

การตรวจวัดไอออนโลหะบางชนิดด้วยตาเปล่าโดยใช้แอมเบอร์ไลท์เอกซ์เอ็ด-7
เคลือบด้วย 1-(2-ไพริดีลเอโซ)-2-แนฟทอล

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NAKED-EYE DETECTION OF SOME METAL IONS USING AMBERLITE
XAD-7 COATED WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

Miss Valentine Juasakul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

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แอมเบอร์ไลต์เอกซ์เอตี-7 เคลือบด้วย 1-(2-ไพริดีลเอโซ)-2-แนฟทอล หรือ PAN ใช้เป็นเซ็นเซอร์
ของแข็งเพื่อตรวจวัดทองแดง(II) โคบอลต์(II) นิกเกิล(II) และสังกะสี(II) ด้วยตาเปล่า ศึกษาพารามิเตอร์สำหรับ
การเคลือบ PAN บนแอมเบอร์ไลต์เอกซ์เอตี-7 เช่น ปริมาณของแอมเบอร์ไลต์เอกซ์เอตี-7 ความเข้มข้นของ PAN
และระยะเวลาในการคนสารละลาย พิสูจน์เอกลักษณ์ของ Amberlite-PAN โดยดีอาร์-ยูวี-วิซิเบิล สเปกโทรโฟโต
เมตรี สังเกตการเปลี่ยนแปลงสีของ Amberlite-PAN จากสีเหลืองเป็นสีม่วง สีเขียว สีชมพู และสีส้ม เมื่อตรวจวัด
กับทองแดง(II) โคบอลต์(II) นิกเกิล(II) และสังกะสี(II) ตามลำดับ ในระบบแบบทซ์พบว่าพีเอช 5 เหมาะสมที่สุด
โดยระยะเวลาในการเปลี่ยนสีของทองแดง(II) เท่ากับ 1 นาที โคบอลต์(II) เท่ากับ 5 นาที นิกเกิล(II) เท่ากับ 20
นาที และสังกะสี(II) เท่ากับ 45 นาที ความเข้มข้นของ PAN ที่เหมาะสมสำหรับเคลือบ PAN บนแอมเบอร์ไลต์
เอกซ์เอตี-7 เท่ากับ 0.5 มิลลิโมลาร์ ซึ่งเหมาะสมต่อการตรวจวัดทองแดง(II) โคบอลต์(II) นิกเกิล(II) และ
สังกะสี(II) ที่ความเข้มข้นต่ำ ชัดจำกัดการตรวจวัดด้วยตาเปล่าของทองแดง(II) โคบอลต์(II) และนิกเกิล(II) เท่ากับ
0.2 มิลลิกรัมต่อลิตร ในขณะที่ขีดจำกัดการตรวจวัดด้วยตาเปล่าของสังกะสี(II) เท่ากับ 4.0 มิลลิกรัมต่อลิตร ช่วง
ความเข้มข้นสำหรับแถบเทียบสีมาตรฐานเท่ากับ 1×10^{-6} - 1×10^{-2} โมลาร์สำหรับทองแดง(II) 1×10^{-6} - 1×10^{-4} โมลาร์
สำหรับโคบอลต์(II) และนิกเกิล(II) และ 1×10^{-6} - 1×10^{-2} โมลาร์สำหรับสังกะสี(II) ใช้ไทโอยูเรียเป็นเอเจนต์มาสคิง
สำหรับทองแดง(II) และใช้โพแทสเซียมคลอไรด์เป็นเอเจนต์มาสคิงสำหรับนิกเกิล(II) นอกจากนี้ยังพบว่า
Amberlite-PAN ใช้เป็นเซ็นเซอร์ของแข็งสำหรับตรวจวัดทองแดง(II) โคบอลต์(II) นิกเกิล(II) และสังกะสี(II)
ด้วยตาเปล่าได้อย่างน้อย 10 สัปดาห์และสามารถนำ Amberlite-PAN กลับมาใช้ซ้ำโดยใช้กรดไนตริกเข้มข้น 1 โม
ลาร์ ได้อย่างน้อยที่สุด 4 ครั้ง การตรวจวัดทองแดง(II) โคบอลต์(II) นิกเกิล(II) และสังกะสี(II) ด้วยตาเปล่าในน้ำ
ตัวอย่างจริงโดยใช้ Amberlite-PAN ภายใต้อุณหภูมิที่เหมาะสมที่สุดประสบความสำเร็จ การตรวจวัดโคบอลต์(II)
นิกเกิล(II) และสังกะสี(II) ในน้ำตัวอย่างจริงที่มีทองแดง(II) อยู่ด้วยและการตรวจวัดสังกะสี(II) ในน้ำตัวอย่างจริง
ที่มีนิกเกิล(II) อยู่ด้วยโดยใช้ Amberlite-PAN ร่วมกับเอเจนต์มาสคิง ทำได้ภายใต้ภาวะที่เหมาะสมที่สุดในการ
ตรวจวัดด้วยตาเปล่า

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....
สาขาวิชา.....เคมี..... ลายมือชื่อ อ.ที่ปริภษาวิทยานิพนธ์หลัก.....
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 VALENTINE JUASAKUL: NAKED-EYE DETECTION OF SOME
 METAL IONS USING AMBERLITE XAD-7 COATED WITH 1-(2-
 PYRIDYLAZO)-2-NAPHTHOL. ADVISOR: ASST. PROF. WANLAPA
 AEUNGMAITREPIROM, Ph.D., 66 pp.

Amberlite XAD-7 coated with 1-(2-pyridylazo)-2-naphthol (PAN) was used as a naked-eye solid sensor for Cu(II), Co(II), Ni(II) and Zn(II). Parameters for coating PAN onto Amberlite XAD-7 such as the amount of Amberlite XAD-7, the concentration of PAN and the stirring time were studied. Amberlite-PAN was characterized by DR-UV-vis spectrophotometry. The color change of Amberlite XAD-7 coated with PAN was observed from yellow to purple, green, pink and orange for Cu(II), Co(II), Ni(II) and Zn(II), respectively. In batch system, the proper pH was found to be 5 with the response time of 1 min for Cu(II), 5 min for Co(II), 20 min for Ni(II) and 45 min for Zn(II). The optimum concentration of PAN for coating PAN onto Amberlite XAD-7 was 0.5 mM which was suitable to detect the lowest concentration of Cu(II), Co(II), Ni(II) and Zn(II). The naked-eye detection limit of Cu(II), Co(II) and Ni(II) was found to be 0.2 mg/L while the detection limit of Zn(II) was found to be 4.0 mg/L. The concentration ranges for color calibrations were 1×10^{-6} - 1×10^{-2} M for Cu(II), 1×10^{-6} - 1×10^{-4} M for Co(II) and Ni(II) and 1×10^{-6} - 1×10^{-2} M for Zn(II). Thiourea was used as a masking agent for Cu(II) and potassium chloride was used as a masking agent for Ni(II). Moreover, the Amberlite-PAN was used as a naked-eye solid sensor for Cu(II), Co(II), Ni(II) and Zn(II) at least 10 weeks and can be reused by 1 M nitric acid regeneration at least 4 times. The determination of Cu(II), Co(II), Ni(II) and Zn(II) in real water samples by naked-eye detection using Amberlite-PAN under the optimum conditions was achieved. The naked-eye determination of Co(II), Ni(II) and Zn(II) in the presence of Cu(II) and the naked-eye determination of Zn(II) in the presence of Ni(II) in real water sample by using Amberlite-PAN with masking agent under the optimum conditions were accomplished.

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CONTENTS

	Page
ABSTRACT (THAI)	iv
ABSTRACT (ENGLISH)	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	ix
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xiv
CHAPTER I INTRODUCTION	1
1.1 Statement of the problem.....	1
1.2 Objectives and scopes of the research.....	2
1.3 Benefit of the research.....	3
CHAPTER II THEORY AND LITERATURE REVIEW	4
2.1 Heavy metal in the environment.....	4
2.2 Naked-eye detection.....	6
2.3 1-(2-Pyridylazo)-2-naphthol (PAN).....	8
2.4 Amberlite XAD-7.....	11
CHAPTER III EXPERIMENTAL	13
3.1 Apparatus.....	13
3.2 Chemicals.....	13
3.3 Preparation of Amberlite-PAN.....	15
3.3.1 Amount of Amberlite XAD-7.....	15

	Page
3.3.2 Concentration of PAN.....	15
3.3.3 Stirring time.....	15
3.4 Preliminary study for naked-eye detection of some metal ions.....	16
3.5 Naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II).....	16
3.5.1 Method detection limit.....	16
3.5.2 Effect of interfering ions.....	16
3.6 Stability life of Amberlite-PAN.....	17
3.7 Reusability of Amberlite-PAN.....	18
3.8 Application to real samples.....	18
CHAPTER IV RESULTS AND DISCUSSION.....	20
4.1 Preparation of Amberlite-PAN.....	20
4.1.1 Amount of Amberlite XAD-7.....	20
4.1.2 Concentration of PAN.....	23
4.1.3 Stirring time.....	24
4.2 Preliminary study for naked-eye detection of some metal ions.....	24
4.3 Naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II).....	28
4.3.1 Method detection limit.....	28
4.3.2 Effect of interfering ions.....	35
4.4 Stability life of Amberlite-PAN.....	39
4.5 Reusability of Amberlite-PAN.....	39
4.6 Application to real samples.....	41
CHAPTER V CONCLUSIONS.....	57
REFERENCES.....	59
VITA.....	66

LIST OF TABLES

Table	Page
2.1 The toxicity of copper, cobalt, nickel and zinc.....	4
2.2 Maximum acceptable concentration of heavy metals in drinking water....	5
2.3 Some of colorimetric solid sensors for cations and anions naked-eye detection.....	8
2.4 Colors of Cu(II), Co(II), Ni(II) and Zn(II) ions with PAN in different solvents.....	9
2.5 Cumulative formation constants for metal complexes with PAN.....	10
2.6 Modification of PAN with several materials for determination of various metal ions.....	10
2.7 Modification of amberlite XAD-7 with various ligand for determination of various metals.....	11
3.1 ICP-OES operating conditions for determination of various metal ions in aqueous solution.....	13
3.2 Chemicals and reagents.....	14
4.1 Colors of Amberlite-PAN complexed with various metal ions in the range of pH 1-7 using batch method	25
4.2 Colors of Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) in function of time.....	27
4.3 Colors of Amberlite-PAN complexed with Cu(II) at different concentrations of PAN.....	28
4.4 Colors of Amberlite-PAN complexed with Co(II) at different concentrations of PAN.....	29
4.5 Colors of Amberlite-PAN complexed with Ni(II) at different concentrations of PAN.....	29
4.6 Colors of Amberlite-PAN complexed with Zn(II) at different concentrations of PAN.....	30
4.7 Colors of Amberlite-PAN (0.5 mM) complexed with Cu(II), Co(II), Ni(II) and Zn(II) ions at different concentrations of metal ions.....	31

Table	Page
4.8 Colors of Amberlite-PAN (0.5 mM) complexed with Cu(II), Co(II), Ni(II) and Zn(II) ions in the presence of masking agents.....	36
4.9 Colors of Amberlite-PAN complexed with Cu(II), Cu(II) and Co(II), Cu(II) and Ni(II) and Cu(II) and Zn(II) with and without thiourea.....	37
4.10 Colors of Amberlite-PAN complexed with Ni(II) and Zn(II) with and without potassium chloride.....	38
4.11 Colors of Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) with and without the regeneration with 1 M HNO ₃	40
4.12 Colors of Amberlite-PAN and regenerated Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II).....	41
4.13 Concentrations of Cu(II),Co(II), Ni(II) and Zn(II) determined by ICP-OES in real water sample solutions.....	42
4.14 Colors calibration of Cu(II) at various concentrations.....	42
4.15 Colors of Amberlite-PAN-Cu at different concentrations of Cu(II).....	43
4.16 Colors calibration of Co(II) at various concentrations.....	43
4.17 Colors of Amberlite-PAN-Co at different concentrations of Co(II).....	43
4.18 Colors calibration of Ni(II) at various concentrations.....	44
4.19 Colors of Amberlite-PAN-Ni at different concentrations of Ni(II).....	44
4.20 Colors calibration of Zn(II) at various concentrations.....	44
4.21 Colors of Amberlite-PAN-Zn at different concentrations of Zn(II).....	45
4.22 Concentrations of Cu(II) and Co(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Co(II).....	46
4.23 Concentrations of Cu(II) and Ni(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Ni(II).....	46
4.24 Concentrations of Cu(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Zn(II).....	46
4.25 Concentrations of Ni(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Ni(II) and Zn(II).....	48

Table	Page
4.26 Concentrations of Cu(II), Ni(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II), Ni(II) and Zn(II).....	49
4.27 Concentrations of Cu(II), Co(II), Ni(II) and Zn(II) determined by naked-eye method and ICP-OES in pond water spiked with unknown samples.....	55

LIST OF FIGURES

Figure	Page
1.1 Structures of (a) Amberlite XAD-7 and (b) PAN.....	3
2.1 The complex formation between metal ions and PAN.....	9
4.1 Colors of (a) Amberlite XAD-7 and (b) Amberlite-PAN.....	21
4.2 DR-UV-vis spectra of Amberlite-PAN in function of amount of Amberlite XAD-7.....	22
4.3 Proposed interaction between Amberlite XAD-7 and PAN.....	22
4.4 DR-UV-vis spectra of Amberlite XAD-7 and Amberlite-PAN in function of PAN concentration.....	23
4.5 Effect of stirring time for coating PAN onto Amberlite XAD-7.....	24
4.6 DR-UV-vis spectra of Amberlite-PAN, Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn.....	26
4.7 (a) DR-UV-vis spectra of Amberlite-PAN with Cu(II) and (b) the relation between f(R) values and the concentrations of Cu(II).....	32
4.8 (a) DR-UV-vis spectra of Amberlite-PAN with Co(II) and (b) the relation between f(R) values and the concentrations of Co(II).....	33
4.9 (a) DR-UV-vis spectra of Amberlite-PAN with Ni(II) and (b) the relation between f(R) values and the concentrations of Ni(II).....	34
4.10 (a) DR-UV-vis spectra of Amberlite-PAN with Zn(II) and (b) the relation between f(R) values and the concentrations of Zn(II).....	35
4.11 The f(R) of Amberlite-PAN in function of time at wavelength 470 nm.....	39
4.12 Colors of Amberlite-PAN (a) original, (b) regenerated 1 time, (c) regenerated 2 times, (d) regenerated 3 times and (e) regenerated 4 times...	40
4.13 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M thiourea and (b) with 1 M thiourea.....	47
4.14 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.....	48
4.15 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M thiourea and 1 M potassium chloride and (b) with 1 M thiourea and 1 M potassium chloride.....	50

Figure	Page
4.16 Diagram of qualitative naked-eye method.....	52
4.17 Colors of Amberlite-PAN-metal ions of unknown sample no. 3, 4, 6, 9, 16, 18, 20, 21, 22, and 24 (a) without 1 M thiourea and (b) with 1 M Thiourea.....	53
4.18 Colors of Amberlite-PAN-metal ions of unknown sample no. 2, 5, 7, 8, 12, 13, 14, 15, 19, and 23 (a) without 1 M thiourea and (b) with 1 M thiourea.....	53
4.19 Colors of Amberlite-PAN-metal ions of unknown sample no. 1, 10, 11 and 17 (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.....	54
4.20 Colors of Amberlite-PAN-metal ions of unknown sample no. 4, 5, 8, 14, 15, 16, 18, 19 and 24 (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.....	54

LIST OF ABBREVIATIONS

pKa	Acid dissociation constant
DI	Deionized water
g	Gram
M	Molar
mg	Milligram
mg/L	Milligram per liter
mL	Milliliter
mM	Millimolar
μ L	Micro liter
nd	Not detectable
nm	Nanometer
PAN	1-(2-Pyridylazo)-2-naphthol
R	Absolute reflectance of the sample
$^{\circ}$ C	Degree Celsius

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Nowadays water pollution is a major global problem requiring continuous evaluation and revision of water contamination at all levels. Heavy metal contamination in water is one of the sources of this problem. These heavy metals consequently harm human health and the natural environment; because drinking water is the most important component for health living and clean water is essential for health. Concentration of trace metals in water is often lower than the limit of detection (LOD) for some instruments. However, there are several techniques used for metal preconcentration such as liquid-liquid extraction (LLE) [1] and solid-phase extraction (SPE) [2]. These techniques have some drawback, for example, the lack of selectivity, large volume of its solvent and high interference from other species with the target analyte.

Spectrometric methods are an efficient technique for determination of metal ions in water such as inductively couple plasma atomic emission spectrometry (ICP-AES) [3] and flame atomic absorption spectrometry (FAAS) [4]. However, these techniques require expensive and complicated instrument and longer operation time interval. Naked-eye detection is a colorimetric method that allows on-site, rapid response time and real-time qualitative or semi-quantitative detection without the use of any complicated spectroscopic instruments. This method detects the color change of sorbent or solution when the ligand interacts with the target analyte [5]. Many researchers studied the naked-eye detection of metal ions in solution using new ligands. For example, Gunnlaugsson et al. [6] designed azobenzene as a chemosensor for Cu(II) detection under physiological pH conditions. The recognition of Cu(II) gave a major color change from red to yellow which was clearly visible to the naked-eye. Murthy et al. [7] reported a new chromogenic chemosensor based on thiocarboxylic acid derivatives for detection of Ni(II) in water sample. Thus, the naked-eye

detections of metal ions using solid sorbents have been also reported. For example, Balaji et al. [8] studied the electrostatic interaction of 4-(2-pyridylazo) resorcinol (PAR) on mesoporous silica anchored with *N*-trimethoxysilylpropyl-*N,N,N*-tri methylammonium chloride (TMAC) for Cd(II) detection. High sensitivity and stability of the material were obtained in comparison with other methods. It was successfully used as a colorimetric optical sensor for qualitative and quantitative detection for Cd(II) at very low concentration in various samples. However, the naked-eye detection of metal ions using solid sorbents is more interesting than the naked-eye detection of metal ions in solution because of the advantage of preconcentration of solid phase. Therefore, the colors of the complexes adsorbed onto surface of the solid phase are easy to observe by naked-eye detection.

In this research, a suitable solid sorbent was modified with a commercial ligand for determination of various metal ions in solution using naked-eye method. 1-(2-Pyridylazo)-2-naphthol (PAN) was chosen as a commercial ligand because PAN can form complex with various metal ions and provide different colors of complex [9]. A solid sorbent of this work was Amberlite-XAD-7 because it is white material and it is simple to modify a chelating ligand onto the surface of Amberlite XAD-7 [10].

1.2 Objectives and scopes of the research

The objectives and scopes of this research were:

- 1) To prepare Amberlite-PAN by coating PAN on the surface of Amberlite XAD-7 for determination of some metal ions by naked-eye method. The structures of Amberlite XAD-7 and PAN are illustrated in Fig. 1.1. Amount of Amberlite XAD-7, concentration of PAN and stirring time were optimized. Amberlite XAD-7 coated with PAN was characterized by diffuse reflectance ultraviolet visible spectrophotometry (DR-UV-vis) technique. The preliminary study for naked-eye detection of 10 metal ions e.g. Cu(II), As(III), Pb(II), Cd(II), Ni(II), Cr(III), Co(II), Mg(II), Mn(II) and Zn(II) was investigated.

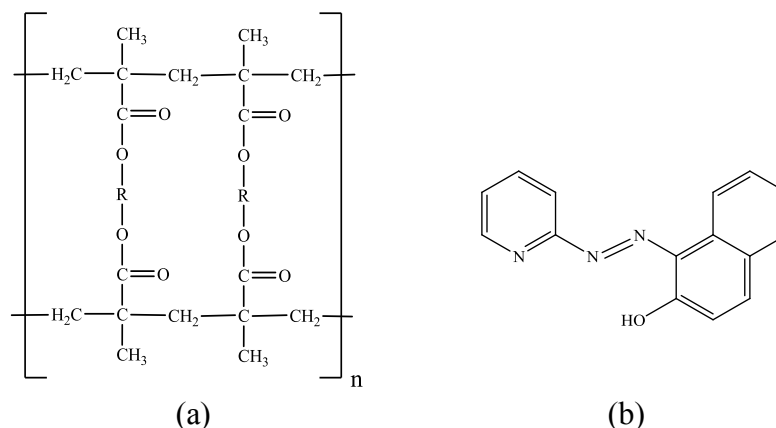


Fig. 1.1 Structures of (a) Amberlite XAD-7 and (b) PAN.

2) To study the naked-eye detection of selected metal ions e.g. Cu(II), Co(II), Ni(II) and Zn(II) in batch system. pH of solution, response time and effect of interfering ions were optimized. Naked-eye detection limit was evaluated by observing the color change of the sorbent under the optimum conditions. Working concentration range for naked-eye calibration colors was also studied.

3) To study stability and reusability of Amberlite-PAN by naked-eye detection method.

4) To apply the proposed naked-eye detection method for qualitative and quantitative determination of Cu(II), Co(II), Ni(II) and Zn(II) in real water samples. The concentration of metal ion in sample solution determined by naked-eye method was compared with the concentration determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES).

1.3 Benefit of the research

In this research, the new solid sensor was developed for determination of some metal ions in an aqueous solution by naked-eye method. The qualitative and semi-quantitative analysis of Cu(II), Co(II), Ni(II) and Zn(II) by Amberlite XAD-7 coated with PAN was achieved. This proposed naked-eye method can detect Cu(II), Co(II), Ni(II) and Zn(II) at low concentration level as same as ICP-OES.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Heavy metal in the environment

Trace metal ion determinations are received intensive attention because the contamination of metal ions is usually present in the environment, in particular heavy metal contamination in water. Heavy metals become toxic because they are not metabolized by the body and accumulated in the soft tissues. Table 2.1 shows the heavy metal toxicity of copper, cobalt, nickel and zinc that can damage and affect to health when these metals are taken into the body.

Table 2.1 The toxicity of copper, cobalt, nickel and zinc.

Metals	Toxicity	
	Acute health effect	Chronic health effect
Copper (Cu)	cause vomiting, hypotension, hematemesis, melena, jaundice and gastrointestinal distress [11].	damage the liver and kidney when uptake the copper in high level [11].
Cobalt (Co)	cause fatigue, nausea, headache, anxiety and irritability [12].	damage the kidney [12].
Nickel (Ni)	cause skin rash, nausea, dizziness, headache, weakness and chest pain [13].	Nickel vapor can lead to swelling of the brain and liver [13].
Zinc (Zn)	Eating large amount of zinc can cause stomach cramps, chills, tachycardia, dyspnea and chest pains [14].	cause anemia and pancreas damage [14].

At low concentration level, heavy metals contaminating in water are a major cause to the human health and environment. The maximum acceptable concentration of some heavy metals in drinking water regulated by the Pollution Control Department of Thailand (PCD) is shown in Table 2.2 [15].

Table 2.2 Maximum acceptable concentration of heavy metals in drinking water.

Heavy metals	Maximum acceptable concentration (mg/L)
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.01
Copper (Cu)	1.0
Chromium (Cr)	0.05
Iron (Fe)	0.5
Lead (Pb)	0.05
Manganese (Mn)	0.5
Mercury (Hg)	0.001
Selenium (Se)	0.01
Silver (Ag)	0.05
Zinc (Zn)	5.0

The determination of heavy metals in water is very important. Spectroscopic methods such as FAAS and ICP-AES have been widely used for this propose. However, the development of novel methods for the detection of heavy metals by simple experiment and without the spectroscopic instrument is still attractive, for instance naked-eye detection method.

2.2 Naked-eye detection

Spectrometric methods were used for determination metal ions such as FAAS, graphite furnace atomic absorption spectroscopy (GFAAS), ICP-AES and mass spectrometry (MS). These techniques provide several interesting characteristics such as low detection limit, high sensitivity and selectivity. Unfortunately, these techniques have some drawbacks for instances expensive instrument, long operation time and require skilled technician of instrument. Therefore many researchers still need to develop novel methods for the detection of metal ions that provide the selectivity to the target analyte, short response time and high sensitivity. Naked-eye detection is a colorimetric method detecting the color change of solution or sorbent when the ligand interacts with the target analyte. There are many advantages of the naked-eye detection such as low cost, allow on-site, rapid response time and real-time qualitative or semi-quantitative detection without any complicated spectroscopic instruments.

The color change of naked-eye detection method depends on a reagent or ligand that interacts with the analyte. The changes of color occurred because the absorption wavelength of ligand molecule was changed when interacting with the target analytes. The selectivity of ligand toward metal ion depends on the hard-soft acid base principle (HSAB) which was the explanation of reaction between metal ions and chelating ligand [16]. Reaction of HSAB is more favorable for hard-hard and soft-soft interactions than for a mix of hard and soft interactions. The binding ability of metal ion and ligand depends on size and change of metal ion and the nature of donor atom of ligand.

The naked-eye method using ligand or sensor molecule was studied in both solution and solid sorbent. For naked-eye detection in solution, many researchers reported the determination of chemical compounds and biomolecules. For example, Cai et al. [17] reported the visual detection of intracellular GSH using RB-functionalized with gold nanoparticles (AuNPs). Jamil et al. [18] synthesized a novel compound, 2-(2-hydroxyphenyl)-1-(phenylamino)-3-(phenylimino)guanidine (AG), for DNA detection and the color was changed from purple to orange in the solution. Vantasin et al. [19] developed the colorimetric analysis of protein content in milk based on an aggregation-induced color change of starch-stabilized AuNPs.

Furthermore, the determination of metal ions by the naked-eye detection in solution was reviewed. Gunnlaugsson et al. [6] designed a colorimetric azobenzene chemosensor for the detection of transition metal ions such as Cu(II) under physiological pH conditions. Suresh et al. [20] developed the colorimetric and ratiometric sensor by using per-6-amino- β -cyclodextrin as a supramolecular host and *p*-nitrophenol as a spectroscopic probe for the detection of Fe(III) and Ru(III) in water. Ruan et al. [21] developed 7-nitrobenzo-2-oxa-1,3-diazole (NBD) with methyl (*S*)-2-(benzyloxycarbonylamino)-6-{4-[(7-nitrobenzo-[*c*] [1,2,5]oxadiazol-4-ylamino) methyl]-1*H*-1,2,3-triazol-1-yl}-hexanoate bearing triazole binding site for selective recognition of Hg(II) in aqueous solution. Tavallali et al. [22] reported the determination of copper and chloride by bromopyrogallol red (BPR) with distinct visual color changes in DMSO/H₂O (9:1 v/v) and this method was applied for the determination of Cu²⁺ and Cl⁻ in water sample. Kumar et al. [23] reported a novel chromogenic thiourea based sensor 4,4'-bis-[3-(4-nitrophenyl)thiourea] diphenyl ether and 4,4'-bis-[3-(4-nitrophenyl) thiourea] diphenyl methane, for the detection of fluoride and cyanide in organic and aqueous media.

From the literature reviews, many researchers reported the determination of metal ions by the solution naked-eye method while the solid naked-eye method was infrequently reported. However, the solid naked-eye detection was more convenient and simpler method than the solution naked-eye detection. Some of colorimetric solid sensors for metal ions by naked-eye method is summarized in Table 2.3.

Table 2.3 Some of colorimetric solid sensors for cations and anions naked-eye detection.

Analyte	Solid support	Limit of detection
Hg(II), Pb(II), Cd(II) [24]	PVC* anchoring chromo- ionophore molecular assemblies	0.034 (Hg(II)), 0.025 (Pb(II)), and 0.031 (Cd(II)) μM ,
Hg(II) [25]	SNT-1** grafted functional azo- coupled macrocyclic receptor	-
Hg(II) [26]	cellulose indicator paper	10 ppm
As(V) [27]	molybdenum-loading chelating resin	1×10^{-7} M
F ⁻ and AcO ⁻ [28]	test paper coated with reduced Schiff base	-

* PVC = polyvinyl chloride

** SNT-1 = silica nanotube

2.3 1-(2-Pyridylazo)-2-naphthol (PAN)

The azo dye, 1-(2-pyridylazo)-2-naphthol (PAN), is one of the chromogenic reagent used for spectrophotometric determination for several metal ions. PAN is usually soluble in organic solvent such as chloroform, amyl alcohol and carbon tetrachloride but insoluble in water [29]. It is a tridentate ligand forming stable complexes with various metal ions through the hydroxyl oxygen, pyridine nitrogen and one of the azo group nitrogen atom (Fig. 2.1) [30].

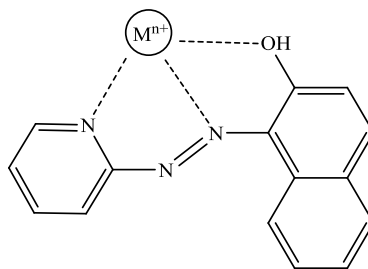


Fig. 2.1 The complex formation between metal ions and PAN.

PAN was applied in complexometric titrations as an indicator because it formed a color chelate with the metal ion. It was also used as an organic reagent for colorimetric determination or spot test. The color of PAN complexes with Cu(II), Co(II), Ni(II) and Zn(II) in different solvents are shown in Table 2.4 [9].

Table 2.4 Colors of Cu(II), Co(II), Ni(II) and Zn(II) ions with PAN in different solvents.

Solvents	Cu(II)	Co(II)	Ni(II)	Zn(II)
water	Deep red	Brownish red	Red	Bright pink
amyl alcohol	Red	Green	Red	Red
CCl ₄	Yellow	Green	Red	Red

PAN was also used as a chelating agent for the preconcentration and separation of heavy metal ions from several media such as natural water [31], waste water [32] and seawater [33]. Cumulative formation constants for metal complexes with PAN are shown in Table 2.5 [34]. Many researchers reported the determination of trace metal ions using PAN modified onto various materials. Table 2.6 shows some modification of PAN onto several materials for the determination of various metal ions.

Table 2.5 Cumulative formation constants for metal complexes with PAN.

Metal	log K₁	log K₂
Co(II)	> 12	-
Cu(II)	16	-
Mn(II)	8.5	16.4
Ni(II)	12.7	25.3
Tl(III)	2.29	-
Zn(II)	11.2	21.7

Table 2.6 Modification of PAN with several materials for determination of various metal ions.

Metal	Materials
Co [32]	immobilized on SDS* -coated alumina
Ni [3]	loaded on Amberlite XAD-2
Zn [33]	modified on polymeric membrane
Pr, Nd, Sm and Y [35]	loaded on silica gel
Pb [4]	modified on microcrystalline naphthaline
Cr, Mn, Fe, Ni, Cu, Cd and Pb [36]	functionalized on Amberlite XAD-1180
Pb [37]	modified on screen-printed carbon electrode
Ce, Dy, La, Sm, Y and U [38]	sorption on C18-silica
Cd [39]	functionalized on multiwalled carbon nanotube
Pb [40]	silica gel coated with PAN

* SDS = sodium dodecyl sulfate

From the literature reviews, the modification of PAN onto various materials for separation or preconcentration of metal ions was reported. Moreover, the modification of solid sorbent with PAN for naked-eye detection was also reported. Kongsung R.[40] studied the naked-eye detection of Pb(II) in drinking water by using silica gel coated with PAN as a solid sensor. It was found that the color of sorbent was

changed from orange to pink and the naked-eye lowest concentration of Pb(II) was 0.8 mg/L. The naked-eye detection limit of Pb(II) is still higher than the maximum acceptable concentration. Then in this work, we desired to modify PAN onto new solid sorbent for determination of various metal ions in solution by solid naked-eye detection. Parameter such as naked-eye detection limit of metal ions and interfering ions was also studied.

2.4 Amberlite XAD-7

Amberlite XAD resin is widely used for preconcentration and separation of trace metal ions by aiding of chelating ligands. XAD resin shows many benefit physical properties such as porosity, high surface area, pore size distribution and chemically homogeneous non-ionic structure [41]. Amberlite XAD resin used for separation and preconcentration of various metal ions was XAD-2 [42], XAD-4 [43], XAD-7 [44] and XAD-1180 [36]. However, Amberlite XAD-7 was successful and popular use for separation and preconcentration because this resin is a polyacrylic ester polymer having hydrophilic surface and moderate polarity. The modifications of Amberlite XAD-7 with various ligands for determination of various metal ions are shown in Table 2.7.

Table 2.7 Modification of Amberlite XAD-7 with various ligands for determination of various metals.

Ligand	Metal	pH
xylenol orange [45]	Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Zn(II)	4.5-5.0 (Cd(II)), 4.5 (Co(II)), 4.0-5.0 (Cu(II)), 4.0 (Fe(III)), 5.0 (Ni(II)) and 5.0-7.0 (Zn(II))
trioctylphosphine oxide [46]	Fe(II)	-
dioctyl sodium	Pb(II)	-
sulphosuccinate-EDTA [47]		
<i>p</i> -xylenol blue [10]	Fe(III), Pb(III), Cr(III)	9.0
toluidine blue <i>o</i> [48]	Cr(VI)	3.0-4.0

From the literature reviews, most researchers reported the modification of various chelating ligands onto Amberlite XAD-7 for separation or preconcentration of metal ions. However, the determination of various metal ions using PAN modified with Amberlite XAD-7 was not found. Thus in this work, we focused on the modification of Amberlite XAD-7 with PAN for the determination of Cu(II), Co(II), Ni(II) and Zn(II) in aqueous solution by the naked-eye method.

CHAPTER III

EXPERIMENTAL

3.1 Apparatus

The Amberlite XAD-7 coated with PAN or Amberlite-PAN was characterized by a diffuse reflectance ultraviolet visible spectrophotometer (DR-UV-vis) with a model of UV-2500 (Shimadzu).

The concentrations of various metal ions in an aqueous solution were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES) model iCAP 6000 series (Thermo Fisher scientific). The operating conditions are listed in Table 3.1.

Table 3.1 ICP-OES operating conditions for determination of various metal ions in aqueous solution.

Operating conditions		
Wavelength for Cu(II)	324.75	nm
Wavelength for Co(II)	228.62	nm
Wavelength for Ni(II)	221.65	nm
Wavelength for Zn(II)	213.86	nm
RF Power	1150	W
Pump rate	50	rpm
Auxiliary gas flow	0.5	L/min
Nebulizer gas flow	0.6	L/min
Coolant gas flow	12	L/min

The pH values of solutions were measured by a Metrohm pH meter model 744.

3.2 Chemicals

All chemicals and reagents were of analytical grade and listed in Table 3.2.

Table 3.2 Chemicals and reagents

Chemicals	Supplier
1,2-(Pyridylazo)-2-naphthol (PAN)	Fluka
Acetic acid	Merck
Amberlite XAD-7	Supelco
Cadmium nitrate	Merck
Cobalt nitrate	Fisher Scientific
Copper nitrate	Merck
Chromium nitrate	Sigma-Aldrich
Disodium hydrogen orthophosphate	BDH
Ethanol	Merck
Methanol	Merck
Hydrochloric acid 37%	Merck
Glycine	Sigma-Aldrich
Lead nitrate	M&B
Magnesium nitrate	Fluka
Manganese chloride	Carlo Erba
Nickel nitrate	Merck
Nitric acid 65%	Merck
Potassium chloride	AJEX Chemicals
Sodium hydroxide	Carlo Erba
Sodium acetate anhydrous	Carlo Erba
Sodium meta-arsenite	BDH
Thiourea	Sigma-Aldrich
Zinc nitrate	QRAC
Cobalt standard solution (1000 mg/L)	BDH
Copper standard solution (1000 mg/L)	Merck
Nickel standard solution (1000 mg/L)	Merck
Zinc standard solution (1000 mg/L)	Merck

3.3 Preparation of Amberlite-PAN

In a 500 mL beaker, methanol was added to Amberlite XAD-7 and then mechanically stirred gently for 15 minutes to ensure a complete mixing. The mixture was filtered and DI water was added. The mixture was stirred for 5-10 minutes. Then the resin was filtered and dried at 80 °C until the resin was dried before use.

3.3.1 Amount of Amberlite XAD-7

In a 100 mL beaker, an amount of Amberlite XAD-7 was magnetically stirred with 20 mL of 0.5 mM PAN dissolved in ethanol at room temperature for 2 hours. The amount of Amberlite XAD-7 was varied from 1 to 4 g. The solid was filtered and dried at room temperature until the resin was dried. The coating of PAN onto Amberlite XAD-7 was examined by DR-UV-vis spectrophotometer at wavelength 470 nm. Amberlite XAD-7 coated with PAN (Amberlite-PAN) was kept in a desiccator before use.

3.3.2 Concentration of PAN

In a 100 mL beaker, an amount of Amberlite XAD-7 was magnetically stirred with 20 mL of PAN of a known concentration in ethanol at room temperature for 2 hours. The concentration of PAN was varied from 0.1-2.5 mM. The solid was filtered and dried at room temperature until the resin was dried. The coating of PAN onto Amberlite XAD-7 was examined by DR-UV-vis spectrophotometer at wavelength 470 nm. Amberlite-PAN was kept in a desiccator before use.

3.3.3 Stirring time

The optimum stirring time for coating PAN onto Amberlite XAD-7 was studied in the range of 1-5 hours. In a 100 mL beaker, 2 g of Amberlite XAD-7 was magnetically stirred with 20 mL of 0.5 mM PAN dissolved in ethanol at room temperature. Then the solid was filtered and dried at room temperature until the resin

was dried. The coating of PAN onto Amberlite XAD-7 was examined by DR-UV-vis spectrophotometer at wavelength 470 nm.

3.4 Preliminary study for naked-eye detection of some metal ions

The naked-eye detection of various metal ions, e.g. Cu(II), As(III), Pb(II), Cd(II), Ni(II), Cr(III), Co(II), Mg(II), Mn(II) and Zn(II) by Amberlite-PAN was studied by batch procedure. Amberlite-PAN (10 mg) was mixed with 1×10^{-4} M metal ions solution (200 μ L) in a well plate for 1 hour. The buffer solution was used for adjusting pH in the range of 1-7 (glycine buffer for pH 1-2, acetate buffer for pH 3-5 and phosphate buffer for pH 6-7). Then the solution was removed from the sorbent using the dropper. Amberlite-PAN was dried until the resin was dried. The color of Amberlite-PAN after being contacted with various metal ions was detected by naked-eye observation.

3.5 Naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II)

3.5.1 Method detection limit

The naked-eye detection limit of Cu(II), Co(II), Ni(II) and Zn(II) was studied by using Amberlite-PAN at the concentrations of 0.1-2.0 mM of PAN and the concentrations of metal ions were varied in a range of 1×10^{-6} - 1×10^{-4} M under the optimum pH. Amberlite-PAN (10 mg) was mixed with metal ions solution (200 μ L) in a well plate. The solution was removed from the sorbent using the dropper. Amberlite-PAN was dried until the resin was dried. The color change of Amberlite-PAN was observed by naked-eye.

3.5.2 Effect of interfering ions

The naked-eye detection of Co(II), Ni(II) or Zn(II) in the presence of Cu(II) was unsuccessful due to the fact that the color of Cu(II)-PAN interfering the color of other complexes. The naked-eye detection of Zn(II) in the presence of Ni(II) was

unsuccessful due to the fact that the color of Ni(II)-PAN interfering the color of Zn(II)-PAN complex. Thus, thiourea used as a masking agent was added to a solution containing the target ions (Co(II), Ni(II) and Zn(II)) in the presence of Cu(II) while a masking agent as potassium chloride was added to a solution containing the target Zn(II) ion in the presence of Ni(II).

Amberlite-PAN (20 mg) was mixed with 0.5 mL of 1 M thiourea solution and 0.5 mL of 1×10^{-4} M Cu(II) and Co(II), Cu(II) and Ni(II) and Cu(II) and Zn(II) solutions in a well plate under the optimum pH for 1 hour. The solution was removed from the sorbent using the dropper. Amberlite-PAN was dried until the resin was dried. The color change of Amberlite-PAN (0.5 mM) was detected by naked-eye assay.

Amberlite-PAN (20 mg) was mixed with 0.5 mL of 1 M potassium chloride solution and 0.5 mL of 1×10^{-4} M Ni(II) and Zn(II) solutions in a well plate under the optimum pH for 1 hour. The solution was removed from the sorbent using the dropper. Amberlite-PAN was dried until the resin was dried. The color change of Amberlite-PAN (0.5 mM) was detected by naked-eye assay.

3.6 Stability life of Amberlite-PAN

Amberlite-PAN was kept in a desiccator at room temperature before use. The stability of Amberlite-PAN was studied for 10 weeks. The colors of Amberlite-PAN with 1×10^{-4} M Cu(II), Co(II), Ni(II) and Zn(II) were investigated once a week for 10 weeks. 10 mg of Amberlite-PAN was mixed with 200 μ L of metal ions solution at pH 5 in a well plate. Then the mixture solution was removed from the solid phase using the dropper. Amberlite-PAN was dried until the resin was dried. The color change of Amberlite-PAN after being contacted with various metal ions was detected by naked-eye. The stability of Amberlite-PAN was examined by DR-UV-vis spectrophotometer at wavelength 470 nm.

3.7 Reusability of Amberlite-PAN

The reusability of Amberlite-PAN was studied by using this sorbent for 4 cycles. The sorbed metal ions on the surface of Amberlite-PAN (100 mg) was regenerated by 1 M HNO₃ (1 mL) and rinsed twice with DI water. The sorbent was dried until the resin was dried before observation the color of sorbent by naked-eye detection. The same manner was repeated for 4 cycles. Then metal ions were detected by used Amberlite-PAN. The colors of used Amberlite-PAN and original Amberlite-PAN with metal ions were compared by naked-eye.

3.8 Application to real samples

Real water samples in this work were pond water, Physics building water and Chamchuri drinking water. The pH value of all real water samples was measured and found to be 6-7. The pond water and Physics building water samples were filtered through a 0.45 μm cellulose membrane followed by milipore membrane filter and adjusted the pH to 3 with 65% HNO₃. Each individual sample was spiked with each individual metal ion to obtain the final concentration of 0.6, 6 and 60 mg/L for Cu(II), Co(II) and Ni(II) and 6 and 60 mg/L for Zn(II). The metal concentration of each spike solution was determined by ICP-OES. Then 0.5 mL of each spike solution was added into a glass vial containing acetate buffer pH 5. After that, 20 mg of Amberlite-PAN (0.5 mM) was added into the glass vial and stood for 1 hour. The solution was removed from the Amberlite-PAN using the dropper. The color of Amberlite-PAN with metal ions had been detected by naked-eye when the Amberlite-PAN was dried until the resin was dried.

The pond water was spiked with species of mixed ions (Cu(II) and Co(II), Cu(II) and Ni(II) or Cu(II) and Zn(II)). The final concentrations of each individual ion were 0.5, 5 and 20 mg/L. The concentration of each spike solution was determined by ICP-OES. Each spike solution (0.5 mL) was added into a glass vial containing acetate buffer pH 5. Thiourea (1 M, 200 μL) was added into the glass vial. 20 mg of Amberlite-PAN (0.5 mM) was added into the glass vial and stood for 1 hour. After

that, the solution was removed from the Amberlite-PAN using the dropper. The color of Amberlite-PAN with metal ions had been detected by naked-eye when the Amberlite-PAN was dried until the resin was dried.

The experiment was performed in the same manner as mentioned above for pond water solution spiked with 0.5, 5 and 20 mg/L of Ni(II) and Zn(II) and 200 μ L of 1 M potassium chloride.

The experiment was performed in the same manner as mentioned above for pond water solution spiked with 0.5, 5 and 20 mg/L of Cu(II), Ni(II) and Zn(II) with 200 μ L of 1 M thiourea and 200 μ L of 1 M potassium chloride.

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion in this chapter present the optimum conditions for preparation of solid phase for the naked-eye detection. Parameters e.g. amount of Amberlite XAD-7, concentration of PAN and stirring time were presented. The preliminary study for naked-eye detection of Cu(II), As(III), Pb(II), Cd(II), Ni(II), Cr(III), Co(II), Mg(II), Mn(II) and Zn(II) was studied. The effect of pH of solution, response time and effect of interfering ions to the naked-eye detection of selected metal ions in batch system was presented. Naked-eye detection limit and working concentration range for naked-eye calibration colors were also studied. Moreover, the stability and reusability of solid phase were studied. Finally, the determination of Cu(II), Co(II), Ni(II) and Zn(II) by naked-eye method in real water samples was presented.

4.1 Preparation of Amberlite-PAN

4.1.1 Amount of Amberlite XAD-7

Amberlite XAD-7 was chosen as a solid support for this work because it is a white material and easy to be modified by a chelating ligand onto its surface. The general modification of Amberlite XAD-7 surface was achieved either through hydrophobic interaction between aliphatic chain (methyl group) of the sorbent and the alkyl group of the chelating ligand or through polar/electrostatic forces [47].

Amberlite XAD-7 was first washed with methanol to eliminate monomeric material and inorganic impurities and followed by DI water to remove chloride-ion impurity before use [48]. The suitable ligand for coating onto Amberlite XAD-7 in this work was PAN because PAN was used as a reagent for colorimetric determination of several metal ions. After coating PAN onto the surface of Amberlite XAD-7, the sorbent obtained was called Amberlite-PAN and the observed color of solid phase changed from white to yellow as shown in Fig 4.1.



Fig 4.1 Colors of (a) Amberlite XAD-7 and (b) Amberlite-PAN.

Amberlite-PAN was characterized by a diffuse reflectance ultraviolet visible spectrophotometer (DR-UV-vis) in the range of wavelength from 200 to 800 nm. The Kubelka-Munk equation is used to describe the reflection and diffusion gradient of solid [49]. It is widely used for colorimetric matching calculation. The Kubelka-Munk equation is shown in equation (4.1)-(4.2).

$$A = -\log R \quad (4.1)$$

$$f(R) = \frac{(1-R)^2}{2R} \quad (4.2)$$

where A is the absorbance,

R is the absolute reflectance of the sample,

Fig 4.2 shows DR-UV-vis spectra of Amberlite-PAN in function of amount of Amberlite XAD-7. They show the maximum wavelength of the observation at 470 nm. This peak corresponds to the absorption of the azo group of PAN. From the results, it was found that when the amount of Amberlite XAD-7 increased, the intensity of signals at wavelength 470 nm decreased due to mole of PAN was constant while surface of Amberlite XAD-7 increased. So, mole PAN per gram of Amberlite XAD-7 decreased with increase of amount of Amberlite XAD-7.

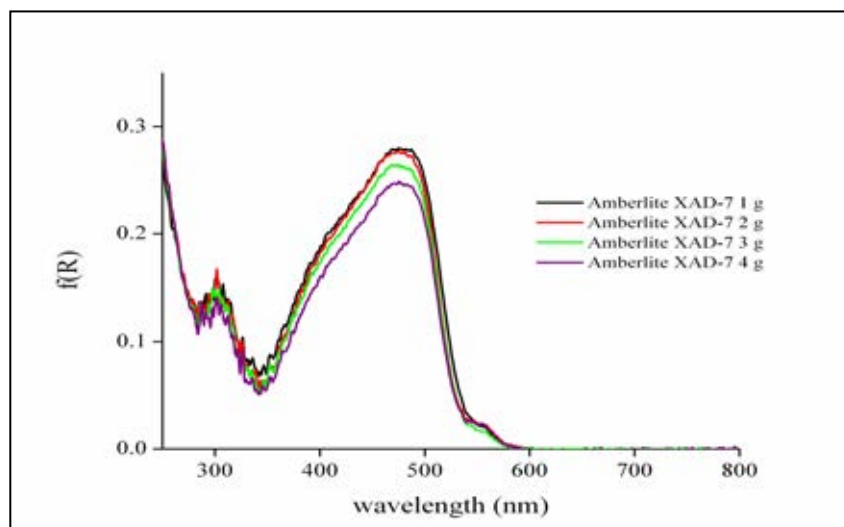


Fig 4.2 DR-UV-vis spectra of Amberlite-PAN in function of amount of Amberlite XAD-7.

However, the insignificant difference of the intensity of signals between 1 to 4 g of Amberlite XAD-7 was obtained (calculated by anova method, P values > 0.05). For the further studies, 2 g of Amberlite XAD-7 was used to obtain the adequate with 20 mL of 0.5 mM PAN.

The coating of PAN onto Amberlite XAD-7 was achieved probably due to the hydrogen bonding between oxygen atom of ester group of Amberlite XAD-7 and hydrogen atom of hydroxyl group of PAN as shown in Fig 4.3

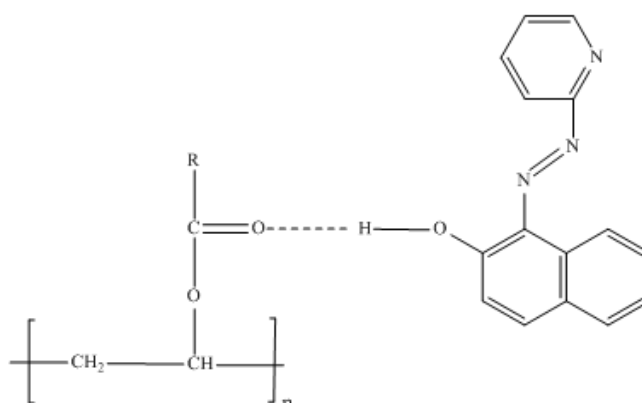


Fig 4.3 Proposed interaction between Amberlite XAD-7 and PAN.

4.1.2 Concentration of PAN

The reflectance spectra of Amberlite XAD-7 modified with different concentrations of PAN (0.1-2.5 mM) and the reflectance spectrum of Amberlite XAD-7 were compared. Fig 4.4 show that the intensity of signals increased with the increase of PAN concentration as considered at a maximum reflectance band at 470 nm. While the reflectance band at 470 nm for Amberlite XAD-7 without PAN was not observed, indicating the existence of PAN onto the surface of Amberlite XAD-7.

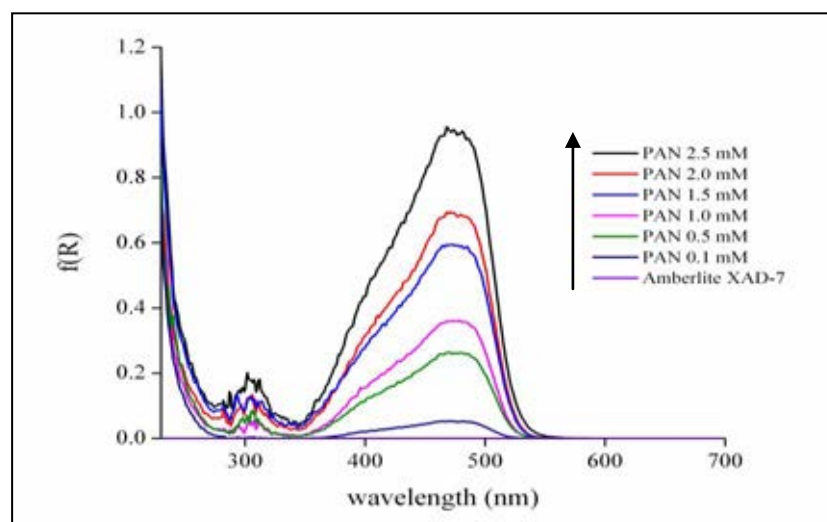


Fig 4.4 DR-UV-vis spectra of Amberlite XAD-7 and Amberlite-PAN in function of PAN concentration.

Moreover, the observed color of solid phase changed from white to yellow within three levels of color intensity: (1) Amberlite-PAN (0.1 mM), (2) Amberlite-PAN (0.5, 1.0, 1.5 mM) and Amberlite-PAN (2.0, 2.5 mM). The concentration of PAN was an important parameter affected to metal ion naked-eye detection at low concentration level. So, the effect of concentration of PAN was also presented in section 4.3.1.

4.1.3 Stirring time

The optimum stirring time for coating PAN onto Amberlite XAD-7 was studied in the range of 1-5 hours using 2 g of Amberlite XAD-7 and 20 mL of 0.5 mM PAN. The coating efficiency was considered by the signals of the reflectance spectra of Amberlite XAD-7 coated with PAN at wavelength 470 nm and the result is shown in Fig 4.5.

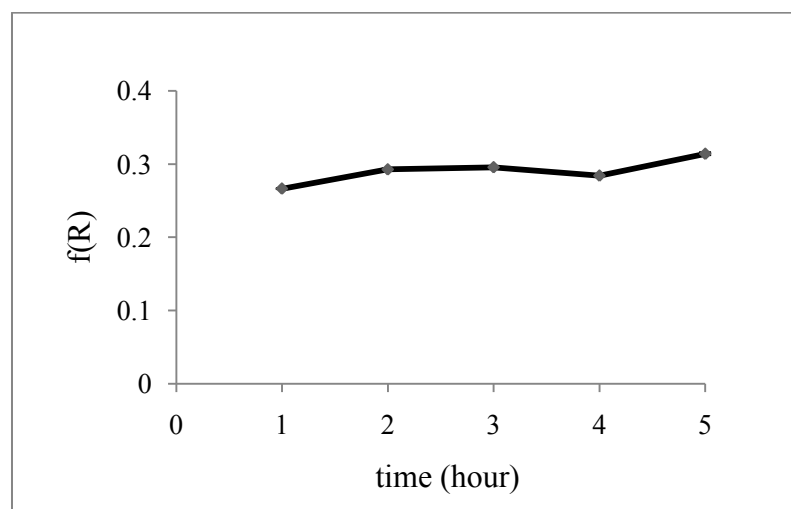























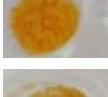









































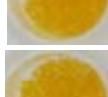













Fig 4.5 Effect of stirring time for coating PAN onto Amberlite XAD-7.

The insignificant difference of the $f(R)$ values for the stirring times between 1 to 5 hours was obtained (calculated by anova method, P values > 0.05), indicating the constant existence of PAN onto the surface of Amberlite XAD-7. The stirring time of 2 hours was selected for further studies.

4.2 Preliminary study for naked-eye detection of some metal ions

The naked-eye detection in colors of Amberlite-PAN and various metal ions e.g. Cu(II), As(III), Pb(II), Cd(II), Ni(II), Cr(III), Co(II), Mg(II), Mn(II) and Zn(II) was studied. The concentration of metal ions used was 1×10^{-4} M and the sorbent was mixed with metal-ion solution in glycine buffer at pH 1-2, acetate buffer at pH 3-5 and phosphate buffer at pH 6-7. Colors of Amberlite-PAN with various metal ions after batch experiments are shown in Table 4.1.

Table 4.1 Colors of Amberlite-PAN complexed with various metal ions in the range of pH 1-7 using batch method.

Metals	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7
Control							
As(III)							
Pb(II)							
Ni(II)							
Cr(III)							
Zn(II)							
Co(II)							
Cu(II)							
Mg(II)							
Mn(II)							
Cd(II)							

The color change of Amberlite-PAN and various metal ions were categorized into 3 groups. The color of Amberlite-PAN with As(III), Pb(II) and Mg(II) was not changed. The color of Amberlite-PAN with Cr(III), Mn(II) and Cd(II) was slightly changed. The color of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) was obviously changed to purple, green, pink and orange, respectively. This indicated that Amberlite-PAN could be used as a solid sensor for some metal ions and provided several colors.

The colors of the sorbent clearly changed with the range of pH 3-7 when Amberlite-PAN interacted with some metal ions such as Ni(II), Co(II) and Cu(II). The observed colors of Amberlite-PAN with Ni(II) at pH 3-7 were not different. It was also observed for Amberlite-PAN complexed with Co(II) and Cu(II).

In this work, acetate buffer at pH 4-5 was chosen as the pH control for further experiments because at these pH values, the colors of Amberlite-PAN and Cu(II), Co(II), Ni(II) and Zn(II) were obviously changed from yellow to purple, green, pink and orange colors, respectively, while the colors of Amberlite-PAN with other metal ions were not changed or changed slightly. Therefore, Amberlite-PAN was used as a solid sensor for Cu(II), Co(II), Ni(II) and Zn(II) naked-eye detection. The conditions of Cu(II), Co(II), Ni(II) and Zn(II) naked-eye detection were optimized.

As mentioned above, the colors of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) were obviously changed to purple, green, pink and orange colors, respectively. The reflectance spectra of Amberlite-PAN, Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn were compared as illustrated in Fig 4.6.

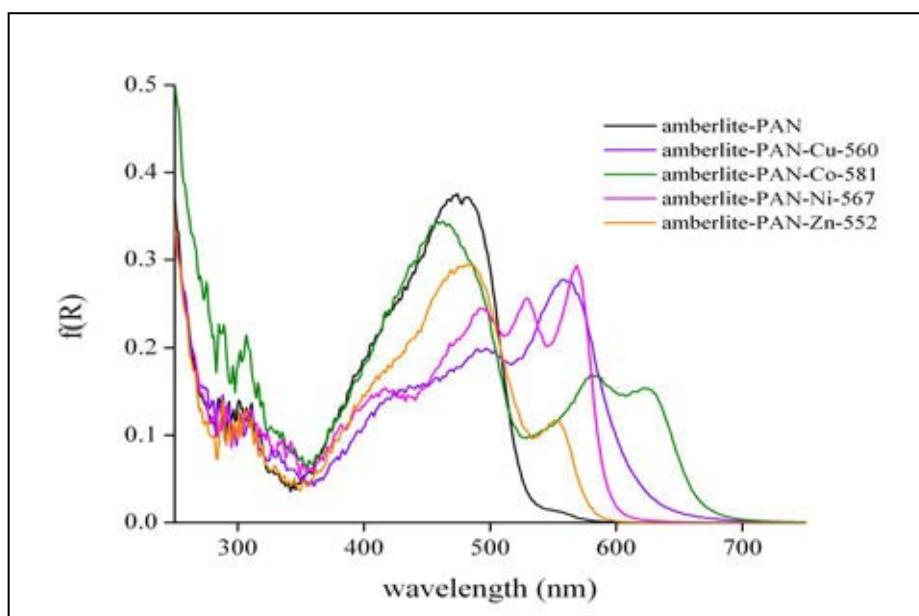






















Fig 4.6 DR-UV-vis spectra of Amberlite-PAN, Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn.

It was found that the reflectance spectrum of Amberlite-PAN differed from those of Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn. The new bands were found into longer wavelength which was observed at wavelength 560, 581, 567 and 552 nm for Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn, respectively. This indicated that the complexation between PAN and Cu(II), Co(II), Ni(II) and Zn(II) occurred onto the surface of Amberlite XAD-7. It could be explained by hard soft acid base principle (HSAB). Borderline metal ions such as Cu(II), Co(II), Ni(II) and Zn(II) prefer to form complexes with borderline donor atoms such as nitrogen of azo and pyridine group [16]. The complex of PAN and Cu(II), Co(II), Ni(II) and Zn(II) was probably formed through the hydroxyl oxygen, pyridine nitrogen and one of the azo group nitrogen atom proposed as illustrated in Fig. 2.1 [30].

The response time of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) at a concentration of 1×10^{-4} M was studied under acetate buffer at pH 5 by batch method. The response time was recorded after the color of sorbent changed. The results are shown in Table 4.2.

Table 4.2 Colors of Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) in function of time.

Metal ions	Control	Time (minutes)			
		1	5	20	45
Cu(II)					
Co(II)					
Ni(II)					
Zn(II)					

It was found that the color change of Amberlite-PAN was clearly observed within 1, 5, 20 and 45 minutes for Cu(II), Co(II), Ni(II) and Zn(II), respectively.

4.3 Naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II)

4.3.1 Method detection limit

The method detection limit was studied by using Amberlite-PAN at the concentrations of PAN in the range of 0.1-2.0 mM and the concentrations of metal ions were varied in a range of 1×10^{-6} - 1×10^{-4} M in acetate buffer at pH 5.

The color change of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) using batch experiments was investigated and the results are shown in Table 4.3-4.6, respectively.

Table 4.3 Colors of Amberlite-PAN complexed with Cu(II) at different concentration of PAN.












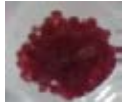








Amberlite-PAN	Control	Cu(II)		
		1×10^{-6} M	1×10^{-5} M	1×10^{-4} M
0.1 mM				
0.5 mM				
1.0 mM				
1.5 mM				
2.0 mM				

Table 4.4 Colors of Amberlite-PAN complexed with Co(II) at different concentration of PAN.





















Amberlite-PAN	Control	Co(II)		
		1×10^{-6} M	1×10^{-5} M	1×10^{-4} M
0.1 mM				
0.5 mM				
1.0 mM				
1.5 mM				
2.0 mM				

Table 4.5 Colors of Amberlite-PAN complexed with Ni(II) at different concentrations of PAN.

















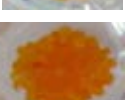

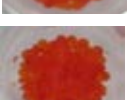
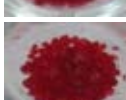




















Amberlite-PAN	Control	Ni(II)		
		1×10^{-6} M	1×10^{-5} M	1×10^{-4} M
0.1 mM				
0.5 mM				
1.0 mM				
1.5 mM				
2.0 mM				





















Table 4.6 Colors of Amberlite-PAN complexed with Zn(II) at different concentrations of PAN.

Amberlite-PAN	Control	Zn(II)		
		1×10^{-6} M	1×10^{-5} M	1×10^{-4} M
0.1 mM				
0.5 mM				
1.0 mM				
1.5 mM				
2.0 mM				

From the results, the colors of Amberlite-PAN were clearly changed when the concentration of Cu(II), Ni(II) and Zn(II) were 1×10^{-4} M while the color change of Amberlite-PAN with Co(II) was clearly observed at 1×10^{-5} - 1×10^{-4} M. However, Amberlite-PAN (0.5 mM) was chosen for further studies, because the observed colors of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) were obviously changed and gave the lowest limit of detection.

To obtain the naked-eye detection limit of Cu(II), Co(II), Ni(II) and Zn(II) ions by Amberlite-PAN, Amberlite XAD-7 coated with 0.5 mM PAN was used. The concentration of metal ions was varied from 1×10^{-6} - 1×10^{-4} M. The naked-eye detection limit was considered by the observed color of Amberlite-PAN with Cu(II), Co(II), Ni(II) and Zn(II) differed from control. The results are shown in Table 4.7.

Table 4.7 Colors of Amberlite-PAN (0.5 mM) complexed with Cu(II), Co(II), Ni(II) and Zn(II) ions at different concentrations of metal ions

Metal ions	Control	1×10^{-6}	3×10^{-6}	1×10^{-5}	6×10^{-5}	1×10^{-4}	(M)
Cu(II)					-		
Co(II)					-		
Ni(II)					-		
Zn(II)			-				

The lowest concentrations of metal ion that could be detected by naked-eye assay are 3×10^{-6} M (or 0.2 mg/L) for Cu(II), Co(II) and Ni(II) and 6×10^{-5} M (or 4.0 mg/L) for Zn(II).

In addition, The reflectance spectra of Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn at different concentrations of metal ions were measured by DR-UV-vis spectrophotometer. The DR-UV-vis spectra of Amberlite-PAN-Cu at different concentrations of Cu(II) and the $f(R)$ values at wavelength 470 and 560 nm and the relation between $f(R)$ values and the concentrations of Cu(II) are shown in Fig 4.7.

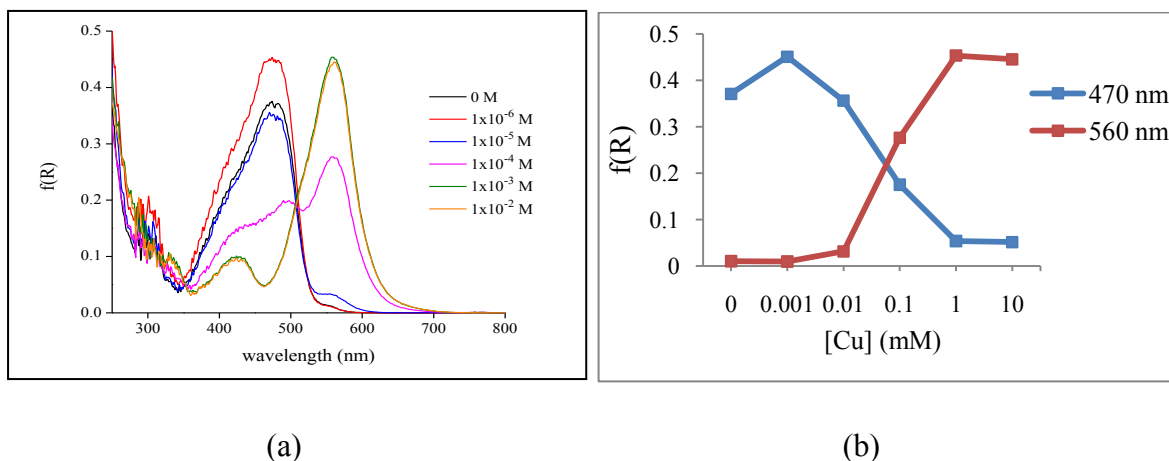


Fig. 4.7 (a) DR-UV-vis spectra of Amberlite-PAN with Cu(II) and (b) the relation between $f(R)$ values and the concentrations of Cu(II).

The change of $f(R)$ values of Amberlite-PAN-Cu at different concentrations of Cu(II) was observed. The $f(R)$ values of Amberlite-PAN-Cu at wavelength 470 nm decreased and the $f(R)$ values of Amberlite-PAN-Cu at wavelength 560 nm increased with the increase of the concentrations of Cu(II). The signal of Amberlite-PAN-Cu at wavelength 560 nm was observed when the concentration of Cu(II) was 1×10^{-5} M, while the color of Amberlite-PAN-Cu observed by naked-eye was lower than 1×10^{-5} M (the naked-eye detection limit of Cu(II) = 3×10^{-6} M).

The DR-UV-vis spectra of Amberlite-PAN-Co at different concentrations of Co(II) and the $f(R)$ values at wavelength 470 and 581 nm and the relation between $f(R)$ values and the concentrations of Co(II) are shown in Fig 4.8.

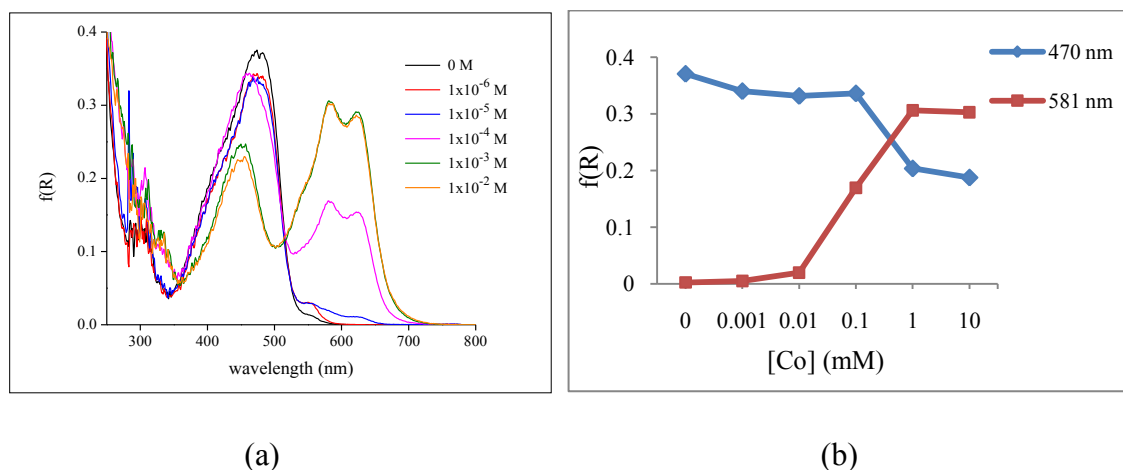


Fig. 4.8 (a) DR-UV-vis spectra of Amberlite-PAN with Co(II) and (b) the relation between $f(R)$ values and the concentrations of Co(II).

The change of $f(R)$ values of Amberlite-PAN-Co at different concentrations of Co(II) was observed. The $f(R)$ values of Amberlite-PAN-Co at wavelength 470 nm decreased and the $f(R)$ values of Amberlite-PAN-Co at wavelength 581 nm increased with the increase of the concentrations of Co(II). The signal of Amberlite-PAN-Co at wavelength 581 nm was observed when the concentration of Co(II) was 1×10^{-5} M, while the color of Amberlite-PAN-Co observed by naked-eye was lower than 1×10^{-5} M (the naked-eye detection limit of Co(II) = 3×10^{-6} M).

The DR-UV-vis spectra of Amberlite-PAN-Ni at different concentrations of Ni(II) and the $f(R)$ values at wavelength 470 and 567 nm and the relation between $f(R)$ values and the concentrations of Ni(II) are shown in Fig 4.9.

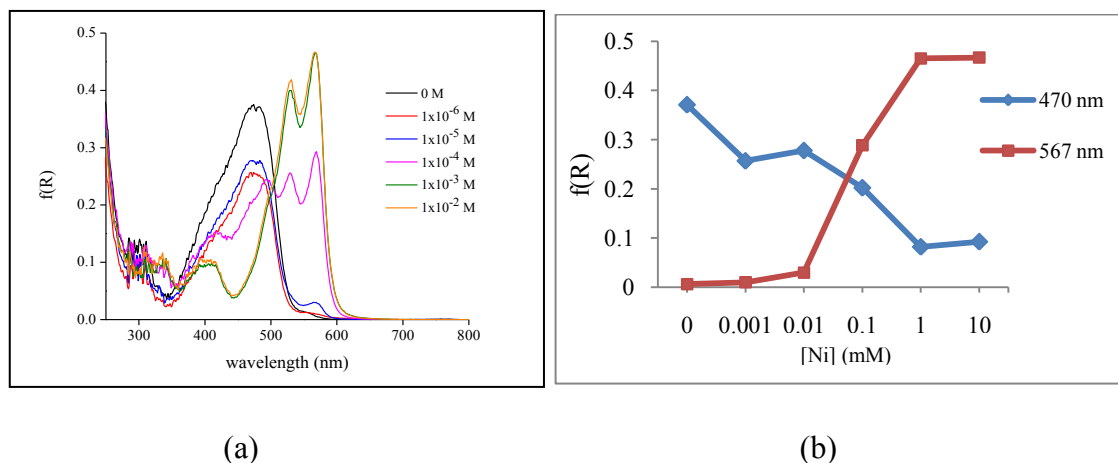


Fig. 4.9 (a) DR-UV-vis spectra of Amberlite-PAN with Ni(II) and (b) the relation between $f(R)$ values and the concentrations of Ni(II).

The change of $f(R)$ values of Amberlite-PAN-Ni at different concentrations of Ni(II) was observed. The $f(R)$ values of Amberlite-PAN-Ni at wavelength 470 nm decreased and the $f(R)$ values of Amberlite-PAN-Ni at wavelength 567 nm increased with the increase of the concentrations of Ni(II). The signal of Amberlite-PAN-Ni at wavelength 567 nm was observed when the concentration of Ni(II) was 1×10^{-5} M, while the color of Amberlite-PAN-Ni observed by naked-eye was lower than 1×10^{-5} M (the naked-eye detection limit of Ni(II) = 3×10^{-6} M).

The DR-UV-vis spectra of Amberlite-PAN-Zn at different concentrations of Zn(II) and the $f(R)$ values at wavelength 470 and 552 nm and the relation between $f(R)$ values and the concentrations of Zn(II) are shown in Fig 4.10.

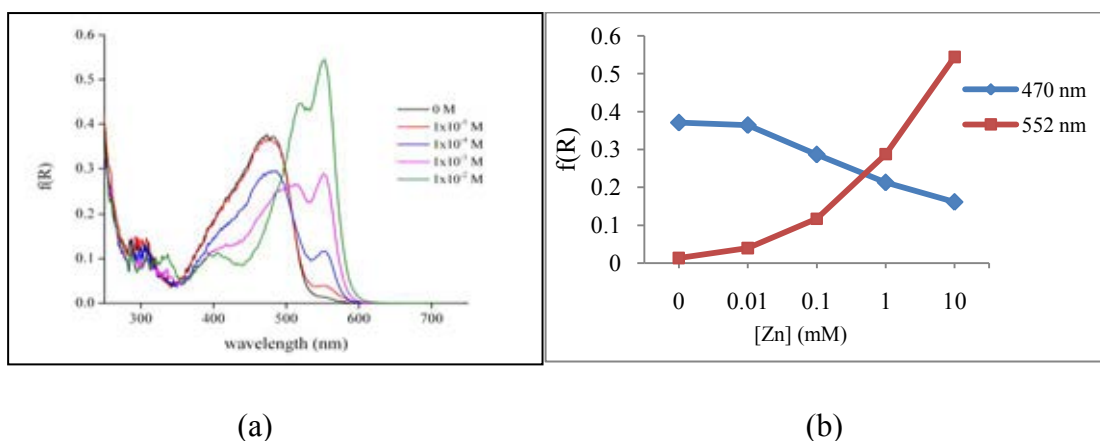


Fig. 4.10 (a) DR-UV-vis spectra of Amberlite-PAN with Zn(II) and (b) the relation between f(R) values and the concentrations of Zn(II).





















The change of f(R) values of Amberlite-PAN-Zn at different concentrations of Zn(II) was observed. The f(R) values of Amberlite-PAN-Zn at wavelength 470 nm decreased and the signal of Amberlite-PAN-Zn at wavelength 552 nm increased with the increase of the concentrations of Zn(II). The signal of Amberlite-PAN-Zn at wavelength 552 nm was observed when the concentration of Zn(II) was 1×10^{-5} M, while the color of Amberlite-PAN-Zn observed by naked-eye was higher than 1×10^{-5} M (the naked-eye detection limit of Zn(II) = 6×10^{-5} M).

4.3.2 Effect of interfering ions

As shown in the previous experiments, the colors of Amberlite-PAN complexed Cu(II), Co(II), Ni(II) and Zn(II) could be observed by naked-eye method under the similar conditions. The colors changed from yellow to purple, green, pink and orange for Cu(II), Co(II), Ni(II) and Zn(II), respectively. Unfortunately, the naked-eye detection of Co(II), Ni(II) or Zn(II) by Amberlite-PAN in the presence of Cu(II) was unsuccessful due to the interference of the color of Amberlite-PAN-Cu with the colors of other complexes. As a results, Co(II), Ni(II) and Zn(II) in the presence of Cu(II) cannot be detected by Amberlite-PAN. The naked-eye detection of Zn(II) in the presence of Ni(II) was unsuccessful due to the fact that the color of Ni(II)-PAN interfering the color of Zn(II)-PAN complex. Therefore, the naked-eye

detection method of a metal ion in the presence of other metal ions by Amberlite-PAN was studied by using masking agent. Masking agent is a chemical reagent reacting with some species that may interfere the target analyte. It was, thus, used for protecting the target analyte from the interference [50]. In addition, the formation constant value (K_f) of masking agent and metal ion should be considered. In this work, thiourea, potassium chloride, potassium cyanide and ethylenediaminetetraacetic acid (EDTA) were used as masking agent because they can form complex with various metal ions. The colors of Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) ions in the presence of masking agents and without masking agents were compared. The results are present in Table 4.8.

Table 4.8 Colors of Amberlite-PAN (0.5 mM) complexed with Cu(II), Co(II), Ni(II) and Zn(II) ions in the presence of masking agents.

	Cu(II)	Co(II)	Ni(II)	Zn(II)
without masking agent				
with 1 M EDTA				
with 1 M KCN				
with 1 M thiourea				
with 1 M KCl				

In case of EDTA, the colors of sorbent changed from purple, green, pink and orange to yellow, indicating that Cu(II), Co(II), Ni(II) and Zn(II) preferred to form complex with EDTA over PAN. Therefore, EDTA could be used as a masking agent for Cu(II), Co(II), Ni(II) and Zn(II).









In case of KCN, the color of only Co(II) complex changed from green to yellow, indicating that only Co(II) preferred to form complex with cyanide over PAN. Therefore, KCN could be used as a masking agent for Co(II). However, we avoided to use KCN in the further experiments because of its toxicity.

In case of thiourea, the color of only Cu(II) complex changed from violet to yellow, indicating that only Cu(II) preferred to form complex with thiourea over PAN. Therefore, thiourea could be used as a masking agent for Cu(II).

In case of KCl, the color of only Ni(II) complex changed from pink to yellow, indicating that only Ni(II) preferred to form complex with chloride over PAN. Therefore, KCl could be used as a masking agent for Ni(II).

To eliminate the interference from Cu(II), thiourea was chosen as a suitable masking agent because of its selectivity to mask only Cu(II), preferentially forming highly stable complex with only Cu(II) under the acidic condition [51]. Thiourea was added to a solution containing two types of the target ions (Co(II), Ni(II) or Zn(II)) in the presence of Cu(II). Table 4.9 demonstrates how thiourea is used to improve the selectivity of Amberlite-PAN.

Table 4.9 Colors of Amberlite-PAN complexed with Cu(II), Cu(II) and Co(II), Cu(II) and Ni(II) and Cu(II) and Zn(II) with and without thiourea.





	Cu(II)	Cu(II)+Co(II)	Cu(II)+Ni(II)	Cu(II)+Zn(II)
without thiourea				
with 1 M thiourea				

From the results, it can be seen that the colors of Amberlite-PAN complexed with Co(II), Ni(II) and Zn(II) in the presence of Cu(II) were purple, but the color of Amberlite-PAN complexed with Co(II), Ni(II) and Zn(II) in the presence of Cu(II) with thiourea were changed to green, pink and orange which were the colors of Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn, respectively. This indicated that thiourea can form complex with Cu(II) more stable than PAN. Then,

PAN was chelated with only Co(II), Ni(II) and Zn(II). Thus, thiourea is successfully to use as a masking agent for Cu(II). Then, Co(II), Ni(II) and Zn(II) in the presence of Cu(II) can be detected by Amberlite-PAN with naked-eye method.

The naked-eye detection of Zn(II) by Amberlite-PAN in the presence of Ni(II) was unsuccessful due to the interference of the color of Amberlite-PAN-Ni with the color of Amberlite-PAN-Zn. To eliminate the interference from Ni(II), potassium chloride was added into a solution containing the target ion (Zn(II)) in the presence of Ni(II) because chloride ion can form complex with transition metal ions, called chloro complexes. Table 4.10 illustrates how potassium chloride is used to improve the selectivity of Amberlite-PAN.

Table 4.10 Colors of Amberlite-PAN complexed with Ni(II) and Zn(II) with and without potassium chloride.

	Ni(II)	Ni(II)+Zn(II)
without KCl		
with 1 M KCl		

From the results, it can be seen that the color of Amberlite-PAN complexed Zn(II) in the presence of Ni(II) was changed to pink, but the color of Amberlite-PAN complexed Zn(II) in the presence of Ni(II) with potassium chloride was changed to orange which was the color of Amberlite-PAN-Zn. This indicated that potassium chloride can form complex with Ni(II) more stable than PAN. Then, PAN was chelated with only Zn(II) and gave orange color. Thus, potassium chloride is successfully to use as a masking agent for Ni(II). Then, Zn(II) in the presence of Ni(II) can be detected by Amberlite-PAN with naked-eye method.

4.4 Stability of Amberlite-PAN

Amberlite-PAN was kept in a desiccator at room temperature before use. The stability of Amberlite-PAN was studied once a week to 10 weeks by DR-UV-vis spectrophotometric technique (illustrated in Fig 4.11) and naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II).

From the results, it was found that Amberlite-PAN kept at different times showed the colors of purple, green, pink and orange for Cu(II), Co(II), Ni(II) and Zn(II), respectively. Moreover, the insignificant difference of the $f(R)$ values at wavelength 470 nm was obtained (calculated by anova method, P values > 0.05). This indicated that the Amberlite-PAN can be used as a solid sensor for Cu(II), Co(II), Ni(II) and Zn(II) naked-eye detection at least within 10 weeks.

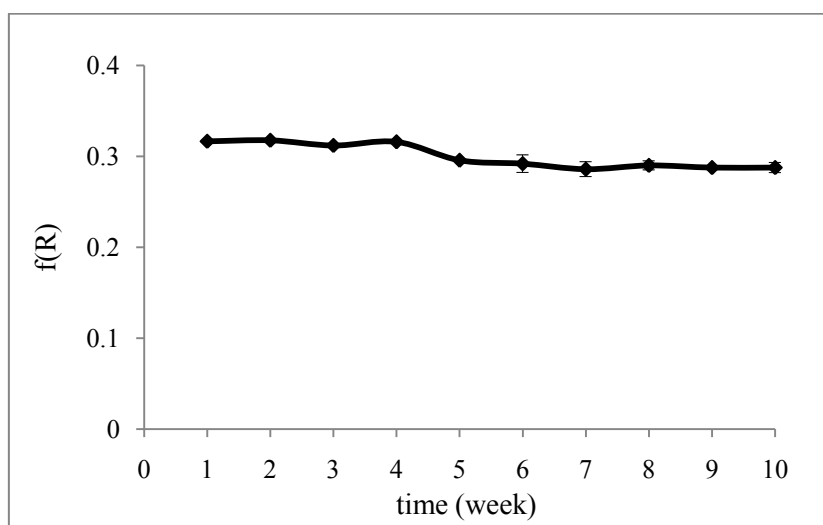












Fig. 4.11 The $f(R)$ of Amberlite-PAN in function of time at wavelength 470 nm.

4.5 Reusability of Amberlite-PAN

In this work, the reagent as nitric acid was used to elute the retained metal ion on Amberlite-PAN. From the results in Table 4.11, it was found that nitric acid cannot elute Co(II) from Amberlite-PAN while Cu(II), Ni(II) and Zn(II) can be eliminated,

that can observe from the disappeared colors. The colors of regenerated Amberlite-PAN were compared to that for original Amberlite-PAN, as shown in Fig 4.12.

Table 4.11 Colors of Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) with and without the regeneration with 1 M HNO₃.

	Control	Cu(II)	Co(II)	Ni(II)	Zn(II)
without 1 M HNO ₃					
with 1 M HNO ₃					

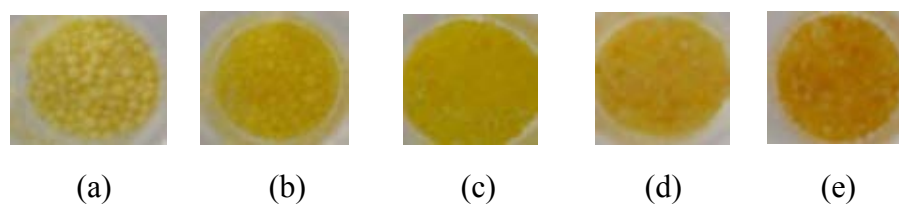

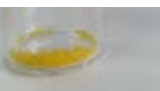















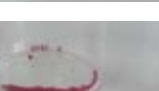

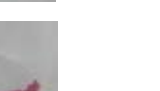







Fig 4.12 Colors of Amberlite-PAN (a) original, (b) regenerated 1 time, (c) regenerated 2 times, (d) regenerated 3 times and (e) regenerated 4 times.

From the results, it was found that the color of original Amberlite-PAN was similar with the color of Amberlite-PAN regenerated 1 time but the color of Amberlite-PAN regenerated more than 1 time slightly differed from original Amberlite-PAN. The color of regenerated Amberlite-PAN changed from bright yellow to deep yellow when reused in several times. Then, the colors of regenerated Amberlite-PAN and original Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II) were compared as shown in Table 4.12.

Table 4.12 Colors of Amberlite-PAN and regenerated Amberlite-PAN complexed with Cu(II), Co(II), Ni(II) and Zn(II).

	regenerated Amberlite-PAN				
	original	1 time	2 times	3 times	4 times
without metal ions					
Cu(II)					
Co(II)					
Ni(II)					
Zn(II)					

Although the color of regenerated Amberlite-PAN was slightly different from that of original Amberlite-PAN, but the colors of regenerated Amberlite-PAN with metal ions were not different from those of original Amberlite-PAN complexed with metal ions. This indicated that the Amberlite-PAN can be used as a solid sensor for the naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II) at least 4 times.

4.6 Application to real samples

Naked-eye determination of Cu(II), Co(II), Ni(II) and Zn(II) by Amberlite-PAN in real water samples was studied. In this work, real water samples were pond water (sample 1), Physics building water (sample 2) and Chamchuri drinking water (sample 3). The effect of matrix in real water sample was investigated by spiked method. Each individual water sample was spiked with each individual ion to obtain the final concentration of 0.6, 6 and 60 mg/L (or 1×10^{-5} , 1×10^{-4} and 1×10^{-3} M,

respectively) for Cu(II), Co(II) and Ni(II) and 6 and 60 mg/L for Zn(II). The concentration of each individual ion was determined by ICP-OES to confirm the concentration of each individual ion in water sample solution. The concentration of Cu(II), Co(II), Ni(II) and Zn(II) determined by ICP-OES in sample solution are shown in Table 4.13. Comparison of the color of Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn with the color calibration of each individual ion by naked-eye method are shown in Table 4.14 and 4.15 for Cu(II), Table 4.16 and 4.17 for Co(II), Table 4.18 and 4.19 for Ni(II) and Table 4.20 and 4.21 for Zn(II).

Table 4.13 Concentrations of Cu(II),Co(II), Ni(II) and Zn(II) determined by ICP-OES in real water sample solutions.

Sample	Spiked (mg/L)	Found (mg/L)				
		Unspiked	Cu(II)	Co(II)	Ni(II)	Zn(II)
1	0.6	nd	0.6	0.6	0.5	-
	6	nd	6.2	6.0	6.2	6.3
	60	nd	58.3	57.0	58.7	58.8
2	0.6	nd	0.6	0.6	0.5	-
	6	nd	6.3	6.0	6.3	6.4
	60	nd	58.0	57.1	58.7	58.3
3	0.6	nd	0.6	0.6	0.7	-
	6	nd	6.4	6.0	6.7	6.1
	60	nd	58.0	67.1	60.0	67.7

nd = not detectable

Table 4.14 Colors calibration of Cu(II) at various concentrations.







Concentration of Cu(II) (M)					
0	1×10^{-6}	3×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-2}
					

Table 4.15 Colors of Amberlite-PAN-Cu at different concentrations of Cu(II).

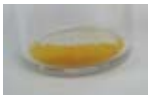








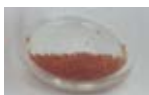


Sample	Concentration of Cu(II) (M)			
	0	1×10^{-5}	1×10^{-4}	1×10^{-3}
1				
2				
3				

Table 4.16 Colors calibration of Co(II) at various concentrations.






Concentration of Co(II) (M)				
0	1×10^{-6}	3×10^{-6}	1×10^{-5}	1×10^{-4}
				

Table 4.17 Colors of Amberlite-PAN-Co at different concentrations of Co(II).













Sample	Concentration of Co(II) (M)			
	0	1×10^{-5}	1×10^{-4}	1×10^{-3}
1				
2				
3				

Table 4.18 Colors calibration of Ni(II) at various concentrations.






Concentration of Ni(II) (M)				
0	1×10^{-6}	3×10^{-6}	1×10^{-5}	1×10^{-4}
				

Table 4.19 Colors of Amberlite-PAN-Ni at different concentrations of Ni(II).

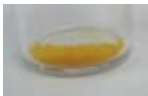











Sample	Concentration of Ni(II) (M)			
	0	1×10^{-5}	1×10^{-4}	1×10^{-3}
1				
2				
3				

Table 4.20 Colors calibration of Zn(II) at various concentrations.





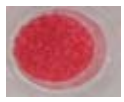










Concentration of Zn(II) (M)					
0	1×10^{-6}	6×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
					

Table 4.21 Colors of Amberlite-PAN-Zn at different concentrations of Zn(II).

Sample	Concentration of Zn(II) (M)		
	0	1×10^{-4}	1×10^{-3}
1			
2			
3			

The colors of Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn at different concentrations of ions in real water samples were compared with the color calibration of each individual ion by naked-eye detection. The concentration ranges for color calibrations were 1×10^{-6} - 1×10^{-2} M for Cu(II), 1×10^{-6} - 1×10^{-4} M for Co(II) and Ni(II) and 1×10^{-6} - 1×10^{-2} M for Zn(II). It was found that the obtained colors of Amberlite-PAN-Cu, Amberlite-PAN-Co, Amberlite-PAN-Ni and Amberlite-PAN-Zn in each concentration were similar to the color of calibration by naked-eye assay and the different samples gave the same color shade.

The sample 1 was spiked with the mixture ions (Cu(II) and Co(II), Cu(II) and Ni(II) or Cu(II) and Zn(II)). The final concentration of each individual ion was 0.5, 5 and 20 mg/L. The concentration of each spiked solution was determined by ICP-OES and the results are shown in Table 4.22-4.24. Then, each spiked solution was added into a glass vial containing 200 μ L of 1 M thiourea at pH 5. The colors of Amberlite-PAN complexed metal ions with and without masking agent were compared. The results are shown in Fig 4.13.

Table 4.22 Concentrations of Cu(II) and Co(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Co(II).

	Added (mg/L)	Found (mg/L)
Cu(II)	0.5	0.4
	5	4.5
	20	19.8
Co(II)	0.5	0.5
	5	5.2
	20	20.7

Table 4.23 Concentrations of Cu(II) and Ni(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Ni(II).

	Added (mg/L)	Found (mg/L)
Cu(II)	0.5	0.4
	5	5.0
	20	19.0
Ni(II)	0.5	0.5
	5	5.0
	20	18.5

Table 4.24 Concentrations of Cu(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II) and Zn(II).

	Added (mg/L)	Found (mg/L)
Cu(II)	0.5	0.5
	5	4.9
	20	19.7
Ni(II)	0.5	0.6
	5	5.6
	20	19.4

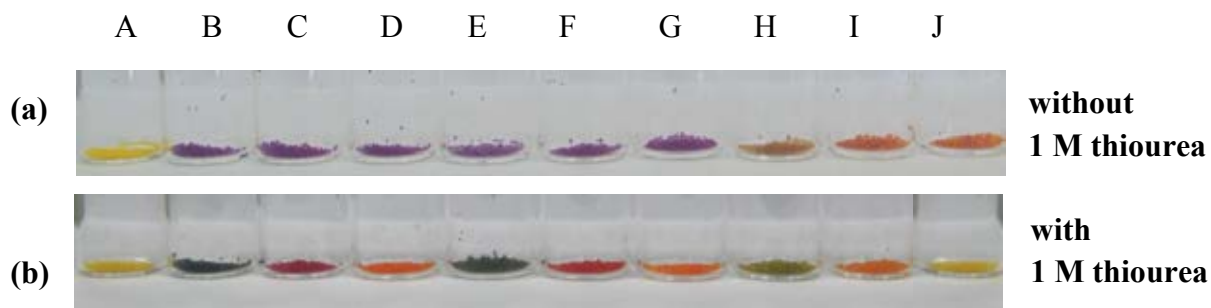


Fig 4.13 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M thiourea and (b) with 1 M thiourea.

The concentrations of A) metal ions = 0 mg/L, B) Cu(II), Co(II) = 20 mg/L, C) Cu(II), Ni(II) = 20 mg/L, D) Cu(II), Zn(II) = 20 mg/L, E) Cu(II), Co(II) = 5 mg/L, F) Cu(II), Ni(II) = 5 mg/L, G) Cu(II), Zn(II) = 5 mg/L, H) Cu(II), Co(II) = 0.5 mg/L, I) Cu(II), Ni(II) = 0.5 mg/L and J) Cu(II), Zn(II) = 0.5 mg/L.

From the results, it was found that the colors of Amberlite-PAN complexed with Co(II), Ni(II) and Zn(II) in the presence of Cu(II) were changed into purple, but the colors of Amberlite-PAN complexed with Co(II), Ni(II) and Zn(II) in the presence of Cu(II) and thiourea were changed into green, pink and orange, respectively. Moreover, the colors of Amberlite-PAN complexed with different concentrations of Co(II), Ni(II) and Zn(II) were changed into the same shade color in comparison with color calibration of each individual ion except that for Amberlite-PAN-Zn at the concentration of 0.5 mg/L. Since Zn(II) can be detected by Amberlite-PAN at the lowest concentration of 4.0 mg/L. Thus, thiourea was used for masking Cu(II) when Amberlite-PAN was used for detecting Co(II), Ni(II) and Zn(II) in the presence of Cu(II) in real water sample by naked-eye method.

The experiment was performed in the same manner as mentioned above for sample 1 spiked with 0.5, 5 and 20 mg/L of Ni(II) and Zn(II) and 200 μ L of 1 M potassium chloride. The concentration of each spiked solution was determined by ICP-OES and the results are shown in Table 4.25. The colors of Amberlite-PAN complexed with metal ions with and without masking agent were examined. The results are shown in Fig 4.14.

Table 4.25 Concentrations of Ni(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Ni(II) and Zn(II).

	Added (mg/L)	Found (mg/L)
Ni(II)	0.5	0.4
	5	4.5
	20	18.9
Zn(II)	0.5	0.5
	5	5.1
	20	18.9

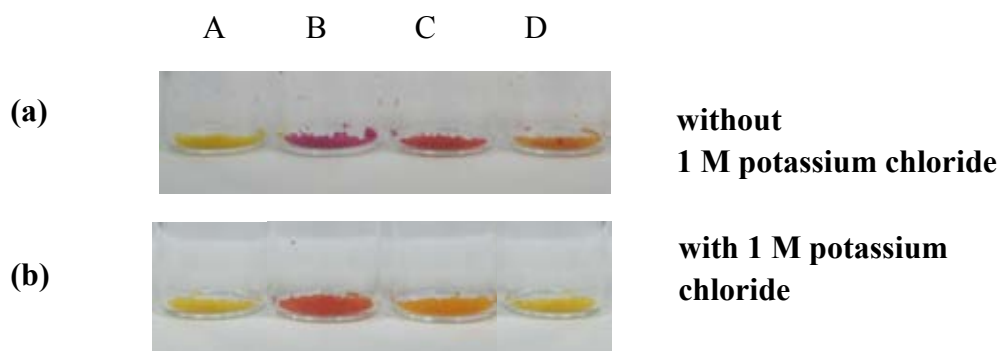


Fig 4.14 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.

The concentrations of A) Ni(II), Zn(II) = 0 mg/L, B) Ni(II), Zn(II) = 20 mg/L, C) Ni(II), Zn(II) = 5 mg/L and D) Cu(II), Zn(II) = 0.5 mg/L.

From the results, it was found that the colors of Amberlite-PAN complexed with Zn(II) in the presence of Ni(II) was changed into pink, but the color of Amberlite-PAN with Zn(II) in the presence of Ni(II) and potassium chloride was changed into orange. Moreover, the colors of Amberlite-PAN complexed with different concentrations of Zn(II) were changed into the same shade color in comparison with the color calibration of Zn(II) except that of Amberlite-PAN-Zn at the concentration of 0.5 mg/L. Thus, potassium chloride was a masking agent for Ni(II) when Amberlite-PAN was used for detecting Zn(II) in the presence of Ni(II) in real water sample by naked-eye method.

The experiment was performed in the same manner as mentioned above for sample 1 spiked with 0.5, 5 and 20 mg/L of Cu(II), Ni(II) and Zn(II) with 200 μ L of 1 M thiourea and 200 μ L of 1 M potassium chloride. The concentration of each spiked solution was determined by ICP-OES and the results are shown in Table 4.26. The colors of Amberlite-PAN complexed with metal ions with and without masking agent were examined. The results are shown in Fig 4.15.

Table 4.26 Concentrations of Cu(II), Ni(II) and Zn(II) determined by ICP-OES in pond water sample spiked with standard solution of Cu(II), Ni(II) and Zn(II).

	Added (mg/L)	Found (mg/L)
Cu(II)	0.5	0.5
	5	4.9
	20	19.9
Ni(II)	0.5	0.5
	5	4.7
	20	18.4
Zn(II)	0.5	0.5
	5	5.4
	20	18.4

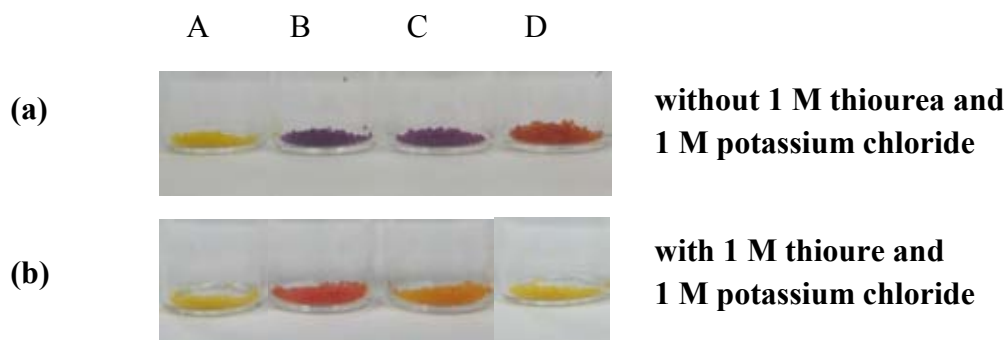


Fig 4.15 Colors of Amberlite-PAN complexed with metal ions (a) without 1 M thiourea and 1 M potassium chloride and (b) with 1 M thiourea and 1 M potassium chloride.

The concentrations of A) Cu(II), Ni(II) and Zn(II) = 0 mg/L, B) Cu(II), Ni(II) and Zn(II) = 20 mg/L, C) Cu(II), Ni(II) and Zn(II) = 5 mg/L and D) Cu(II), Ni(II) and Zn(II) = 0.5 mg/L.

From the results, it was found that the colors of Amberlite-PAN complexed with Zn(II) in the presence of Cu(II) and Ni(II) was changed into purple, but the color of Amberlite-PAN complexed with Zn(II) in the presence of Cu(II) and Ni(II) and thiourea and potassium chloride was changed into orange. Moreover, the colors of Amberlite-PAN complexed with different concentrations of Zn(II) was changed in the same shade color in comparison with the color calibration of Zn(II) except Amberlite-PAN-Zn at the concentration of 0.5 mg/L. Thus, thiourea and potassium chloride can serve as a masking agent for Cu(II) and Ni(II), respectively when Amberlite-PAN was used for detecting Zn(II) in the presence of Cu(II) and Ni(II) in real water sample by naked-eye method.

The qualitative and semi-quantitative analysis of Cu(II), Co(II), Ni(II) and Zn(II) by this proposed method was examined. The 24 unknown sample solutions were prepared by using pond water spiked with Cu(II),Co(II),Ni(II) and Zn(II) under the condition as follows:

- The stock solutions of Cu(II),Co(II),Ni(II) and Zn(II) with known concentrations were labeled as A, B, C and D, respectively. These solutions were used as standard solution spiked into unknown samples.
- The unknown samples were prepared by spiking the standard solutions A, B, C and D in pond water as follows:
 - spike only A, B, C or D
 - spike A and B, A and C, A and D or C and D
 - spiked A, C and D
- The minimum concentration of each standard solution was 0.6 mg/L. The final volume was 10 mL.

The qualitative analysis was performed as follows by Fig 4.16. 0.5 mL of unknown sample solution and 2 drops of acetate buffer pH 5 were added into a glass vial. Then 20 mg of Amberlite-PAN (0.5 mM) was added into the glass vial and standed for 1 hour. If the color of Amberlite-PAN changed from yellow to purple, 200 μ L of 1 M thiourea was added into the glass vial. If the color of Amberlite-PAN changed from yellow to pink, 200 μ L of 1 M potassium chloride was added into the glass vial. After that, the solution was removed from the Amberlite-PAN using a dropper. The color of Amberlite-PAN complexed with metal ions had been observed by naked-eye after Amberlite-PAN was dried. The semi-quantitative analysis was performed by comparing the color of Amberlite-PAN in sample solution with the color calibration of Cu(II),Co(II),Ni(II) and Zn(II) and the concentrations obtained from the naked-eye method were also compared with the concentrations determined by ICP-OES.

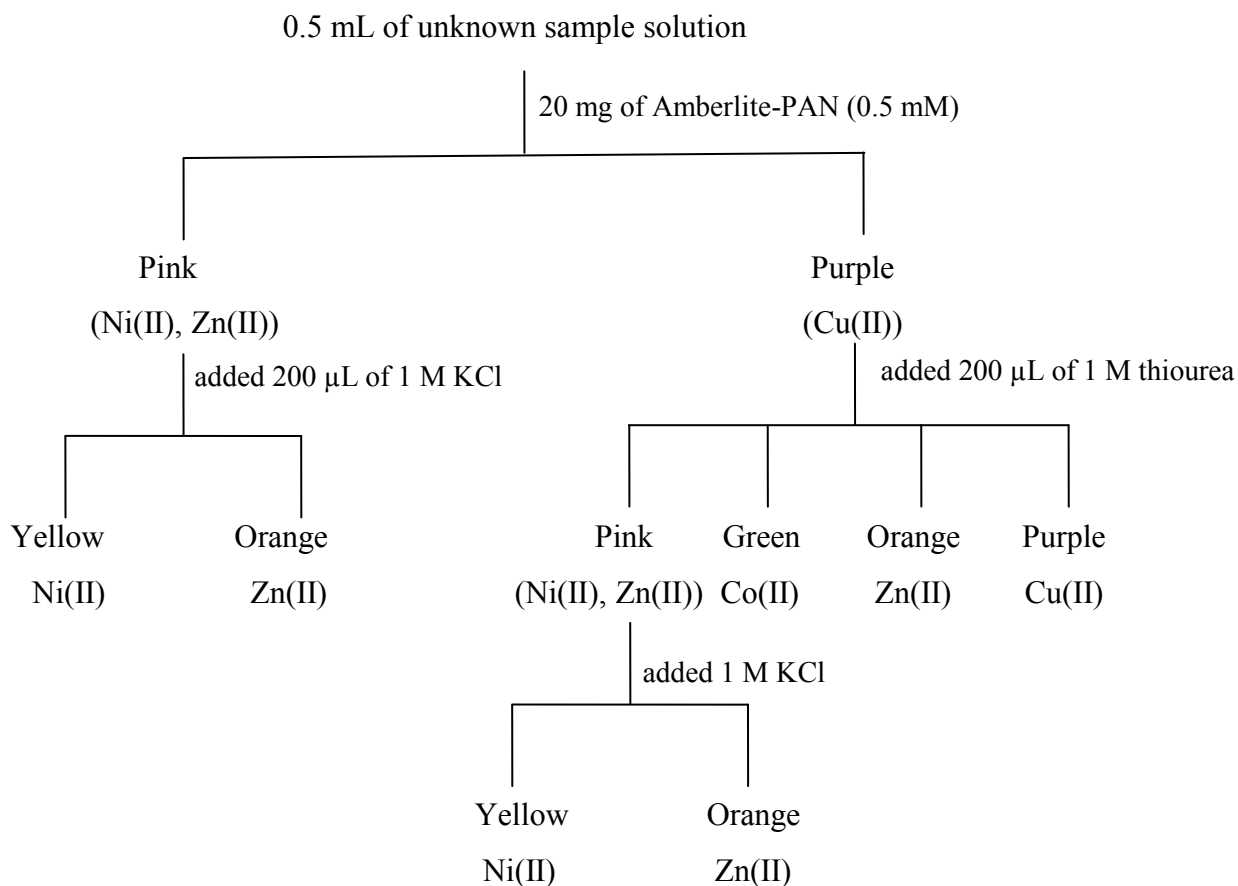


Fig 4.16 Diagram of qualitative naked-eye method.

The observed colors of Amberlite-PAN-metal ions of unknown sample no. 3, 4, 6, 9, 16, 18, 20, 21, 22 and 24 were purple (represent in Fig 4.17(a)), indicating that all unknown samples contained Cu(II) ion. After adding 1 M thiourea, the colors of Amberlite-PAN-metal ions changed from purple to orange, pink and green as shown in Fig 4.17(b), indicating that all unknown samples contained more than one metal ion.

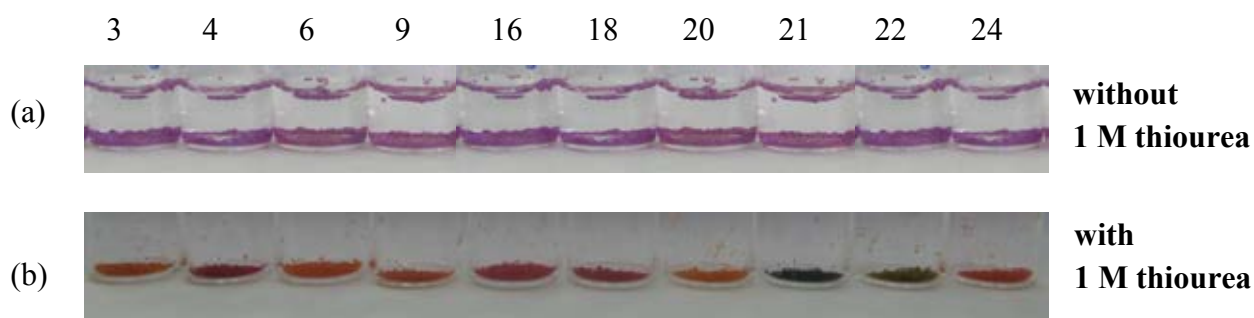


Fig 4.17 Colors of Amberlite-PAN-metal ions of unknown sample no. 3, 4, 6, 9, 16, 18, 20, 21, 22, and 24 (a) without 1 M thiourea and (b) with 1 M thiourea.

The observed colors of Amberlite-PAN-metal ions of unknown sample no. 2, 5, 7, 8, 12, 13, 14, 15, 19 and 23 were slightly purple (represent in Fig 4.18(a)), indicating that all unknown samples contained Cu(II) ion at very low concentration. After adding 1 M thiourea, the colors of Amberlite-PAN-metal ions changed from purple to orange, pink and green as shown in Fig 4.18(b), indicating that all unknown samples contained more than one metal ion.

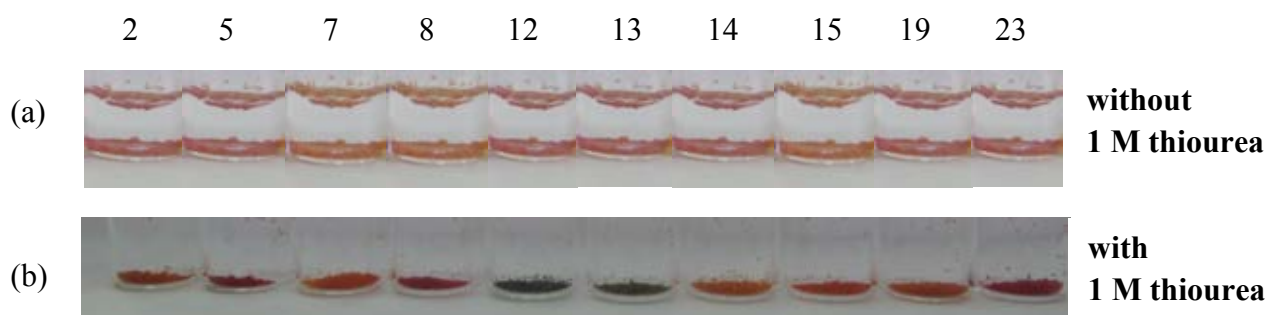


Fig 4.18 Colors of Amberlite-PAN-metal ions of unknown sample no. 2, 5, 7, 8, 12, 13, 14, 15, 19, and 23 (a) without 1 M thiourea and (b) with 1 M thiourea.

The observed colors of Amberlite-PAN-metal ions of unknown sample no. 1, 10, 11 and 17 were slightly pink (represent in Fig 4.19(a)), indicating that all unknown samples contained Ni(II) ion at very low concentration. After adding 1 M potassium chloride, the colors of Amberlite-PAN-metal ions changed from pink to orange and bright pink as shown in Fig 4.19(b), indicating that all unknown samples contained Zn(II) ion.

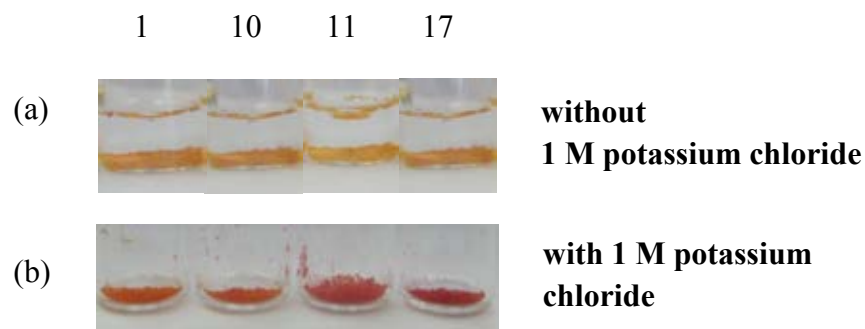


Fig 4.19 Colors of Amberlite-PAN-metal ions of unknown sample no. 1, 10, 11 and 17 (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.

After added 1 M thiourea, the observed colors of Amberlite-PAN-metal ions of unknown sample no. 4, 5, 7, 8, 14, 15, 16, 18, 19 and 24 were slightly pink and bright pink (represent in Fig 4.20(a)), indicating that all unknown samples contained Ni(II) ion. After adding 1 M potassium chloride, the colors of Amberlite-PAN-metal ions changed from slightly pink and bright pink to bright orange as shown in Fig 4.20(b), indicating that all unknown samples contained Zn(II) ion.

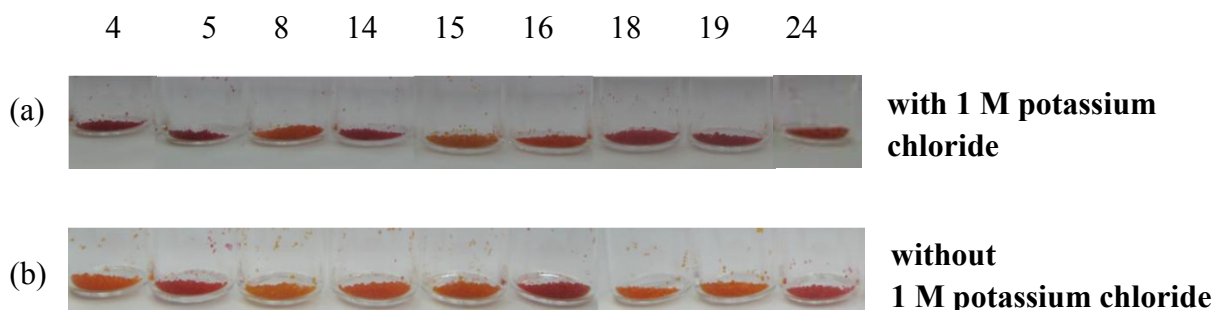


Fig 4.20 Colors of Amberlite-PAN-metal ions of unknown sample no. 4, 5, 8, 14, 15, 16, 18, 19 and 24 (a) without 1 M potassium chloride and (b) with 1 M potassium chloride.

From the qualitative naked-eye results, it was found that the unknown samples no. 1, 10, 11 and 17 contained Ni(II) and Zn(II) ions, the unknown sample no. 12, 13, 21 and 22 contained Cu(II) and Co(II) ions, the unknown sample no. 2, 3, 6, 7, 9, 20 and 23 contained Cu(II) and Zn(II) ions and the unknown sample no. 4, 5, 8, 14, 15, 16, 18, 19 and 24 contained Cu(II), Ni(II) and Zn(II) ions. The concentrations obtained from the naked-eye method of 24 unknown samples were compared with the concentrations determined by ICP-OES presented in Table 4.27.

Table 4.27 Concentrations of Cu(II), Co(II), Ni(II) and Zn(II) determined by naked-eye method and ICP-OES in pond water spiked with unknown samples.

Unknown sample no.	Concentration of metal ions (mg/L)							
	Naked-eye detection				ICP-OES			
	Cu(II)	Co(II)	Ni(II)	Zn(II)	Cu(II)	Co(II)	Ni(II)	Zn(II)
1	-	-	0.6-1	6	nd	nd	0.5	7.0
2	0.6-1	-	-	0.6-6	0.6	nd	0.5	nd
3	6-10	-	-	0.6-6	5.8	nd	nd	0.6
4	6-10	-	6-60	6-30	5.8	nd	5.6	6.3
5	0.6-1	-	6-60	6-30	0.6	nd	5.6	nd
6	6-10	-	-	6-30	5.6	nd	nd	19.7
7	0.6-1	-	-	6-30	0.6	nd	nd	19.7
8	0.6-1	-	6-60	6-30	0.6	nd	5.6	19.7
9	6-10	-	-	6-30	5.6	nd	0.5	6.7
10	-	-	0.6-1	6-30	nd	nd	0.5	19.6
11	-	-	6-60	30-60	nd	nd	5.6	6.7
12	0.6-1	6-20	-	-	0.6	5.7	nd	nd
13	0.6-1	0.6-1	-	-	0.6	0.6	nd	nd
14	0.6-1	-	0.6-1	6-30	0.6	nd	nd	6.7
15	0.6-1	-	0.6-1	6-30	0.6	nd	nd	19.6
16	6-10	-	6-60	6-30	5.5	nd	5.7	19.6
17	-	-	6-60	6-30	nd	nd	5.5	19.6
18	0.6-1	-	6-60	6-30	5.5	nd	5.5	6.7
19	0.6-1	-	6-60	6-30	0.6	nd	5.5	6.6
20	0.6-1	-	-	6-30	5.5	nd	0.5	6.6
21	6-10	6-20	-	-	5.6	5.7	nd	nd
22	6-10	0.6-1	-	-	5.6	0.6	nd	nd
23	0.6-1	-	-	6-30	0.6	nd	nd	6.7
24	6-10	-	6-60	6-30	5.4	nd	nd	19.5

nd = not detectable

From the results, it was found that the concentrations of each individual ion detected by naked-eye assay were similar to the concentrations determined by ICP-OES except Ni(II) and Zn(II) at low concentration. Because at low concentration of Ni(II) and Zn(II), the color of Amberlite-PAN complex slightly changed from yellow to bright orange with the same color shade such as sample no. 2, 5, 9, 11, 14, 15, 20 and 24. Then, Amberlite-PAN cannot be detected Ni(II) and Zn(II) at low concentration. However, the concentration of the unknown sample containing different concentrations of Ni(II) and Zn(II) such as sample no. 1, 10 and 17 can be determined by Amberlite-PAN naked-eye method.

As a consequence, Amberlite-PAN (0.5 mM) can be used as a solid sensor for detecting ion of Cu(II), Co(II), Ni(II) and Zn(II) at the different concentrations of metal ions in real water sample by naked-eye assay.

CHAPTER V

CONCLUSIONS

A new solid sensor was developed for naked-eye detection of some metal ions in water by using Amberlite-XAD 7 coated with PAN. The preliminary results showed that Amberlite-PAN forms the complexes with Cu(II), Co(II), Ni(II) and Zn(II). Its color changed from purple to green, pink and orange, respectively. Therefore, Amberlite-PAN can serve as a solid sensor for naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II). The optimum conditions for preparation of Amberlite-PAN were: the amount of Amberlite-XAD 7 = 2 g, the concentration of PAN (in ethanol) = 0.5 mM and the stirring time for coating PAN onto Amberlite-XAD 7 = 2 hours. Amberlite-PAN obtained was characterized by DR-UV-vis spectrophotometer. The maximum $f(R)$ wavelength of Amberlite-PAN was observed at around 470 nm while the $f(R)$ signal of Amberlite XAD-7 was not found at the same wavelength, indicating that PAN was coated onto the surface of Amberlite XAD-7.

The naked-eye detection of Cu(II), Co(II), Ni(II) and Zn(II) by Amberlite-PAN in batch experiment was studied under acetate buffer at pH 5. The response time between Amberlite-PAN and Cu(II), Co(II), Ni(II) and Zn(II) (1×10^{-4} M) was clearly observed within 1 min, 5 min, 20 min and 45 min, respectively. The lowest concentration of Cu(II), Co(II), Ni(II) and Zn(II) in solution that can be detectable the color by naked-eye assay. The results showed that the concentration of PAN which was capable to detect the lowest concentration of metal ions was 0.5 mM. The lowest concentrations detected by naked-eye were 0.2 mg/L for Cu(II), Co(II) and Ni and 4.0 mg/L for Zn(II).

An individual metal ion can be detected by Amberlite-PAN under the similar conditions. The naked-eye detection of Co(II), Ni(II) or Zn(II) in the presence of Cu(II) was unsuccessful due to the color of Cu(II)-PAN interfering the color of other complexes and the naked-eye detection of Zn(II) in the presence of Ni(II) was

unsuccessful due to the color of Ni(II)-PAN interfering the color of Zn(II)-PAN. To eliminate the interference from Cu(II), thiourea, a suitable masking agent, was added to a solution containing the target ion (Co(II), Ni(II) or Zn(II)) in the presence of Cu(II). No color of Amberlite-PAN-Cu in the presence of thiourea was observed indicating that thiourea can be used as a masking agent for Cu(II). Therefore, Amberlite-PAN can detect Co(II), Ni(II) and Zn(II) in the presence of Cu(II) in the solution. To eliminate the interference from Ni(II), potassium chloride, a masking agent, was added to a solution containing the target ion (Zn(II)) in the presence of Ni(II). No color of Amberlite-PAN-Ni in the presence of potassium chloride was observed indicating that potassium chloride can be used as a masking agent for Ni(II). Consequently, Amberlite-PAN can detect Zn(II) in the presence of Ni(II) in the solution.

Amberlite-PAN can be used as a naked-eye solid sensor for Cu(II), Co(II), Ni(II) and Zn(II) at least 10 weeks and Amberlite-PAN can be regenerated by 1 M nitric acid at least 4 times. The naked-eye determination of Cu(II), Co(II), Ni(II) and Zn(II) in water by using Amberlite coated with 0.5 mM PAN solution under the optimum conditions was achieved. The naked-eye determination of Co(II), Ni(II) and Zn(II) in the presence of Cu(II) and naked-eye determination of Zn(II) in the presence of Ni(II) in pond water by using Amberlite-PAN with masking agent (thiourea or potassium chloride) under the optimum conditions were accomplished.

Suggestions for future work

It is necessary to find out a suitable masking agent to eliminate the interference of Co(II). Since the naked-eye detection of Ni(II) and Zn(II) in the presence of Co(II) was unsuccessful due to the color of Co(II)-PAN interfering the colors of other complexes.

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