentration and charge of ion \(i\), respectively. So, the ionic strength of the adsorption experiment can be calculated by Eq. 3.4 as follow:

\[
I = \frac{1}{2} ([\text{Na}^+] + [\text{ClO}_4^-]) = \frac{1}{2} (0.01 + 0.01) = 0.01\text{M}
\]

According to Stumm [], the ionic strength is related to activity coefficient \((\gamma)\). The Güntelberg approximation that can be used to calculate the relationship of ionic strength and activity coefficient. The Güntelberg approximation is described as follow:

\[
\text{Log}_{10}Y_i = -0.5z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}}
\] (3.5)

The equilibrium condition is influenced by the ionic strength of the solution. The mixed stability constant \(K'\) has been related to stability constant \(K\) by following equation:

\[
\text{pK'} = \text{pK} + \text{Log}_{10}Y
\] (3.6)

Using Eq. 3.6 to adjust the stability constant listed in Table 3.4. For copper ion, the charge is +2 and the ionic strength is 0.01 M. By using Eq. 3.5 to calculate the activity coefficient of copper ion was shown as follow:

\[
\text{Log}_{10}Y_{Cu^{2+}} = -0.5z_{Cu}^2 \frac{\sqrt{I}}{1 + \sqrt{I}} = -0.5 \times 2^2 \times \frac{\sqrt{0.01}}{1 + \sqrt{0.01}} = -0.18
\]

Table 3.5 shows the stability constant correction of copper speciation in the ionic strength of 0.01 M.
Table 3.5  Stability constant correction of copper speciation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0.01 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{CuOH}^+ + \text{H}^+$</td>
<td>$\log_{10} K_1' = -7.82$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_2 + 2\text{H}^+$</td>
<td>$\log_{10} \beta_2' = -16.02$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_3^- + 3\text{H}^+$</td>
<td>$\log_{10} \beta_3' = -26.62$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_4^{2-} + 4\text{H}^+$</td>
<td>$\log_{10} \beta_4' = -39.72$</td>
</tr>
</tbody>
</table>

Fig. 3.14 shows the meta speciation of Cu(II) with 0.01M ionic strength.

![Figure 3.14](image)

**Figure 3.14**  Copper (Cu) speciation. Ionic strength = 0.01 M

For the metal speciation of Co(II), the total cobalt concentration, $[\text{Co}]_T$, is the amount of four copper speciation, $[\text{Co}^{2+}]$, $[\text{CoOH}^+]$, $[\text{Co(OH)}_2]$, and $[\text{Co(OH)}_3^-]$, in
aqueous system. Eq. 3.7 shows the relation of the copper species.

\[
[Co]_T = [Co^{2+}] + [CoOH^+] + [Co(OH)_2] + [Co(OH)_3^-]
\]

\[
= [Co^{2+}] (1 + ^*K_1[H^+]^{-1} + ^*\beta_2[H^+]^{-2} + ^*\beta_3[H^+]^{-3}) \quad (3.7)
\]

The stability constant of cobalt speciation is shown in Table 3.6.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0) [57]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co^{2+} + H_2O ↔ CoOH^+ + H^+</td>
<td>Log_{10}^*K_1 = -9.9</td>
</tr>
<tr>
<td>Co^{2+} + 2H_2O ↔ Co(OH)_2 + 2H^+</td>
<td>Log_{10}^*\beta_2 = -18.8</td>
</tr>
<tr>
<td>Co^{2+} + 3H_2O ↔ Co(OH)_3^- + 3H^+</td>
<td>Log_{10}^*\beta_3 = -31.5</td>
</tr>
</tbody>
</table>

Using Eq. 3.6 to adjust the stability constant listed in Table 3.6. For cobalt ion, the charge is +2 and the ionic strength is 0.01 M. By using Eq. 3.5 to calculate the activity coefficient of cobalt ion was shown as follow:

\[
\log_{10}^\gamma_{Co^{2+}} = -0.5 \frac{z_{Co}^2}{1 + \sqrt{I}} \frac{\sqrt{I}}{1 + \sqrt{0.01}} = -0.5 \times 2^2 \times \frac{\sqrt{0.01}}{1 + \sqrt{0.01}} = -0.18
\]

Table 3.7 shows the stability constant correction of cobalt speciation in the ionic strength of 0.01 M.
Table 3.7  Stability constant correction of cobalt speciation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0.01 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{CoOH}^+ + \text{H}^+$</td>
<td>$\log_{10} K_1' = -9.72$</td>
</tr>
<tr>
<td>$\text{Co}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Co(OH)}_2 + 2\text{H}^+$</td>
<td>$\log_{10} \beta_2' = -18.62$</td>
</tr>
<tr>
<td>$\text{Co}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Co(OH)}_3^- + 3\text{H}^+$</td>
<td>$\log_{10} \beta_3' = -31.32$</td>
</tr>
</tbody>
</table>

Fig. 3.15 shows the meta speciation of Co(II) with 0.01M ionic strength.

Figure 3.15  Cobalt (Co) speciation. Ionic strength = 0.01 M
For the metal speciation of Zn(II), The total zinc concentration, \([Zn]_T\), is the amount of five zinc speciation, \([\text{Zn}^{2+}]\), \([\text{ZnOH}^+]\), \([\text{Zn(OH)}_2^-]\), \([\text{Zn(OH)}_3^-]\), and \([\text{Zn(OH)}_4^{2-}]\), in aqueous system. Eq. 3.8 shows the relation of the copper species.

\[
[Zn]_T = [\text{Zn}^{2+}] + [\text{ZnOH}^+] + [\text{Zn(OH)}_2^-] + [\text{Zn(OH)}_3^-] + [\text{Zn(OH)}_4^{2-}]
\]

\[
= [\text{Zn}^{2+}] (1 + \kappa_1 [H^+] + \kappa_2 [H^+]^2 + \kappa_3 [H^+]^3 + \kappa_4 [H^+]^4)
\]

The stability constant of zinc speciation is shown in Table 3.8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0.01 M) [58]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Zn}^{2+}] + \text{H}_2\text{O} \leftrightarrow \text{ZnOH}^+ + \text{H}^+)</td>
<td>(\log_{10}\kappa_1 = -8.96)</td>
</tr>
<tr>
<td>([\text{Zn}^{2+}] + 2\text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_2^- + 2\text{H}^+)</td>
<td>(\log_{10}\kappa_2 = -17.82)</td>
</tr>
<tr>
<td>([\text{Zn}^{2+}] + 3\text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_3^- + 3\text{H}^+)</td>
<td>(\log_{10}\kappa_3 = -28.05)</td>
</tr>
<tr>
<td>([\text{Zn}^{2+}] + 4\text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_4^{2-} + 4\text{H}^+)</td>
<td>(\log_{10}\kappa_4 = -40.41)</td>
</tr>
</tbody>
</table>

Using Eq. 3.6 to adjust the stability constant listed in Table 3.8. For zinc ion, the charge is +2 and the ionic strength is 0.01 M. By using Eq. 3.5 to calculate the activity coefficient of zinc ion was shown as follow:

\[
\log_{10} \gamma_{\text{Zn}^{2+}} = -0.5z_{\text{Zn}}^2 \frac{\sqrt{I}}{1 + \sqrt{I}} = -0.5 \times 2^2 \times \frac{\sqrt{0.01}}{1 + \sqrt{0.01}} = -0.18
\]

Table 3.9 shows the stability constant correction of zinc speciation in the ionic strength of 0.01 M.
Table 3.9  Stability constant correction of zinc speciation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0.01 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$ + H$_2$O ↔ ZnOH$^+ + H^+$</td>
<td>Log$_{10}^*K_1' = -8.78$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2H$_2$O ↔ Zn(OH)$_2^+ + 2H^+$</td>
<td>Log$_{10}^*\beta_2' = -17.64$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 3H$_2$O ↔ Zn(OH)$_3^− + 3H^+$</td>
<td>Log$_{10}^*\beta_3' = -27.87$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 4H$_2$O ↔ Zn(OH)$_4^{2−} + 4H^+$</td>
<td>Log$_{10}^*\beta_4' = -40.23$</td>
</tr>
</tbody>
</table>

Fig. 3.16 shows the meta speciation of Zn(II) with 0.01M ionic strength.

Figure 3.16  Zinc (Zn) speciation. Ionic strength = 0.01 M
For the metal speciation of Ni(II), the total nickel concentration, \([\text{Ni}]_T\), is the amount of five nickel speciation, \([\text{Ni}^{2+}]\), \([\text{NiOH}^+]\), \([\text{Ni(OH)}_2]\), \([\text{Ni(OH)}_3^-]\), and \([\text{Ni(OH)}_4^{2-}]\), in aqueous system. Eq. 3.9 shows the relation of the copper species.

\[
[\text{Ni}]_T = [\text{Ni}^{2+}] + [\text{NiOH}^+] + [\text{Ni(OH)}_2] + [\text{Ni(OH)}_3^-] + [\text{Ni(OH)}_4^{2-}]
= [\text{Ni}^{2+}] (1 + \beta_1[H^+] - 1 + \beta_2[H^+]^2 + \beta_3[H^+]^3 + \beta_4[H^+]^4)
\]  

(3.9)

The stability constant of nickel speciation is shown in Table 3.10.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298 K, I = 0) [57]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{NiOH}^+ + \text{H}^+)</td>
<td>Log(_{10})(\beta_1) = -9.9</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_2 + 2\text{H}^+)</td>
<td>Log(_{10})(\beta_2) = -19.0</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_3^- + 3\text{H}^+)</td>
<td>Log(_{10})(\beta_3) = -30.0</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_4^{2-} + 4\text{H}^+)</td>
<td>Log(_{10})(\beta_4) = -38.8</td>
</tr>
</tbody>
</table>

Using Eq. 3.6 to adjust the stability constant listed in Table 3.10. For nickel ion, the charge is +2 and the ionic strength is 0.01 M. By using Eq. 3.5 to calculate the activity coefficient of nickel ion was shown as follow:

\[
\text{Log}_{10} \gamma_{\text{Ni}^{2+}} = -0.5z_{\text{Ni}}^2 \frac{\sqrt{I}}{1 + \sqrt{I}} = -0.5 \times 2^2 \times \frac{\sqrt{0.01}}{1 + \sqrt{0.01}} = -0.18
\]

Table 3.11 shows the stability constant correction of nickel speciation in the ionic strength of 0.01 M.
Table 3.11  Stability constant correction of nickel speciation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (298K, I = 0.01 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{NiOH}^+ + \text{H}^+ )</td>
<td>( \log_{10} \text{K}_1' = -9.72 )</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_2 + 2\text{H}^+ )</td>
<td>( \log_{10} \beta_2' = -18.82 )</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_3^- + 3\text{H}^+ )</td>
<td>( \log_{10} \beta_3' = -29.82 )</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}_4^{2-} + 4\text{H}^+ )</td>
<td>( \log_{10} \beta_4' = -38.62 )</td>
</tr>
</tbody>
</table>

Fig. 3.17 shows the meta speciation of Ni(II) with 0.01M ionic strength.
Compared with the metal speciation in different pH with the net heavy metal removal efficiency, it is seen that the formation of heavy metal in the highest removal effect of G0 dendrimer. For copper, the highest removal efficiency is in the pH range from 5.7 to 6.3 and the dominant of copper(II) species in this pH range is Cu$^{2+}$. For cobalt(II), the highest removal efficiency is from pH 6.9 to 7.3 and the corresponding speciation in that pH range is Co$^{2+}$. For nickel, the highest removal efficiency is from pH 7.0 to 7.4 and the corresponding speciation in that pH range is Ni$^{2+}$. For zinc, the highest removal efficiency is in the pH range from 6.3 to 6.8 and the dominant of copper species in this pH range is Zn$^{2+}$.

### 3.5.4 Surface Speciation and Intrinsic Stability Constants

According to Huang et al.[56], the surface group behaves amphoterically in aqueous system:

\[
\begin{align*}
R-NH_3^+ &\leftrightarrow R-NH_2 + H^+ ; K_{a1}^{\text{int}} \\
R-NH_2 &\leftrightarrow R-NH^- + H^+ ; K_{a2}^{\text{int}}
\end{align*}
\]

Where $R-NH_3^+$, $R-NH_2^+$, and $R-NH^-$ represent protonated, neutral and ionized surface amine groups, respectively. The intrinsic acidity constant, $K_{a1}^{\text{int}}$ and $K_{a2}^{\text{int}}$, are defined as follows:

\[
\begin{align*}
K_{a1}^{\text{int}} &= \frac{\{R-NH_2\}\{H^+\}}{\{R-NH_3^+\}} \quad (3.5) \\
K_{a2}^{\text{int}} &= \frac{\{R-NH^-\}\{H^+\}}{\{R-NH_2\}} \quad (3.6)
\end{align*}
\]

Where $\{i\}$ represent the surface concentration of ith species.

The total surface acidity sites, $S$, is the sum of the three hydroxyl groups:

\[
S_t = \{R-NH_3^+\} + \{R-NH_2\} + \{R-NH^-\} \quad (3.7)
\]
At pH < pH_{zpc}, the surface is predominantly positively charged, therefore:

\[ S_t = \{R-NH_3^+\} + \{R-NH_2\} \quad (3.8) \]

At pH > pH_{zpc}, the surface is predominantly negatively charged, therefore:

\[ S_t = \{R-NH_2\} + \{R-NH^-\} \quad (3.9) \]

When pH < pH_{zpc},

\[ \{R-NH_3^+\} = \sigma^+ \quad (3.10) \]

By substituting the above relationship into Eq. 3.5 and with further mathematical arrangement, Eq. 3.5 can be convert to linear formation as follow:

\[ \frac{1}{\{H^+\}} = \frac{S_t}{K_{a1}^\text{int}} \sigma + \frac{1}{K_{a1}^\text{int}} \quad (3.11) \]

Plot \( \frac{1}{\{H^+\}} \) vs \( \frac{1}{\sigma^+} \) in the linear Eq. 3.11, the slope is \( \frac{S_t}{K_{a1}^\text{int}} \) and intercept is \( -\frac{1}{K_{a1}^\text{int}} \).

When pH > pH_{zpc},

\[ \{R-NH^-\} = \sigma^- \quad (3.12) \]

By substituting the above relationship into Eq. 3.6 and with further mathematical arrangement, Eq. 3.6 can be convert to linear formation as follow:

\[ \{H^+\} = \frac{S_tK_{a2}^\text{int}}{\sigma} - \frac{1}{K_{a2}^\text{int}} \quad (3.13) \]

Plot \( \{H^+\} \) versus \( \frac{1}{\sigma^-} \), in the linear Eq. 3.13 the slope is \( S_tK_{a2}^\text{int} \) and intercept is \( \frac{1}{K_{a2}^\text{int}} \).

In Eq. 3.11 and Eq. 3.13, \( \{H^+\} \) represent the surface concentration of protons which is not directly measurable. But it can be calculate from the pH measured in bulk phase, \( [H^+] \), by the Boltzmann equation:

\[ \{H^+\} = [H^+] e^{-\frac{\psi_0}{RT}} \quad (3.14) \]

Where \( \psi_0, F, R, \) and T represent the surface potential (volt), Faraday constant (96485 C mol\(^{-1}\)), molar gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and absolute temperature (T).
The surface charge density $\sigma$ ($\mu$C cm$^{-2}$) is related to surface potential $\psi_0$ (volt) according to Gouy-Chapman theory which is shown as follow:

$$\sigma = (8\varepsilon_0 n_{skb}T)^{\frac{1}{2}} \sinh \left( \frac{z\psi_0}{RT} \right)$$

$$= 0.1174c_s^{\frac{1}{2}} \sinh \left( \frac{z\psi_0}{RT} \right)$$  \hspace{1cm} (3.15)

Where $c_s$ represent ionic strength (M); $z$ represent valence of ion.

From Fig. 2.7, we obtained the zeta potential of G0 dendrimer, so we used Eq. 3.18 to convert the surface potential to surface charge density. Fig. 3.18 shows the surface charge density of G0 dendrimer. From Fig. 3.18, we can also convert pH measured in bulk phase, i.e., $[H^+]$ to surface concentration, i.e., $\{H^+\}$ according to Eq. 3.13. In Fig 3.6, 3.7, 3.8, and 3.9, we can find the pH range of G0 dendrimer adsorption on heavy metal is from 3.8 to 9.3 and that is below the ZPC of G0 dendrimer, which is equal to 9.6. Therefore, to obtain the K value of G0 dendrimer, we can use Eq. 3.11 which is suitable for pH below pHzpc. Fig. 3.19 is the plot to obtain surface acidity constant and total surface site of G0 dendrimer. Table 3.12 shows the intrinsic stability constants and some other parameter of G0 dendrimer.
Figure 3.18  Surface charge density of G0 dendrimer

Figure 3.19  Plot to obtain surface acidity constant and total surface site of G0 dendrimer.
Table 3.12  Intrinsic stability constants of G0 dendrimer

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>(10^{-1}M)</th>
<th>(10^{-2}M)</th>
<th>(10^{-3}M)</th>
<th>(S_t)</th>
<th>(pH_{zpc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pK_{a1}^{int})</td>
<td>8.96</td>
<td>8.37</td>
<td>7.31</td>
<td>0.51</td>
<td>9.6</td>
</tr>
<tr>
<td>(pK_{a2}^{int})</td>
<td>10.24</td>
<td>10.83</td>
<td>11.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G0 dendrimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.5.5 Equilibrium Constants

For the adsorption process, the reaction was shown as follow:

\[
\text{R-NH}_3^+ + \text{Me}^{2+} \leftrightarrow \text{R-NH}_2\text{-Me}^{2+} + \text{H}^+; K
\]

(3.16)

Where R-NH\(_3^+\), Me, and R-NH\(_2\)-Me\(^{2+}\) represent surface species, heavy metal and absorbed heavy metal, respectively. The reaction equilibrium constant, K, defined as follow:

\[
K = \frac{[\text{R-NH}_2\text{-Me}^{2+}][\text{H}^+]}{[\text{R-NH}_3^+][\text{Me}^{2+}]}
\]

(3.17)

The three species SOH\(_2^+\), SOH, and SO\(^-\) were described as follow:

\[
\alpha_{R-NH_3^+} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}
\]

(3.18)

\[
\alpha_{R-NH_2} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}
\]

(3.19)

\[
\alpha_{R-NH^-} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}
\]

(3.20)

The major effective surface species of G0 dendrimer is R-NH\(_3^+\) and it defined as Eq. 3.18.

Based on Eq. 3.18, 3.19, and 3.20, the surface speciation of G0 dendrimer modified magnetite particles is shown as Fig. 3.20.
Figure 3.20 The surface speciation of G0 dendrimer modified magnetite particles. Experiment condition: [G0] = 5 g/L; I = 0.01 M; T = 298 ± 1 K.

Fig. 3.21, 3.22, 3.23, and 3.24 is the distribution of free metal ion, absorbed metal ion, and total metal minus precipitated metal in the adsorption process of Cu(II), Co(II), Zn(II), and Ni(II), respectively.
According to Eq. 3.17, we can obtain the equilibrium constant $K$ for Cu(II) absorbed on G0 dendrimer in the pH range from 4.0 to 6.3, that is $\log K = -3.79 \pm 0.09$. 
Figure 3.22  Distribution of Co(II) in adsorption process. Experiment condition: Co(II) = 4.21 × 10^{-3} M; C(NaClO_4) = 0.01M; T = 298 ± 1 K.

According to Eq. 3.17, we can obtain the equilibrium constant K for Co(II) absorbed on G0 dendrimer in the pH range from 5.3 to 7.1, that is logK = -5.18 ± 0.19.
According to Eq. 3.17, we can obtain the equilibrium constant $K$ for Zn(II) absorbed on G0 dendrimer in the pH range from 4.5 to 6.7, that is $\log K = -4.03 \pm 0.58$. 

Figure 3.23 Distribution of Zn(II) in adsorption process. Experiment condition: Zn(II) = $3.46 \times 10^{-3}$ M; C(NaClO$_4$) = 0.01M; $T = 298 \pm 1$ K.
Figure 3.24  Distribution of Ni(II) in adsorption process. Experiment condition: 
Cu(II) = 4.24 × 10^{-3} \text{M}; C(\text{NaClO}_4) = 0.01\text{M}; T = 298 \pm 1 \text{K}.

According to Eq. 3.17, we can obtain the equilibrium constant K for Ni(II) 
absorbed on G0 dendrimer in the pH range from 5.8 to 7.1, that is logK = -4.70 \pm 0.21.

3.6 Conclusions

Among the four heavy metals, the total removal followed the order: Cu(II) > 
Ni(II) > Zn(II) > Co(II). Cu(II), Ni(II), Zn(II), and Co(II) was totally removed at pH 6.7, 
7.3, 7.5, and 9.3, respectively.

In term of net heavy metal removal efficiency, the order was: Ni(II) > Cu(II) > 
Zn(II) > Co(II). The highest net removal efficiency of Ni, Cu, Zn, and Co was 85, 65, 55, 
and 42\%, respectively.

The adsorption process of four heavy metals can be fitted with the Langmuir 
adsorption model.
The maximum adsorption capacity of G0 dendrimer for Cu(II), Co(II), Zn(II), and Ni(II) was 49.02, 21.69, 28.17, and 22.73 mg/g, respectively.

The total surface site of G0 dendrimer is 0.51 μcoul/cm².

The logK value of adsorption reaction of Cu, Co, Zn, and Ni is -3.79 ± 0.09, -5.13 ± 0.38, -4.03 ± 0.58, and -4.70 ± 0.21, respectively.
Chapter 4

FUTURE RESEARCH

From current research, G0 dendrimer modified magnetite particles show the adsorption capacity of Cu(II), Co(II), Zn(II), and Ni(II). In future research, more heavy metals, such as Cd(II), As(III), and As(V), may be applied in the adsorption experiment to test the adsorption capacity.

For the materials, higher generation can be introduced to the surface of magnetite particles. Based on the dendrimer structure, high generation associated more functional group exposed on the surface. In future research, higher generation, G2 and G4, will grow on the magnetite particle. The G2 and G4 dendrimer modified magnetite particles will be used as new absorbent to test the removal efficiency of heavy metals.

To investigate the regeneration ability of dendrimer modified magnetite particles, the adsorption-desorption experiment will be conducted in the future research.
REFERENCES


[57] NIST Standard Reference Databases 46.
