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Hydroxyapatite for colorimetric detection of nickel(II) ion

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โดย

นายอิทธินันท์ ดวงงาม

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By	Mr. Itthinan Duangngam

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Bachelor of Science degree

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บทคัดย่อ

เตรียมไฮดรอกซีอะพาไทต์ (HAp) ที่เคลือบด้วย 1-(2-ไพริดิลเอโซ)-2-แนฟทอล (PAN) หรือ HAp-PAN เพื่อใช้เป็นตัวตรวจวัดไอออนนิกเกิล(II) โดยผิวของไฮดรอกซีอะพาไทต์ที่ดัดแปรด้วยวิธีเคลือบและวิธีการดูดซับ ทำการพิสูจน์เอกลักษณ์วัสดุที่ได้ด้วยเครื่อง X-Ray diffraction spectrometer แบบผง (Powder XRD), Zetasizer และ Thermogravimetric analyzer (TGA) ในวิธีเคลือบไฮดรอกซีอะพาไทต์ถูกดัดแปรด้วยเฮกซะเดกซิลไตรเมธิลแอมโมเนียมโบรไมด์ (CTAB) ก่อนนำไปเคลือบด้วย PAN ซึ่ง HAp-PAN ที่เตรียมโดยใช้ PAN ความเข้มข้น 1.0 มิลลิโมลาร์สามารถตรวจวัดไอออนนิกเกิล(II) ที่ความเข้มข้น 100 และ 1000 ไมโครกรัม/ลิตรได้ และพบการหลุดออกของ PAN จากผิวของไฮดรอกซีอะพาไทต์ขณะทำการตรวจวัด ในส่วนของวิธีการดูดซับ HAp ถูกดัดแปรผิวด้วยการผสมกับ PAN ในสารละลาย CTAB เมื่อนำวัสดุไปทดสอบกับสารละลายนิกเกิล(II) พบว่าวัสดุเปลี่ยนสีจากสีเหลืองอ่อนในสภาวะที่ไม่มีไอออนนิกเกิล (II) เป็นสีชมพูหรือม่วงตามความเข้มข้นของไอออนนิกเกิล(II) ที่เพิ่มมากขึ้น โดยสภาวะที่เหมาะสมสำหรับการเตรียม HAp-PAN คือ ใช้ความเข้มข้นของสารละลาย PAN เป็น 1.2 มิลลิโมลาร์และใช้เวลาในการดูดซับ 5 นาที และ pH ที่เหมาะสมสำหรับตรวจวัดไอออนนิกเกิล(II) คือ pH 6 อีกทั้ง HAp-PAN ที่เตรียมได้จากวิธีการดูดซับสามารถตรวจวัดไอออนนิกเกิล(II) ด้วยตาเปล่าที่ความเข้มข้น 300 และ 700 ไมโครกรัม/ลิตร

คำสำคัญ: ไฮดรอกซีอะพาไทต์, 1-(2-ไพริดิลเอโซ)-2-แนฟทอล, การตรวจวัดเชิงสี, ไอออนนิกเกิล(II)

Project Title	Hydroxyapatite for colorimetric detection of nickel(II) ion		
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Abstract

Hydroxyapatite (HAp) coated with 1-(2-pyridylazo)-2-naphthol (PAN) was prepared for the use as a sensor for Ni^{2+} designated as HAp-PAN. HAp surface modification was performed by impregnation method and adsorption method. The materials were characterized by powder X-Ray diffraction spectrometer (Powder XRD), Zetasizer, and thermogravimetric analyzer (TGA). In impregnation method, HAp was modified with hexadecyltrimethylammonium bromide (CTAB) and further impregnated with PAN solution. HAp-PAN prepared by using 1.0 mM PAN solution could be used to detect 100 and 1000 μg/L Ni^{2+}. The leaching of PAN from the obtained material was observed when tested with Ni^{2+} solution. In the adsorption method, HAp was modified by mixing HAp with PAN in CTAB solution. The obtained material was used in Ni^{2+} detection. The solid turned from pale yellow in the absence of Ni^{2+} to pink or purple in increasing Ni^{2+} concentration. The suitable condition to prepare HAp-PAN was by using a 1.2 mM PAN solution and 5 mins of adsorption time. The suitable pH for Ni^{2+} detection was pH 6. The HAp-PAN obtained by adsorption method could detect 300 and 700 μg/L Ni^{2+} by naked eyes.

Keywords: Hydroxyapatite, 1-(2-pyridylazo)-2-naphthol, colorimetric detection, nickel(II) ion

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LIST OF ABBREVIATIONS

HAp	Hydroxyapatite
CTAB	Hexadecyltrimethylammonium bromide
PAN	1-(2-Pyridylazo)-2-naphthol
DI	Deionized
RO	Reverse osmosis
mg	milligram
g	gram
M	Molar
mM	millimolar
mg/L	milligram per liter
µg/L	microgram per liter
mL	milliliter
µL	microlitter
^{o}C	Degree Celsius
eq.	equivalent
hr(s).	hour(s)
min(s)	minute(s)
rpm	round(s) per minute(s)

Chapter 1

Introduction

1.1 Statement of the problem

Nickel is one of heavy metals which are widely used as alloys due to its anti-corrosion property. Nickel is used in various industrial manufacturing, for example, production of car parts, batteries, stainless steel, accessories, and cooking utensils. However, if nickel is released into the environment and absorbed in human body, its toxicity would lead to hand eczema, lung and nasal cancer, and allergic response. High concentration of nickel leads to DNA damage [1,2]. In Thailand, nickel was found in Samrong canal and Bang Nang Kreng canal, Samut Prakan province in 2010. The contamination was likely because of the release of industrial waste water into the environment [3]. Therefore, monitoring of nickel level in water is necessary to control the contamination problems. To determine the level of nickel in water samples, various techniques can be used including atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy. Furthermore, nickel sensors, for example, electrochemical sensors using chelating agent [4], electrochemical composite sensors [5], and sensors from nanoparticle [6] were developed. However, these techniques require laboratory skill for sensors synthesis and analytical instruments. Therefore, some colorimetric sensors for Ni^{2+} detection were proposed and the color change of these sensors could be observed by naked eyes without the use of any instrument [7,8]. In this project, a colorimetric solid sensor is prepared for Ni^{2+} detection using hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) as solid support and 1-(2-pyridylazo)-2-naphthol (PAN) as colorimetric reagent. HAp was chosen because it is non-toxic and easily synthesized [9] and PAN is a tridentate ligand that forms complex with Ni^{2+} and change its color [10]. It was expected to improve the sensivity in Ni^{2+} detection at low concentration. To modify HAp surface with PAN, hexadecyltrimethylammonium bromide (CTAB) is also used in the process [11].

1.2 Objective and scope of the research

To synthesize modified hydroxyapatite for colorimetric detection of Ni^{2+}.

1.3 Literature review, theory and concept

1.3.1 Hydroxyapatite (HAp)

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, has either hexagonal or monoclinic crystal structure. Its space group symmetry of hexagonal phase is $P6_3/m$ with lattice parameters of a = b = 9.432 Å, c = 6.881 Å, and angle between c-axis and a-axis is 120°. In addition, HAp can be formed with Ca/P ratio of 1.67 [12]. Its phosphate groups are on c-plane [13] and they exhibit negative charge on the plane. In nature, it is found in bones and teeth [14] and it is often used in medical and dental applications [13].

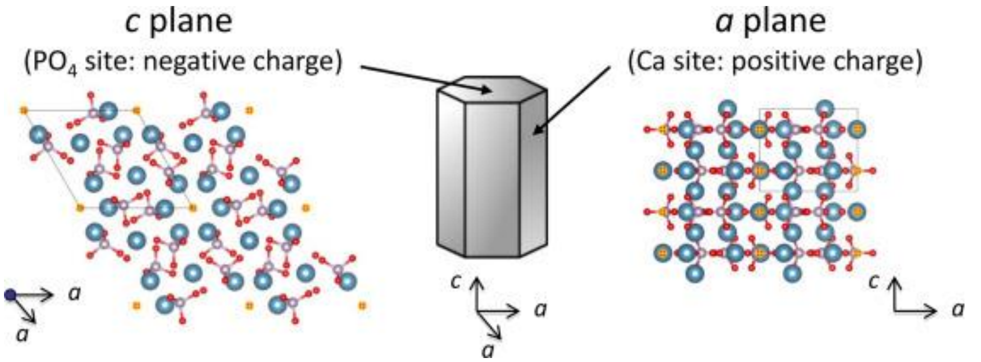


Figure 1.1 Crystal structure and illustration of stoichiometric hydroxyapatite (HAp) [13]

In laboratory, HAp can be synthesized through various approaches. They can be classified into 2 main methods; dry method and wet method. In dry methods, solid of several compounds are ground and mixed together and the mixture is calcined at high temperature. Pramanik et al. introduced the preparation of their HAp from CaO, P_2O_5, and SiO_2. The inorganic component mixture was ground and compacted under pressure. Then, the mixture was sintered at 1250 $^{\circ}C$ [15]. Moreover, Guo et al. synthesized HAp from the solid-state reaction using $Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4$, and $NaHCO_3$ as substrates at room temperature to study the effect of calcining temperature on HAp particle size [16].

In wet methods, the calcium-source and phosphate-source compounds are dissolved in aqueous solution and used as starting solutions for the synthesis of HAp [17].

These methods are divided into 5 synthetic routes which are co-precipitation method, sol-gel method, emulsion method, hydrolysis method, and hydrothermal method. Firstly, in precipitation method, the formation of HAp relates to nucleation-growth mechanism. Yelten-Yilmaz and Yilmaz reported the preparation of HAp based on the neutralization reaction between $Ca(OH)_2$ suspension and H_3PO_4 solution. This reaction resulted in a white precipitate that was further treated at 120 ^{o}C to get HAp [17]. Verwilghen et al. used $CaCO_3$ suspension mixed with $(NH_4)_3PO_4$ in DI water. The mixture was stirred at 60 ^{o}C for 72 hr. After solid separation and drying, a fine powder of HAp was obtained [18].

Secondly, in sol-gel method, the formation of HAp relates to the mineralization of precursors. Bezzi et al. used $Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4$, EDTA, and urea dissolved in DI water containing 7% ammonia. The mixture was stirred for 2 hr. at 90-120 ^{o}C to hydrolyze urea. The white gel was obtained. It was dried at high temperature to yield a white powder which was composed of HAp, **β**-TCP and CaO. Then, $(NH_4)_2HPO_4$ was added into the aqueous suspension of the powder to correct Ca/P ratio to 1.667. The pure HAp powder was formed after it was dried at 120 ^{o}C [19]. Eshtiagh-Hosseini et al. proposed a water-based sol-gel process. $Ca(NO_3)_2.4H_2O$ solution in DI water was mixed with sol of triethyl phosphate ($(C_2H_5O)_3PO$, TEP) in anhydrous ethanol. The mixture was heated, aged, dried, and calcined to obtain HAp [20].

Thirdly, in emulsion method, surfactants are used in the synthesis. $Ca(NO_3)_2.4H_2O$ and H_3PO_4 are mostly used as calcium- and phosphate-source, respectively. Saha et al. reported the synthesis of HAp by reverse microemulsion technique using $Ca(NO_3)_2.4H_2O$ and H_3PO_4 aqueous solutions as starting materials. In addition, several surfactants (i.e. dioctyl sulfosuccinate sodium salt (AOT), dodecyl phosphate (DP), NP5 (poly(oxyethylene)$_5$ nonylphenol ether), and NP12 (poly(oxyethylene)$_{12}$ nonylphenol ether)) were used to form emulsion in organic solvents [21].

The forth method is hydrolysis method. HAp was synthesized via hydrolysis of calcium phosphates used as precursors. Graham and Brown synthesized stoichiometric HAp from hydrolysis reactions of octacalcium phosphate (OCP) with tetracalcium phosphate (TetCP) and calcium hydroxide were used to adjust Ca/P ratio [22]. Duracan and Brown obtained HAp from direct hydrolysis reaction of **α**-tricalcium phosphate (**α**-TCP,

α-$Ca_3(PO_4)_2$) which was synthesized from solid state reaction between $CaCO_3$ and calcium pyrophosphate ($Ca_2P_2O_7$) [23].

Finally, in hydrothermal methods, HAp size and morphology can be controlled [24]. Bensalah et al. synthesized HAp nanorods from phosphogypsum waste and potassium dihydrogenphosphate (KH_2PO_4). The effect of synthesis parameters, for example, synthesis time, temperature, and pH of the solution were investigated [24]. Meanwhile Wang et al. prepared HAp through low-temperature hydrothermal method and CTAB was used as a template for nucleation and crystal growth control [25].

1.3.2 Modification of hydroxyapatite

Modification of HAp surface is quite difficult because of interface interaction between hydrophilic surface of HAp and hydrophobic compounds of reagents. Emulsifying agents and bridging agents are used to solve this problem. Moreover, there are 4 techniques for surface modification including direct reaction, coating, grafting and polymerization [26].

The first method is direct reaction. HAp is directly stirred with chemicals used for modification. Kim modified HAp with oleic acid which is an amphiphilic surfactant. After solid separation, the solid was further stirred with poly(ε-caprolactone) (PCL) and solvent extraction was used to solidify the mixture solution. Then, the obtained product was dried under vacuum over 3 days [27].

The second method is coating technique. Zhao et al. coated silane coupling agent diluted in acetone onto HAp via condensation reaction. HAp was synthesized by the wet method. After that, silane coupling agent solution was added onto HAp powder and stirred for 30 mins. The dried HAp with or without silane treatment was stirred with epoxy to prepare HAp-epoxy composite and heated at 130 °C [28].

The third method is grafting technique. Hong et al. grafted L-lactide which reacted with hydroxyl groups on surface of the HAp via ring-opening polymerization reaction using $Sn(Oct)_2$ as a catalyst. HAp was suspended in dried xylene and heated at 90 °C before the L-lactide solution was added dropwise into the mixture. The reaction was performed under nitrogen atmosphere at 120 °C for 3-48 hrs. and cooled down to room temperature. PLLA-g-HAp was obtained and was washed to remove residual poly (L-lactide). Finally, it was dried in a vacuum-oven [29].

The last method is polymerization technique. Wei et al. modified HAp which was treated with 3-aminopropylthriethoxysilane (APS). Its terminal amino groups further reacted with **γ**-benzyl-L-glutamate N-carboxyanhydride via the ring opening polymerization [30].

1.3.3 Colorimetric detection of Ni^{2+}

As color changes are easy to be observed by naked eyes, therefore a large number of colorimetric detection methods have been developed and used to determine metal ions. In this work, colorimetric solid sensors for Ni^{2+} detection are focused. First, Juasakul demonstrated the use of amberite XAD-7 coated with 1-(2-pyridylazo)-2-naphthol for Ni^{2+} detection. When this solid was tested with Ni^{2+}, its color changed from yellow to pink [10]. Meanwhile, Dhaka et al. applied benzimidazole-based sensor on paper to detect Ni^{2+}. The first sensor was prepared by coating 2-(benzimidazol-2-yl-4-phenylazo)phenol on paper and the another paper based sensor was coated with 2-(benzimidazol-2-yl-4-(4-methoxyphenyl)azo)phenol, respectively. For both sensors, the paper color changed from white to yellow when it was exposed to Ni^{2+} [31].

1.4 Expected benefits

To obtain a method for preparation of a new solid sensor for colorimetric detection of Ni^{2+}.

Chapter 2

Experimental

2.1 Instruments

Table 2.1 List of instruments

Instruments	Brand and Model
Powder X-Ray diffraction spectrometer	Rigaku, Dmax-2200 Ultima$^+$
Thermogravimetric analyzer	Perkin-Elmer, Pyris 1
Zetasizer	Malvern, version 7.04

2.2 Chemicals

Table 2.2 List of chemicals

Chemicals	Purity	Suppliers
1-(2-Pyridylazo)-2-naphthol (PAN)	≥ 97.0%	Fluka Analytical
Ammonia solution	25%	EMSURE®
Calcium nitrate tetrahydrate ($Ca(NO_3)_2•4H_2O$)	99.0-103.0%	Ajax Finechem
Ethanol (CH_3CH_2OH)	100%	EMSURE®
Hexadecyltrimethylammonium bromide (CTAB)	≥ 96.0%	Fluka Analytical
Nickel Standard for AAS 1000 ± 4 mg/L	CRM	Sigma-Aldrich
Nitric acid (HNO_3)	≥ 65.0%	EMSURE®
Orthophosphoric acid (H_3PO_4)	85-87%	CARLO ERBA
Potassium bromide (KBr)	≥ 99.0%	Sigma-Aldrich
Sodium hydroxide pellets (NaOH)	≥ 99.0%	EMSURE®

2.3 Characterization

2.3.1 Powder X-ray diffraction (Powder XRD)

XRD pattern of HAp was recorded at 2θ in a range of 5-60° by a Rigaku, Dmax-2200 Ultima$^+$ diffractometer equipped with a fixed monochromator and a Cu Kα radiation source at an accelerating voltage of 40 kV and applied current of 30 mA. Scan speed was 2.000 degrees/min.

2.3.2 Thermogravimetric analysis

The samples, HAp, CTAB, PAN, HAp-PAN from impregnation method and adsorption method, were dried in the oven at 80 ^{o}C overnight. After that, they were cooled in a desiccator. Their thermograms were recorded using a thermogravimetric analyzer (Perkin-Elmer, Pyris 1) in a temperature range of 100-550 ^{o}C.

2.3.3 Zeta potential

HAp and HAp-PAN from adsorption method using 0.8 mM of PAN solution were dispersed in 5 mL of RO water. After that, the values of zeta potential were measured by a zetasizer (Malvern, version 7.04) at The Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University.

2.4 Procedures

2.4.1 Synthesis of hydroxyapatite

Hydroxyapatite (HAp) was synthesized using precipitation method [32]. To obtain approximately 2 g of HAp, 4.70 g of $Ca(NO_3)_2.4H_2O$ (19.9 mmol, 10 eq.) were weighed in a 250-mL beaker and dissolved with 50 mL of RO water. Then, 10 mL of 1.19 M H_3PO_4 solution (11.9 mmol, 6 eq.) was added in the $Ca(NO_3)_2$ solution. Mole ratio of Ca to P is 1.67 which is equal to Ca/P ratio found in HAp [15]. The pH of the solution was adjusted to 11 with 25% NH_3 solution and the solution was stirred for 2 hrs. After that, the mixture was centrifuged at 3500 rpm for 5 mins in order to separate the solid HAp from the solution. The obtained HAp was washed with RO water to remove NH_3 residue and dried in an oven at 120 ^{o}C overnight. Finally, it was cooled in a desiccator and hand-grounded to powder.

2.4.2 Synthesis of HAp modified with PAN using impregnation method

The HAp was prepared as previously described using precipitation method. After adjusting the pH of the mixture to 11, 10 mL of 1 mg/mL CTAB solution was added and stirred at room temperature for 2 hrs. After that, the mixture was centrifuged at 3500 rpm for 1 min in order to discard the solution. Next, 10 mL of 1 mM PAN solution in methanol was added onto the solid and stirred for 30 mins. The PAN-impregnated HAp was dried in an oven at 80 ^{o}C overnight. Then, it was cooled in a desiccator and hand-grounded to powder. The solid was called HAp-PAN IP1. Furthermore, the HAp was impregnated with PAN solution of different concentrations (i.e. 0.17 mM, 0.25 mM, 0.34 mM) and called HAP-PAN-IP0.17, HAP-PAN-IP0.25, and HAP-PAN-IP0.34. The obtained materials were characterized by TGA and used to detect Ni^{2+}.

2.4.3 Synthesis of HAp modified with PAN using adsorption method

2.4.3.1 Effect of adsorption time

A 0.8 mM PAN in 60 mM CTAB solution was prepared and used for HAp modification. 49.8x mg of PAN was dissolved in 50 mL of 60 mM CTAB solution and 5 mL of ethanol (10% ethanol by volume). After stirring for 1 min, 50 mL of 60 mM CTAB solution was added in the PAN solution and the mixture was stirred at 80 ^{o}C for 30 mins. Then, the volume of the solution was adjusted to 250 mL in a volumetric flask to obtain 0.8 mM PAN solution. The HAp was modified with PAN using different contact times. 20 mL of 0.8 mM PAN solution was stirred with 0.500x g of HAp for 5 mins, 30 mins, 1 hr. or 3 hrs. in a 100-mL beaker. The mixture was centrifuged at 3500 rpm for 1 min to discard the solution. The obtained solid was washed with RO water twice and dried in the oven at 80 ^{o}C for 10-12 hrs. Finally, the solid was hand-grounded to powder and kept for characterization.

2.4.3.2 Effect of PAN concentration

A 1.2 mM PAN in 60 mM CTAB solution was prepared and used as stock solution. 14.9x mg of PAN was dissolved in 1 mL of ethanol and 10 mL of 60 mM CTAB solution (10% ethanol by volume). After stirring the PAN solution for 1 min, 20 mL of 60 mM CTAB solution was added and the mixture was stirred at 80 ^{o}C for 30 mins. The volume of the solution was adjusted to 50 in a volumetric flask to obtain a 1.2 mM PAN solution. This solution was diluted to prepare a 0.4 and 0.8 mM PAN solution using 60 mM CTAB solution as diluent. To modify the HAp, 20 mL of 0.4, 0.8 or 1.2 mM PAN solution was stirred with 0.500x g of HAp for 1 hr. in a 100-mL beaker. The mixture was centrifuged at 3500 rpm for 1 min to discard the solution. The obtained HAp-PAN solid was washed with RO water twice and dried in an oven at 80 ^{o}C for 10-12 hrs. Finally, the solid was hand-grounded to powder, weighed and they were named HAp-PAN-AP0.4, HAp-PAN-AP0.8, and HAp-PAN-AP1.2, respectively corresponding to PAN concentration. The materials were characterized and used to test Ni^{2+} in solution.

2.4.4 Detection of Ni^{2+} in solution

2.4.4.1 Detection of Ni^{2+} by HAp-PAN from impregnation method

For preliminary study, 0.500x g of HAp-PAN-IP1 were washed by stirring the material in 10 mL of DI water for 5 mins. Then, they were dried in an oven at 50 ^{o}C for 10-12 hrs and hand-grounded to powder. Then, 10 and 100 µg/L Ni^{2+} solutions were prepared by diluting a 1000 mg/L Ni^{2+} standard solution and 10.00 mL of each Ni^{2+} solution was stirred with HAp-PAN-IP1 for 15 mins. After that, the solution was discarded. The slurry was dropped on a piece of filter paper and its photos were immediately taken. The experiment was performed in duplicate and RO water was used as blank solution.

2.4.4.2 Detection of Ni^{2+} by HAp-PAN from adsorption method

2.4.4.2.1 Effect of solution pH

Solutions of 1 mg/L Ni^{2+} which had pH 3, 6 and 8 were prepared by diluting a 1000 mg/L Ni^{2+} standard solution with RO water and adjusting the pH using 0.1 M NaOH solution and/or 0.1 M HNO_3 solution. Next, 10.00 ± 0.09 mg HAp-PAN-AP0.8 was weighed into a test tube. 10.00 mL of 1 mg/L Ni^{2+} solution (pH 3, 6 or 8) was added. Then, the mixture was stirred for 5 mins and further kept still for the solid to precipitate for 5 mins. After that, the solution was discarded. The slurry was dropped onto a piece of filter paper and the photo of the solid was immediately taken. The experiment was performed in triplicate and RO water of different pH was used as blank solution in the detection.

2.4.4.2.2 Effect of PAN concentration

First, 10.00 ± 0.09 mg of HAp-PAN-AP0.4, HAp-PAN-AP0.8, and HAp-PAN-AP1.2 were weight into test tubes. Next, 10.00 mL of Ni^{2+} solutions containing 300 μg/L, 500 μg/L, 700 μg/L or 1 mg/L Ni^{2+} (pH 6) was added into the solid in each tube and stirred for 5 mins. After that, the solution was discarded and its pH was measured. The slurry was dropped on a piece of filter paper and its photos were immediately taken. The experiment was performed in triplicate and RO water was used as blank solution.

Chapter 3

Results and Discussion

3.1 Synthesis and characterization of hydroxyapatite

Hydroxyapatite (HAp) was synthesized through the precipitation method for the use as a solid support. A white HAp powder was obtained and further characterized by a Powder X-ray diffraction to observe its crystal structure (Figure 3.1).

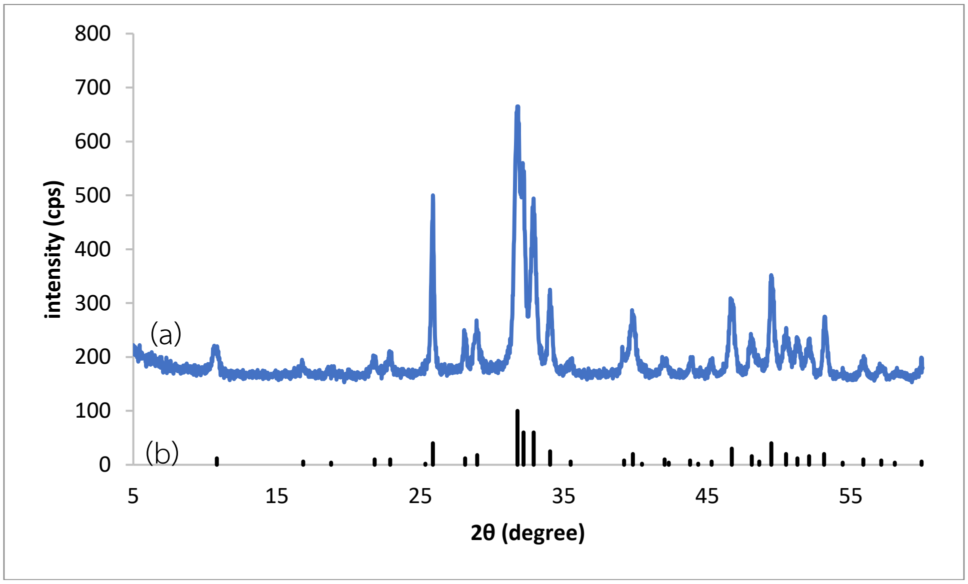


Figure 3.1 XRD pattern of (a) HAp synthesized by precipitation method and (b) standard structure of HAp (JCPDS card number 09-0432).

According to Figure 3.1, both XRD pattern of HAp synthesized by precipitation method and HAp standard structure from JCPDS card number 09-0432 are similar indicating that the crystal structure of the solid was hexagonal. Therefore, the synthesized solid was confirmed to be HAp.

3.2 Synthesis and characterization

3.2.1 HAp modified with PAN using impregnation method

To prepare HAp modified with PAN by using impregnation method, HAp was precipitated under basic condition and CTAB was immediately added into the suspension. Under basic condition (pH = 11), the surface of HAp would contain negative charges regarding to its pI value (pI = 10) [33]. Therefore, the electrostatic interaction with CTAB could occur on the solid surface. The coating of CTAB on HAp surface would help to increase surface hydrophobicity for further modifying with PAN. In this experiment, PAN solution of different concentrations (0.17 – 1 mM) was used to modify HAp and the obtained materials were called HAp-PAN-IP0.17, HAp-PAN-IP0.25, HAp-PAN-IP0.34, and HAp-PAN-IP1, respectively. The materials were characterized by thermogravimetric analysis compared to the starting materials (Figure 3.2-3.3).

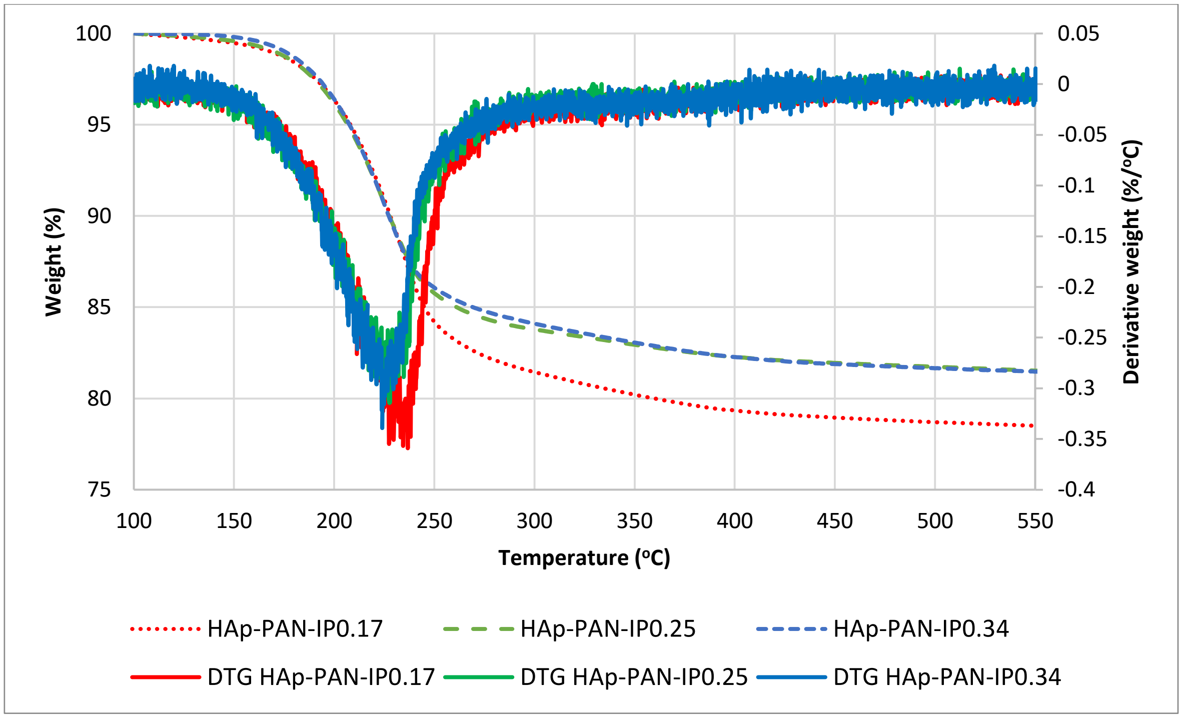


Figure 3.2 Thermograms and derivative thermograms of HAp-PAN-IP0.17, HAp-PAN-IP0.25 and HAp-PAN-IP0.34

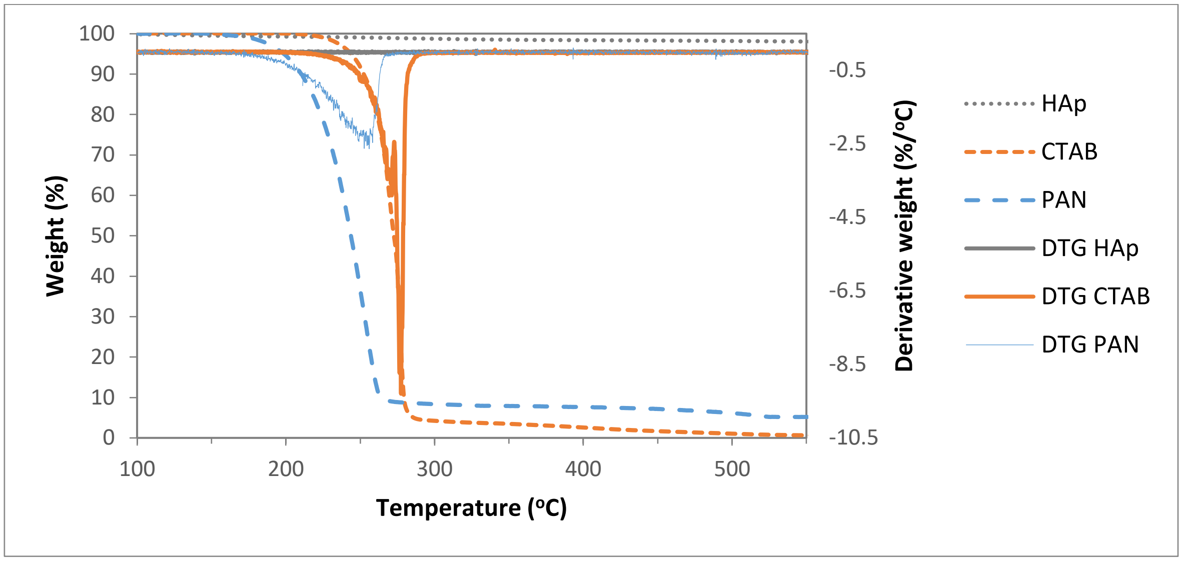


Figure 3.3 Thermograms and derivative thermograms of HAp, CTAB and PAN.

According to Figure 3.2, thermograms of HAp-PAN-IP0.17, HAp-PAN-IP0.25, and HAp-PAN-IP0.34 show a weight loss in the temperature range of 150-275 °C. On the other hand, the thermogram of non-modified HAp did not show any weight loss in the temperature range of 100-550 °C (Figure 3.2). Meanwhile, pure CTAB and pure PAN decomposed in the temperature range of 201-277 °C and 150-256 °C, respectively. For HAp-PAN analysis, the weight loss occurred at the same decomposition temperature range of CTAB and PAN. Therefore, the weight loss observed in the HAp-PAN materials could be attributed to the decomposition of CTAB and PAN on the materials. The organic contents on HAp-PAN-IP0.17, HAp-PAN-IP0.25, and HAp-PAN-IP0.34 were 17%, 15%, 15%, respectively. These results indicate that PAN could be modified on HAp through impregnation method.

It should be noticed that the organic content on these materials observed by TGA did not correspond with the concentration of PAN solution used in the impregnation. Nevertheless, it was observed that the materials prepared by using higher concentration of PAN had more intense yellow color. During impregnation process, in particular methanol evaporation by heating, it may lead to nonhomogeneous coating of HAp surface with PAN. In addition, the thermogravimetric analysis was performed only once each material. These explained the trend of weight loss that did not correspond to the concentration of PAN used in the modification. To obtain more reliable results, TGA analysis should be performed several times.

3.2.2 HAp modified with PAN using adsorption method

To prepare HAp modified with PAN using adsorption method, PAN in CTAB micelles was adsorbed onto HAp through electrostatic interaction. In this experiment, the effect of adsorption time and PAN concentration were studied.

In the first experiment, HAp was modified with 0.8 mM PAN solution. The obtained material (HAp-PAN-AP0.8) was analyzed by a zetasizer to measure zeta potential of the solid surface, compared to bare HAp. The results are shown in Table 3.1.

Table 3.1 Zeta potential of HAp and HAp-PAN-AP*0.8*

Material	**Average zeta potential (mV)**
HAp	3.1 ± 0.2
HAp-PAN-AP0.8	21.7 ± 0.8

According to the results in Table 3.1 , the value of zeta potential of both HAp and HAp-PAN was positive, indicating that the net surface charge of these materials was positive (at pH 7). Furthermore, HAp-PAN surface had much higher positive potential than HAp surface. In aqueous solution under the condition used in this study, CTAB might form positively charged admicelles or micelles and trap PAN inside. When these micelles adsorbed on HAp surface, the surface charge of HAp would be more positive. These results reveal that HAp surface could be coated with PAN entrapped in CTAB micelles.

To optimize the adsorption amount of PAN on HAp, the effect of adsorption time was studied. HAp was modified with a 0.8 mM PAN solution using contact time of 5 mins, 30 mins, 1 hr. or 3 hrs. The materials were characterized by thermogravimetric analysis (Figure 3.4).

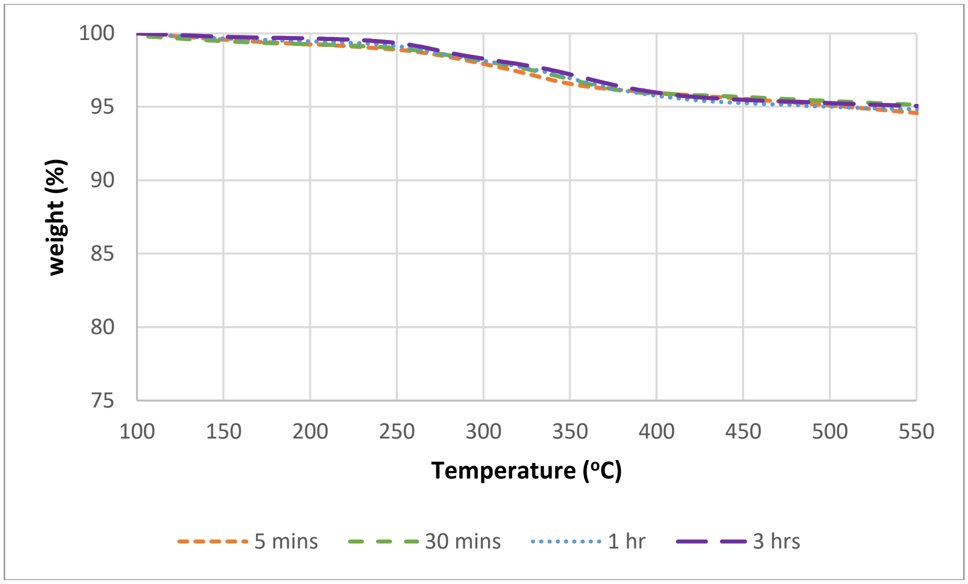


Figure 3.4 Thermograms of materials prepared by using an adsorption time of 5 mins, 30 mins, 1 hr., and 3 hrs.

According to the results in Figure 3.4, thermograms of HAp-PAN-AP0.8 materials prepared by using adsorption time of 5 mins, 30 mins, 1 hr. and 3 hrs. show an organic decomposition in a temperature range of 150 – 430 °C. Regarding the temperature of weight loss, it is likely that the weight loss of these materials was attributed to the decomposition of CTAB and PAN on the surface. The organic contents on HAp were 2%, 3%, 4%, and 4%, when the adsorption time of 5 mins, 30 mins, 1 hr., and 3 hrs. were applied, respectively. It shows that the amount of PAN on HAp was not remarkably increased when adsorption time period was longer. Therefore, the suitable adsorption time was 5 mins.

It should be noticed that the amount of organic contents on HAp-PAN prepared by adsorption method was much less than that on HAp-PAN prepared by using impregnation method. In adsorption method, the amount of PAN adsorbed depends on the adsorption capacity of HAp, which is probably low and limited by its surface area. Therefore, only a small amount of PAN was adsorbed on HAp.

Furthermore, PAN solution of different concentrations (0.4 – 1.2 mM) was used to modify HAp and the obtained materials were called HAp-PAN-AP0.4, HAp-PAN-

AP0.8, HAp-PAN-AP1.2, respectively. The materials were characterized by thermogravimetric analysis compared to the starting materials (Figure 3.3,3.5).

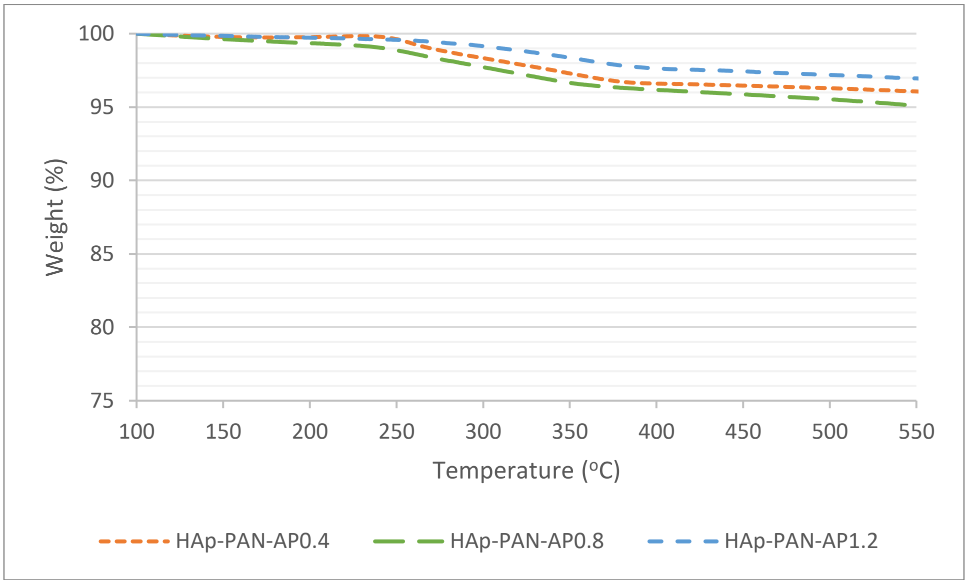


Figure 3.5 Thermograms of HAp-PAN-AP0.4, HAp-PAN-AP0.8, and HAp-PAN-AP1.2.

According to the results in Figure 3.5, thermograms of HAp-PAN-AP0.4, HAp-PAN-AP0.8, HAp-PAN-AP1.2 show a weight loss in a temperature range of 150 – 400 °C. The organic content on these materials was 2 - 3% which were not obviously different despite an increase of PAN concentration used in the preparation. It was probably due to the limited surface area of HAp for PAN adsorption and saturation of PAN on HAp surface may occur. Nevertheless, the TGA was performed only once each material. The materials were further tested with Ni^{2+} solutions to observe the color change.

3.3 Detection of Ni^{2+}

3.3.1 Detection of Ni^{2+} using HAp-PAN from impregnation method

To clearly observe color change, HAp-PAN-IP1 was chosen in this experiment to detect 10 µg/L, 100 µg/L, and 1000 µg/L Ni^{2+} solution. The results are shown in Table 3.2.

Table 3.2 Color of HAp-PAN materials used in Ni^{2+} detection

Ni^{2+} concentration (μg/L)	**Initial pH**	**1**	**2**
Blank	5.98		
10	6.10		
100	6.28		
1000	5.68		

The color of HAp-PAN-IP1 was more purple than the color of the blank (0 μg/L Ni^{2+} solution) when used to detect 100 μg/L and 1000 μg/L Ni^{2+} solution while the color of HAp-PAN-IP1 tested with 10 μg/L Ni^{2+} solution did not different from the color of blank. It was observed that while the solid was stirred with Ni^{2+} solution, the solution color turned to pink and the solid color was paler. Meanwhile, the color of blank solution turned from colorless to yellow. It seems that an excess of PAN on HAp leached out from the solid and it may competitively react with Ni^{2+} in the solution. It would affect to the extent of complex on HAp surface and this phenomenon might be uncontrollable. In order to remove excess amount of PAN on HAp, the materials (i.e. HAp-PAN-IP0.17, HAp-PAN-IP0.25 and HAp-PAN-IP0.34) were washed several times with DI water. The color of the materials turned to the original HAp color as most of PAN leached out from solid into the solution. Therefore, they were not used to detect Ni^{2+}.

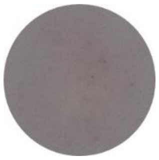
The leaching of PAN from solid is an important problem encountered. In impregnation method, all of PAN was deposited or coated on HAp surface after solvent evaporation. However, HAp surface has a limited capacity to adsorb PAN and hence, there was certainly an excess or unattached PAN on the solid. These PAN could easily leach from the solid when the material was in contact with water. Furthermore, it seems that the interaction of PAN with HAp surface was weak. As a result, PAN could be desorbed from the surface easily. Therefore, the impregnation method was not a suitable method to prepare HAp-PAN and an adsorption method was introduced to overcome the leaching problem. In adsorption method, PAN in CTAB micelles was adsorbed on HAp surface according to the adsorption capacity of HAp and hence, excessive amount of PAN-CTAB was low.

3.3.2 Detection of Ni^{2+} using HAp-PAN from adsorption method

To detect Ni^{2+} in the solution using HAp-PAN, two parameters were studied. The first parameter was pH of Ni^{2+} solution. It affects to the complexation reaction between PAN and Ni^{2+} and the adsorption of Ni^{2+}-PAN complex in the solution back to HAp. Another parameter was PAN concentration used in the modification of HAp. Different concentrations of PAN may affect to Ni^{2+} extraction and color change of the HAP-PAN material.

To study the pH effect, 1000 μg/L Ni^{2+} solution was used because it showed an intense color. It was extracted by HAp-PAN-AP0.8 for 5 mins. Then, the mixture was kept still for some times in order to precipitate HAp-PAN out of the solution. The color of the materials is shown in Table 3.3.

Table 3.3 Color of HAp-PAN materials used in Ni^{2+} detection at different pH

Initial pH of Ni^{2+} solution	Blank	1 mg/L Ni^{2+} solution		
3.00				
6.25				
8.67				

The color of materials used at pH 3 and 8 was pink, while it turned purple at pH 6. Therefore, pH 6 was chosen because the solid had deep color tone. However, the materials were not used under strong acid and strong basic condition because hydroxyapatite can dissolve in strong acid solution [34] and $Ni(OH)_2$ can precipitate in strong base solution [35]. The color of the material was very intense in this experiment as the contact time between the material and Ni^{2+} solution was long (about 15-30 mins) and the complexation reaction continued to occur. To shorten the analysis time, the contact time was decreased to 5 mins.

To study the effect of PAN concentration, HAp-PAN-AP0.4, HAp-PAN-AP0.8, and HAp-PAN-AP1.2 were prepared and used in the detection of Ni^{2+} in the concentration range of 0-1000 μg/L at pH 6. The contact time between the material and metal solution was 5 mins and the color of the solid was observed immediately after that. The results were observed by naked eyes and the photos of the materials were analyzed for color intensity by using ImageJ software in a green mode. The green mode was used because the color of material after extraction was pink or purple and green color which is an opposite color was adsorbed. The results are shown in Table 3.4-3.6. It should be noted that in this experiment, the camera setting was changed from 1/2000 sec., f/5.6, and 160 of ISO to 1/320 sec. f/9 and 200 of ISO. It affected the brightness of the pictures and the color of pictures seems to be more bright and paler than those reported in previous section.

Table 3.4 Color of HAp-PAN-AP0.4 materials used in Ni^{2+} detection

Nickel concentration (µg/L)	Solid color	Mean color intensity in green mode
0 (blank)		204 ± 5
300		197 ± 3
500		194 ± 1
700		190 ± 1
1000		192 ± 3

By naked eye observation, color of HAp-PAN-AP0.4 clearly changed to pale pink at 700 µg/L Ni^{2+}. When compared the color intensities of the material used in blank solution and in Ni^{2+} solution by T-test, the color intensity of HAp-PAN-AP0.4 used in 300 µg/L and 500 µg/L Ni^{2+} solution was not significantly different from blank color intensity at 95% confidence level ($p = 0.289$ and 0.087, respectively). Nonetheless, the color intensity of HAp-PAN-AP0.4 used in 700 µg/L Ni^{2+} solution was significantly different from blank color intensity at 95% confidence level. It was in agreement with the observation by naked eyes. However, the color intensity of HAp-PAN-AP0.4 used to detect 1000 µg/L Ni^{2+}

was paler than that observed in lower concentration. Therefore, the color response seems not be accurately related to concentration change.

Table 3.5 Color of HAp-PAN-AP0.8 materials used in Ni^{2+} detection

Nickel concentration (μg/L)	Solid color	Mean color intensity in green channel
0 (blank)		198 ± 1
300		189 ± 4
500		186 ± 3
700		184 ± 7
1000		179 ± 4

By naked eye observation, color of HAp-PAN-AP0.8 clearly changed to pale pink at 300 μg/L Ni^{2+}. When compared the color intensities of the material used in blank solution and in Ni^{2+} solution by T-test, the color intensity of HAp-PAN-AP0.8 used in 300 μg/L was significantly different from blank color intensity at 95% confidence level (p = 0.023) which is in agreement with the observation by naked eyes. Nonetheless, the color intensity of HAp-PAN-AP0.8 used in 300, 500, 700, and 1000 μg/L Ni^{2+} solution were not significantly different from each other at 95% confidence level. Therefore, the color response seems not to be accurately related to concentration change from 300 to 1000 μg/L Ni^{2+}. Furthermore, the color of the materials used at this concentration range could not be distinguished clearly by naked eyes.

Table 3.6 Color of HAp-PAN-AP1.2 materials used in Ni^{2+} detection

Nickel concentration (μg/L)	Solid color	Mean color intensity in green channel
0 (blank)		198 ± 3
300		193 ± 12
500		188 ± 6
700		171 ± 1
1000		168 ± 5

By naked eye observation, color of HAp-PAN-AP1.2 clearly changed to pale pink at 300 μg/L Ni^{2+}. When compared the color intensities of HAp-PAN used in blank solution and in Ni^{2+} solution by T-test, the color intensity of HAp-PAN-AP1.2 used in 300 μg/L was not significantly different from blank color intensity at 95% confidence level (p = 0.169) but they were different from each other by naked eyes. It was probably due to the high deviation of color intensities obtained by Image J program. Moreover, the color intensity of HAp-PAN-AP1.2 used to detect 700 μg/L Ni^{2+} was significantly different from color intensity of the blank and that of 300 μg/L Ni^{2+} at 95% confidence level (p = 0.003, 0.004). The color observed at 700 μg/L was more intense than that observed in lower concentrations but close to the color observed in 1000 μg/L Ni^{2+}. Therefore, it showed a clear color change at 300 μg/L and 700 μg/L Ni^{2+}.

In summary, HAp-PAN-AP0.4 and HAp-PAN-AP0.8 could detect Ni^{2+} only at 700 μg/L and 300 μg/L, respectively. Meanwhile, HAp-PAN-AP1.2 could be used to detect Ni^{2+} at 300 μg/L and 700 μg/L. The deviation of solid color was observed despite being used to detect Ni^{2+} of the same concentration. It was probably due to the effect of using different speed of mixing during the detection. Therefore, the detection process should be carefully performed in order to obtain precise and accurate results.

Chapter 4

Conclusions

4.1 Conclusion

Hydroxyapatite was successfully synthesized by precipitation method. It was modified with PAN through impregnation and adsorption methods.

By impregnation method, HAp could be modified with PAN confirmed by the results from thermogravimetric analysis. Using PAN solution with a concentration range of 0.17-0.34 mM PAN for HAp modification did not remarkably affect to the amount of PAN on HAp surface. Moreover, HAP-PAN-IP1 showed color change from yellow to pink or purple when used to test with 100 and 1000 µg/L Ni^{2+} solution. However, the leaching of PAN from HAp-PAN was observed.

By adsorption method, HAp could be successfully modified with PAN. The adsorption time in the range of 5 – 30 mins did not obviously affect the amount of PAN modified on HAp surface. In addition, difference of PAN concentration used in the modification affected to color change of HAp-PAN. HAp-PAN-AP1.2 material showed a clear color change at 300 µg/L and 700 µg/L Ni^{2+}. The suitable pH for Ni^{2+} detection was pH 6.

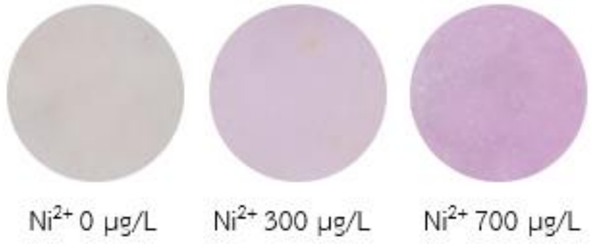


Figure 4.1 HAp-PAN-AP1.2 after extraction with Ni^{2+} solution

4.2 Suggestion

The effect of several parameters should be further investigated, for example;

1) Interference: The effect of Co^{2+}, Cu^{2+} and Zn^{2+} should be studied as they can form complex with PAN [11].

2) Detection time

3) Solid to liquid ratio

Finally, the method using HAp-PAN should be validated by comparing with standard methods (i.e. ICP-OES, atomic absorption spectroscopy [9])

4.3 Obtained benefits

Methods for HAp-PAN preparation were obtained.

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