

การดูดซับไอออนโลหะหนักด้วยพอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์]ที่เชื่อมขวางด้วย  
ไตรเอทิลีนเททระมีน

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
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ADSORPTION OF HEAVY METAL IONS BY  
POLY[*N*-ISOPROPYLACRYLAMIDE] CROSSLINKED WITH  
TRIETHYLENETETRAMINE

Miss Khanitta Kamchudbhai

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

Department of Chemistry

Faculty of Science

Chulalongkorn University

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ขนิษฐา กำจัดภัย: การดูดซับไอออนโลหะหนักด้วยพอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์]ที่เชื่อมขวางด้วยไตรเอทิลีนเทระมีน. (ADSORPTION OF HEAVY METAL IONS BY POLY[N-ISOPROPYLACRYLAMIDE] CROSSLINKED WITH TRIETHYLENE TETRAMINE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. อภิชาติ อิ่มยิ้ม, 43 หน้า.

สังเคราะห์โคพอลิเมอร์ชนิดใหม่ระหว่าง พอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์] กับกรดมาเลอิก โดยใช้ไตรเอทิลีนเทระมีนเป็นสารเชื่อมขวาง ผ่านปฏิกิริยาพอลิเมอไรเซชันแบบฟรีแรดิคัล โดยใช้อัตราส่วนโดยโมลระหว่าง เอ็น-ไอโซโพรพิลอะคริลาไมด์ต่อกรดมาเลอิกเท่ากับร้อยละ 65 ต่อ 35 และใช้แอมโมเนียมเปอร์ซัลเฟตเป็นตัวริเริ่มปฏิกิริยา สังเคราะห์โคพอลิเมอร์ที่อุณหภูมิ 60-80 องศาเซลเซียส และทำให้เกิดปฏิกิริยาการเชื่อมขวางแบบเอมิเคชันด้วยความร้อนที่อุณหภูมิ 145 องศาเซลเซียส หาลักษณะเฉพาะของพอลิเมอร์ด้วยเทคนิคอินฟราเรดสเปกโตรเมตรี ทำการศึกษาภาวะที่เหมาะสมในการดูดซับไอออนตะกั่ว(II) ทองแดง(II) และ โครเมียม(III) โดยใช้การสกัดแบบแบทช์ พบว่าโคพอลิเมอร์ที่มีไตรเอทิลีนเทระมีนสามารถดูดซับไอออนโลหะหนักทุกชนิด ได้ดีกว่าโคพอลิเมอร์ที่ไม่ได้เชื่อมขวางด้วยไตรเอทิลีนเทระมีน พีเอชที่เหมาะสมสำหรับการดูดซับไอออนตะกั่ว(II) ทองแดง(II) เท่ากับ 5 และ โครเมียม(III) เท่ากับ 4-5 เมื่อใช้แท่งพอลิเมอร์ที่มีเส้นผ่านศูนย์กลาง 0.7 เซนติเมตร ความยาว 1 เซนติเมตร และทำการดูดซับที่อุณหภูมิ 28-30 องศาเซลเซียส พบว่าการดูดซับเข้าสู่สมดุลสำหรับไอออนตะกั่ว(II) ทองแดง(II) และ โครเมียม(III) ในเวลา 2, 5 และ 7 ชั่วโมงตามลำดับ โดยไอออนตะกั่ว(II) ทองแดง(II) และ โครเมียม(III) ที่ถูกดูดซับบนพอลิเมอร์สามารถชะออกได้โดยใช้ กรดไฮโดรคลอริก 15% (v/v) ภายในเวลา 0.5-1 ชั่วโมงที่อุณหภูมิต่ำกว่า 25 องศาเซลเซียส

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KHANITTA KAMCHUDBHAI: ADSORPTION OF HEAVY METAL IONS BY POLY[*N*-ISOPROPYLACRYLAMIDE] CROSSLINKED WITH TRIETHYLENETETRAMINE ADVISOR: ASST.PROF. APICHAT IMYIM, Ph.D., 43 pp.

A new copolymer poly[*N*-isopropylacrylamide-co-maleic acid] crosslinked with triethylenetetramine was prepared by free radical polymerization. The percent mole ratio of *N*-isopropylacrylamide to maleic acid was fixed at 65:35 and using ammonium persulphate as an initiator. The copolymer was synthesized at the temperature ranging of 60-80 °C followed by a heat-induced amidation crosslinking reaction at 145 °C. The copolymer was characterized by Fourier transforms infrared spectroscopy. Adsorption behavior of lead(II), copper(II) and chromium(III) ions was examined by bath method. The result showed that the copolymer crosslinked with triethylenetetramine had more adsorption capacity than copolymer without triethylenetetramine. The optimum pH value for the adsorption of lead(II) Cu(II) was 5 and 4-5 for Cr(III) when using a rod shape copolymer (0.7 cm diameter and 1 cm length). The adsorption equilibrium reached within 2, 5 and 7 hours for Pb(II), Cu(II) and Cr(III), respectively at 28-30 °C. The desorption of Pb(II), Cu(II) and Cr(III) ions equilibria reached within 0.5-1 hour at temperature lower 25 °C by 15% (v/v) HCl.

Department: ..... Chemistry ..... Student's Signature .....

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## LIST OF ABBREVIATIONS

LCST	Lower Critical Solution Temperature
NIPA	<i>N</i> -isopropylacrylamide
°C	Degree Celsius
MA	Maleic acid
FT-IR	Fourier Transforms Infrared Spectroscopy
FAAS	flame atomic absorption spectrometer
CST	Critical Solution Temperature
mol <sup>-1</sup>	Per mole
TETA	Triethylenetetramine
g mol <sup>-1</sup>	Gram per mole
cm <sup>-1</sup>	Per centimeter
FT	Fourier Transform
v	Stretching vibration
nm	Nanometre
mA	Milli ampere
mL min <sup>-1</sup>	Millilitre per minute
ATR	Attenuated Total Reflection
MBAA	<i>N,N'</i> -Methylenebisacrylamide
APS	Ammonium persulfate
DI	Deionization
mol L <sup>-1</sup>	Mol per liter
i.d.	Internal diameter
H <sup>+</sup>	Proton

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of the problem

Polymer properties change by external factors as stimuli-responsive polymer [1], which differently referred to as environmentally-sensitive, smart or intelligent polymers, when stimulated by temperature [2-4], pH [1, 3, 5-7], light [2], electric field [8-10]. As the result, it changes in conformation, in solubility, alteration of the hydrophilic/hydrophobic balance, etc [2]. Thermo-responsive polymers show the phase transition occurred at certain temperature which has been called lower critical solution temperature (LCST) or the lowest temperature of the phase separation. That is the polymer shrink and swell when the temperature is higher and lower than this value respectively [2]. Thermo-responsive polymer have received considerable attention in wide applications such as drug delivery system [11-12], biochemical [13], immobilize enzyme [14], separation process [15] and remove metal from aqueous solution [16-18].

*N*-isopropylacrylamide (NIPA) is one kind of thermo-responsive polymers whose the LCST falls in the region of 32-36 °C. Below this value water molecules are form hydrogen bonds with the amide group of *N*-isopropylacrylamide, which makes it water-soluble polymer, when a temperature exceeds its LCST, the polymer phase separated from water and agglutinated to form collapse as a result of the disruption of hydrogen bonds [19-20].

For extensive applications, the polymer properties was changed by copolymerization between two or more monomers, be effective alteration of properties such as shifting of the LCST, solubility change etc. Wei Wang et al. [21] synthesized copolymers *N*-isopropylacrylamide (NIPA), *N*-vinyl-2-pyrrolidone (NVP), chlorophyllin and sodium copper salt (CHL) (copolymer PNNC) for partition

of biomolecules in aqueous two-phase system which could be effectively recycled and reused.

Due to the property of phase transition around its LCST, poly (*N*-isopropylacrylamide) was selected for removal of heavy metal ions from aqueous solution. And to improve efficiency of this research, the properties of polymer were changed by synthesis of copolymer using poly (*N*-isopropylacrylamide) as monomer, maleic acid as comonomer and triethylenetetramine as crosslinker. The new synthetic copolymer was expected to improve adsorption capacity toward metal ions. Because this molecule of triethylenetetramine possesses 4 figures of amine group in which nitrogen atom acts as a donor atom for metal ions.

This research focused on the synthesis by free radical polymerization and characterization of copolymer of poly (*N*-isopropylacrylamide) with maleic acid crosslinked with triethylenetetramine for adsorption of Cu(II), Pb(II) and Cr(III) ions from aqueous solution.

## **1.2 Objectives**

1.2.1. Synthesize and characterization copolymer of poly (*N*-isopropylacrylamide) and Maleic acid (MA) crosslinked with Triethylenetetramine

1.2.2. Study adsorption and desorption properties of Cu(II), Pb(II) and Cr(III) ions from aqueous solution

## **1.3 Scope of the research**

A new copolymer between poly(*N*-isopropylacrylamide) and maleic acid crosslinked with triethylenetetramine was synthesized. Fourier Transforms Infrared Spectroscopy (FT-IR) was used for characterization of polymer. Afterwards the polymer was brought to adsorb and desorb Cu(II), Pb(II) and Cr(III) ions from aqueous solution by batch method. Adsorption capacities of copolymer crosslinked with triethylenetetramine and without triethylenetetramine were compared. Moreover

suitable conditions of adsorption and desorption were studied i.e. effect of pH, effect of adsorbent size and surface area, effect of time and temperature (in desorption study). The concentration of metal ions was determined by Flame Atomic Absorption Spectrometry (FAAS).

#### **1.4 The benefits of this research**

New copolymers poly(*N*-isopropylacrylamide) and maleic acid crosslinked with triethylenetetramine which could adsorb Cu(II), Pb(II) and Cr(III) ions was achieved.

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Stimuli responsive polymer

Polymers that respond when physical or chemical properties change are called stimuli responsive polymer. List of their various properties are shown in Table 2.1.

**Table 2.1** List of various properties that can activate such dramatic behavior [22]

Physical	Chemical	Biochemical
Temperature	pH	Enzyme substrates
Ionic strength	Specific ions	Affinity ligands
Solvents	Chemical agents	
Radiation (UV, visible)		
Electric field		
Mechanical stress		
High pressure		
Sonic radiation		
Magnetic field		

### 2.1.1 Thermo responsive polymer

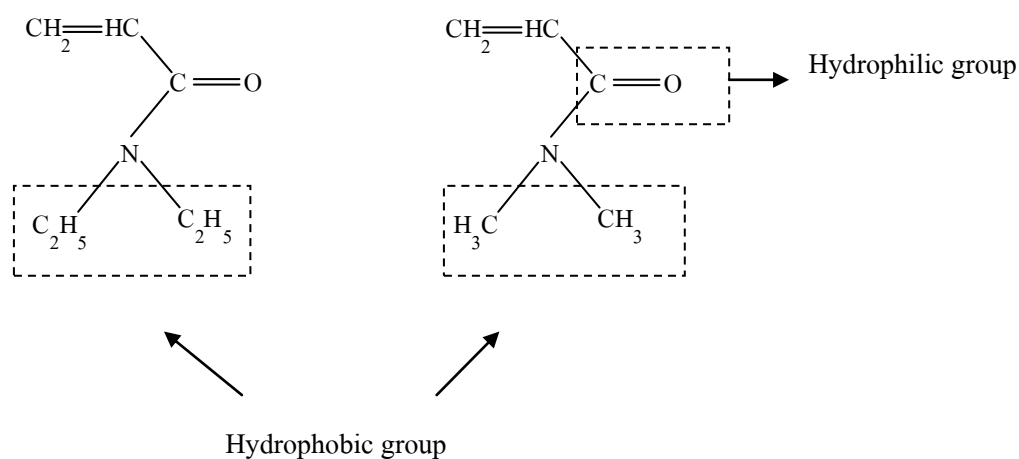
Thermo responsive polymer exhibits a critical solution temperature (CST). Critical solution temperature is the temperature at which the phase or property of polymer is changed [23]. The polymer behaves in water absorption to swollen state at the temperature below CST and shrinks when increasing the temperature above CST because the alteration of hydrophobicity and hydrophilicity. The minimum temperature at which the precipitation of polymer starts is called a lower critical solution temperature (LCST).

The hydrogels have much attractive and been widely used for many applications especially for the removal of heavy metal ions from aqueous medium. Ufuk Yildiz et al. (2010) [29] prepared a hydrogel by synthesis of copolymer of *N*-vinyl-2-pyrrolidone with methylacrylate (MA). The hydrogel was used as binding materials for different heavy metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) from wastewater. Hideaki Tokuyama et al. (2005) [30] synthesized a novel thermosensitive gel adsorbent to adsorb and/or desorb Cu(II) by temperature swing technique. The thermosensitive gel was prepared from *N*-isopropylacrylamide as a monomer and 4-(vinylbenzyl) ethylenediamine (VBEDA) as a chelating agent and crosslinker. The temperature swing was carried out at 283-307 K. Ningmei Wu et al. (2013) [31] synthesized a novel poly(hydroxyethyl methacrylate/maleamic acid) (p(HEA/MALA)) hydrogel by  $^{60}\text{Co}$ - $\gamma$  induced copolymerization, which was used for removal of Pb(II), Cd(II), Ni(II) and Cu(II) from aqueous solution. Han Yana et al. (2011) [32] modified chitosan hydrogel beads (CS) with the etherification agent of chloroacetic acid (carboxymethylated chitosan beads (CMC)) for enhancing an adsorption capacity of Cu(II), Pb(II) and Mg(II) from aqueous solutions, moreover the CMC also improved the selectivity of adsorption for Cu(II). Alain Graillet et al. (2013) [33] removed metal ions from wastewater by thermosensitive copolymers, which were prepared by free radical copolymerization between *N*-*n*-propylacrylamide (NnPAAm) and (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1) followed by a hydrolysis the phosphonated esters into phosphonic diacid groups (hMAPC1), poly(NnPAAm-stat-hMAPC1) copolymers. The adsorption was studied in a

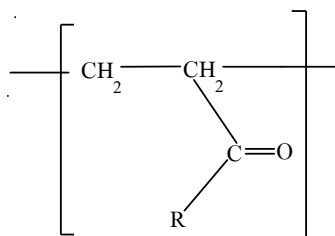


temperature range of 22-26 °C which could separate copolymer-metal complexes from water and led to the cheaper processes.

One kind of thermo responsive polymer is *N*-substituted polyacrylamides (Figure 2.1 and 2.2) which has attracted of attention because their unique thermal response in aqueous medium. The hydrogen bond between water molecules and the NH or C=O groups of polymer is broken at the temperature above LCST as a result the phase transition from coil to hydrophobic globule and the subsequent precipitation of the polymer out of solution.


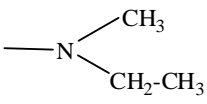
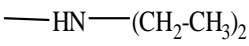
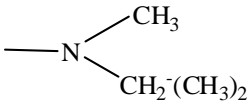
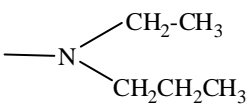
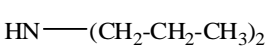


**Figure 2.1** Molecule structure of two monomers (*N*-substituted polyacrylamides) and identification of their hydrophilic and hydrophobic regions [24]

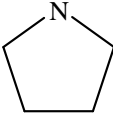
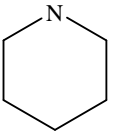


**Figure 2.2** Molecular structure of *N*-substituted acrylamide [24]

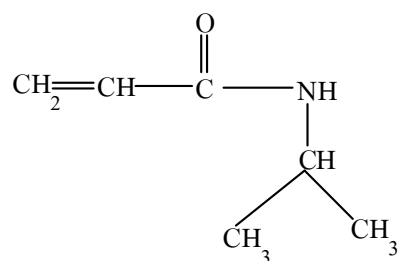
**Table 2.2** LCST of aqueous solutions of poly (*N*-substituted acrylamides) [24]

<b>R</b>	<b>Poly (<i>N</i>-alkylacrylamide)</b>	<b>LCST (°C)</b>
NH	Poly(acrylamide)	no LCST, insoluble in water
NH-CH <sub>3</sub>	Poly( <i>N</i> -methylacrylamide)	no LCST, insoluble in water
NH-CH <sub>2</sub> -CH <sub>3</sub>	Poly( <i>N</i> -ethylacrylamide)	82
NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Poly( <i>N</i> -propylacrylamide)	22
NH-CH-(CH <sub>3</sub> ) <sub>2</sub>	Poly( <i>N</i> -isopropylacrylamide)	32-34
NH- 	Poly( <i>N</i> -cyclopropylacrylamide)	47
NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Poly( <i>N</i> -butylacrylamide)	no LCST, insoluble in water
N-C(CH <sub>3</sub> ) <sub>3</sub>	Poly( <i>N</i> - <i>t</i> -butylacrylamide)	no LCST, insoluble in water
N-(CH <sub>3</sub> ) <sub>2</sub>	Poly( <i>N,N'</i> -dimethylacrylamide)	no LCST, insoluble in water
	Poly( <i>N</i> -ethyl, <i>N</i> -methylacrylamide)	56
	Poly( <i>N,N</i> -diethylacrylamide)	32-42
	Poly( <i>N</i> -isopropyl, <i>N</i> -methylacrylamide)	25
	Poly( <i>N</i> -ethyl, <i>N</i> -propylacrylamide)	no LCST, insoluble in water
	Poly( <i>N,N</i> -dipropylacrylamide)	no LCST, insoluble in water

**Table 2.2** LCST of aqueous solutions of poly (*N*-substituted acrylamides) [24] (cont.)

<b>R</b>	<b>Poly (<i>N</i>-alkylacrylamide)</b>	<b>LCST (°C)</b>
	Poly( <i>N</i> -acryloylpyrrolidine)	55
	Poly( <i>N</i> -acryloylpiperidine)	4

The phase transition temperature in aqueous of *N*-substituted polyacrylamides depends on chemical structure of the side chain (see Table 2.2). *N*-isopropylacrylamide (Figure 2.3) has been received much attention for many applications due to their ability exhibiting quickness thermo-reversible in aqueous medium. Its properties are illustrated in Table 2.3.

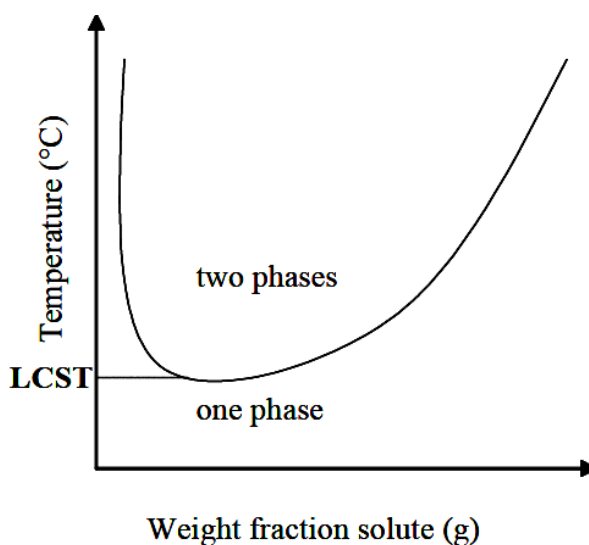
**Figure 2.3** The structure of *N*-isopropylacrylamide monomer.

**Table 2.3** Physical and chemical properties of *N*-isopropylacrylamide monomer [25]

<b>Properties</b>	<b>Value</b>
Appearance	White crystalline solid
Synonym	2-Propenamide
Formula	C <sub>6</sub> H <sub>11</sub> NO
Molecular weight (g mol <sup>-1</sup> )	113.16
Melting point	60-63 °C
Boiling point	89-92 °C
Water solubility	Soluble

### 2.1.2 Properties of poly(*N*-isopropylacrylamide)

The polymer becomes insoluble and phase separation occurs when the temperature rise to above 32 °C and it becomes soluble in the aqueous phase once the temperature drops below the LCST [26]. The phase transition responsible for the aggregation and the subsequent precipitation of the polymer out of solution is taking place since hydrogen bonding becomes weaker and breaks as the temperature is raised. Temperature-sensitive polymers change from hydrated random coil to hydrophobic globule. As the temperature rises and approaches the phase transition point, the first step of the phase separation is the breaking up of the relatively strong hydrogen bonds, formed around the polymer coil between water molecules and the NH or C=O groups of the temperature-sensitive polymers, followed by the collapse of the polymer molecule into a hydrophobic globule [24].



**Figure 2.4** Phase diagram of a system exhibiting lower critical solution temperature (LCST) [24].

Poly(*N*-isopropylacrylamide) or pNIPA is a hydrogel that had been much attractive and widely used in many applications especially in removal of heavy metal ion. Hideaki Tokuyama et al. (2010) [18] reported the adsorption of heavy metal ions (Cu(II), Cr(III)) and humic acid (HA) in aqueous solution by flocculation technique. The metal ions and HA were formed complexes (metal-HA) by being heated above LCST and adsorbed on grafted copolymer. The grafted copolymer was prepared using NIPA copolymer with *N,N*-dimethylaminopropylacrylamide (DMAPAA) or *N,N*-dimethylaminopropylacrylamide, methyl chloride quarternary (DMPAA-Q) and grafted onto a polypropylene film. Sachio Fukuoka et al. (2010) [34] synthesized *N,N,N',N'*-(tetrakis-2-pyridylmethyl)ethylenediamine (TPEN) and was subjected to *N*-isopropylacrylamide, poly(TPEN-NIPA) gels which used for extraction of Cd(III) ion from aqueous solution. In addition, the number of terminal polymerizable double bonds which towards improved molecular design of the polymer gel and affected the extraction temperature was studied.

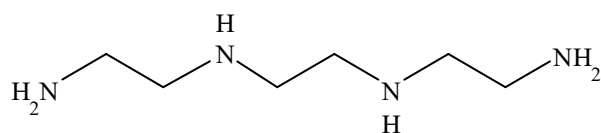
### 2.1.3 Preparation of poly(*N*-isopropylacrylamide)

The synthesis of pNIPA copolymers by radical polymerization technique has been widely used. The polymerization was carried out in water at temperature above

LCST under nitrogen atmosphere. Rzaev et al (2007) [20] synthesized of copolymer of NIPA with 2-(dimethylmaleimido)-*N*-ethylacrylamide in 1,4-dioxane which was initiated by AIBN under nitrogen atmosphere at a temperature of 70 °C . Hirata et al (2004) [35] synthesized poly(*N*-isopropylacrylamide) at the temperature range of 60-80 °C and the solution was degassed to initiate the polymerization. Zhao et al (2008) [36] synthesized the hydrogel in two ways including a normal water bath heating method and a microwave irradiation method, *N*-isopropylacrylamide was a monomer and *N,N*-methylenebisacrylamide was an initiator, the mixture reacted in water bath at 80 °C under nitrogen atmosphere for the first method and another way, the mixture was dissolved in degassed acetone and bubbled N<sub>2</sub>. The polymerization was carried out in a microwave accelerator at 80 °C.

## 2.2 Triethylenetetramine

Triethylenetetramine (TETA) is a useful ligand for metal complexing agent. Its structure and physical and chemical properties are presented in Figure 2.5 and Table 2.4, respectively.



**Figure 2.5** The molecular structure of Triethylenetetramine

**Table 2.4** Physical and chemical properties of Triethylenetetramine [39]

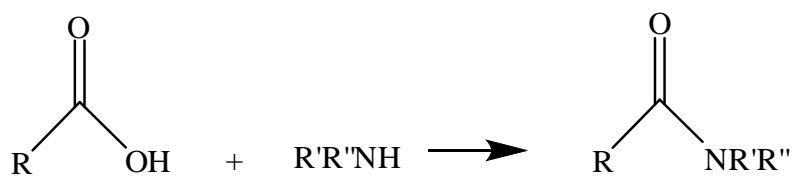
<b>Properties</b>	<b>Value</b>
Appearance	Liquid (Oily liquid) yellowish
Synonym	<i>N,N'</i> -Bis(2-aminoethyl)ethane-1,2-diamine
Formula	$C_6H_{18}N_4$
Molecular weight (g mol <sup>-1</sup> )	146.24
Melting point	12 °C
Boiling point	266°C
Water solubility	Easily soluble in cold water

TETA as a crosslinker introduces functional groups that hence improve the adsorption behavior of the polymer, these structure has nitrogen atoms which contain lone pair electron defining as an electron pair donor and a metal ion as an electron pair acceptor to form stable metal complexes with a variety of metal ions [27]. Zhang et al (2010) [37] modified activated carbon with triethylenetetramine (TETA) to obtain (AC-TETA) for preconcentration and determination of trace Cr(III), Fe(III) and Pb(II) in the water sample. These method was relatively high capacity and faster rate of adsorption and desorption and convenient. Mahmoud et al (2013) [38] prepared the adsorbent by the direct surface impregnation of magnetic nano-iron oxide with nano-silicon oxide and immobilization of triethylenetetramine to be a nano-sorbent (Nano-Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-TETA) sorbent. The sorbent was used for removal of heavy metal ions such as Cu(II) and Pb(II) from water samples using both bath and microcolumn techniques.

## 2.3 Amide formation

### 2.3.1 Heat induced amidation reaction

Carboxylic acids and amines can react together to form salts, strong heating of these salts can lead to amide formation. This reaction is carried out in hot acetic acid with continuous distillation to remove excess acetic acid and water. Therefore the reaction is driven towards the amide in 1993 (Figure 2.6). The preparation of a range of amides by heating a mixture of different amines and carboxylic acids in the absence of any catalyst or coupling agent was reported [15]. The optimum conditions for the heating of carboxylic acid amine mixtures were found to be between 160-180 °C for 10-30 minutes [28].



**Figure 2.6** The amidation reaction from carboxylic acid and amine [28]

## 2.4 Adsorption

Adsorption is the process in which atoms, ions or molecules from a substance (it could be gas, liquid or dissolved solid) adhere to a surface of the adsorbent. Adsorption is a surface-based process where a film of adsorbate is created on the surface while absorption involves the entire volume of the absorbing substance.

### *Physisorption*

This physical adsorption is the attraction between adsorbates and adsorbents via van der Waals force. The geometrical structure and electronic characteristics of the adsorbed molecule or atom and also of the surface are essentially preserved.



### Chemisorption

Chemical adsorption occurs when there is the formation of a chemical (often covalent) linkage between adsorbate and substrate which is stronger than van der Waals force found in physisorption.

## **2.5 Determination of metal**

Flame atomic absorption spectroscopy (FAAS) is one of techniques used to determine qualitatively and quantitatively of analyte in a liquid sample. Process of atomization by flame starts that liquid sample is aspirated into a nebulizer to form aerosol. The aerosol is introduced into flame. The step of atomization is desolvation, evaporation and finally atomization. An atom let through the fire a light beam with such a wavelength that can be absorbed by ground state atoms and thus the decrease of light intensity of free atoms of analyte is measured in the atomizer.

### Flames

Air-acetylene flame (2,000-2,300 °C): for readily atomizable metals (alkali metals, Mg, Ca in the absence of interferents, Zn, Cu, Cd, Pb, Mn, Fe, casually Cr)

Nitrous oxide- acetylene flame (2,800-3,000 °C): for hardly atomizable elements (Sr, Ba, V, Cr, Mo, Al, Si, B etc.) [40]

The relationship between the decrease of light intensity at the wavelength of the examined metal and the concentration of free atoms in a unit of volume is described by

$$\text{Lambert-Beer law as follows: } A = \log \frac{I_0}{I} = a.c.l$$

where A = absorbance

$I_0$  = initial light intensity before absorption

I = light intensity after absorption

$a$  = absorption coefficient (constant depending on material properties)

$c$  = number of free ground state atoms in the atomizing unit (flame)

$l$  = length of way passing the light in the atomizing unit [41]

## 2.6 Characterization technique of copolymer

Infrared spectroscopy is an absorption method in the wavelength region of 1 to 100  $\mu\text{m}$  in that extends the region of the visible light to longer wavelengths and smaller frequencies/energies. The energy of infrared light excites vibrational and rotational motions in molecules. IR spectroscopy is used to investigate structural elements of biological systems but it is limited by the presence of water. In biological molecules the interesting resonance frequencies of the C=N, C=O, N-H or O-H vibrations are often hidden by the strong IR absorption of water at around 1600 and 3400  $\text{cm}^{-1}$ . Infrared spectra are usually presented by a plot of the percentage of transmission and the wave number in  $\text{cm}^{-1}$ . A typical IR spectrum is therefore recorded from about 4000 to 10000  $\text{cm}^{-1}$  (upper limit) to about 100-800  $\text{cm}^{-1}$  (lower limit).

Conventional spectroscopy is frequency domain spectroscopy in which radiant power data are recorded as function of frequency. In time domain spectroscopy, which is achieved by Fourier Transform (FT), the whole spectrum in the magnetic resonance, microwave and infrared regions was recorded simultaneously.

In this signal, its output will be an oscillating signal, again of frequency  $\nu$ . The detector output is considered a function of time (time domain spectroscopy instead of frequency domain spectroscopy) [42].

Infrared spectroscopy is a very useful technique for characterization of polymers.

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Apparatus

##### 3.1.1 Flame atomic absorption spectrometer

A flame atomic absorption spectrometer (FAAS) (Perkin-Elmer) was used for the determination of metal concentration. The instrumental parameters are listed in Table 3.1.

**Table 3.1** FAAS conditions for the determination of metal concentration.

Operating condition	Cu(II)	Pb(II)	Cr(III)
Wave length (nm.)	324.8	283.3	357.9
Slit width (nm.)	0.7	0.7	0.7
Lamp type	HCL	HCL	HCL
Lamp current (mA.)	15	10	25
C <sub>2</sub> H <sub>2</sub> flow rate (mL min <sup>-1</sup> )	3	2	3
Air flow rate (mL min <sup>-1</sup> )	10	10	10

##### 3.1.2 Fourier transforms infrared spectrometer

A Fourier Transforms Infrared Spectrometer model Nicolet FT-IR 6700 was used for the characterization of polymer by using Attenuated Total Reflection (ATR) mode and infrared spectra were recorded in the wave number range of 400 – 4,000 cm<sup>-1</sup>.

### 3.1.3 pH Meter

The pH values of solution were measured by pH Meter Metrohm model 744.

### 3.1.4 Thermostatic water bath and ultrasonic bath

A thermostatic water bath model RCS 6-D (Lauda Brinkmann) was used to control temperature in the process of adsorption of metal ions at various temperatures.

An ultrasonic bath was used to sonicate the polymer solution.

## 3.2 Chemicals and preparation of reagents

### 3.1.1 Chemicals

All Chemicals were AR grade listed in Table 3.2

**Table 3.2** Chemical list

Chemicals	Supplier
<i>N</i> -isopropylacrylamide (NIPA)	Sigma-Aldrich
Maleic acid 99% (MA)	Sigma-Aldrich
<i>N,N'</i> -Methylenebisacrylamide 98% (MBAA)	Sigma-Aldrich
Ammonium persulfate 98% (APS)	Fluka
Triethylenetetramine 60% (TETA)	Sigma-Aldrich
Chromium(III)Nitrate Standard solution (1,000 mg L <sup>-1</sup> )	Merck
Copper(II)Nitrate Standard solution (1,000 mg L <sup>-1</sup> )	Merck
Lead(II)Nitrate Standard solution (1,000 mg L <sup>-1</sup> )	Fisher Chemical
Nitric acid 65%	Merck
Hydrochloric acid 37%	Merck
Sodium hydroxide	Merck
Nitrogen gas 99.999%	BIG

### **3.2.2 Preparation of reagent**

All solutions were prepared by using deionized (DI) water.

#### **(a) Chromium(III), copper(II) and lead(II) standard solutions**

All metal stock standard solutions were prepared by dilution of 1,000 mg.L<sup>-1</sup> stock standard solution to the required concentrations.

#### **(b) Nitric acid**

Nitric acid (1, 5, 10, 15 % v/v and 1 mol.L<sup>-1</sup>) were prepared for adjusting pH and desorbing of metal ions by dilution from the concentration solution.

#### **(c) Sodium hydroxide**

Sodium hydroxide (1, 5% w/v and 1 mol.L<sup>-1</sup>) solutions were prepared by dissolving the appropriate amount of NaOH in DI water to required concentration for pH adjustment.

#### **(d) Hydrochloric acid**

Hydrochloric acid (5, 10 and 15% v/v) were prepared for desorbing of metal ions by dilution from the concentration solution

### **3.3 Synthesis of copolymers**

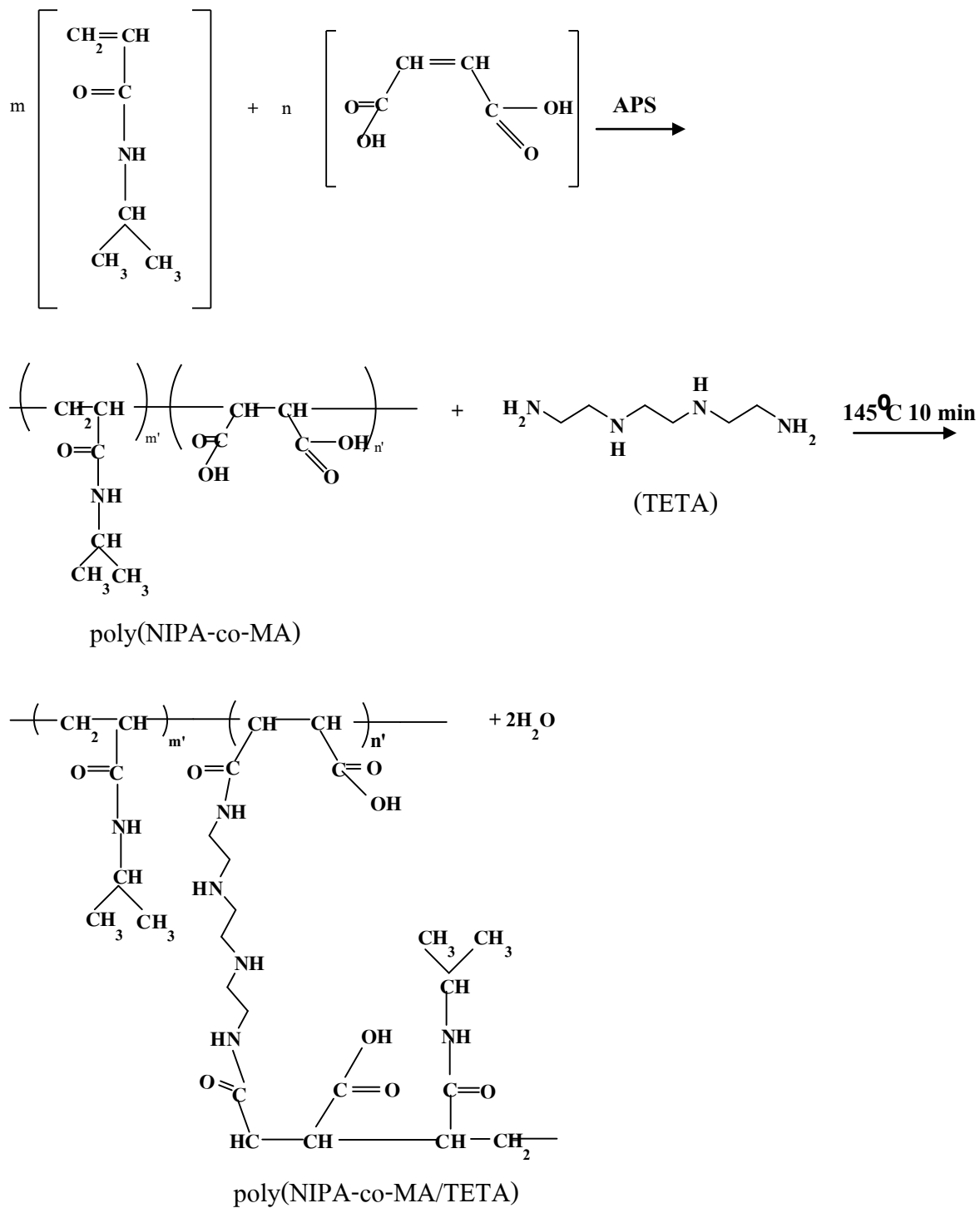
The preparation conditions of copolymerization are shown in Table 3.3.

**Table 3.3** Synthesis conditions of copolymer

<b>Chemical substance</b>	<b>Function</b>	<b>Final concentration (mM)</b>
<i>N</i> -isopropylacrylamide (NIPA)	monomer	1,660
Maleic acid (MA)	comonomer	880
<i>N,N'</i> -Methylenebisacrylamide (MBAA)	co-crosslinker	68
Ammonium persulfate (APS)	initiator	10
Triethylenetetramine (TETA)	crosslinker	4,103

*N*-isopropylacrylamide (NIPA), maleic acid (MA) and *N,N'*-methylenebisacrylamide (MBAA) were dissolved in 9 mL of DI water in a test tube (0.7 cm i.d.). After that the solution was sonicated at room temperature for 15 minutes, the solution was kept under nitrogen atmosphere for 30 minutes and heated in water bath at 60-80 °C. The polymerization took place when added 1 mL of ammonium persulfate (APS) in to the solution. The duration of gelation was 1 hour. After that the polymer gel was cut in to pieces having a length of 1 cm. The hydrogel polymer was dried at 100 °C until constant weight. Later the hydrogel polymer was soaked in triethylenetetramine (TETA) solution for 24 hours, followed by a heat-induced amidation crosslinking reaction at 145 °C for 10 minutes in an oven, the polymer was dried to constant weight at 100 °C and was washed repeatedly by DI water several times to remove the unreacted crosslinker. Then drying overnight was performed again to obtain a constant weight. The copolymer obtained is shown in Figure 3.1.

**Figure 3.1** Picture of copolymer rods



**Figure 3.2** The synthesis pathway of copolymer

### **3.4 Characterization**

The synthesized copolymer was characterized by Fourier transforms infrared spectrometry.

### **3.5 Chromium(III), copper(II) and lead(II) ions adsorption**

#### **3.5.1 Effect of pH**

The effect of pH of metal solution was investigated in the range of pH 1.0-7.0. pH adjustments were made with HNO<sub>3</sub> (1 and 5 %v/v) and KOH (1 and 5 %w/v). The two categories of copolymer, with TETA and without TETA were equilibrated by immersing in 10 mL of metal solution as Pb(II) (20 mg.L<sup>-1</sup>), Cr(III) (5 mg L<sup>-1</sup>) and Cu(II) (5 mg L<sup>-1</sup>), and shaking for 12 hours. Thereafter, the initial and residual concentrations of all metals in the solution were determined by FAAS.

#### **3.5.2 Effect of adsorption time**

The polymer gels crosslinked with TETA were immersed in each metal solution (10 mL) with the same concentration as used in Section 3.5.1 and shaken at room temperature. To investigate the effect of adsorption time, a range of 0.5-12 hours was studied. The initial and residual concentrations of all metals in the solution were determined by FAAS.

#### **3.5.3 Effect of adsorbent size and surface area**

The effect of adsorbent size and surface area was evaluated using 10 mL of individual metal solution with the same concentration as presented in 3.5.1.

Different sizes of the cylindrical shape of hydrogel adsorbents with 0.7 cm diameter, varying lengths from 0.25-1.0 cm were immersed in metal solution and shaken at room temperature for 8 hours. A 1 cm length adsorbent was divided into 2, 4 and 8 pieces to increase its surface area and put into a metal solution and shaken at



room temperature for 8 hours. The remaining metal concentration in the solutions was determined by FAAS.

#### **3.5.4 Effect of temperature**

The size of adsorbents was 0.7 cm diameter and 1.0 cm length. The initial concentration of Pb(II) was 20 mg L<sup>-1</sup>, and 5 mg L<sup>-1</sup> for Cr(III) and Cu(II). The adsorption investigation was done using the optimum pH and adsorption time. The effect of temperature was studied by varying the temperature in the range of 23-80 °C.

### **3.6 Chromium(III), copper(II) and lead(II) ions desorption**

#### **3.6.1 Types of desorbing solution**

The copolymers containing adsorbed each metal ions under optimum pH, adsorption time and temperature were immersed for 2 hours in 3 mL of HCl and HNO<sub>3</sub> with the concentrations of 5, 10, and 15 % (v/v). The concentration of metal in desorbing solution was determined by FAAS.

#### **3.6.2 Effect of desorption time**

The range of desorption time of 10 minutes to 1 hour was investigated using the appropriate desorbing solution. The concentrations of all metals were determined by FAAS.

#### **3.6.3 Effect of temperature**

The effect of temperature was investigated by varying the temperature in the range of 25-60 °C for 2 hours. The concentration of all metal ions in desorbing solutions was determined by FAAS.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of copolymers

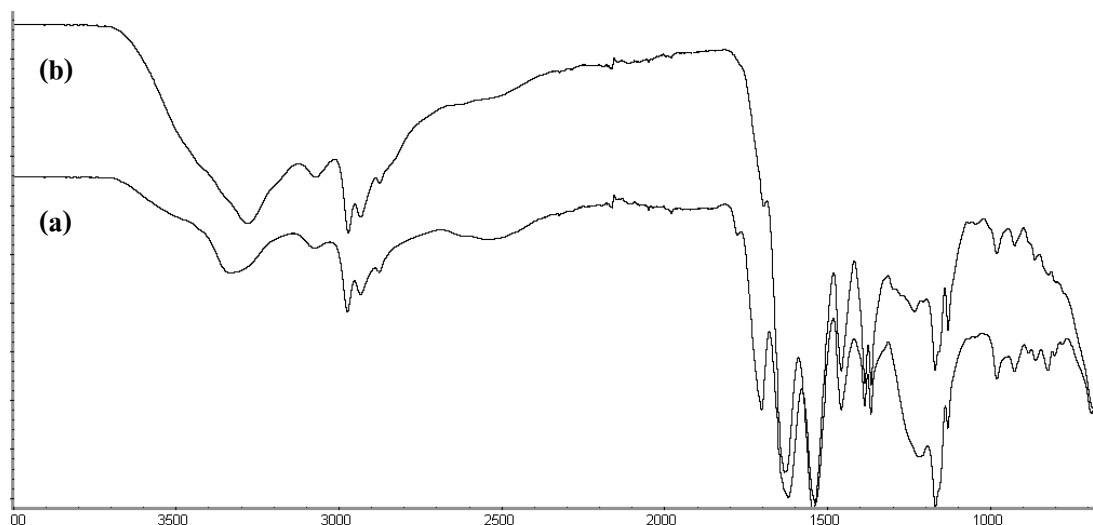
The copolymers consisting of *N*-isopropylacrylamide (NIPA), maleic acid (MA) *N,N'*-methylenebisacrylamide (MBAA), the mole ratio of *N*-isopropylacrylamide to maleic acid was fixed at 65:35 and triethylenetetramine as a crosslinker which were synthesized by free radical copolymerization, initiated by ammonium persulfate (APS). The crosslinking was done by heat induced amidation reaction at a temperature of 145 °C for 10 minutes. This condition was chosen based on the literature [28].

As mentioned in Chapter III, two kinds of copolymer crosslinked with TETA and without TETA were compared for adsorption efficiency.

#### 4.2 Characterization of Copolymers

Two kinds of copolymer were characterized by Fourier transform infrared spectroscopy (FTIR) as mentioned in Chapter III. The FT-IR spectra of poly(NIPA-co-MA) and poly(NIPA-co-MA)/TETA are displayed in Figure 4.1 (a and b). The poly(NIPA-co-MA)/TETA showed IR spectrum in the wave numbers of 1690-1630  $\text{cm}^{-1}$  which was the characteristic peaks of carbonyl group of amide but the characteristic peak of carbonyl group of carboxylic acid being in the wave numbers of 1705-1720  $\text{cm}^{-1}$  were not present. This position was different from poly(NIPA-co-MA). The result concluded that the amide bond between amine group of TETA and carboxylic group of maleic acid occurred by heat induced amidation reaction.

In conclusion, FT-IR characterization was entirely clear for confirming the crosslinking of TETA onto the poly(NIPA-co-MA).



**Figure 4.1** FT-IR spectra of (a) poly(NIPA) without TETA, (b) poly(NIPA) crosslinked with TETA

### 4.3 Chromium(III), copper(II) and lead(II) ions adsorption

The synthesized copolymers were used in adsorption study for chromium(III), copper(II) and lead(II) ions in aqueous solution using batch method. The adsorption of various parameters such as pH and temperature of metal ion solution, adsorption time, adsorbent size and surface area were investigated.

The adsorption capacity was presented in quantity of metal (mg) per one gram of polymer calculated according to Equation 4.1.

$$\text{Adsorption capacity} = \frac{C_i - C_e}{1000} \times V \times \frac{1}{w} \dots\dots\dots(4.1)$$

where  $C_i$  = initial concentration of metal ion in the solution ( $\text{mg L}^{-1}$ )

$C_e$  = equilibrium concentration of metal ion in the solution ( $\text{mg L}^{-1}$ )

$V$  = volume of metal solution (mL)

$w$  = weight of polymer (g)

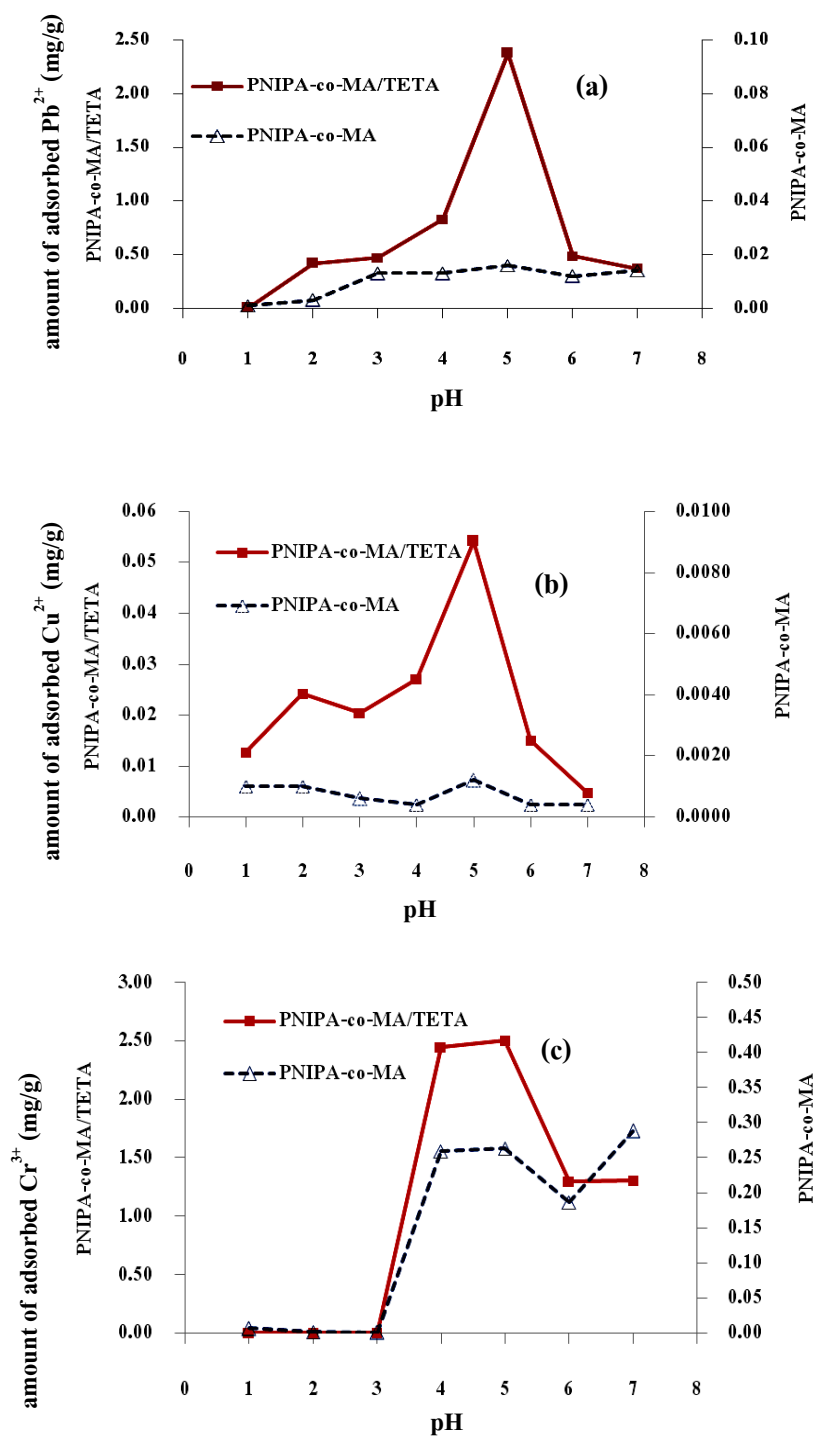
### 4.3.1 Effect of pH

The pH of metal solution affected the precipitation of metal ion. Therefore, the effect of pH metal adsorption should be preliminary studied.

The effect of metal solution with the pH range of 1-7 was investigated, and the adsorption time was fixed at 12 hours. The result of metal adsorption on the adsorbent was displayed as a function of pH in Figure 4.2 (a-c).

The adsorption of all metal ions were compared between the adsorbent of poly(NIPA-co-MA)/TETA and poly(NIPA-co-MA) and the result showed that copolymer crosslinked with TETA had more adsorption efficiency than the copolymer without TETA. Therefore, TETA, which crosslinked on copolymer, enhanced the adsorption efficiency of metal ions by forming a complex of metal-TETA.

The optimum pH for the adsorption of metal was 5 and the adsorption efficiency reduced in the pH range of 1-4 because the amine functional group in TETA might be protonated by proton ( $H^+$ ) in solution and at high pH, the precipitation of metal hydroxide occurred; as a result, the adsorption efficiency also decreased.

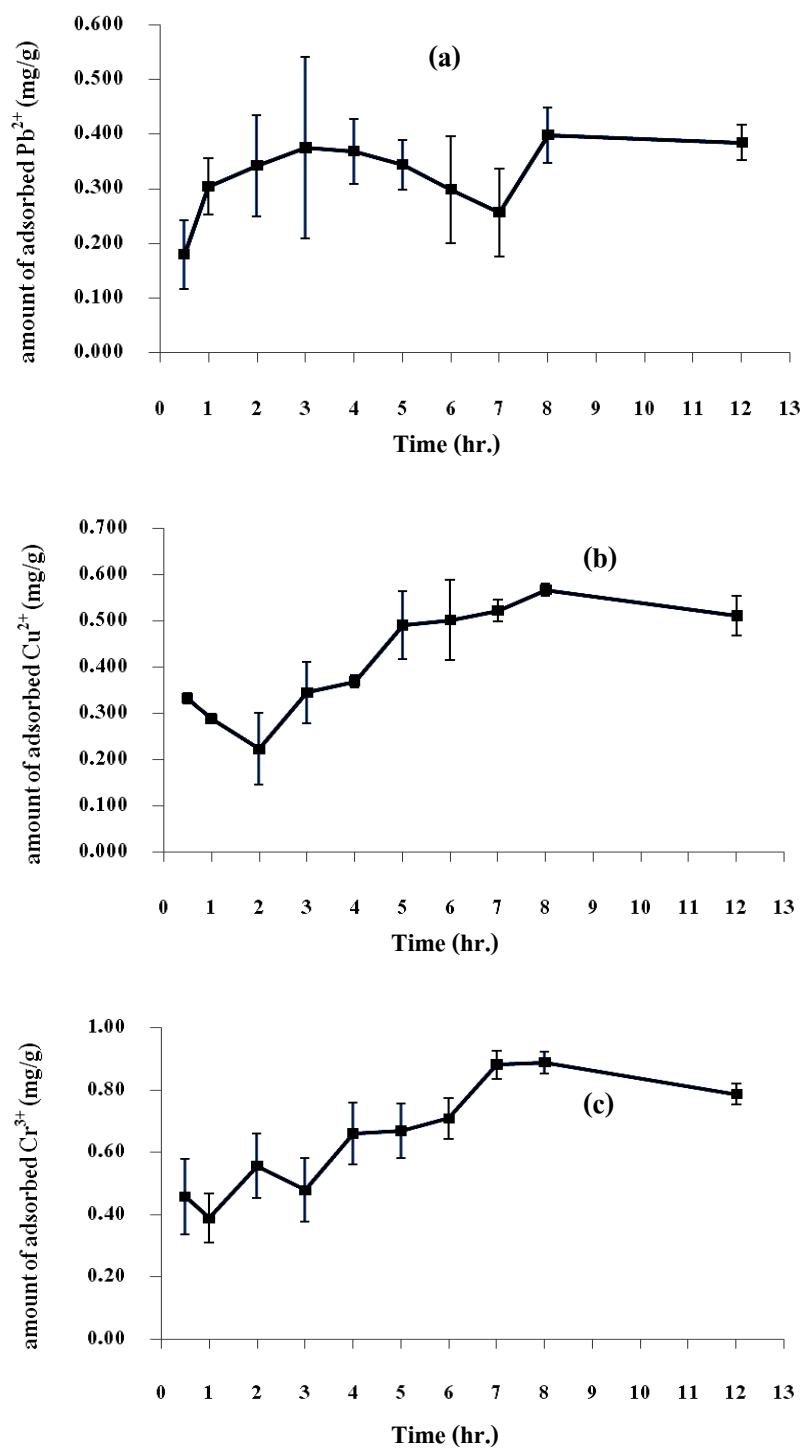


**Figure 4.2** Amount of adsorbed metal ions by copolymer crosslinked with TETA and without TETA (a) Pb(II), (b) Cu(II), (c) Cr(III)

### **4.3.2 Effect of adsorption time**

The effect of adsorption time for metal ions onto the polymeric adsorbent at optimum pH with various times was studied. The estimation could be performed by increasing time until the adsorbent provided the constant value of adsorption. The result, as shown in Figure 4.3, indicated that the adsorption capacity increased with the increasing of adsorption time and reached the equilibrium within different times for each metal ion.

The adsorption efficiency slightly increased by increasing adsorption time and reached the equilibrium after 2 hours for Pb(II), 5 hours for Cu(II) and 7 hours for Cr(III).



**Figure 4.3** Effect of adsorption time by copolymer cross linked with TETA (a)  $Pb(II)$ , (b)  $Cu(II)$ , (c)  $Cr(III)$

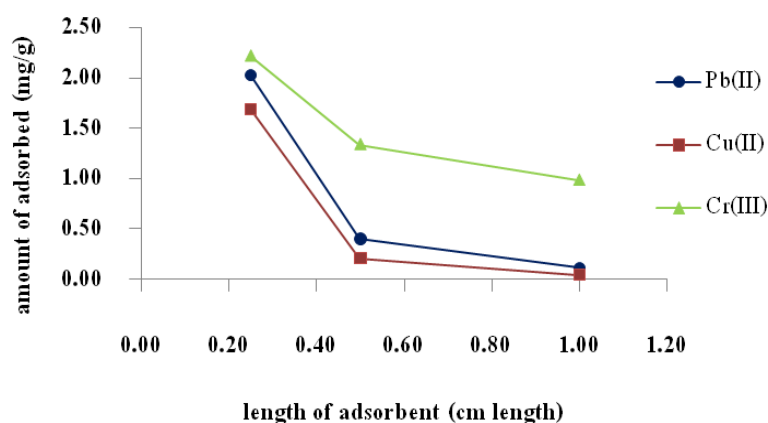
However, the adsorption amount of each experiment fluctuated (high standard deviation value) possibly due to the heterogeneous surface of the adsorbent resulting from the heterogeneous copolymeric hydrogel that was prepared at the temperature over the LCST.

#### 4.3.3 Effect of adsorbent size and surface area

The effects of adsorbent size and surface area were studied. Adsorption behavior of the sorbent was investigated by varying the size of 0.7 cm diameter adsorbent including 0.25, 0.50, 1.0 cm length. In addition, the surface area of adsorbent was increased by splitting the 1.0 cm length gel into 2, 4 and 8 pieces.

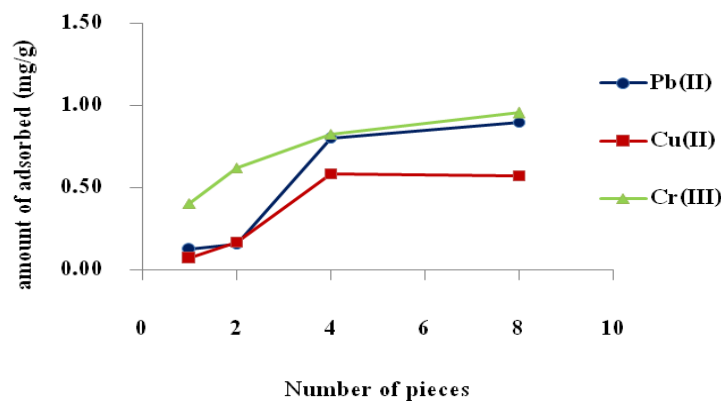
Increasing of length of polymer, as a result the adsorption efficiency decreased because the ratio of surface area to weight was reduced.

Increasing the number of pieces of adsorbent or increasing the surface area, the result showed that the adsorption efficiency increased. And the efficiency of adsorbent slightly increased from 4 to 8 pieces. It concluded that the optimum surface area is 4 pieces of adsorbent.



**Figure 4.4** Effect of size of adsorbent by copolymer crosslinked with TETA



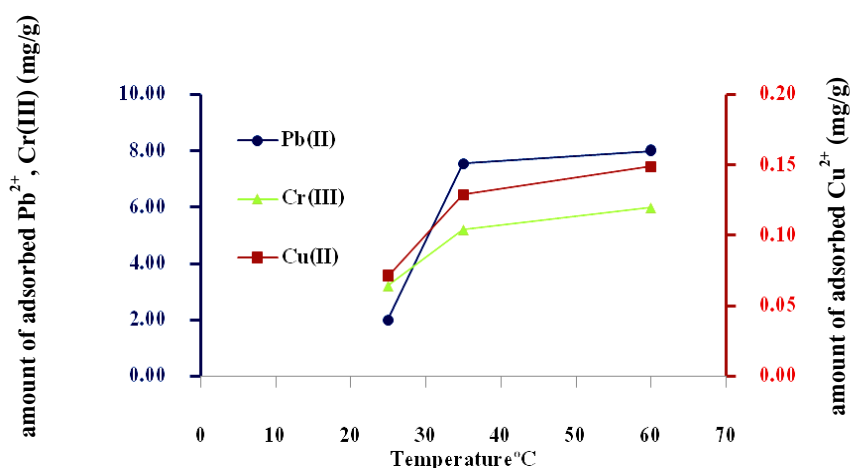


**Figure 4.5** Effect of surface area of adsorbent by copolymer crosslinked with TETA

#### 4.3.4 Effect of temperature

The adsorption capacity towards metal ions was investigated as a function of temperature at optimum pH and appropriate contact time. From the literature it has been known that poly(NIPA) hydrogel was a representative of temperature-responsive polymer since it exhibits a sharp phase transition in water. It has a lower critical solution temperature (LCST) in the vicinity of 32 °C. It means that at a temperature lower the LCST, the hydrogel exhibits poor adsorbability towards metal ions and exhibits hydrophilic and swelling behavior. When the temperature increases above LCST, the hydrogel can trap metal ions, because in this state hydrogen bonds between hydrogel and water were broken, as a result the hydrogel exhibited hydrophobic and collapsed.

The temperatures of 25, 35 and 60 °C were investigated for adsorption of all metal ions. The adsorption efficiency obviously increased when the temperature rose due to the unique property of hydrogel that shrinks and can trap metal ions at high temperature. For all metal ions, the adsorption efficiency slightly increased from the temperature of 35-60 °C, denoting the adsorption efficiency not only depended on temperature because the polymer contains TETA as a crosslinker and also increased the adsorption efficiency.



**Figure 4.6** Effect of temperature on metal adsorption by copolymer crosslinked with TETA

#### 4.4 Chromium(III), copper(II) and lead(II) ions desorption

The metal ions desorption efficiency is expressed in term of percentage desorption or elution, calculated according to Equation 4.4.

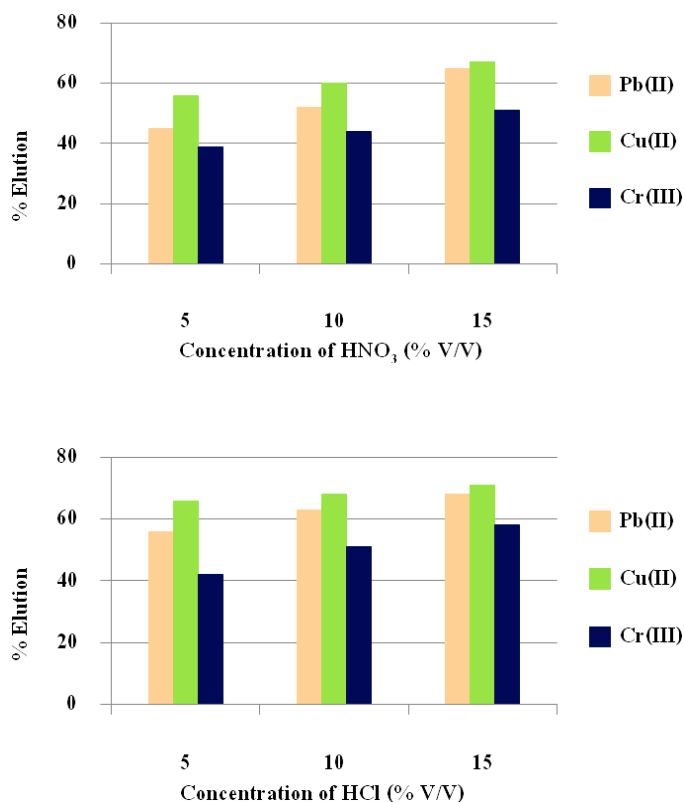
$$\% \text{ elution} = \frac{m_d}{m_a} \times 100 \quad (4.4)$$

where  $m_d$  = amount of metal ion eluted from adsorbent (mg)

$m_a$  = amount of metal ion adsorbed onto adsorbent (mg)

##### 4.4.1 Types of desorbing solution

The desorption of metal ion was studied using different types and concentrations of eluent. Suitable eluent has to be compatible with the determination technique if an analytical application is desired. The selection of eluent depends on the adsorption mechanism and the possibility to perturb interactions between metal ion and functional group of polymer. The result is presented in Figure 4.7.

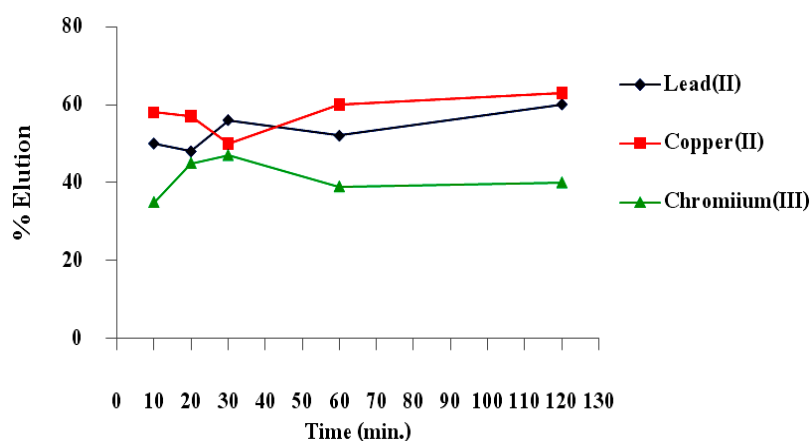


**Figure 4.7** Desorption percentage of metal ions in different types of desorbing solution

HCl showing the desorption percentage of 40-70 %, seemed to be a quite better desorbing solution than HNO<sub>3</sub> with the desorption percentage of 38-65 %. When the concentration of acid increased, the desorption percentage increased for both acid solutions. The order of desorption percentage was Cu(II) > Pb(II) > Cr(III). It could be described that in acidic solution, the amine moieties could be protonated by protons hence releasing metal ions. However, the desorption percentage could be improved by increasing desorption time and acid concentration or varying desorption temperature.

#### 4.4.2 Effect of desorption time

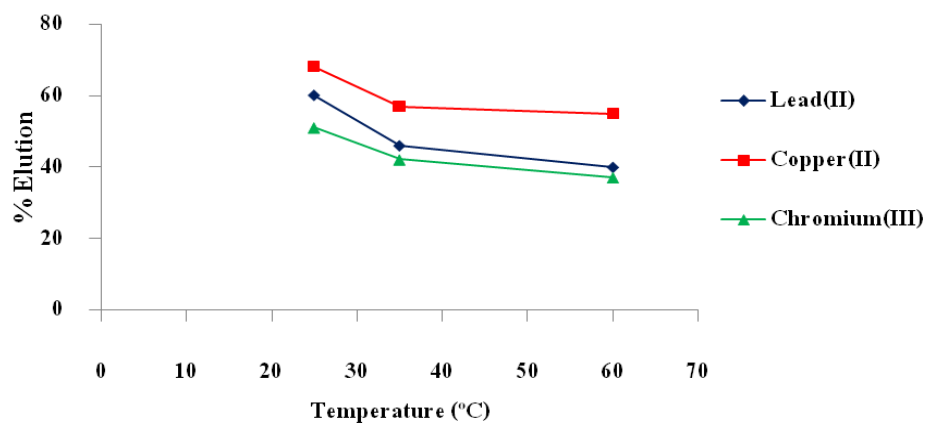
The rate of desorption was investigated at 25 °C. The results in Figure 4.8 showed the desorption of metal ions by 15 % (v/v) HCl as a function of time. Metal ions adsorbed from polymers hence the elution percentages increased gradually until 1 hour after that the equilibrium was attained. The highest elution percentages occurred after 2 hours.



**Figure 4.8** Effect of desorption time on metal ion desorption at 25°C.

#### 4.4.3 Effect of temperature

The desorption of metal ions from the adsorbent polymer was examined in term of temperature using its appropriate eluent and 2 hours desorption time. The results are presented in Figure 4.9.



**Figure 4.9** Effect of temperature on metal ion desorption onto polymer

The desorption percentage of all metal ions decreased when increasing temperature. This phenomenon could be explained by a special property of hydrogel that when temperature increases the hydrogel shrinks due to breaking of hydrogen bonding and losing water molecules. The metal ions were hardly eluted from the hydrogel sorbent. In conclusion, the temperature was significant for the desorption of metal ion from poly(NIPA) gels.

## CHAPTER V

### CONCLUSION

A new copolymer poly(NIPA-co-MA)/TETA consisting of monomers which are *N*-isopropylacrylamide (NIPA) and maleic acid crosslinked with triethylenetetramine was successfully synthesized through free radical copolymerization in an aqueous system using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as initiator at 60 °C. The synthesized copolymers were exposed to metal ion adsorption comparing with poly(*N*-isopropylacrylamide) without TETA or poly(NIPA-co-MA). Various parameters influencing the adsorption and desorption were studied. The percent mole ratio of *N*-isopropylacrylamide to maleic acid was fixed at 65:35 and crosslinked by heat induced amidation reaction at the temperature of 145 °C. The synthetic copolymers were characterized by Fourier Transforms Infrared (FT-IR) Spectroscopy. The result could evidently confirm the successful copolymerization.

The synthesized polymers were used for the adsorption of Pb(II), Cu(II) and Cr(III) ions in aqueous solution using batch method. The effect of pH and temperature, adsorption time, adsorbent size and surface area was investigated. Moreover, in the desorption study, the effect of types of desorbing solution, desorption time and temperature was investigated. The adsorption and desorption conditions were suggested in Table 5.1.

**Table 5.1** Adsorption and desorption conditions of poly(NIPA-*co*-MA)/TETA

Conditions	Pb(II)	Cu(II)	Cr(III)
Adsorption			
pH	5	5	4-5
Temperature (°C)		> 35	
Adsorption time (hours)	2	5	7
Size	Small pieces		
Surface area	1 cm length rod polymer, divided into 4 pieces		
Desorption			
Desorbing solution		15 % (v/v) HCl	
Desorption time (min)	30	60	30
Temperature		< 25	

### Suggestions for future works

- The synthesized copolymers shall be applied for real wastewater samples.
- Only rod form of the synthesized hydrogels was proposed in this study. There was limitation in the application. Other preparation method shall be examined to obtain other forms such as thin film, small particles or fiber in order to increase the specific or exchange surface area.
- These copolymers may be applied to prepare composite incorporating absorbents by filling inorganic constituent such as silica, hydroxyapatite for developing their properties.
- Adsorption isotherm shall be studied.

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