การแยกและการเพิ่มความเข้มข้นไอออนโลหะจากน้ำโดยใช้แอนไอออนเอกซ์เชนจ์เรซินโหลดด้วย
ไพเพอราซีนไดไทโอคาร์บาเมต

นางสาวศุภาวรรณ ออกฉิม

SEPARATION AND PRECONCENTRATION OF METAL IONS FROM WATER
USING ANION-EXCHANGE RESIN LOADED WITH
PIPERAZINEDITHIOCARBAMATE

Miss Supawan Augchim

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
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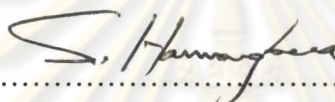
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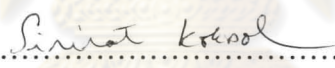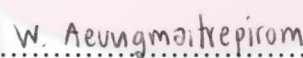By   Miss Supawan Augchim
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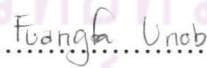
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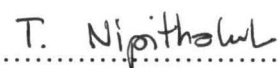
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ศุภาวรรณ ออกฉิม : การแยกและการเพิ่มความเข้มข้นไอออนโลหะจากน้ำโดยใช้แอน
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PRECONCENTRATION OF METAL IONS FROM WATER USING ANION-
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อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. วัลภา เอื้องไมตรีภิรมย์, 76 หน้า.

แอนไอออนเอกซ์เชนจ์เรซินโหลดด้วยไพเพอราซีนไดไทโอคาร์บาเมตเกิดได้โดยผ่านกลไก
การแลกเปลี่ยนแอนไอออน พิสูจน์เอกลักษณ์ของคอมเพลกซิงเรซินชนิดใหม่ที่สังเคราะห์ได้ด้วย
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มีค่าเท่ากับ 3.5 ไมโครโมลต่อกรัม ศึกษาการแยกไอออนโลหะได้แก่ เงิน ทองแดง ตะกั่ว และทอง
ในระบบแบชท์พบว่า ค่าพีเอชที่เหมาะสมในการแยกเงินและทองแดงเท่ากับ 7 และ 2 ตามลำดับ
ส่วนค่าพีเอชที่เหมาะสมในการแยกตะกั่วและทองเท่ากับ 5 เวลาในการสกัดที่เหมาะสมสำหรับ
เงินและตะกั่วอยู่ที่ 15 และ 20 นาที ตามลำดับ ในขณะที่ทองแดงและทองใช้เวลาในการสกัดสูง
ถึง 60 นาที พฤติกรรมการดูดซับไอออนโลหะทั้ง 4 ชนิดเป็นไปตามโมเดลของแลงเมียร์ มีค่าความ
จุการดูดซับตามลำดับดังนี้ ตะกั่ว > เงิน > ทองแดง > ทอง โดยมีค่าความจุการดูดซับสูงสุดเป็น
81.1, 74.2, 43.5 และ 21.9 ไมโครโมลต่อกรัม ตามลำดับ สำหรับระบบคอลัมน์ศึกษาการแยก
และการเพิ่มความเข้มข้นของเงินและตะกั่ว พบว่าอัตราการไหลที่เหมาะสมของสารละลายเงิน
และตะกั่ว เท่ากับ 3.0 และ 4.0 มิลลิลิตรต่อนาที ตามลำดับ ตัวชะที่เหมาะสมของไอออนเงิน
ได้แก่ สารละลายไทโอยูเรีย 0.5 โมลต่อลิตรในกรดไฮโดรคลอริก 1 โมลต่อลิตร ที่อัตราการไหล
0.25 มิลลิลิตรต่อนาที ปริมาตร 5.0 มิลลิลิตร และไอออนตะกั่วถูกชะด้วยสารละลายอีดีทีเอ 0.2
โมลต่อลิตรในกรดไฮโดรคลอริก 0.1 โมลต่อลิตร ที่อัตราการไหล 1.0 มิลลิลิตรต่อนาที ปริมาตร
5.0 มิลลิลิตร มีแฟกเตอร์การเพิ่มความเข้มข้นเป็น 10 และ 50 สำหรับไอออนเงินและตะกั่ว
ตามลำดับ ทั้งนี้ไอออนโซเดียม โพแทสเซียม และแคลเซียม ไม่มีผลต่อการแยกไอออนโลหะเมื่อ
เปรียบเทียบกับการแยกด้วยแคตไอออนเอกซ์เชนจ์เรซิน นำวิธีที่ได้ไปประยุกต์ในการเพิ่มความ
เข้มข้นของไอออนเงินและตะกั่วจากน้ำประปาและน้ำทะเล ด้วยวิธีการเติมก่อนตรวจวัดปริมาณ
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SUPAWAN AUGCHIM: SEPARATION AND PRECONCENTRATION OF METAL IONS FROM WATER USING ANION-EXCHANGE RESIN LOADED WITH PIPERAZINEDITHIOCARBAMATE. ADVISOR: ASST. PROF. WANLAPA AEUNGMAITREPIROM, Ph. D., 76 pp.

The anion exchange resin was successfully loaded with piperazinedithio-carbamate via anion exchange mechanism. The new synthesized complexing resin was characterized by IR spectroscopy. The loading capacity of complexing ligand onto resin at pH 5 during loading times of 8 min was found to be 3.5 μmol g^{-1}. The separation of the metal ions as Ag(I), Cu(II), Pb(II) and Au(III) was studied in batch method. The optimum pHs for the sorption of Ag(I) and Cu(II) were found to be 7 and 2, respectively. The optimum pH of Pb(II) and and Au(III) of 5 was obtained. The suitable contact time of Ag(I) and Pb(II) were found to be at 15 and 20 min, respectively. While Cu(II) and Au(III) showed long sorption kinetic within 60 min. The sorption behaviors of all metal ions fit well to the Langmuir's model and the sorption capacities in the order of Pb(II) > Ag(I) > Cu(II) > Au(III) were observed with the maximum sorption capacities of 81.1, 74.2, 43.5 and 21.9 μmol g^{-1}, respectively. For the flow system, the separation and preconcentration of Ag(I) and Pb(II) were studied. The optimum sample flow rates of Ag(I) and Pb(II) were obtained at 3.0 and 4.0 mL min^{-1}, respectively. The elution of Ag(I) was achieved by using 5.0 mL of 0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl at the flow rate of 0.25 mL min^{-1} and the Pb(II) was desorbed by 5.0 mL of 0.2 mol L^{-1} EDTA in 0.1 mol L^{-1} HCl at the flow rate of 1.0 mL min^{-1}. The preconcentration factor of 10 and 50 for Ag(I) and Pb(II) were obtained, respectively. Coexisting cations such as Na$^+$, K$^+$ and Ca^{2+} did not affect the recoveries of metal ions in comparison with cation exchange resin. The proposed method can be applied to preconcentrate Ag(I) and Pb(II) from tap water and sea water with spiked sample method before determination of Ag(I) and Pb(II) with FAAS resulting in high accuracy and precision.

Department :	Chemistry	Student's Signature :	Supawan Augchim
Field of Study :	Chemistry	Advisor's Signature :	W. Aeungmaitrepirom
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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

SPADNS	Trisodium salt of 2-(*p*-sulfophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulfonic acid
ATPS	Azothiopyrinesulfonic acid
ARS	Sodium 1,2-dihydroxyanthraquinone-3-sulfonate
BCS	2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline
Bromopyrogallol	Dibromopyrogallolsulfonphthaleine
Bismuthiol II	5-Mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione, potassium salt
EDTA	Ethylenediaminetetraacetic acid
Tiron	Disodium 1,2-dihydroxybenzene-3,5-disulfonate
Thoron	(1-(2-Arsonophenylazo)-2-hydroxy-3,6-naphthalenedisulfinic acid sodium salt
PV	Pyrocatechol Violet
HOx	5-sulfo-8-quinolinol
ANS	8-amino-naphthalene-2-sulfonic acid
$mg\ L^{-1}$	Milligram per litre
$\mu g\ L^{-1}$	Milcrogram per litre
$g\ mol^{-1}$	Gram per mole
cm^{-1}	Wave number
$g\ cm^{-3}$	Gram per cubic centimetre
$°C$	Degree celsius
$\mu\Omega$	Micro-ohm
LLE	Liquid liquid extraction
SPE	Solid phase extraction
FAAS	Flame atomic absorption spectroscopy
DCP-AES	Direct current plasma-Atomic emission spectrometry
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma-Mass spectrometry
^{1}H-NMR	Proton nuclear magnetic resonance
FT-IR	Fourier transforms infrared spectroscopy
DI	Deionized water
g	Gram

mmol	Millimole
mmol L^{-1}	Millimole per litre
mL	Millilitre
h	Hour
min	Minute
mm	Millimetre
nm	Nanometre
ppm	Part per million
ppb	Part per billion
meq L^{-1}	Milliequivalent per litre
meq g^{-1}	Milliequivalent per gram
μmol	Micromole
μmol g^{-1}	Micromole per gram
P.F.	Preconcentration factor
LOD	Limit of detection
LOQ	Limit of quantitation

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

The main drawback of heavy metals separation from water using conventional cation exchange resin is low selectivity. The development of the modified resin or the complexing resin can improve the selective separation of heavy metals from water. The anion exchange resin loaded with complexing ligands has been interesting for many years. The advantage of complexing resin is not only selective sorption of heavy metals but also preconcentration of many trace heavy metals [1-4].

The complexing ligands possessing anionic groups in their molecules come into contact with the anionic resin by means of anion exchange process. In particular, the binding sites such as O, N and S in their molecules can chelate with metal ions. The complexing ligands such as trisodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate [5], tetrakis (4-carboxyphenyl) porphyrin [6], and 1,8-dihydroxy-2-(pyrazol-5-ylazo)-naphthalene-3,6-disulphonic acid [7] were loaded onto surface of anion exchange resin for separation and preconcentration of heavy metals from water samples. Fortunately, dithiocarbamates are bidentate anionic ligands, offering two sulphur donor atoms (illustrated in Figure 1.1) and formed stable complexes with a large number of elements [8-10].
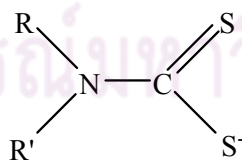
R, R′ = H, Alk, Ar

Figure 1.1 Chemical structures of dithiocarbamate derivatives.

From the anionic properties and their dithiocarbamate complexes, we attempt to modify dithiocarbamate ligand onto anion exchange resin since the selectivity and preconcentration of trace heavy metals from water become to inspiration of this thesis.

1.2 Research objectives

The aims of this work were focused on the modification of anion exchange resin with bis(sodium dithiocarbamate) piperazine as complexing ligand containing selective binding sites to heavy metals. Next, the complexing resin was applied for separation and preconcentration of trace metals from real water samples.

1.3 Scope of the research

The scopes of this work were the synthesis and characterization of the complexing ligand by FT-IR spectroscopy and ^{1}H-NMR spectroscopy. Then, the loading conditions of complexing ligand onto anion exchange resin were studied in parameter of solution pH, loading time, and complexing ligand concentration. Afterwards, the sorption of heavy metals such as Ag(I), Cu(II), Pb(II) and Au(III) on complexing resin were studied under static and dynamic methods. In static method, parameters such as solution pH, sorption time, concentration of metal ion solution and interfering ions were studied. The parameters of the flow rate of metal and eluent solution, sample volume, and reusability of complexing resin were evaluated in dynamic method.

Furthermore, the optimum conditions of this method were applied to real water samples as tab water and seawater with spiked method.

1.4 The benefits of the research

The selectivity and the enrichment of trace heavy metals were achieved using a new complexing resin before determination by FAAS.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Dithiocarbamate derivatives

Dithiocarbamates are widely used in several fields, e.g., agriculture as fungicides and pesticides, intermediates in organic synthesis, radio protectors in pharmaceuticals, vulcanizing agents in rubber chemistry and chelating agents in material chemistry [11-19].

An especially in a part of modified material chemistry, dithiocarbamates were added onto different solid supports for heavy metals removal, separation purposes or sometimes achieving more satisfying subsequent instrumental analysis [20-34]. The examples of their applications are listed in Table 2.1. Unfortunately, the properties of dithiocarbamates are often changed by thermal temperature and acid environment. Therefore, the stability of dithiocarbamates as a function of thermal decomposition and decomposition mechanism of dithiocarbamates in acid media were seriously considered [35- 40].

Table 2.1 The dithiocarbamate derivatives modified onto various solid materials and their applications

Dithiocarbamate derivatives	Type of modification	Type of solid material	Application	Ref.
N-(2-aminoethly-3-aminopropyl) dithiocarbamate	Immobilization	Silica gel	Adsorption of heavy metals	[20]
Sodium dithiocarbamate	Grafting	Poly(styrene-g-ethylene glycols)	Adsorption of heavy metals	[21]
Benzyl dithiocarbamate	Grafting	Polystyrene microspheres	Selective removal of Hg(II) ion	[22]
Uni-dithiocarbamate	Grafting	Silica gel	Extraction of Co(II)	[23]
Polydithiocarbamate	Immobilization	Polystyrene resin	Preconcentration and removal of trace heavy metals from waters	[24]
Polydithiocarbamate	Grafting	Macroreticular resin	Preconcentration of trace Mn(II) from mineral and tap water	[25]
Tris-dithiocarbamate	Grafting	Silica gel	Selective extraction of Hg(II) ion	[26]
Sodium salt of dithiocarbamate	Grafting	Silica gel	Removal of Hg(II)	[27]
Morphiline dithiocarbamate	Impregnation	Bagasse	Preconcentration of trace heavy metals from natural waters	[28]
Poly(acrylaminophosphonic) dithiocarbamate	Ion-exchanger	Polyacrylonitrile fiber	Preconcentration of rare earth element from seawater	[29]
Hexamethyleneammonium-hexamethylenedithiocarbamate	-	Amberlite XAD-16 resin	Preconcentration of trace metals from seawater and wastewater samples	[30]
Pyrrolinide dithiocarbamate	-	C_{18}-bonded Silica gel	Preconcentration of trace metal from seawater	[31]
1-Benzylpiperazinedithiocarbamate	-	Microstalline naphthalene	Preconcentration of Cd(II) from water samples	[32]
Sodium diethyldithiocarbamate	Immobilization	Silica gel	Preconcentration of trace metals from aqueous solution	[33]
Pyrrolidinedithiocarbamate and piperidinedithiocarbamate	Impregnation	Amberlite XAD-4 resin	Preconcentration of trace metals from saline matrices	[34]

2.2 Anion exchange resin

Anion exchange resins are spherical beads consisted of a network of cross-linked polymers containing functional groups with fixed cations that are positive charges located on each functional group along the resin surface. The functional groups on the surface of resin such as chloride ion or hydroxide ion that can be exchanged negative ions with negative charge of analyte ions in the bulk solution.

When the anion exchange resin (saturated with A^-) is immersed in solution, there is a tendency for A^- to diffuse into the bulk solution and B^- into the resin because of the concentration differences between the solution and the resin phases. The anion exchange mechanism is shown in equation 2.1.

$$R^+A^- \ + \ B^- \ \rightleftharpoons \ R^+B^- \ + \ A^- \hspace{2cm} (2.1)$$

where R^+ = the positive charge or fixed cation on the resin surface
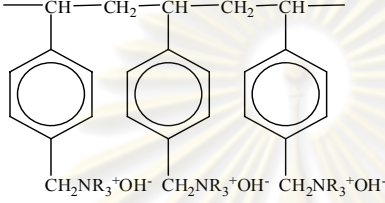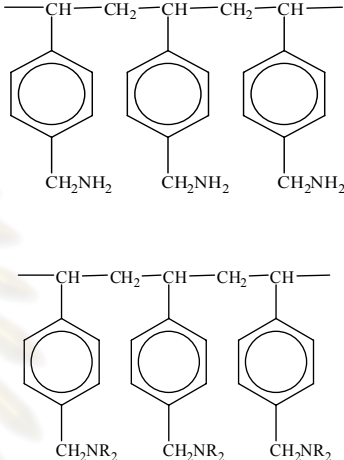
A^- = the negative charge or active anion group on the resin surface

B^- = the analyte ion in the bulk solution

The types and functional groups of anion exchange resin are summarized in Table 2.2.

Table 2.2 The types of anion exchange resin [41]

	Strong anion exchange resin	Weak anion exchange resin
Functional groups	- $[N(CH_3)_3]^+$ - $[N(CH_3)_2C_2H_4OH]^+$	- NR_2 - NHR - NH_2
Structures		
Trade names	Amberlite IRA-400, 401, 402, 405 Dowex -1, 11 MP-600 Zeo-Karb 226 Lewatit MN	Amberlyst 21 Dowex A-1, M-43, Monosphere77 Duolite 43

Modification of complexing ligand onto anion exchange resin

In general case, if we separate heavy metals from real water sample using ion exchange resin, the cation exchange resin is usually considered but the cation exchange resin often gives low selectivity. So, the modification of anion exchange resin with complexing ligand to improve the selectivity of heavy metals is interesting.

The modification of resin depends on the physical and chemical properties of the exchanging ion and resins. The nature of the resin is one factor to influence the selectivity of modified resin including the type of functional groups on the polymer chains. The complexing ligand loaded onto resin depends on various factors such as the ability of the ion-exchangers and solution pH. The characteristic property of

complexing ligand loaded onto resin consists of an ion-exchanger with the resin, the selectivity of the analyte, and the physical adsorption on the resin matrix.

The preparation and regeneration pathways of anion exchange resin with terfunctional properties of complexing ligand are shown in Figure 2.1.

The complexing ligands containing terfunctional properties such as Alizarin Red S, Bromopyrogallol, Napthol blue black, 8-hydroxyquinoline-5-sulfonic acid and pyrocatechol violet loaded onto anion exchange resin are shown in Figure 2.2. Furthermore, other complexing ligands like EDTA, Bismuthiol II and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (illustrated in Figure 2.3) can be successfully loaded onto anion exchange resin. These modified resins had excellent selectivity and they could be used to preconcentrate some heavy metals. They also showed higher recoveries than those of unmodified resins because of the donor sites on surfaces of modified resins [43].

$$R{-}N^+, Cl^- \quad + \quad X-R^{'}-SO_3^-Na^+ \quad \longrightarrow \quad R-N^+SO_3^--X \quad + \quad Na^+, Cl^-$$

Anion-exchange resin   Complexing ligand

$$\overset{|}{R'}$$

Loaded anion-exchange resin

$$\downarrow \text{Y (analyte)}$$

$$R-N^+SO_3^--X \qquad\qquad R-N^+SO_3^--X-Y$$
$$\overset{|}{R'} \qquad\qquad\qquad\qquad \overset{|}{R'}$$

$$+ \quad Y$$

Regeneration of loaded anion-exchange resin   Recovery of Y

$$\downarrow$$

$$R-N^+, Cl^- \quad + \quad X-R^{'}-SO_3^-Na^+ \quad + \quad Y$$

Regeneration of anion-exchange resin   Complexing ligand   Recovery of Y

-------- physical interaction
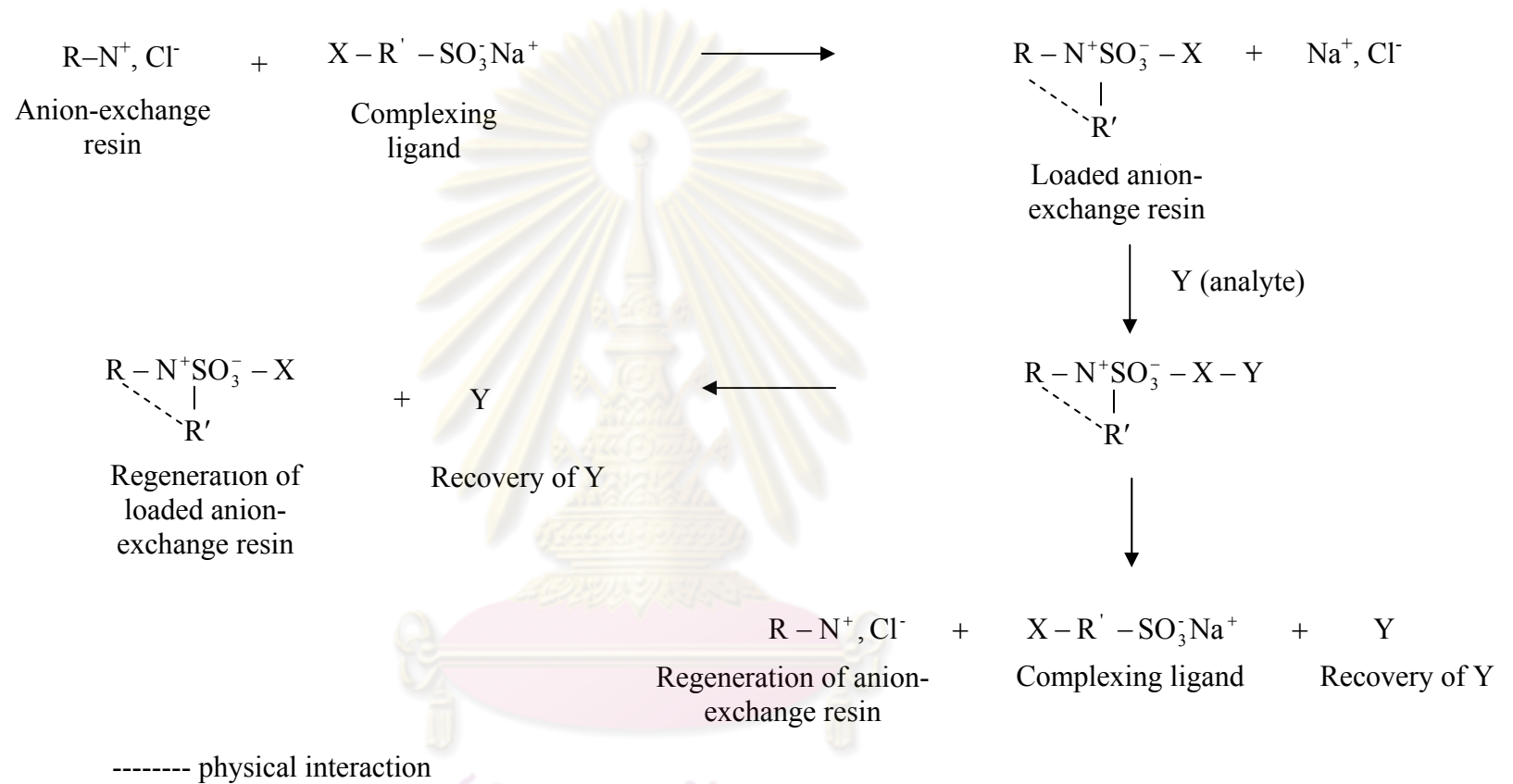
Figure 2.1 Preparation and regeneration pathways of anion exchange resin loaded with terfunctional properties of complexing ligand.[42]
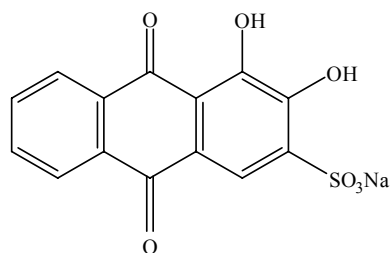
Alizarin Red S
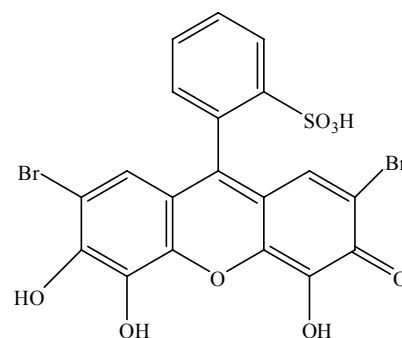
Bromopyrogallol
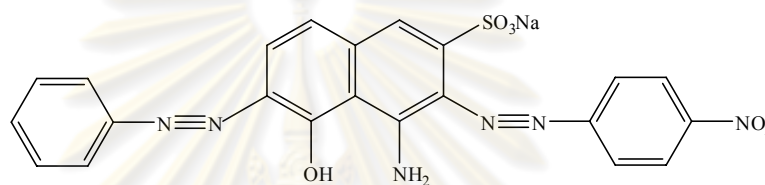
Napthol blue black
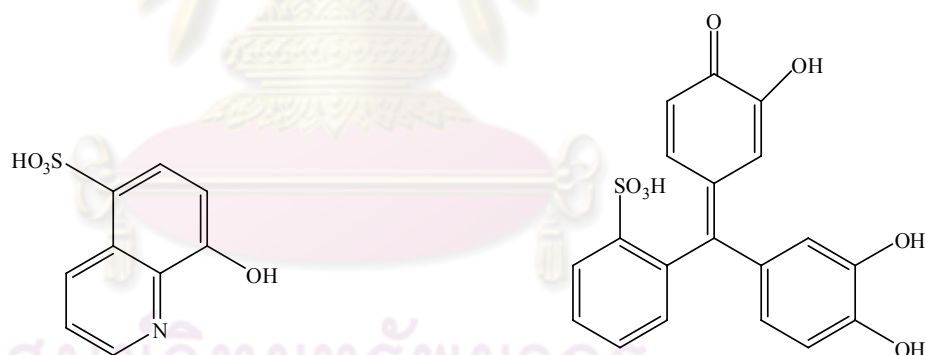
8-hydroxyquinoline-5-sulfonic acid

pyrocatechol violet

Figure 2.2 Some complexing ligands with sulfonate group.
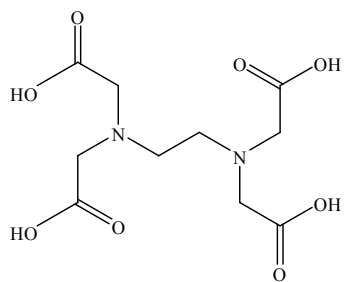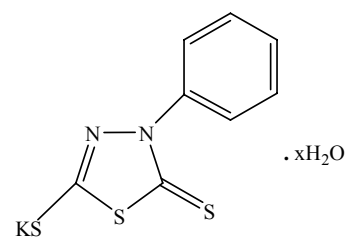
EDTA   Bismuthiol II
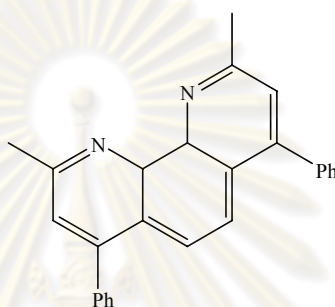
2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline

Figure 2.3 Some complxing ligands without sulfonate group in their molecules.

Some complexing resins applied to separate and preconcentrate trace metal ions from various samples are reported in Table 2.3.

Table 2.3 Applications of loaded anion exchange resin with several complexing ligands

Anion-exchange resin	Complexing ligand	Metal ions	Applications	Method of determination	Ref.
Dowex 1X-8	Alizarin Red S	Cu(II), Mn(II), Zn(II)	Separation and preconcentration of Cu(II), Mn(II) and Zn(II) in saline samples	AAS	[44]
Amberlite IRA 400	SPADNS	Cu(II) and Fe(III)	Preconcentration of Cu(II) and Fe(III) in drinking water	AAS	[45]
Amberlyst A-26	Thoron	Fe(III)	Separation and preconcentration of Fe(III) from Cu(II), Ni(II), Zn(II), Ca(II) and Mg(II) in natural water samples	AAS	[46]
Dowex 2x4	Pyrocatechol violet	Sn(IV)	Preconcentration of Sn(IV) in a nickel sample	DCP-AES	[47]
Amberlite IRA 400	Bismuthiol II	Sn(IV)	Selective collection of Se(IV) from environmental water	Spectrofluorometry	[48]
Dowex 1x4	BCS	Hg(I)	Selective collection of Hg(I) in natural water samples	Neutron activation analysis	[49]
Amberlyst A-26	Tiron	Ag(I), Co(II), Fe(II), Cd(II)	Separation of heavy metals from water samples	AAS	[50]

BCS = 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline

SPADNS = trisodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate

For the chelation of the metal ions on the surface of complexing resin, there are many factors such as suitable extraction condition, the nature of donor sites of complexing resin, and geometrical structure of the complexes to be considered.

In case of the nature of donor atoms of complexing resin, the donor atoms such as nitrogen, oxygen and sulfur are usually observed. In general case, the order of soft Lewis base is $S > N > O$. The complexes between metal ion and donor sites of complexing resin refer to hard-soft acid-base principle as hard likes hard and soft likes soft [51]. The hard-soft acid-base definitions are summarized in Table 2.4.

Table 2.4 Definition and examples of hard-soft acid-base

	Acid	Base
Hard	- high positive charge, small size, low polarizability	- high electronegativity and low polarizability
	- Mn^{2+}, Cr^{3+}, Fe^{3+}, Ti^{4+}, V^{5+}	- F^-, OH^-, NO_3^-, Cl^-, SO_4^{2-}
Borderline	- Intermediate behavior	- Intermediate behavior
	- Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}	- N_3^-, NO_2^-, NCS^-, SO_3^{2-}
Soft	- low positive charge, large size, high polarizability	- low electronegativity and high polarizability
	- Au^+, Ag^+, Cd^{2+}, Hg^{2+}, Pd^{2+}	- I^-, CN^-, SCN^-, CO, R_2S, RSH

2.3 Heavy metals in the environment

Heavy metals are mobilized by various physical, chemical and biological circulations so the mobility of heavy metals in the environmental media has been important factor. The mechanism including sorption process, redox reactions and speciation of heavy metals are studied. These processes are controlled by chemical driving factor such as pH, redox potential and chemical species formed.

In this section, the metal ions as silver ion, copper ion, lead ion and gold ion are represented in a detail of physical and chemical properties, common oxidation states in natural, main resources and toxicity.

2.3.1 Silver

Silver is a lustrous and bright white metal, which is ductility and malleability. Silver has atomic number of 47, an atomic weight of 107.87 and a specific gravity of 10.5 g cm^{-3}. Silver is found in four oxidation states in nature: 0, +1, +2 and +3, that is commonly in occurring 0 and +1 while the oxidation state of +2 and +3 are rarely. Ag$^+$ is very reactive and forms stable complexes with negative binding sites in suspended soils and sediments.

The most important sources of silver are metallic Ag, argentite (Ag$_2$S) and silver chloride (AgCl). Other sources of silver are found nearly electrolytic copper refining and smelting of Nickel ores. In the main industrial, silver was used for photographic manufacturing, this amounts to more than 40% of the world's total silver requirement. It's used for electrical contacts and conductors, catalysts, batteries, sterling ware, jewellery, silverplate, mirrors and others. The main toxicity of silver is an influence by chemical speciation, such as water hardness, pH, alkalinity, chloride ions (Cl$^-$) and dissolved organic carbon (DOC). In humans, silver is relatively nontoxic. The prediction of Eh-pH stability field for silver is shown in Figure 2.4.
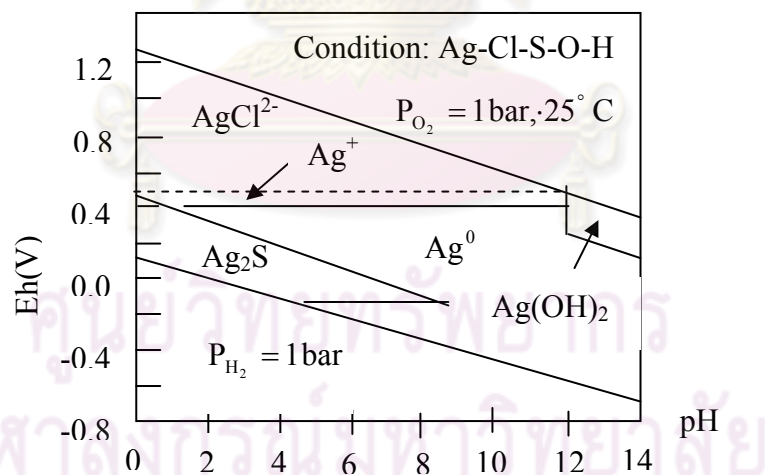
Figure 2.4 Predicted Eh-pH stability field of silver, modified from Bradl, H. B. [52].

2.3.2 Copper

Copper is a reddish, malleable, ductile metal with very good heating and electrical conductivity. It belongs to group I-B of the periodic table, which has an atomic number of 29, an atomic weight of 63.55, a melting point of 1083 °C and

a specific gravity of 8.96 g cm^{-3}. There are two natural isotopes, ^{63}Cu and ^{65}Cu, with relative abundances of 69.10% and 30.90%, respectively. The oxidation states of copper are occurring +1 and +2. For the +2 state, it is isomorphous with Zn^{2+}, Mg^{2+} and Fe^{2+}. Copper can be formed with variety of sulfides, sulfates and carbonates. The main resources of copper are copper fertilizers (for example $CuSO_4 \cdot 5H_2O$, CuO, Cu_2O and $CuSO_4 \cdot 3Cu\,(OH)_2$) which are widely used in agriculture. Copper is widely used for wire production and in electrical industry. Other applications are kitchenware, water delivery systems, fertilizers, bactericides and fungicides and feed additives.

In aquatic systems, the free Cu^{2+} ion is considered because it has toxicity form of copper to aquatic life more than the complex forms. The concentrations levels of copper in various environmental media [52] are shown in Table 2.5.

Table 2.5 Commonly observed copper concentrations (mg L^{-1}) in various environmental media

Material	Average concentration	Range
Igneous rocks	125	80 – 200
Sandstone	30	6 – 46
Limestone	6	0.6 – 13
Shale and clay	35	23 – 67
Coal	17	1 – 49
Fly ash	185	45 – 1452
Sewage sludges	690	100 – 1000
Soils	30	2 – 250
Freshwater (µg L^{-1})	3	0.2 – 3
Seawater (µg L^{-1})	0.25	0.05 – 12

2.3.3 Lead

Lead is a bluish-gray metal, malleable, ductile, a poor electrical conductivity and very resistant to corrosion. It belongs to group IV-A of the periodic, which has an atomic number of 82, an atomic weight of 207.2, a melting point of 328 °C and a specific gravity of 11.4 g cm^{-3}. They occurs four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb

and [208]Pb, with relative abundances of 1.48%, 23.6%, 22.6% and 52.3%, respectively. There are two oxidation states, +2 and +4. Mostly is found the +2 oxidation state in inorganic compound.

Species forms of lead depend on pH. At low pH values, lead performs hydrolysis reaction and displays multiple hydrolysis reactions. Above pH 9, the formation of $Pb(OH)_2$ is important, while as pH range 6-10 the formation of $Pb(OH)^+$ is predominant. The species distribution of lead as a function of pH is illustrated in Figure 2.5.
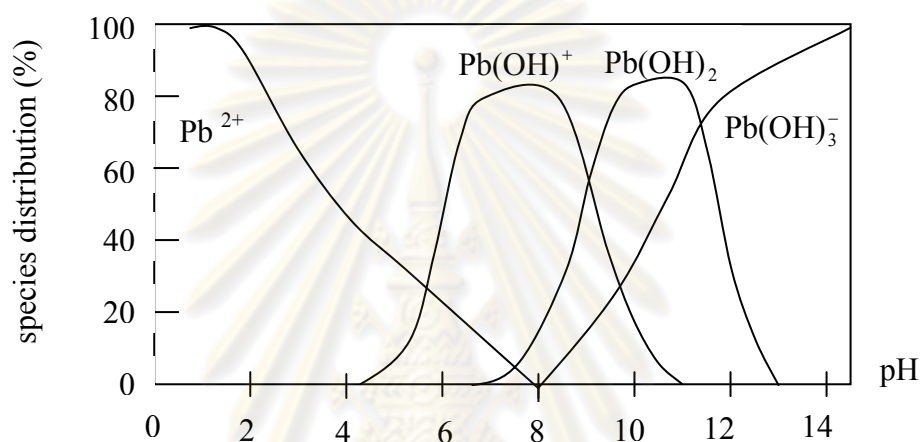
Figure 2.5 Species distribution of lead as a function of pH, modified from
Bradl, H. B. [52].

The concentrations levels of lead in various environmental media [52] are shown in Table 2.6.

Table 2.6 Common values of lead concentrations (mg L^{-1}) in various environmental media

Material	Average concentration	Range
Igneous rocks	15	2 – 30
Sandstone	7	1 – 31
Limestone	9	-
Shale	20	16 – 50
Coal	16	up to 60
Fly ash	170	21 – 220
Sewage sludges	1832	136 – 7627
Soils agricultural	-	2 – 300
Freshwater (µg L^{-1})	3	0.06 – 120
Seawater (µg L^{-1})	0.03	0.03 – 13

2.3.4 Gold

Gold is a metallic yellow, bright luster, ductility and stability in air. Metallic gold also has high electrical and conductivity properties that lead to widespread use in industries. List of some physical properties of gold is shown in Table 2.7.

Table 2.7 Physical properties of gold

Physical properties	
molar atomic weight	196.967 g mol^{-1}
melting point	1064 °C
boiling point	2808 °C
density(at 20 °C)	19.32 g cm^{-3}
electrical resistivity (at 20 °C)	2.35 µΩ cm
electronegativity	2.4

Gold is a soft metal and is found in oxidation states from -1 to +5. Main forms of gold ion like aurous (Au^{1+}) and auric (Au^{3+}) oxidation state. The coordination number of aurous ion is usually found of 2 and the complex of this ion is a linear

geometry. In the case of auric ion, the common coordination number of 4 and a square planar geometry were always found [53].

Although the stability complexes of gold ion and ligands have in a wide ranges. The stability of gold complexes is related not only the complexing ligand properties, but also more specifically to the donor atom of the ligand that is bonded directly to the gold atom. In water, Au^{1+} and Au^{3+} can form complexes as $Au(H_2O)_2^+$ and $Au(H_2O)_4^{3+}$, respectively, although they are generally represented as Au^+ and Au^{3+}. In chloride media, the distribution species forms of gold as a function of pH are differently as shown in Figure 2.6.
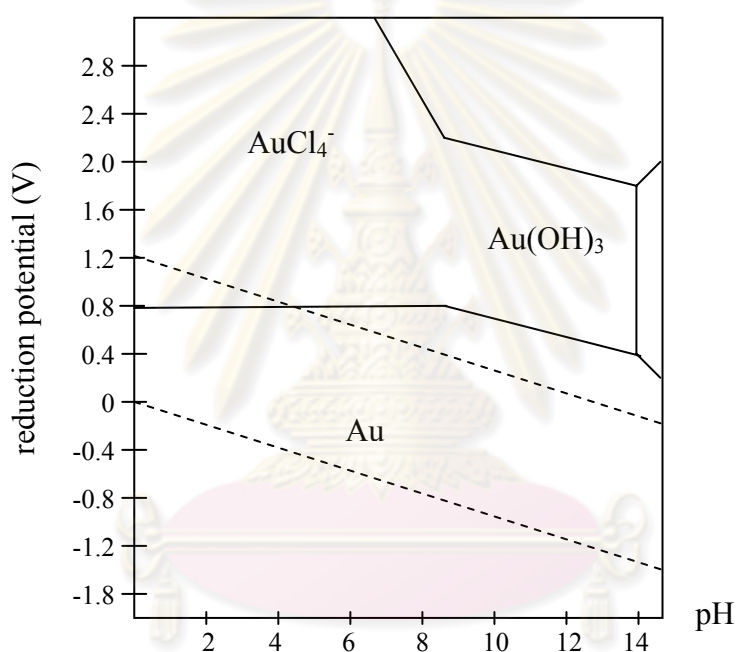
Figure 2.6 Diagram of the Au-H_2O-chloride ion system at 25 °C when $[Au^{3+}] = 0.01$ mol L^{-1} and $[Cl^-] = 2.0$ mol L^{-1}, modified from Finkelstein, N. P. and Hancock, R. D. [54].

2.4 Solid phase extraction

Solid phase extraction (SPE) is one of useful sample preparation technique for isolation and concentration of analytes from a gas or liquid by their transfer and sorption on the solid surface. The SPE method is more efficient than LLE with several

advantages such as, yields quantitative extractions, enrichment of analytes, easy to operate, automation and reduction of lab times.

SPE method consists of four main steps: conditioning, loading, washing and elution, respectively (illustrated in Figure 2.7) [55].
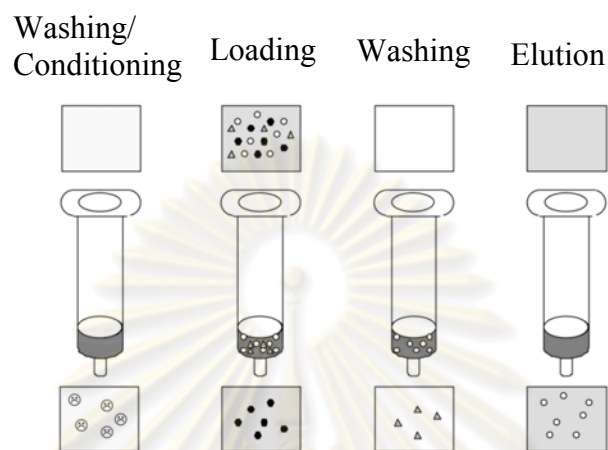
☹ impurity, ● partitioning component, Δ interfering component and ○ analyte

Figure 2.7 Four typical steps of SPE method.

The first step, an appropriate solvent is used to condition on the solid sorbent, and to remove the initial impurities on the sorbent surface or the packing material. The second step, the sample is throughout onto the solid sorbent. During this step, the analytes are accumulated on the sorbent surface. The solid sorbent (that is saturated with the analytes) is washed with an appropriate solvent in the third step. The appropriate solvent should be lower elution strength and can eliminate matrix components on the surface of sorbent. The last step is elution. The analytes (sorbed on solid sorbent) are eluted by an appropriate eluent, without eluting of matrix components. The analytes in the final step continue to the detector for quantitative determination.

2.5 Adsorption isotherm

For the characteristic adsorption behavior of the analytes onto sorbent surface, the adsorption isotherm is considered. Adsorption isotherm is defined that the analytes are contacted with the sites surface of sorbent in an aqueous phase under

thermodynamic equilibrium. The surface coverage of analytes to sorbent depends on the enthalpy of adsorption. There are many types of isotherm (such as Langmuir isotherm or Freundlich isotherm) which are based on different assumptions in each model.

In this subheading, the Langmuir isotherm for sorption behavior of analytes onto surface of sorbent is explained.

The Langmuir isotherm is a model to predict the analytes in a gas phase or an aqueous phase accumulated onto sorbent surface in a monolayer adsorption on the pressure of the gas above the surface at a constant temperature. The Langmuir equation [56] is represented in equation 2.2.

$$\frac{C}{N_f} = \frac{1}{bN^s_f} + \frac{C}{N^s_f} \tag{2.2}$$

In this expression, C is the residual concentration (mol L^{-1}) of the analyte at equilibrium, N_f is the mole of analyte per gram of sorbent, N^s_f is the maximum sorption capacity of the sorbent and $b = K_{eq}/a$, where "a" represents the activity of the solvent in solution. By plotting C/N_f versus C (illustrated in Figure 2.8), the linearity of model and the slope of $1/N^s_f$ are obtained.
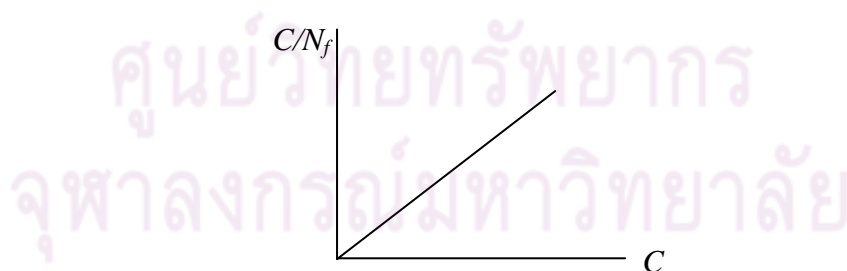
Figure 2.8 The linearity from Langmuir isotherm.

2.6 Flame Atomic Absorption Spectroscopy (FAAS)

Flame atomic absorption spectroscopy (FAAS) is one technique which is used to determine the quanlitative and quantitative analysis in a milligram per litre of concentration level of analyte in a liquid sample. The metal ion is separated and mixed as an aerosol by combustible gases such as acetylene gas and air, or acetylene gas and nitrous oxide. The mixture is ignited in a flame under temperature between 2100 to 2800 °C. During combustion, metal atom in the sample is reduced to the atomic state and a light beam from a hallow cathode lamp of analyte is working through the flame into a monochromator and detector, respectively. The common instrument is shown in Figure 2.9.
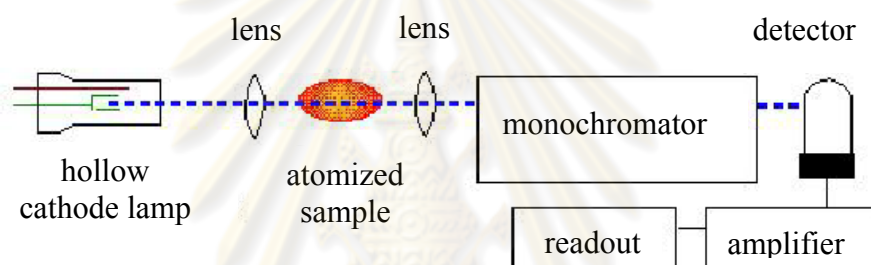
Figure 2.9 General atomic absorption spectrometer [57].

However, FAAS has a restriction in a poor detection limit than the other techniques such as inductive couple plasma (ICP) and inductive couple plasma-mass spectrometry (ICP-MS). The limits of detection of FAAS are shown in Table 2.8. Therefore, a good choice to improve this problem requires a sample preparation method such as solid phase extraction, co-precipitation, and coagulation because their methods have an enrichment of analyte.

Table 2.8 Detection limits of FAAS [58]

Element	Detection limit (mg L^{-1})
Al	0.03
As	0.10
Cd	0.001
Cu	0.002
Fe	0.005
Hg	0.50
Mn	0.002
Mo	0.03
Ni	0.005
Pb	0.01
Sn	0.02
Zn	0.002

CHAPTER III

PREPARATION OF PIPERAZINEDITHIOCARBAMATE
ON ANION EXCHANGE RESIN

In this chapter, we attempted to synthesize the piperazinedithiocarbamate as complexing ligand and to characterize the synthesized product, followed by the loading of the piperazinedithiocarbamate onto an anion exchange resin. The effect of loading parameters such as pH, loading time and concentration of complexing ligand was investigated. Moreover, the stability of the complexing resin after loading was also studied in coexisting anions medium such as NO_3^- and Cl^-.

3.1 Chemicals

All chemicals were of analytical grade and listed in Table 3.1. They were used without further purification unless otherwise noted.

Table 3.1 Chemicals list

Chemicals	Supplier
Acetone	Fisher Scientific
Amberlite IRA 402 anion exchange resin	Fluka
Carbon disulfide	MERCK
Deuterium oxide	Fluka
Diethyl ether	MERCK
Hydrochloric acid 37%	MERCK
2-Propyl alcohol	CARLO ERBA
Piperazine anhydrous	MERCK
Potassium bromide	MERCK
Sodium chloride	CARLO ERBA
Sodium hydroxide	MERCK
Sodium nitrate	CARLO ERBE

3.2 Synthesis of bis(sodium dithiocarbamate) piperazine and its characterization

The bis(sodium dithiocarbamate) piperazine or piperazine dithiocarbamate was prepared with adaptable method of Fabretti et al. [59]. The synthetic pathway is shown in scheme 3.1.
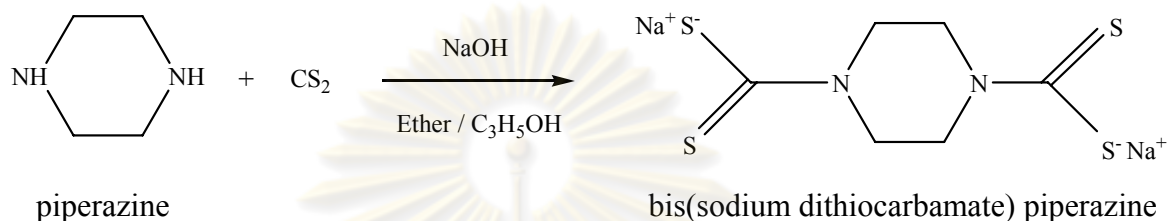
Scheme 3.1 The synthetic pathway of bis(sodium dithiocarbamate) piperazine.

A mixture of piperazine anhydrous (1.0 g, 11.6 mmol) and 50 mL of diethyl ether in a 250 mL two-necked round bottom flask was stirred under nitrogen gas at room temperature for 1 h. Then, a mixture of 2-propyl alcohol (30 mL) and carbon disulfide (5 mL, 6.3 mmol) was added dropwise, followed by 10 mL of sodium hydroxide solution (1.0 g, 25.0 mmol). The reaction mixture was continuously stirred over 5 h. The crude product was purified by recrystallization in acetone and the crystal white product was obtained (1.8 g, 6.4 mmol, yield = 55.2 %, melting point = 247.5-250 °C decompose). The product was kept in a desiccator.

The characterization of the complexing ligand was carried out on UV-Vis spectrophotometry (HP 8453, Hewllet Packard), Fourier Transform Infrared spectroscopy (Nicolet Impact 410) in transmittance mode between 500-4000 cm^{-1} with KBr pellet technique and ^{1}H-NMR spectroscopy (Varian Mercury plus 400) in order to determine its chromophore, functional groups and molecular structure, respectively.

The absorption spectrum of the synthesized product in deionized water is shown in Figure 3.1.

This complexing ligand showed the maximum absorbance in the ultraviolet regions at 283 nm and 265 nm, respectively. These two absorption bands were owing

to a transition of the unshared electron pairs of the dithiocarbonyl sulfur which is characteristic of the NCS$_2$ group [60].
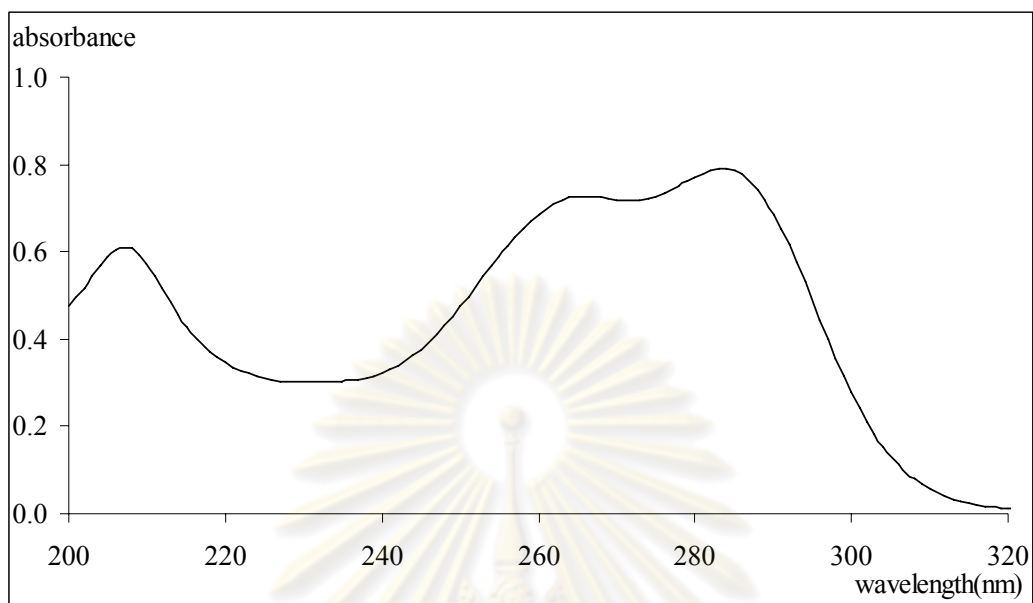
Figure 3.1 Absorption spectrum of complexing ligand in deionized water at pH 7.0 $(4.0 \times 10^{-4}$ mol L$^{-1})$.

The FT-IR spectra of complexing ligand in comparison with piperazine are illustrated in Figure 3.2.
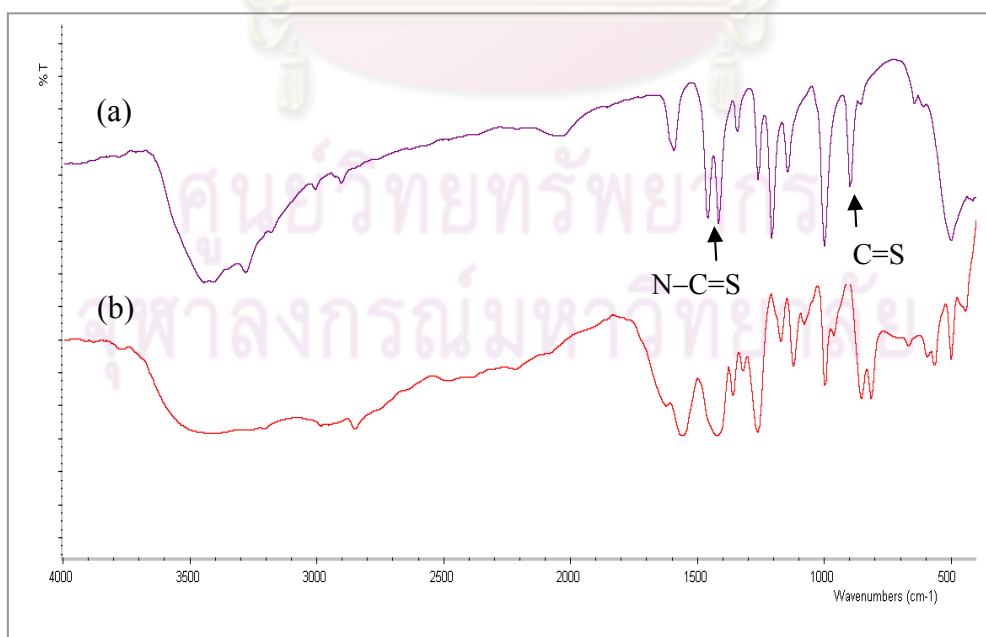
Figure 3.2 FT-IR spectra of (a) complexing ligand and (b) piperazine.

The most important absorption bands of complexing ligand found at around 940 and 1500 cm^{-1} were attributed to the C=S group and N−C=S partial double bond stretching, respectively, which were similar to the previous researches [61-62]. In addition, a characteristic band of dithiocarbamate in the range of 1450-1580 cm^{-1} contributed to N−C=S stretching defined bond order between a single bond and a double bond.

The ^{1}H NMR spectrum of complexing ligand (Figure 3.3) showed the abundances of hydrogen atoms in the CH$_2$ group of piperazine. The singlet characteristic peak of complexing ligand was obtained at the chemical shift of 4.30 ppm, meanwhile the chemical shift of piperazine was presented at 3.00 ppm as shown in Figure 3.4.
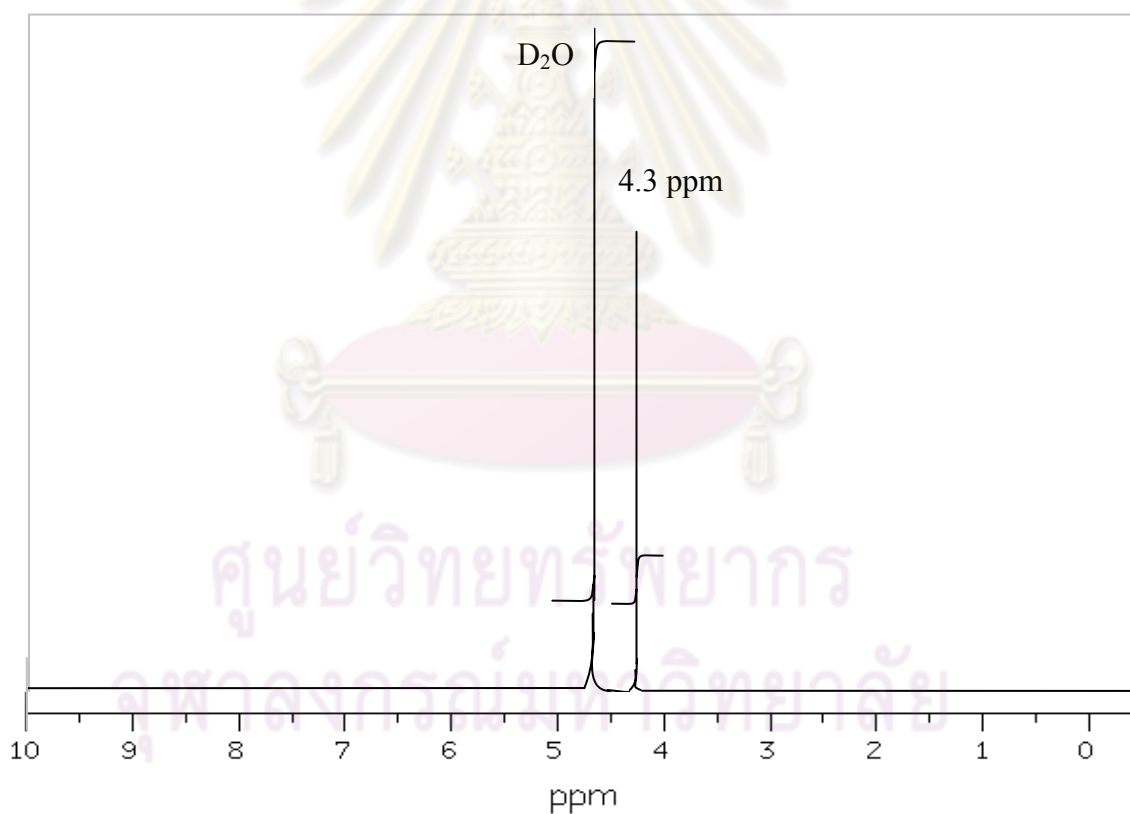
Figure 3.3 ^{1}H NMR spectrum of complexing ligand.
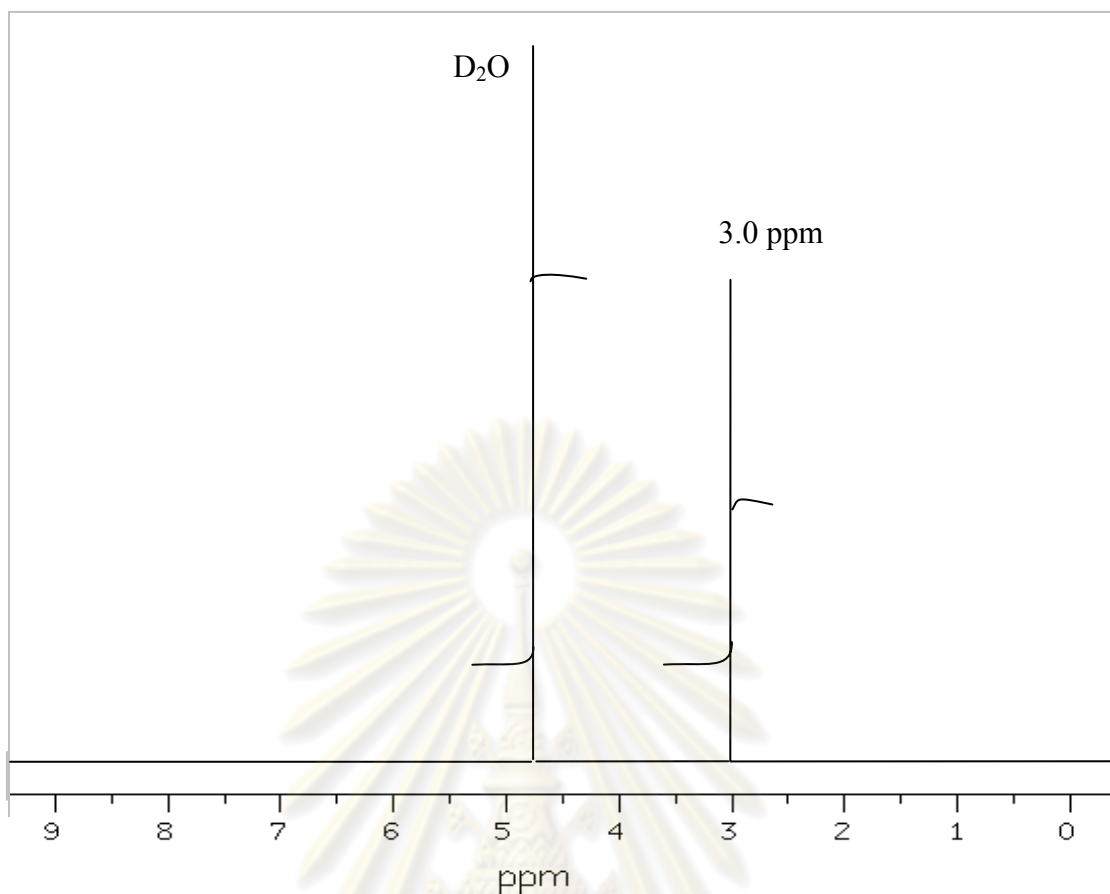
Figure 3.4 ^{1}H NMR spectrum of piperazine.

The characterization data described above indicated that we accomplished to synthesize the bis(sodium dithiocarbamate) piperazine as complexing ligand.

3.3 Loading of bis(sodium dithiocarbamate) piperazine onto anion exchange resin

In this section, the loading of complexing ligand onto anion exchange resin was studied in batch method. The conventional anion exchange resin in this experiment was Amberlite IRA 402 in chloride form. The properties of solid material are listed in Table 3.2.

Table 3.2 Properties of Amberlite IRA 402 anion exchange resin

Properties	Components
Matrix type	styrene-divinylbenzene (gel)
Anionic active group	chloride ion
Fixed cationic group	quaternary ammonium functional group
Cross-linkage	6%
Moisture	53%
Operating pH	0-14
Particle size	16-50 mesh
Capacity	1.2 meq mL^{-1} by wetted bed volume
	4.1 meq g^{-1} by dried weight

The structure of Amberlite IRA 402 anion exchange resin is shown in Figure 3.5.
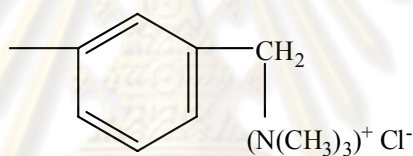
Figure 3.5 The structure of Amberlite IRA 402 anion exchange resin.

The effect of loading parameters such as pH, loading time and concentration of complexing ligand was investigated. Moreover, the stability of the complexing resin after loading was also studied in coexisting anions medium such as NO_3^- and Cl^-. The amount of complexing ligand was determined by UV-Vis spectrophotometer model HP 8453 at 283 nm using deionized water as blank. The loading experiments were performed in triplicate (n=3). The loading capacity of complexing ligand onto anion exchange resin was calculated according to equation 3.1.

$$\text{loading capacity } (\mu\text{mol g}^{-1}) \; = \; \frac{n_{before} - n_{after}}{m_{resin}} \tag{3.1}$$

where n_{before} = the amout of complexing ligand in solution before loading (μmol)

n_{after} = the amout of complexing ligand in residual solution after loading (μmol)

m_{resin} = the weight of anion exchange resin (g)

The loading pathway of complexing ligand onto Amberlite IRA 402 anion exchange resin was proposed in scheme 3.2.
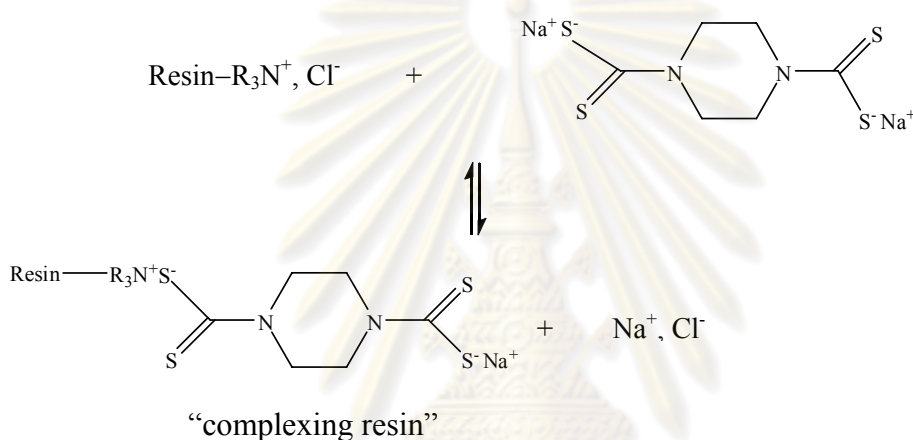
Scheme 3.2 Loading pathway of complexing ligand onto Amberlite IRA 402.

3.3.1 Preparation of solutions

(1) Hydrochloric acid solution (0.1 mol L^{-1}) was prepared by direct dilution of the concentrated hydrochloric acid in deionized water.

(2) Sodium chloride solution (0.01 and 0.1 mol L^{-1}) was prepared by dissolving an appropriate amount of NaCl in deionized water.

(3) Sodium hydroxide solution (0.1 mol L^{-1}) was prepared by dissolving an appropriate amount of NaOH in deionized water.

(4) Sodium nitrate solution (0.01 and 0.1 mol L^{-1}) was prepared by dissolving an appropriate amount of NaNO$_3$ in deionized water.

(5) Complexing ligand solution (80 mg L^{-1}) was prepared by dissolving an exactly appropriate amount of complexing ligand in deionized water in an appropriate volumetric flask.

3.3.2 Loading parameters

3.3.2.1 Effect of pH

The pH effect for loading of complexing ligand onto anion exchange resin was investigated as follows:

A suspension of 30 mg of Amberlite IRA 402 in 10.00 mL of 80 mg L^{-1} complexing ligand solution at a pH range of 2-10 (adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH) in a beaker was stirred at room temperature for 3 h. The resin was separated by filtration and the amount of residual complexing ligand in solution was determined by UV-Vis spectrophotometer. The experiments were performed in triplicate (n=3).

The loading capacity of complexing ligand in a function of pH is shown in Figure 3.6.
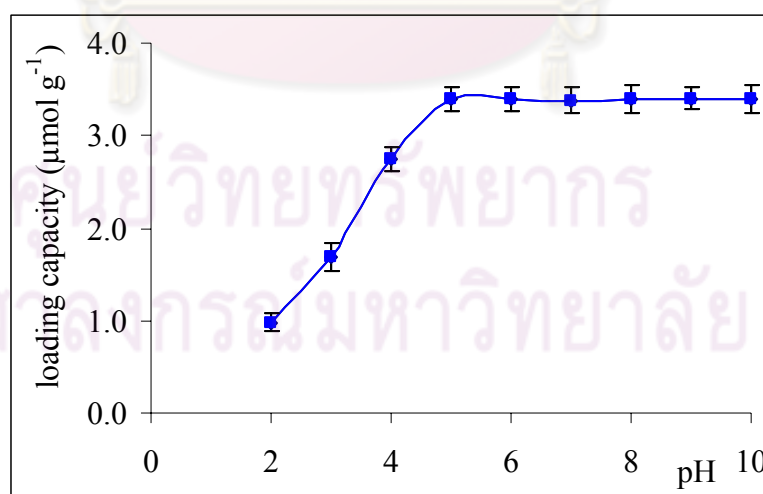
Figure 3.6 Effect of pH on loading capacity.

In strong acidic solution, loading capacity decreased. When increased solution pH, increasing of loading capacity was obtained. The constant loading capacity of complexing ligand onto anion exchange resin as a function of pH was found since pH = 5 with the maximum loading capacity of 3.5 μmol g^{-1}. Therefore, the suitable solution pH of 5-6 for loading complexing ligand onto anion exchange resin was selected for next experimental study.

Figure 3.7 shows the experimental results of the absorption spectra of complexing ligand in deionized water at pH between 2 to 10.
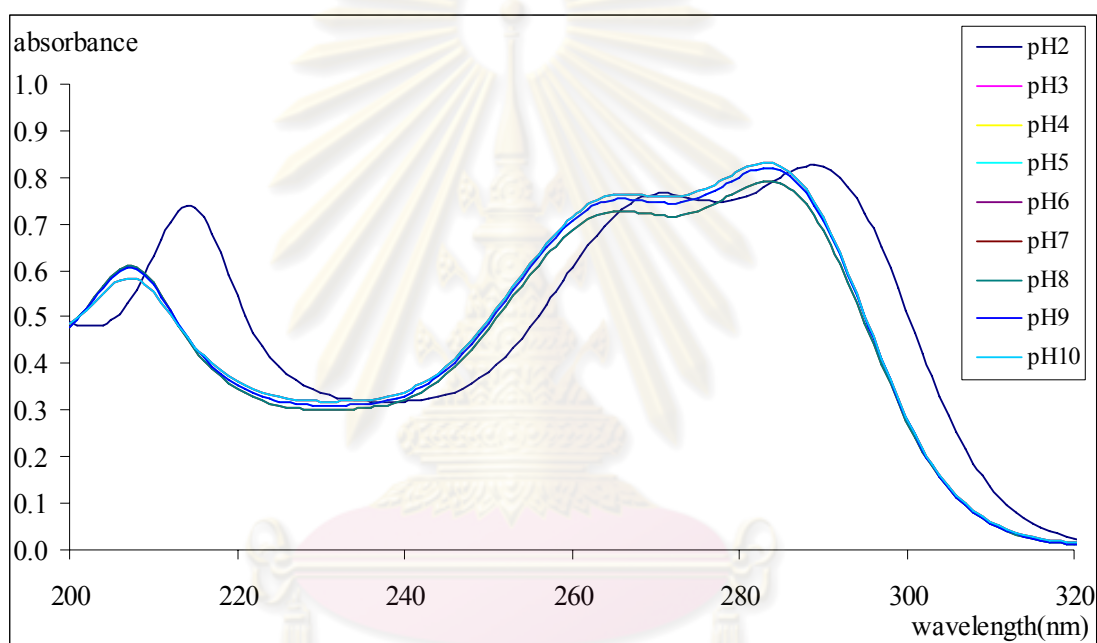
Figure 3.7 Absorption spectra of complexing ligand in deionized water at different pHs (4×10^{-4} mol L^{-1}).

The absorption bands at 207, 265 and 283 nm were observed at pH 4-10. At lower pH 2-3, the bathochromic shifts of the complexing ligand peaks at all three peaks were clearly seen. These indicated the formation of the protonated form of complexing ligand.

The protonation of dianion piperazinedithiocarbamate as the following mechanism:
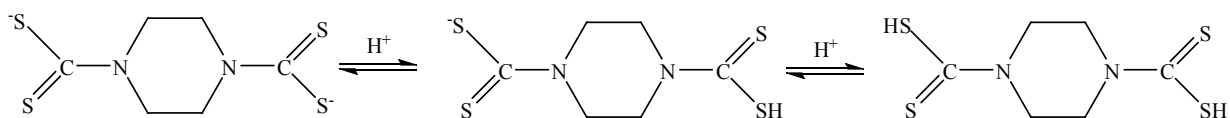
gave the monoanion or neutral molecule which had less efficiency to exchange with Cl$^-$ on the resin surface resulting in lower loading capacities.

Moreover, the color change of complexing resin was clearly observed from white (Amberlite IRA 402) to brown. This indicated that the anion exchange between Cl$^-$ and piperazinedithiocarbamate was achieved.

The FT-IR spectrum of the complexing resin synthesized at pH 6 was compared with unloaded Amberlite IRA 402 as shown in Figure 3.8.
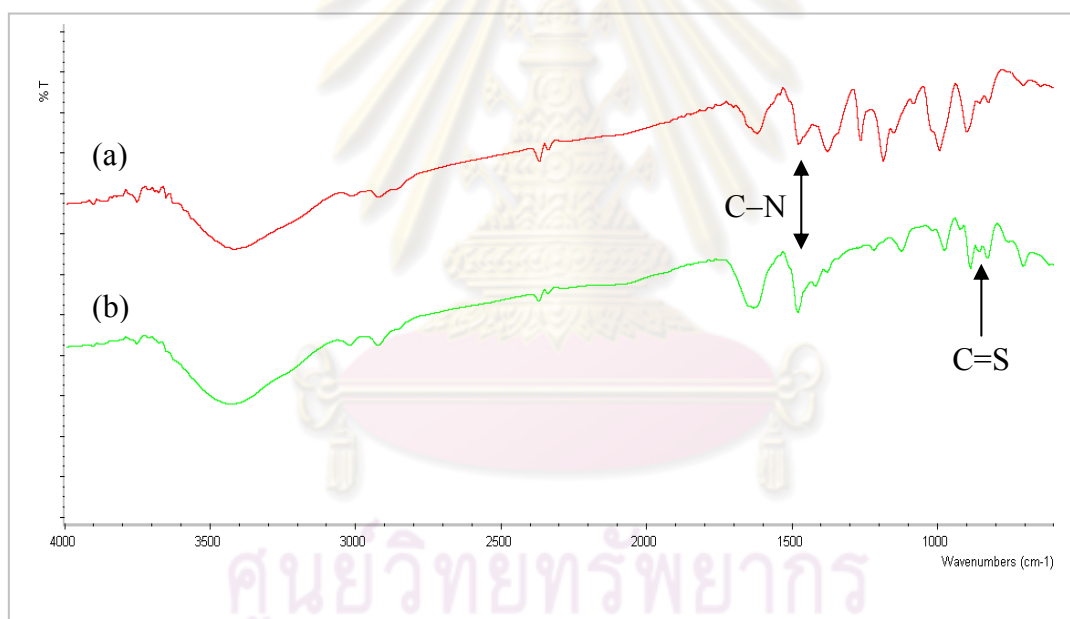
Figure 3.8 FT-IR spectra of (a) Amberlite IRA 402 and (b) complexing resin.

The FT-IR spectra showed very small difference between Amberlite IRA 402 and the complexing resin. The absorption bands of complexing resin mainly belonged to Amberlite IRA 402 structure due to low capacity of the piperazinedithiocarbamate on resin (3.5 μmol g^{-1}). However, the characteristic peak of C=S group was found at 940 cm^{-1} in complexing resin spectrum while the Amberlite IRA 402 did not appear. This indicated that the complexing resin had piperazinedithiocarbamate.

3.3.2.2 Effect of loading time

The effect of loading time was studied between 2-20 min. The loading kinetics of complexing ligand onto anion exchange resin was determined under the following conditions:

10.00 mL of 80 mg L^{-1} complexing ligand solution at pH 5-6 (adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH) was continuously stirred with 30 mg of Amberlite IRA 402 at room temperature. The resin was filtered off and the amount of residual complexing ligand in solution was determined by UV-Vis spectrophotometer. The experiments were performed in triplicate (n=3).

The results are shown in Figure 3.9.
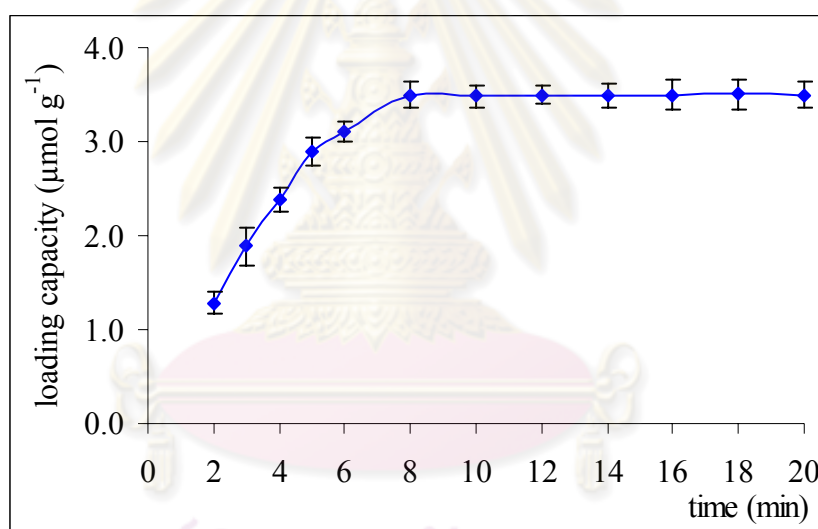
Figure 3.9 Effect of loading time on loading capacity.

The loading capacity of complexing ligand onto Amberlite IRA 402 as a function of loading time showed the constant retention of complexing ligand within 8 min. This loading kinetic was faster than other complexing ligands such as napthol blue-black loaded anion exchange resin [63]. The time required to reach complete loading capacity of napthol blue-black onto anion exchange resin was found to be ≥ 90 min.

In next parameter, the loading time at least 8 min was used for loading of complexing ligand onto Amberlite IRA 402.

3.3.2.3 Effect of complexing ligand concentration

The concentration of complexing ligand was an important factor to determine the maximum loading capacity of complexing ligand onto anion exchange resin. The loading capacity as a function of initial complexing ligand concentration was studied as follows:

10.00 mL of complexing ligand solution in the concentration range of 10-140 mg L^{-1} at pH 5-6 (adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH) was continuously agitated with 30 mg of anion exchange resin at 25 °C for 8 min. The resin was filtered off and the amount of residual complexing ligand in solution was determined by UV-Vis spectrophotometer. The experiments were performed in triplicate (n=3).

The loading capacity as a function of initial concentration of complexing ligand is shown in Figure 3.10.
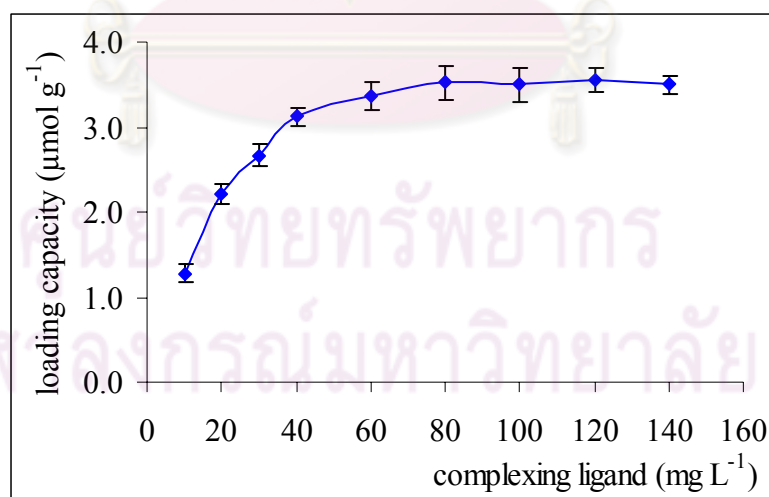
Figure 3.10 Loading capacity as a function of complexing ligand concentration.

The maximum loading capacity of piperazinedithiocarbamate onto Amberlite IRA 402 was found to be 3.50 µmol g^{-1} when the initial concentrations of complexing

ligand solution of 80-140 mg L^{-1} were used. The concentration of 80 mg L^{-1} was good enough for loading of complexing ligand onto Amberlite IRA 402.

The loading behavior of complexing ligand onto anion exchange resin was confirmed by Langmuir isotherm. The experimental data plotted C/N_f versus C with isotherm model illustrated in Figure 3.11 showed satisfied correlation coefficient of 0.9957, indicating that these results fit well to the Langmuir model. Langmuir model also allowed to estimate the maximum loading capacity of 3.5 μmol g^{-1}.
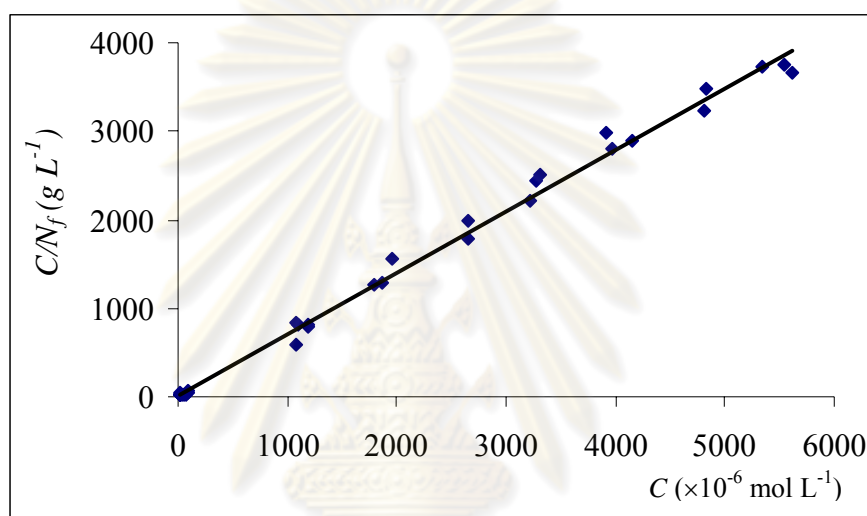
Figure 3.11 Langmuir isotherm fitting at 25 °C.

According to the maximum loading capacity of the piperazinedithiocarbamate onto Amberlite IRA 402 of 3.5 μmol g^{-1} was lower than the ion-exchange capacity of Amberlite IRA 402 (see Table 3.2). Therefore, the loading mechanism of piperazinedithiocarbamate onto Amberlite IRA 402 was only ion-exchange process.

3.4 Stability of complexing resin

The stability of complexing resin in different matrix coexisting anion solutions depends on the ability of complexing ligand retained on anion exchange resin and the matrix anion competition in bulk solution [43]. So the effect of matrix coexisting anions to leach the complexing ligand from loaded complexing resin was seriously considered.

In this experiment, the coexisting anions such as NO_3^- and Cl^- were selected to study because these anions were usually found in natural water. The stability of complexing resin was studied by determining the complexing ligand in solution after shaking with NaCl or $NaNO_3$ solutions of different concentrations (0.01 and 0.1 mol L^{-1}) and at various pHs in comparison with deionized water. The procedure was carried out as follows:

A 30 mg of complexing resin was continuously stirred in 10.00 mL of an individual matrix coexisting anion solution at various pHs of 2-10 (adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH) at room temperature for 30 min. The complexing resin was filtered off and the leached complexing ligand in solution was determined by UV-Vis spectrophotometer. The experiments were performed in triplicate (n=3).

The %release of complexing ligand from complexing resin was calculated according to equation 3.2.

$$\% \text{ release} = \frac{n_{release}}{n_{resin}} \times 100 \qquad (3.2)$$

where $n_{release}$ = the amount of complexing ligand in solution (μmol)

   n_{resin} = the amount of complexing ligand onto solid material (μmol)

The results are presented in Table 3.3.

Table 3.3 % Release[*] of complexing ligand from complexing resin

pH	DI	NaCl		NaNO$_3$	
		0.01 mol L^{-1}	0.10 mol L^{-1}	0.01 mol L^{-1}	0.10 mol L^{-1}
2	0.50 (0.02)	1.35 (0.04)	10.38 (0.07)	1.64 (0.05)	24.18 (0.07)
3	0.49 (0.05)	1.10 (0.06)	10.70 (0.05)	1.76 (0.03)	24.08 (0.09)
4	0.51 (0.03)	0.90 (0.03)	8.92 (0.08)	1.79 (0.07)	23.48 (0.10)
5	0.53 (0.05)	0.95 (0.03)	7.60 (0.04)	1.55 (0.06)	22.82 (0.83)
6	0.19 (0.02)	0.65 (0.04)	7.17 (0.05)	1.36 (0.02)	22.71 (0.14)
7	0.21 (0.03)	0.60 (0.05)	7.87 (0.08)	1.24 (0.05)	22.45 (0.09)
8	0.21 (0.04)	0.57 (0.02)	7.58 (0.03)	1.22 (0.06)	19.98 (0.17)
9	0.18 (0.03)	0.59 (0.06)	7.00 (0.06)	1.29 (0.04)	20.48 (0.11)
10	0.18 (0.05)	0.61 (0.02)	7.16 (0.04)	1.20 (0.03)	20.04 (0.18)

[*] mean values (SD)

It was found that the complexing resin was able to resist in the presence of deionized water, 0.01 mol L^{-1} NaCl and 0.01 mol L^{-1} NaNO$_3$ at pH 2-10 with %release < 2%. A comparison of NaCl and NaNO$_3$ at similar concentration, higher %release of complexing ligand from complexing resin in nitrate medium was observed, indicating that the stability of complexing resin was in the order of NaCl > NaNO$_3$. It was probably due to higher hydrophobic property of nitrate ion than that of chloride ion [64]. In addition, the polystyrene-divinylbenzene as polymer matrix on the anion exchange resin is major component and the amount of piperazinedithiocarbamate loaded onto Amberlite IRA 402 was very low.

In the case of the different concentrations of NaCl solution, %release of complexing ligand in 0.10 mol L^{-1} NaCl were higher than those of in 0.01 mol L^{-1} NaCl. It might be explained by the following equilibrium:

In the presence of high concentration of NaCl, the equilibrium will go forward resulting in high %release. In addition, the similar phenomena in $NaNO_3$ medium was obtained.

Furthermore, the release of complexing ligand as a function of time was considered. In this study, the medium as deionized water at pH 6 was chosen. The results in Table 3.4 showed that no significant release of complexing ligand was observed.

Table 3.4 The releasing time effect in deionized water at pH 6

Time (min)	Release (%) [*]
10	0.17 (0.01)
20	0.20 (0.01)
30	0.19 (0.02)
40	0.20 (0.01)
50	0.17 (0.01)
60	0.18 (0.02)
70	0.19 (0.01)
80	0.20 (0.03)
90	0.19 (0.01)
100	0.21 (0.02)

[*] mean values (SD)

In summary, we succeeded to loading of the piperazinedithiocarbamate onto Amberlite IRA 402 anion exchange resin. The optimum loading conditions of

complexing ligand onto Amberlite IRA 402 were solution pH > 5, loading time of 8 min and the complexing ligand concentration of 80 mg L^{-1}.

We expected that the complexing ligand was loaded on anion exchange resin in a position of sulfur binding atom and another sulfur binding sites in its molecule could form complex with metal ions, leading to separate and preconcentrate metal ions from aqueous solution.

CHAPTER IV

SEPARATION AND PRECONCENTRATION OF HEAVY METALS ON COMPLEXING RESIN

In this chapter, we described the extraction properties of the complexing resin towards Ag(I), Cu(II), Pb(II) and Au(III) in static and dynamic methods. The parameters in static method such as solution pH, extraction time, concentration of metal solution and interfering cations were studied. In dynamic method, the flow rates of sample and eluent solution, sample volume and reusability of complexing resin were investigated. Furthermore, the preconcentration of trace heavy metals in real water samples with the suitable condition under dynamic method was also evaluated.

The metal extraction efficiency and elution efficiency were reported in the term of sorption capacity and %elution which can be calculated by equations 4.1 and 4.2, respectively.

$$\text{sorption capacity (mg g}^{-1}) = \frac{N_{before} - N_{after}}{m_{cpx\ resin}} \qquad (4.1)$$

where N_{before} = the amount of metal ion before extraction (mg)

N_{after} = the amount of metal ion in residual solution after extraction (mg)

$m_{cpx\ resin}$ = the weight of complexing resin (g)

$$\% \text{ elution} = \frac{N_e}{N_s} \times 100 \qquad (4.2)$$

where N_e = the amount of metal ion eluted from complexing resin (mg)

N_s = the amount of metal ion sorbed on complexing resin (mg)

The metal ion concentrations were determined by a flame atomic absorption spectrophotometer (FAAS) model AAnalyst 100 (Perkin-Elmer). The instrumental conditions are listed in Table 4.1.

Table 4.1 FAAS conditions for determination of metal ions solution

Operating conditions	Ag	Au	Cu	Pb
Wavelength (nm)	328.1	242.8	324.8	283.3
Slit width (nm)	0.7	0.7	0.7	0.7
Lamp type	HCL*	HCL*	HCL*	HCL*
Lamp current (mA)	15	15	15	10
C_2H_2 flow-rate (mL min^{-1})	3	3	3	3
Air flow-rate (mL min^{-1})	10	10	10	10

* Hollow cathode lamp

All metal ion solutions were prepared using deionized water by stepwise dilution of 1000 mg L^{-1} standard solution.

4.1 Chemicals

All chemicals were of analytical grade and listed in Table 4.2. They were used without further purification unless otherwise noted.

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Table 4.2 Chemicals list

Chemicals	Supplier
Amberlite cation exchange resin	Mazuma
Calcium chloride	Fluka
Ethylenediaminetetraacetic acid disodium salt dehydrate	Fluka
Hydrochloric acid 37%	MERCK
Lithium chloride	Fluka
Magnesium chloride	Fluka
Potassium chloride	Ajax Chemical
Sodium chloride	CARLO ERBE
Sodium hydroxide	MERCK
Sodium nitrate	CARLO ERBA
Thiourea	Sigma-Aldrich
Ag standard solution (1000 mg L^{-1})	BDH SpectrosoL$^{®}$
Au standard solution (1000 mg L^{-1})	BDH SpectrosoL$^{®}$
Cu standard solution (1000 mg L^{-1})	BDH SpectrosoL$^{®}$
Pb standard solution (1000 mg L^{-1})	BDH SpectrosoL$^{®}$

4.2 Extraction study in static method

In batch or static method, the various parameters such as solution pH, extraction times, metal ion concentrations, and interfering cations were investigated.

4.2.1 Effect of solution pH

The solution pH is the most important factor to the efficiency of sorption capacity of metal ion on complexing resin because the binding sites of complexing ligand are controlled by solution pH.

In general case, the binding sites of complexing ligand can be protonated in acid solution. While in basic solution, binding sites of the complexing ligand were completely deprotonated. However, in strong basic solution, the metal ion can

precipitate in hydroxide form so the extractions of metal ion are not successfully obtained.

Experiments were performed by using 2.5 mg L^{-1} of Ag(I), 5.0 mg L^{-1} of Cu(II), 10.0 mg L^{-1} of Pb(II) and 6.0 mg L^{-1} of Au(III). The metal solutions were adjusted to the appropriate pH ranging from 2 to 9 using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NaOH. A suspension of 10.0 mg of complexing resin and 5.00 mL of a metal solution in a test tube was mechanically stirred for 3 h at room temperature. The aqueous solution was bringing off and the amount of residual metal ion in the solution was determined by FAAS. The experiments were performed in triplicate (n=3).

The retentions of Ag(I), Cu(II), Pb(II) and Au(III) on the complexing resin as a function of pH are illustrated in Figure 4.1.
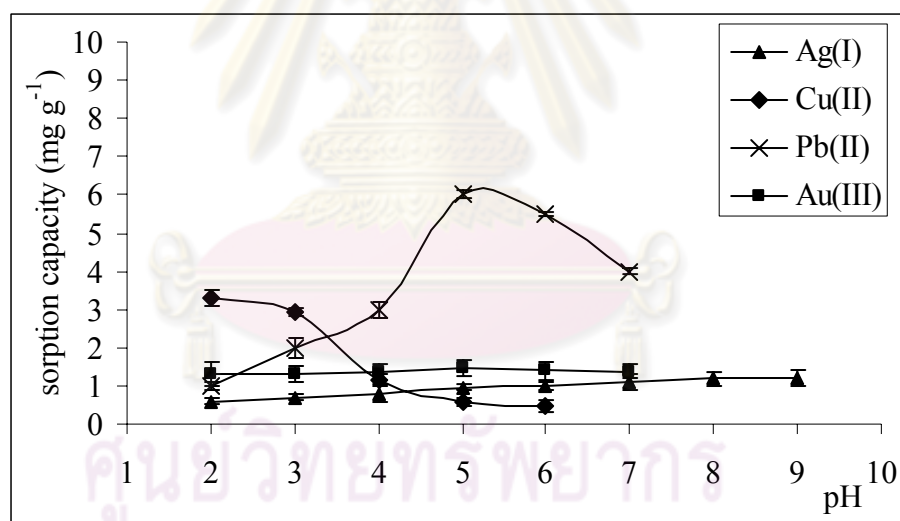
Figure 4.1 Effect of solution pH on the metal extraction.

In the case of Cu(II), the sorption capacity rapidly decreased from pH 3 to pH 4. At pH 5-6, the sorption capacities of 0.5 mg g^{-1} were obtained while the maximum sorption capacity of 3.3 mg g^{-1} was found at pH 2. The experiments were not performed at pH > 6 because of the occurrence of Cu(II) hydroxide precipitation.

The sorption capacity of Pb(II) increased with increasing the solution pH until pH 5 resulting in the maximum sorption capacity of 6.0 mg g^{-1}. The sorption

capacities rapidly decreased between pH 5 to pH 7, probably because $Pb(OH)^+$ became to be the dominant species of Pb(II) which can not chelate to dithiocarbamate groups. Lower sorption capacities at low pH for Pb(II) were probably due to the protonation of $-S^-$ resulting in $-SH$ which had less efficiency to chelate with Pb(II). But for Cu(II), the higher sorption capacities were found at lower pH indicating that Cu(II) probably preferred $-SH$ donor site more than $-S^-$ donor site.

On the other hand, the pH of metal solution slightly affected to the sorption capacity of Ag(I) and Au(III).

According to the hard-soft acid base principle and the assumption of the chelate complexes by dithiocarbamate derivatives with copper ion [65], lead ion [66] and silver ion [67], we proposed that Cu(II), Pb(II) and Ag(I) would bind to the SS moiety of dithiocarbamate group in 1:2 metal-to-ligand ratio.

The retention of Au(III) probably occurred via two mechanisms as follows:

(1) At low pH, Au(III) is mainly form of $AuCl_4^-$ which can exchange with Cl^- or piperazinedithiocarbamate on resin surface as the following chemical equations:

$$\text{Resin} - R_3N^+, Cl^- + AuCl_4^- \;\rightleftharpoons\; \text{Resin} - R_3N^+, AuCl_4^- + Cl^-$$
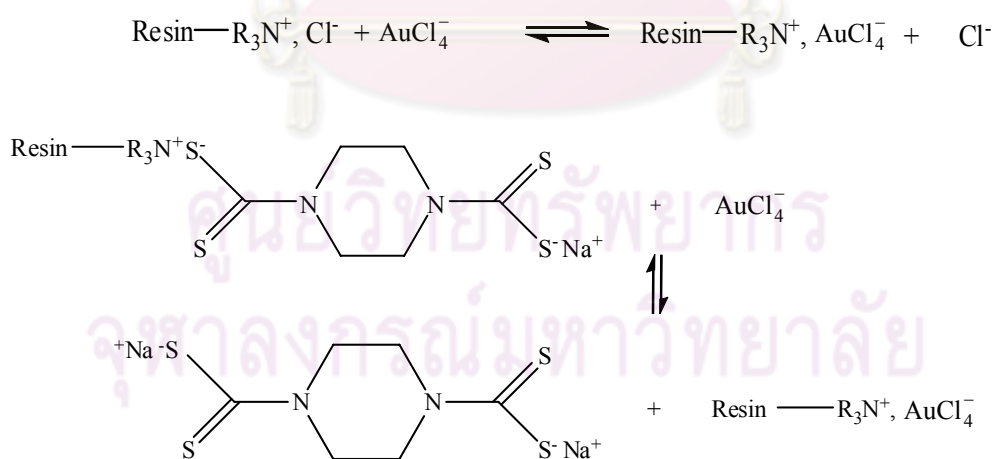
(2) The chelation between Au(III) and piperazinedithiocrbamate.

The Au-dithiocarbamate ratios of 1:1, 1:2 and 1:3 were proposed as follows [68]:

1:1	1:2	1:3
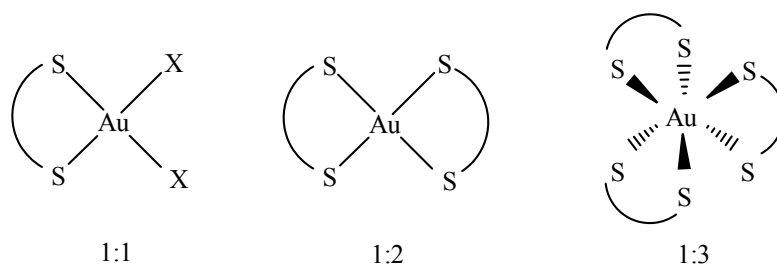
4.2.2 Effect of extraction time

The extraction time of metal ion is one of the important parameters because the application to flow system requires fast kinetic of equilibrium.

The effect of extraction time of metal ion on the complexing resin was studied using the metal ion solution at optimum pH as follows:

2.5 mg L^{-1} of Ag(I) at pH = 7

5.0 mg L^{-1} of Cu(II) at pH = 2

10.0 mg L^{-1} of Pb(II) at pH = 5

6.0 mg L^{-1} of Au(III) at pH = 5

A suspension of 10 mg of complexing resin and 5.00 mL of an individual metal solution in a test tube was mechanically stirred for different times between 5 to 120 min at room temperature. The aqueous solution was bringing off and the amount of residual metal ion in the solution was determined by FAAS.

The results of each metal extraction as a function of time are shown in Figure 4.2.
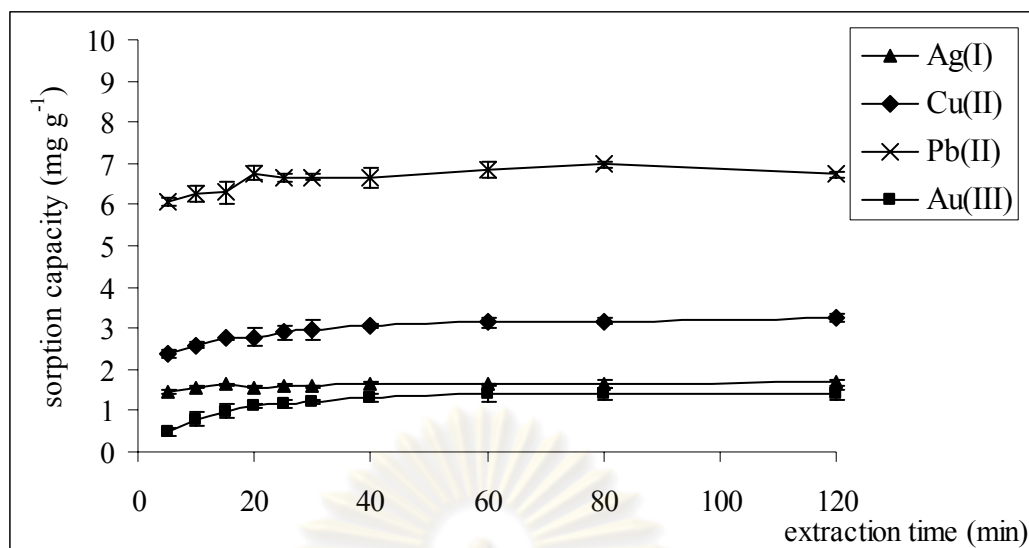
Figure 4.2 Sorption kinetics of metal-ligand on complexing resin.

The extraction time of Ag(I) and Pb(II) was fairly rapid at 15 and 20 min, respectively. While the extraction time of Cu(II) and Au(III) on complexing resin was found to be 60 min as long sorption kinetics. Therefore, the rapid sorption kinetics of Ag(I) and Pb(II) can be applied in column method.

4.2.3 Effect of initial concentration

The effect of initial metal concentration on sorption capacity was performed using the following procedure:

A suspension of 10 mg of complexing resin in 5.00 mL of a metal solution of which the concentration were varied between 2.5-100.0 mg L^{-1} for Ag(I), 10.0-120.0 mg L^{-1} for Cu(II), 5.0-100.0 mg L^{-1} for Pb(II) and 5.0-10.0 mg L^{-1} for Au(III) under the optimum pH as section 4.2.2 in a test tube. The mixture was mechanically stirred for 15, 60, 20 and 60 min for Ag(I), Cu(II), Pb(II) and Au(III), respectively. The temperature was controlled at 25 °C. The amount of residual metal ion in solution was determined by FAAS. The experiments were performed in triplicate (n=3).
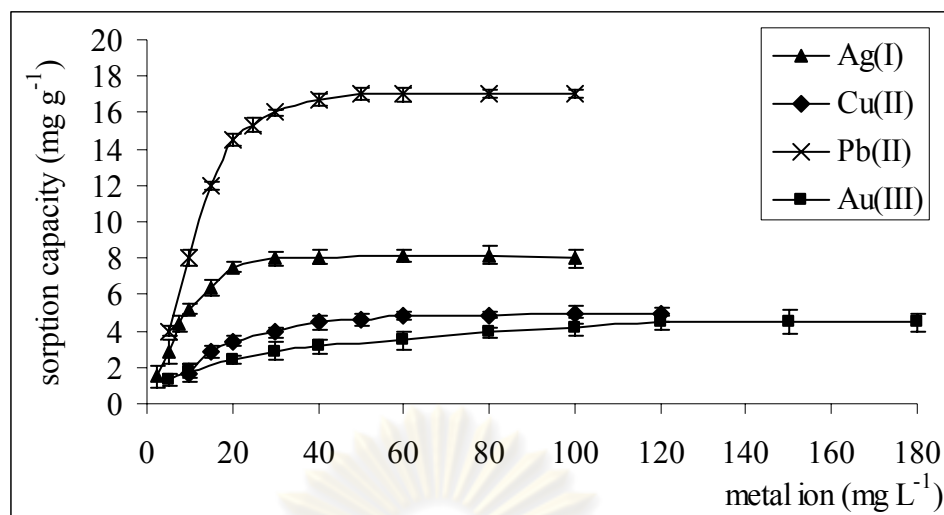
Figure 4.3 Effect of initial concentration for sorption capacity of metal ions.

Figure 4.3 showed the maximum sorption capacity of Ag(I), Cu(II), Pb(II) and Au(III) on the complexing resin with the initial concentration of 40, 60, 50 and 120 mg L^{-1}, respectively. The estimated maximum sorption capacities of complexing resin for Ag(I), Cu(II), Pb(II) and Au(III) were found to be 8.0, 4.9, 16.8 and 4.5 mg g^{-1}, respectively.

The sorption model of metal ion on the complexing resin according to the Langmuir model was used to analyze the sorption data. The information obtained from this model was used to describe the adsorption phenomena of investigated metal ion on solid-liquid interface.

The experimental data plotted C/N_f versus C, the linear curves were obtained with the R^2 > 0.99 (illustrated in Figure 4.4). These curves yielded the slope = 1/N_f^s. The maximum sorption capacities (N_f^s) calculated by 1/slope and Langmuir constant are given in Table 4.3.
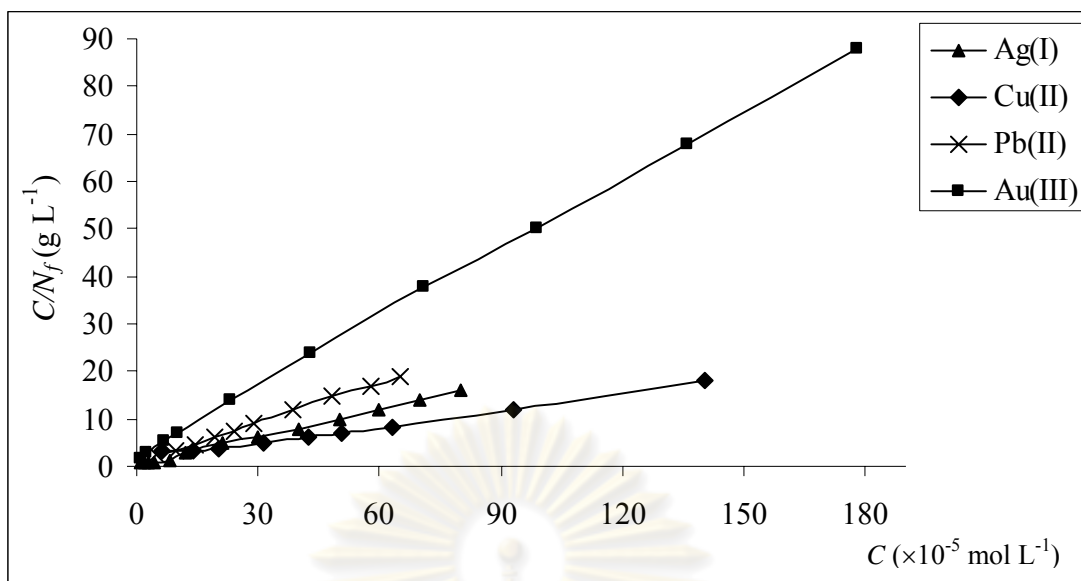
Figure 4.4 Langmuir plots for Ag(I), Cu(II), Pb(II) and Au(III) at 25 °C.

Table 4.3 Langmuir data

Metal ion	R^2 value	b value ($\times 10^4$ L mol^{-1})	N_f^s value ($\times 10^{-6}$ mol g^{-1})
Ag(I)	0.9913	2.97	74.2
Cu(II)	0.9975	1.53	43.5
Pb(II)	0.9936	1.47	81.1
Au(III)	0.9948	1.87	21.9

These results showed the important characteristic of the metal ions behaviors based on the Langmuir model in which the monolayer sorption process via chemisorption. Furthermore, the sorption capacities of each metal ion on complexing resin were different. The maximum sorption capacities (N_f^s) in the order of Pb(II) > Ag(I) > Cu(II) > Au(III) were obtained.

The b value represented the activity of the solution or bonding energy coefficient. This results showed that the maximum b value of Ag(I) was obtained on the complexing resin surface.

4.2.4 Effect of eluent

The effects of eluents on the %elution of metal ion from complexing resin were investigated. The metal ion released from surface of complexing resin depends on the metal-ligand stability. The formation constant values of metal-eluent component must be higher than the formation constant values of metal-ligand on complexing resin.

In this experiment, the effect of eluents on the elution of metal ion from complexing resin was also investigated in two steps as follows:

(1) Retention of metal ion on complexing resin.

A suspension of 10 mg of complexing resin and 5.00 mL of an individual metal ion solution in a test tube was mechanically stirred for 15 min for Ag(I), 60 min for Cu(II), 20 min for Pb(II) and 60 min for Au(III) at room temperature. Next, the residual metal ion solution was determined by FAAS and the complexing resin was washed with 5.00 mL of deionized water.

(2) Elution of metal ion from complexing resin.

5.00 mL of an eluent solution was added and mechanically agitated for elution time of 2 h at room temperature. The aqueous solution was bringing off and the amount of metal ion in the solution was determined by FAAS.

The experiments were performed in triplicate (n=3).

4.2.4.1 Eluent type and their concentrations

For desorption of Ag(I) and Au(III), the series of eluent type such as thiourea and thiosulfate were considered because their complexes have high formation constant values. In the case of Cu(II) and Pb(II), the eluent as EDTA was chosen because of the high formation constant values of 6.3×10^{18} for Cu(II)-EDTA complexes and 1.1×10^{18} for Pb(II)-EDTA complexes at pH 3 [69].

Moreover, the mineral acid such as hydrochloric acid was added in the eluent solution to increase the elution efficiency of Ag(I), Pb(II) and Au(III) from the complexing resin. Because the Ag(I), Pb(II) and Au(III) can be retained on complexing resin at pH 7.0, 5.0 and 5.0, respectively.

In the case of Cu(II), the retention of Cu(II) was found at pH 2.0 so the elution of Cu(II) from the complexing resin should be occurred in basic solution. The sodium hydroxide was added in the EDTA solution to improve the elution efficiency of Cu(II) from complexing resin.

The %elution of metal ion from complexing resin are shown in Table 4.4.

Table 4.4 %Elution in various eluents

Metal ion	Eluent type	Elution (%) [*]
Ag(I)	0.1 mol L^{-1} thiourea	70.5 (1.2)
	0.1 mol L^{-1} thiourea in 1 mol L^{-1} HCl	83.2 (2.4)
Cu(II)	0.1 mol L^{-1} EDTA	58.6 (1.7)
	0.1 mol L^{-1} EDTA in 0.05 mol L^{-1} NaOH	101.3 (2.0)
Pb(II)	0.1 mol L^{-1} EDTA	65.1 (2.3)
	0.1 mol L^{-1} EDTA in 0.5 mol L^{-1} HCl	88.4 (1.0)
Au(III)	0.1 mol L^{-1} thiourea	81.6 (0.7)
	0.1 mol L^{-1} thiourea in 1 mol L^{-1} HCl	101.0 (1.4)

[*] mean values (SD), n=3

The results showed that the Cu(II) and Au(III) were completely eluted using 0.1 mol L^{-1} EDTA in 0.05 mol L^{-1} NaOH and 0.1 mol L^{-1} thiourea in 1 mol L^{-1} HCl, respectively. But the uncomplete elutions of Ag(I) and Pb(II) were obtained. To ensure the desorption of Ag(I) and Pb(II) from complexing resin, a term of eluent concentration was considered.

The %elution of Ag(I) and Pb(II) as a function of eluent concentration level are shown in Table 4.5.

Table 4.5 %Elution[*] of Ag(I) and Pb(II)

	Concentration (mol L^{-1})	Ag(I)	Pb(II)
Thiourea[a]	0.1	82.1(3.3)	-
	0.3	98.0 (2.7)	-
	0.5	100.4 (1.9)	-
	0.7	102.1 (2.1)	-
EDTA[b]	0.1	-	87.6 (1.8)
	0.2	-	102.0 (0.9)
	0.3	-	101.1 (2.3)
	0.4	-	101.2 (1.5)

[*] mean values (SD), [a] in 1 mol L^{-1} HCl, [b] in 0.5 mol L^{-1} HCl, n=3

The results showed that the eluent as 0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl gave a complete elution of Ag(I) and Pb(II) was quantitatively eluted using 0.2 mol L^{-1} EDTA in 0.5 mol L^{-1} HCl.

The suitable eluent solutions for each metal ion are summarized in Table 4.6.

Table 4.6 Suitable eluents for metal desorption

Metal ion	Eluent
Ag(I)	0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl
Cu(II)	0.1 mol L^{-1} EDTA in 0.05 mol L^{-1} NaOH
Pb(II)	0.2 mol L^{-1} EDTA in 0.5 mol L^{-1} HCl
Au(III)	0.1 mol L^{-1} thiourea in 1 mol L^{-1} HCl

Moreover, the metal desorbed from complexing resin as a function of time was also investigated in next subheading. Because desorption of metal ion can be applied in a column method if the metal ion was rapidly eluted from complexing resin.

4.2.4.2 Elution time

The elution time of metal ion from complexing resin was also investigated as follows:

A suspension of 10 mg of complexing resin and 5.0 mL of a metal ion solution in a test tube was mechanically stirred for 15 min for Ag(I), 60 min for Cu(II), 20 min for Pb(II) and 60 min for Au(III) at room temperature. Next, the residual metal solution was bringing off and determined by FAAS and the metal-piperazinedithiocarbamate complexes on complexing resin was washed using 5.00 mL of deionized water. Afterward 5.00 mL of an eluent solution was added and mechanically stirred for different times between 5 to 90 min at room temperature. The aqueous solution was bringing off and the amount of metal ion in the solution was determined by FAAS. The experiments were performed in triplicate (n=3).

The results of each metal desorption as a function of time are shown in Figure 4.5.
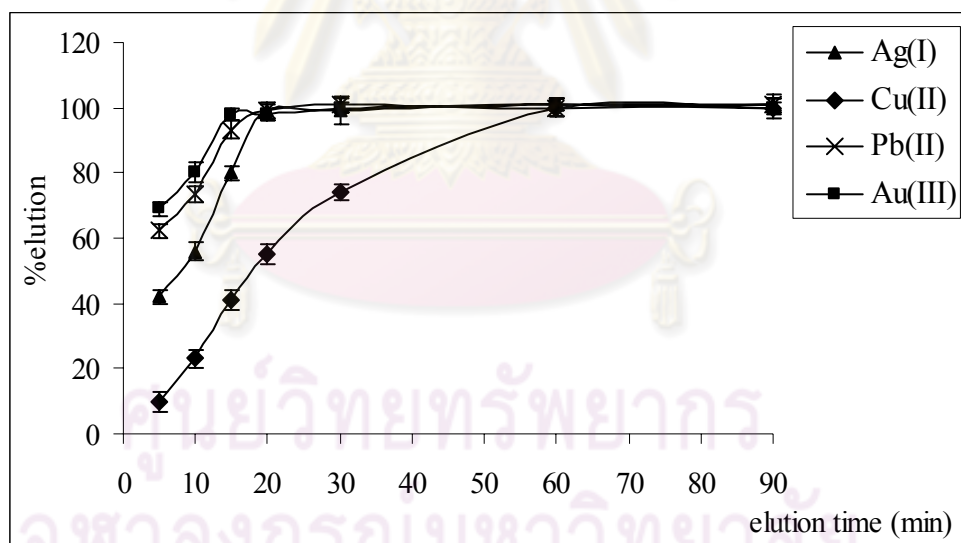
Figure 4.5 Effect of elution time.

The results showed that the elution times of Ag(I), Cu(II), Pb(II) and Au(III) were found to be 20, 60, 20 and 15 min, respectively. The desorption kinetics of Cu(II) was long times meanwhile Ag(I), Pb(II) and Au(III) desorbed from complexing resin was fairly rapid. Thus the desorption of Ag(I), Pb(II) and Au(III) can be applied in a flow system. Unfortunately, the sorption kinetics of Au(III) on complexing resin

became to 60 min as long sorption times while the sorption kinetics of Ag(I) and Pb(II) on complexing resin completed only 15 and 20 min, respectively (see section 4.2.2). So the sorption and desorption profiles of Ag(I) and Pb(II) were considered in a flow system.

4.2.5 Effect of coexisting cations

Common coexisting cations such as Na^+, Ca^{2+} and Mg^{2+} as chloride salts found in the natural water samples were used to investigate the selective of metal sorption on modified resin reported in term of % sorption.

The sorption efficiency of metal ion was calculated by the following equation 4.3.

$$\%\text{sorption} \quad = \quad \frac{C_i - C_r}{C_i} \times 100 \qquad (4.3)$$

where C_i = the initial concentration of metal ion before extraction (mg L^{-1})

C_r = the residual concentration of metal ion after extraction (mg L^{-1})

Experiments were performed by using 2.5 mg L^{-1} of Ag(I), 5.0 mg L^{-1} of Cu(II) and 10.0 mg L^{-1} of Pb(II). To ensure that the complexing resin can make trace metal ion separation from coexisting cation matrix with high selectivity, the comparison test between the complexing resin and the conventional cation exchange resin (Amberlite in sulfonic acid form) under the optimum conditions was performed using the following procedure:

A suspension of 10 mg of complexing resin and 5.00 mL of binary mixture containing metal ion and one of the coexisting cation in a test tube was mechanically stirred for 15 min for Ag(I), 60 min for Cu(II) and 20 min for Pb(II) at room temperature. The aqueous solution was bringing off and the amount of residual metal ion in the solution was determined by FAAS.

The effects of coexisting cations on the %sorption of metal ion are presented in Table 4.7.

Table 4.7 Comparison of the %sorption[*] on complexing resin and cation exchange resin

Coexisting cation (mg L^{-1})	Complexing resin			Cation exchange resin		
	Ag(I)	Cu(II)	Pb(II)	Ag(I)	Cu(II)	Pb(II)
Without coexisting cation	100.3 (0.4)	102.1 (1.0)	101.0 (1.4)	101.1 (0.5)	100.4 (2.3)	101.7 (1.2)
Li^+ 5	103.1 (0.4)	-	-	78.3 (2.3)	-	-
25	70.5 (1.2)	-	-	54.1 (3.1)	-	-
50	60.2 (2.5)	-	-	29.5 (1.9)	-	-
100	-	102.3 (0.7)	101.2 (2.3)	-	97.2 (2.4)	101.4 (1.1)
1000	-	98.1 (1.4)	100.1 (0.6)	-	78.5 (0.6)	85.3 (3.2)
Na^+ 5	100.2 (2.0)	-	-	32.2 (1.8)	-	-
25	89.4 (1.9)	-	-	21.1 (2.9)	-	-
50	71.2 (0.6)	-	-	11.6 (1.7)	-	-
100	-	100.8 (1.7)	100.3 (1.5)	-	86.8 (2.1)	91.2 (0.7)
1000	-	101.1 (3.2)	100.8 (2.2)	-	69.4 (2.0)	83.6 (1.2)
K^+ 5	101.3 (2.1)	-	-	43.2 (1.9)	-	-
25	94.1 (1.7)	-	-	31.0 (2.0)	-	-
50	88.7 (1.4)	-	-	17.4 (3.0)	-	-
100	-	101.4 (1.7)	99.4 (2.7)	-	90.2 (1.1)	99.1 (1.6)
1000	-	95.7 (0.9)	92.2 (1.2)	-	74.1 (2.5)	62.8 (2.3)
Mg^{2+} 10	101.2 (1.7)	100.2 (2.0)	100.0 (2.7)	100.1 (1.0)	101.0 (1.8)	100.2 (3.4)
100	102.5 (0.8)	100.4 (3.9)	98.4 (1.1)	70.8 (1.2)	71.9 (2.7)	89.6 (1.9)
1000	89.3 (2.0)	98.8 (0.6)	95.1 (2.9)	53.6 (1.5)	45.3 (1.0)	81.4 (2.8)
Ca^{2+} 10	101.2 (1.7)	100.1 (0.4)	100.5 (3.2)	100.4 (2.4)	99.2 (2.3)	100.2 (1.9)
100	103.1 (0.8)	100.0 (1.2)	96.3 (1.1)	77.5 (2.1)	76.0 (3.1)	95.5 (2.2)
1000	101.8 (2.0)	102.3 (2.5)	93.2 (1.5)	57.2 (1.3)	50.6 (1.9)	86.1 (1.4)

[*] mean values (SD), n=3

In the case of non coexisting cation, it was found that the cation exchange resin had similar retention efficiency in comparison with the complexing resin with high %sorption. In the presence of any coexisting cation, higher %sorption of Ag(I), Cu(II) and Pb(II) were obtained for complexing resin. When the concentration of coexisting cation increased, %sorption of interested metal ions significantly decreased for cation exchange resin, with ion-exchange retention mechanism. While coexisting cations had less effect for the complexing resin, indicating that the chelating agent as

piperazinedithiocarbamate enhanced the selectivity via the chelation mechanism. This loaded complexing resin had potential to apply to separate Cu(II) and Pb(II) from real water sample that contained alkaline and alkaline earth metal ions at high concentration level. The sorptions of Ag(I) in the presence of alkaline and alkaline earth at high concentrations on complexing resin were higher than those of cation exchange resin. Therefore, the complexing resin showed the good selectivity of Ag(I), Cu(II) and Pb(II) from coexisting cations media while conventional cation exchange resin can not obtain.

4.3 Extraction study in dynamic method

In column or dynamic method, the silver ion and lead ion were selected for sorption and desorption study because their retention time and release time were fairly rapid in batch method. The various parameters such as sample flow rate, eluent flow rate, sample volume and reusability of complexing resin were investigated.

In this study, a laboratory-made mini-column (i.d. 2.79 mm) was packed with 10 mg of complexing resin and 5.00 mL of metal solution containing 2.5 mg L^{-1} for Ag(I) at pH = 7.0 or 10.0 mg L^{-1} for Pb(II) at pH = 5.0 was passed through the mini-column controlled by a peristaltic pump model ISMATEC with Tygon tubing R 3607 i.d. 2.79 mm wall 0.86 mm. Then the residual concentration of metal ion was determined by FAAS. All experiments were performed in triplicate (n=3).

4.3.1 Flow rate of sample solution

The sample flow rate is an important parameter to obtain quantitative retention of metal ion on complexing resin. The flow rate of sample solution was studied in a range of 0.5-5.0 mL min^{-1} for sorption of Ag(I) and Pb(II).

The results are shown in Figure 4.6.
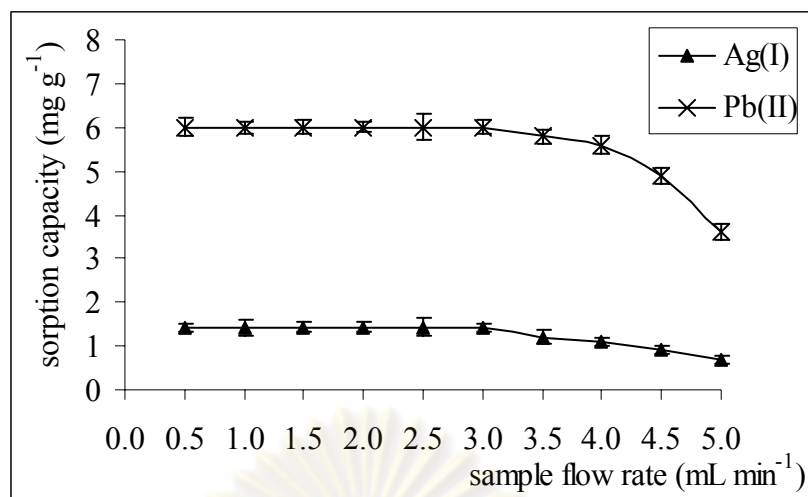
Figure 4.6 Effect of sample flow rate.

The efficiencies of sample flow rates were found to be 3.0 mL min^{-1} and 4.0 mL min^{-1} for Ag(I) and Pb(II), respectively. When the sample flow rate increased, the sorption efficiency decreased due to less contact of metal ion to binding sites of complexing resin.

Therefore, the sample flow rates of 3.0 mL min^{-1} for Ag(I) and 4.0 mL min^{-1} for Pb(II) were used to study in next experiments.

4.3.2 Flow rate of eluent solution

0.5 mol L^{-1} Thiourea in 1 mol L^{-1} HCl and 0.2 mol L^{-1} EDTA in 0.1 mol L^{-1} HCl were selected for elution of Ag(I) and Pb(II), respectively.

In this study, 5.00 mL of the eluent solution at a flow rate of 0.25-2 mL min^{-1} was also investigated the percentage elution of Ag(I) and Pb(II) from complexing resin.

The elutions as a function of eluent flow rate are shown in Figure 4.7.
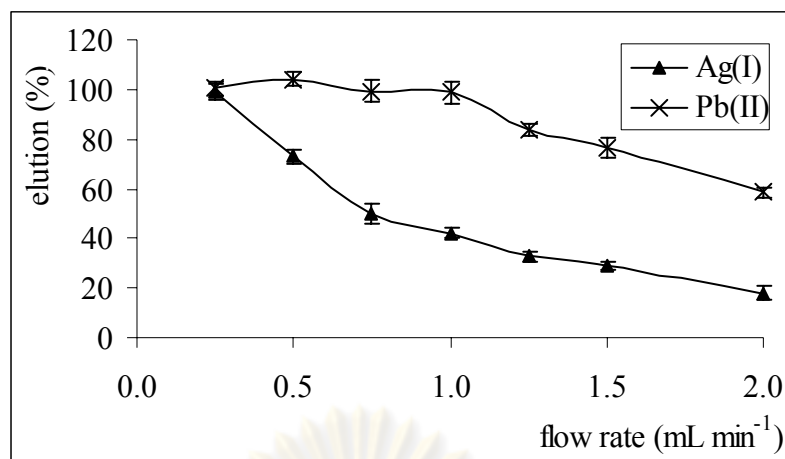
Figure 4.7 Effect of eluent flow rate on the elution of Ag(I) and Pb(II).

The quantitative elution of Ag(I) was obtained at the flow rate of 0.25 mL min^{-1} and the eluent flow rate of 1.0 mL min^{-1} was obtained for Pb(II). When increasing eluent flow rate, the %elution of metal ion decreased due to a rapid elution time.

4.3.3 Reusability of complexing resin

To evaluate the reuse of the complexing resin, the retention and the elution of Ag(I) and Pb(II) were performed under the optimum conditions as shown in Table 4.8.

Table 4.8 The optimum operating conditions for metal sorption and desorption on
10 mg of complexing resin

	Ag(I)	Pb(II)
Sorption conditions		
Concentration (mg L^{-1})	2.5	10.0
Solution pH	7.0	5.0
Sample flow rate (mL min^{-1})	3.0	4.0
Sample volume (mL)	5.0	5.0
Desorption conditions		
Eluent solution	0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl	0.2 mol L^{-1} EDTA in 0.1 mol L^{-1} HCl
Eluent flow rate (mL min^{-1})	0.25	1.0
Eluent volume (mL)	5.0	5.0

The retention and elution cycle consisted of four steps:

(1) retention by passing 5.00 mL of metal ion solution, then the metal ion in residual solution was determined by FAAS,

(2) washing by passing 5.00 mL of deionized water,

(3) elution by passing 5.00 mL of eluent solution, then the metal ion eluted was determined by FAAS,

(4) washing by passing 5.00 mL of deionized water,

The reusability diagram of complexing resin is represented in Figure 4.8.
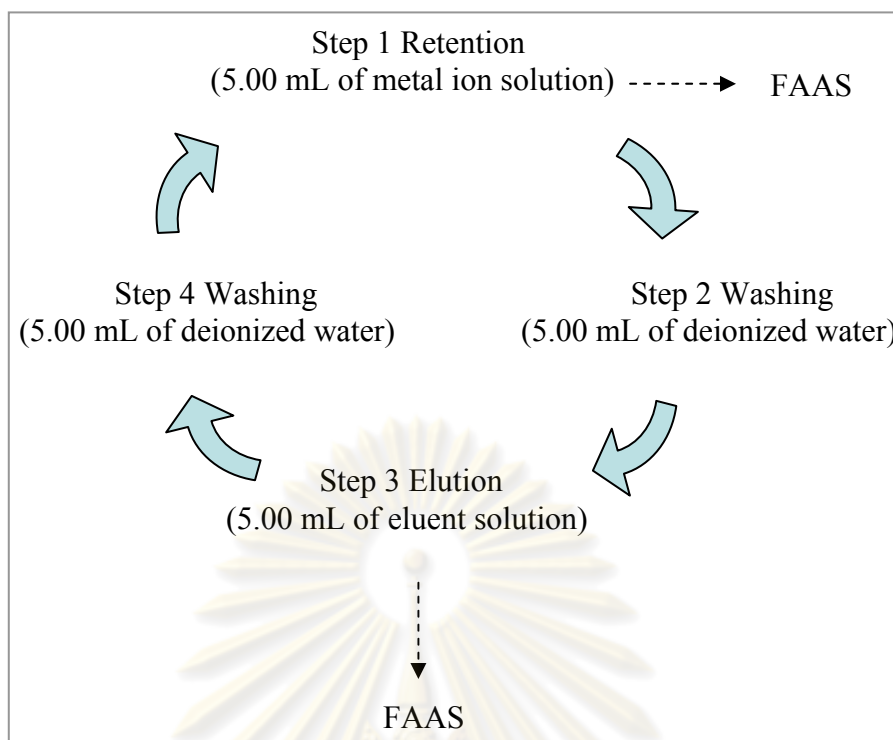
Figure 4.8 Metal sorption and desorption cycle diagram.

The experimental results were reported in term of the percentage recovery which was calculated by equation 4.4.

$$\% \text{ recovery } = \frac{N_e}{N_i} \text{ x } 100 \qquad (4.4)$$

where N_e = the amount of metal ion eluted from complexing resin (mg)

   N_i = the initial amount of metal ion (mg)

The recoveries of Ag(I) and Pb(II) as a function of cycle number are shown in Figure 4.9.
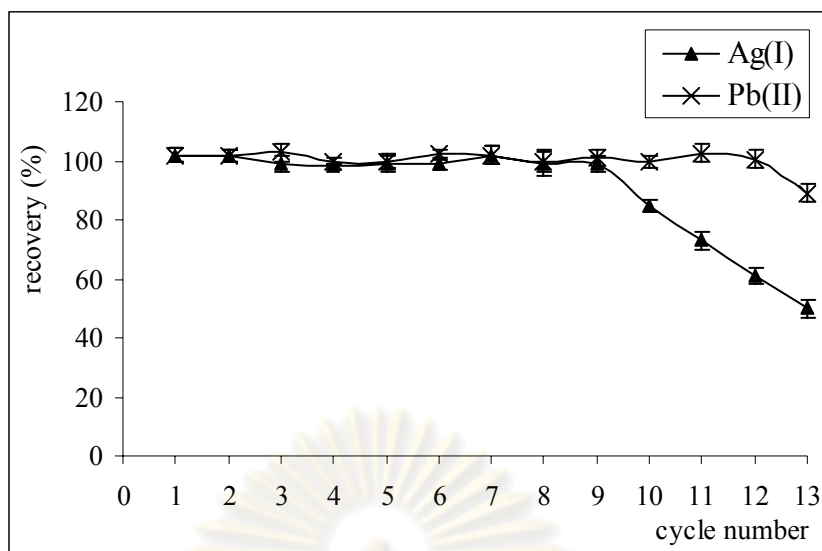
Figure 4.9 Reusability of complexing resin for Ag(I) and Pb(II).

The results showed that %recoveries significantly decreased since the cycle number of 10 for Ag(I) while %recoveries of Pb(II) were constant until the 12th repeated cycle. This indicated that the laboratory-made mini-column showed the reproducibility in both within and between columns at least 9 cycles for Ag(I) and 12 cycles for Pb(II).

4.3.4 Preconcentration study

The preconcentration of trace metal ion in term of the sample volume is one of the important parameters to obtain high preconcentration factor.

The Ag(I) volumes of 10-90 mL at a concentration of 50 μg L^{-1} and the Pb(II) volumes of 50-400 mL at a concentration of 100 μg L^{-1} were used in this experiment under the optimum conditions mentioned in Table 4.8.

The recoveries of Ag(I) and Pb(II) as a function of sample volume are illustrated in Figures 4.10 and 4.11, respectively.
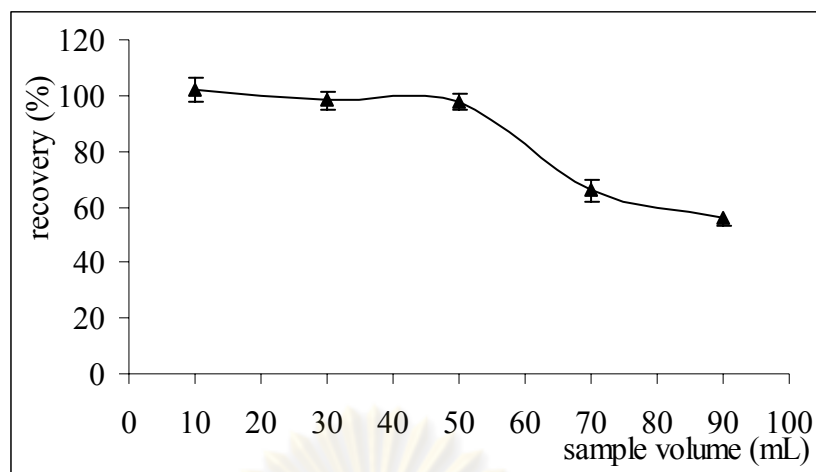
Figure 4.10 Effect of sample volume on the %recovery of Ag(I).
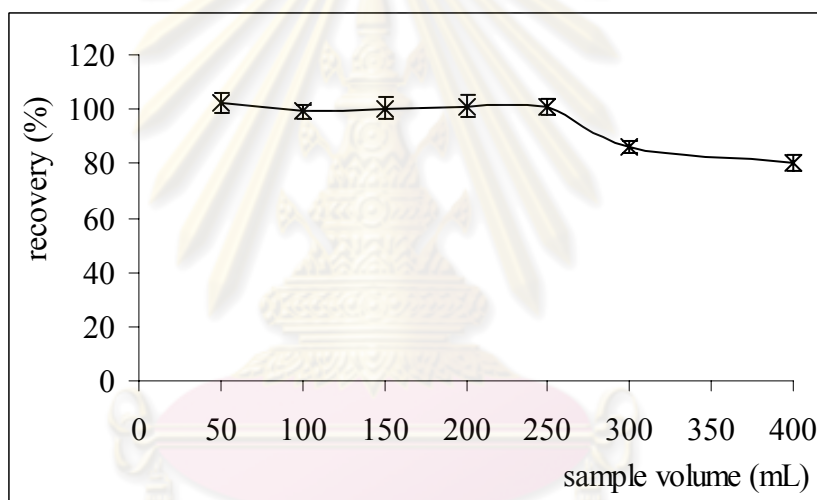
Figure 4.11 Effect of sample volume on the %recovery of Pb(II).

The sample volumes of 50 mL for Ag(I) and 250 mL for Pb(II) yielded acceptable recoveries. When sample volume increased, the %recovery of metal ion decreased probably due to the overloading of metal ion on complexing resin.

4.4 Analytical performance of method detection limit

The method detection limits provide a useful method for capability of the method. The method detection limit is restricted by the instrument detection limit.

Commonly, the instrument detection limit of system is always determined using blank solution. The detection limit and quantitation limit are defined as follows [70]:

1. Limit of detection (LOD) or detection limit is the lowest concentration level that can be determined from three times standard deviation of the signal of blank solution according to equation 4.5:

$$LOD_{(signal)} = y_{B(signal)} + 3SD_{B(signal)} \qquad (4.5)$$

2. Limit of quantitation (LOQ) or lower limit of quantitation is the concentration level above that quantitative result was obtained from ten times standard deviation of the signal of blank solution according to equation 4.6:

$$LOQ_{(signal)} = y_{B(signal)} + 10SD_{B(signal)} \qquad (4.6)$$

where $y_{B(signal)}$ = blank signal

$SD_{B(signal)}$ = standard deviation of blank signal according to equation 4.7

$$SD_{B(signal)} = \sqrt{\frac{\sum_{i}(X_i - \overline{X})^2}{N}} \qquad (4.7)$$

where N = number of data

X_i = signal value of blank

$\overline{X}$ = mean signal value of blank

Moreover, method detection limit (MDL) and method quantitation limit (MQL) of the method can be determined according to equations 4.8-4.9, respectively.

$$MDL = \frac{LOD}{P.F.} \qquad (4.8)$$

$$MQL = \frac{LOQ}{P.F.} \tag{4.9}$$

where P.F. = Preconcentration Factor = $\dfrac{\text{Sample volume (mL)}}{\text{Eluent volume (mL)}}$

The experimental data in section 4.3.4 showed the optimum sample volumes of 50 mL for Ag(I) and 250 mL for Pb(II) with the eluent solution of 5.00 mL. Therefore the preconcentration factors of 10 and 50 were obtained for Ag(I) and Pb(II), respectively.

In this manner, the blank solution as the eluent solution was used to determine the detection limit of FAAS without passing through the complexing resin column. The summary results of detection limit are shown in Table 4.9.

Table 4.9 Preconcentration factor, LOD and LOQ of Ag(I) and Pb(II)

Metal ion	Preconcentration Factor	LOD (mg L^{-1})	LOQ (mg L^{-1})
Ag(I)[*]	10	0.02	0.07
Pb(II)[**]	50	0.06	1.91

[*] blank solution = 0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl

[**] blank solution = 0.2 mol L^{-1} EDTA in 0.1 mol L^{-1} HCl

4.5 Application to real water samples

The complexing resin was applied to preconcentrate Ag(I) and Pb(II) in real water samples as tap water and sea water with spiked method under the optimum preconcentration conditions in a column method. These experiments were performed 9 replicates (n=9).

The Ag(I) volume of 50 mL and the Pb(II) volume of 250 mL were used in this experiment under the optimum conditions mentioned in Table 4.8.

The results are shown in Table 4.10.

Table 4.10 Recoveries of the Ag(I) and Pb(II) preconcentration from tap water and sea water[*], respectively

Element	Tap water				Sea water			
	Spiked, $\mu g\ L^{-1}$	Found[**], $\mu g\ L^{-1}$	recovery (%)	RSD (%)	Spiked, $\mu g\ L^{-1}$	Found[**], $\mu g\ L^{-1}$	recovery (%)	RSD (%)
Ag	0	n.d.	-	-	0	n.d.	-	-
	25	24.7 ± 1.0	98.8	5.4	25	22.5 ± 3.5	90.0	10.1
	50	51.4 ± 0.6	102.8	3.2	50	43.6 ± 2.0	87.2	7.6
	100	100.5 ± 1.5	100.5	2.5	100	88.6 ± 1.2	88.6	4.9
Pb	0	n.d.	-	-	0	n.d.	-	-
	50	50.9 ± 2.4	101.6	4.8	50	44.7 ± 1.3	89.4	4.7
	100	99.8 ± 2.0	99.8	3.7	100	94.1 ± 1.4	94.1	2.4

[*] Resource: Phetchburi province, [**] mean $\pm \dfrac{t_{0.05}s}{\sqrt{n}}$, n.d. = not detectable, n = 9

The results showed the high percentage recoveries and good RSD for Ag(I) and Pb(II) preconcentration in both tap water and sea water. Although the recoveries of Ag(I) and Pb(II) in sea water were less than in tap water probably due to their matrix, however the accuracy and the precision of this proposed method showed the satisfactory results in comparison with Table 4.11. This indicated that this system can be applied for determination of Ag(I) and Pb(II) in tap water and sea water.

Table 4.11 Analyte recovery and precision at different concentrations [71]

Analyte, (%)	Analyte ratio	Unit	Mean recovery, (%)	RSD, (%)
100	1	100%	98-102	1.3
10	10^{-1}	10%	98-102	1.8
1	10^{-2}	1%	97-103	2.7
0.1	10^{-3}	0.1%	95-105	3.7
0.01	10^{-4}	100 ppm	90-107	5.3
0.001	10^{-5}	10 ppm	80-110	7.3
0.0001	10^{-6}	1 ppm	80-110	11
0.00001	10^{-7}	100 ppb	80-110	15
0.000001	10^{-8}	10 ppb	60-115	21
0.0000001	10^{-9}	1 ppb	40-120	30

4.6 Comparison of complexing resin properties with literatures

The piperazinedithiocarbamate was loaded onto Amberlite IRA 402 anion exchange resin. The characteristic properties, in term of loading parameter and metal sorption, of this modified resin were compared to other resins in literatures, as shown in Table 4.12.

Table 4.12 Comparison of the characteristic properties of loaded anion exchange resin with literatures

Loaded complexing ligand	Types of sample	Loading time (min)	Loading capacity (μmol g^{-1})	Metal ions	Sorption time (min)	Sorption capacity (mg g^{-1})	Weight of complexing resin (mg)	Preconcentration Factor	Method of determination	Ref.
SPADNS	Drinking water	-	-	Cu(II)	-	-	1800	10	FAAS	[5]
ARS	Sea water	-	-	Cu(II)	90	50	750	5	FAAS	[43]
				Mn(II)	≥ 60					
Thoron	Natural water	-	200	Fe(III)	-	-	200	50	GF-AAS	[45]
PV	Nickel sample	-	10	Sn(IV)	≥ 120	-	100	10	DCP-AES	[46]
Napthol blue black	Pharmaceutical sample	≥ 90	3.9×10^9	Cu(II), Zn(II)	-	-	1500	-	FAAS	[67]
ANS	Copper ores	-	200	Ag(I)	-	-	200	-	FAAS	[68]
Piperazine dithiocarbamate	Tap water, Sea water	≥ 8	3.5	Ag(I)	15	8.1	10	10	FAAS	This work
				Cu(II)	60	4.9		-		
				Pb(II)	20	16.9		50		
				Au(III)	60	4.5		-		

ARS = Alizarin Red S

ANS = 8-amino-naphthalene-2-sulfonic acid

PV = Pyrocatechol violet

SPADNS = trisodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate

Thoron = (1-(2-arsonophenylazo)-2-hydroxy-3,6-naphthalenedisulfonic acid sodium salt

The literature data indicated that the complexing ligand in this work was rapidly loaded on Amberlite IRA 402 anion exchange resin although the loading capacity of 3.5 μmol g^{-1} was obtained in compared with others. Moreover, the sorption kinetics of metal ions on piperazinedithiocarbamate resin were faster than other complexing resins.

Furthermore, the preconcentration factors of 10 for Ag(I) and 50 for Pb(II) were obtained when the only 10 mg of piperazinedithiocarbamate resin was used in column method.

CHAPTER V

CONCLUSION

The complexing ligand as piperazinedithiocarbamate was synthesized and characterized by FT-IR and ^{1}H-NMR spectroscopies. A complexing ligand rapidly loaded anion exchange resin was found at pH $\geq$ 5.0 and the maximum loading capacity of the piperazinedithiocarbamate onto anion exchange resin of 3.5 μmol g^{-1} was obtained.

A new complexing resin was used to separate heavy metals such as silver ion, copper ion and lead ion from spiked sample water under static and dynamic method. In static method, the parameters such as solution pHs, sorption kinetics and concentrations of metal ion were studied. Moreover, the sorption behaviors of all metal ions fit well to the Langmuir model and the high selectivity was obtained in comparison with the conventional cation exchange resin. The parameters in column method consisted of flow rate of metal solution, flow rate of eluent solution, reuse of complexing resin and sample volume were considered. The complexing resin can be reused in several times, nine cycles for silver ion and twelve cycles for lead ion, respectively. Especially, silver ion and lead ion showed a high precencentration factors of 10 and 50 when the complexing resin was used only 10 mg.

The optimum operating conditions for preconcentration of silver ion and lead ion on 10 mg of complexing resin as following:

	Ag(I)	Pb(II)
Sorption conditions		
Concentration (μg L^{-1})	50.0	100.0
Solution pH	7.0	5.0
Sample flow rate (mL min^{-1})	3.0	4.0
Sample volume (mL)	50.0	250.0
Desorption conditions		
Eluent solution	0.5 mol L^{-1} thiourea in 1 mol L^{-1} HCl	0.2 mol L^{-1} EDTA in 0.1 mol L^{-1} HCl
Eluent flow rate (mL min^{-1})	0.25	1.0
Eluent volume (mL)	5.0	5.0

Furthermore, the complexing resin was applied for the preconcentration of trace silver ion and lead ion from real water samples as tap water and sea water under the optimum preconcentration in a column method. The results showed a good %recovery and %RSD of metal ions with the acceptable range. Therefore, the proposed method has high accuracy and high precision.

Suggestions in the future works

The efficient methods for synthesis of piperazinedithiocarbamate yielded in good purity should be established. The loading capacity of complexing ligand onto anionic resin should be improved in order to obtain the higher preconcentration factor and the lower limit of detection. Moreover, a more effective and comfortable system may be developed to the on-line preconcentration-FAAS system.

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