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碩士論文

以螯合劑自鉻化砷酸銅防腐材萃取鉻、銅及砷

陳品叡

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Extraction of Chromium, Copper, and Arsenic from CCA Treated Wood by Using Chelating Agents

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Extraction of Chromium, Copper, and Arsenic from CCA
Treated Wood by Using Chelating Agents

本論文係陳品叡君（R96625045）在國立臺灣大學森林環境暨資源學研究所完成之碩士學位論文，於民國 98 年 05 月 15 日承下列考試委員審查通過及口試及格，特此證明

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摘要

鉻化砷酸銅（Chromated copper arsenate, CCA）是一種被廣泛使用的水溶性木材防腐藥劑，由鉻、砷及銅三種金屬氧化物混合而成。CCA 防腐材廢棄物在焚燒或掩埋之後，容易釋放重金屬，因此 CCA 防腐材廢棄物若能先移除一部分重金屬，將能有效降低對環境的污染。CCA 防腐材之處理有許多方法，其中水溶液萃取是最有效且被廣泛使用的方法之一。本研究使用 CCA-C 型防腐劑（含有氧化鉻 47.5%，氧化銅 18.5%，五氧化二砷 34.0%）經滿胞法處理之南方松(*Pinus taeda*)，螯合劑使用具生物可分解性之螯合劑：EDTA(Ethylenediaminetetracetic acid)，EDDS（*S*, *S*-Ethylenediaminedisuccinic acid）及 NTA（Nitrilotriacetic acid）等三種。萃取條件包括：溶液酸鹼值、濃度、萃取溫度與萃取時間。三種金屬均在酸性條件下（pH 2.0-4.0）的萃取效果最好，因此推論此三種螯合劑較適合於酸性條件下反應。螯合劑濃度結果顯示在濃度範圍為 0.01 至 0.1 M 時，0.1M 可以達到最好的萃取效果。溫度之結果可發現在 75$^{\mathrm{o}}$C 時即可達到十分良好之重金屬移除效率。萃取時間可看出各金屬之萃取速度並不一致，鉻和砷為萃取速率較慢之重金屬，萃取時間對其結果影響較大；銅的萃取速率較快，5~6 小時左右就可以移除 93%。綜合以上最適條件，最好之移除效率分別為鉻 53%-66%，銅 84%-93%，砷 55%-62%。固液比對 EDDS-CCA 化學藥劑比之指數函數結果可看出 EDDS 對於銅之螯合能力最佳，鉻次之，砷最弱;且固液比為 10 時萃取效果較好。序列萃取結果顯示未以 EDDS 萃取之 CCA 防腐材，85.6%之鉻存在於有機相分離部及殘餘相分離部；銅有 49%存在於可交換分離部及殘餘相分離部。有機相分離部及殘餘相分離部則含有 80.2%的砷。本研究顯示以生物可分解性較強之螯合劑 EDDS 與 NTA，可有效去除 CCA 防腐材中之重金屬，且效果比一般經常使用之生物可分解性螯合劑 EDTA 更佳，除了可降低 CCA 防腐材廢棄物對於環境之污染，也能使此技術應用層面更廣。

關鍵詞：鉻化砷酸銅防腐材，金屬螯合劑，鉻化砷酸銅（CCA），序列萃取。

Abstract

Chromated copper arsenate (CCA) is the most widely used wood preservative. It is formulated with copper, chromium, and arsenic oxides. Better disposal methods of CCA treated wood waste would be needed to alleviate secondary pollution induced by waste land-filling or incineration.

There are many methods to remediate CCA treated wood waste. Aqueous extraction is the most one. In this study, the materials are southern pine (*Pinus taeda*) that is pressure-treated with CCA type C preservative (hexavalent chromium as CrO_3, 47.5%; copper as CuO, 18.5%; arsenic as As_2O_5, 34.0%). Chelating agents are biodegradable chelating agents: ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and [S, S]-Ethylenediaminedisuccinic acid (EDDS). This study investigates impact of various parameters including pH, chelating concentration, temperature, and chelating duration on chromium, copper, and arsenic extraction efficiencies. Results indicates that lower pH (pH 2.0-4.0) are more effective than higher pH (pH>6) for extraction of chromium, copper, and arsenic. By changing solution concentration from 0.01 to 0.1M, the optimal extraction efficiencies for three metals were obtained at 0.1 M. Optimal extraction temperature for CCA metals was 75^{o}C. The results of duration of extraction presented the chelating rates of metals. There is great extraction efficiencies of copper between 5 and 6 hours extraction. Under these best conditions, the highest percentage removals of chromium, copper and arsenic are 53%-66%, 84%-93%, 55%-62%, respectively.

In the results of EDDS-CCA stoichiometric ratios, EDDS concentrations above unit stoichiometric requirement are required to remove CCA metals at optimal. And the extraction efficiencies are illustrated when solution to wood ratio is 10. The results of sequential extractions demonstrated that chromium was mainly existed in the organic and residual fractions (85.6%); copper is mainly existed in exchangeable and residual fractions (49%); arsenic is mainly existed in organic and residual fractions (80.2%).

This study indicates the extraction efficiencies for chromium, copper, and arsenic by EDTA, EDDS and NTA are satisfactory. Besides, EDDS and NTA are more biodegradable, and more effect in CCA treated wood remediation. In the near future, EDDS and NTA could be applied broadly to remove heavy metals from wastes.

Key words: CCA treated wood, chelating agent, Chromated copper arsenate (CCA), sequential extraction.

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Chapter 1 Introduction

Chromated copper arsenate (CCA) is one of the most widely used wood preservative to protect the wood which is attacked by fungi, wood attacking insects and a lot of types of marine organisms. CCA also improves the weather-resistance of treated timber, and it can assist paint adherence in the long term (Hingston J. A. *et al*., 2000).

With the use of CCA, the volume of CCA treated wood is very large in the United States. In 2004, CCA has been prohibited from using in house use wood like furniture and outdoor desks by U.S. Environment Protection Agency (USEPA). In Taiwan, the government prohibited CCA from house-use wood and materials, which may contact human skin in 2007. But around the world, CCA is not all prohibited, CCA and CCA treated wood are only used less than before in some areas. CCA treated wood can be utilized more than 50 years. The waste of CCA treated wood would be a big problem in waste disposal, because CCA treated wood waste, which is not treated by any pretreatment, will cause the diffusion of toxins into the atmosphere (as in the case of incineration) or into the soil and groundwater (as in the case of land-filling). Options for recycling and reusing CCA treated wood waste include dimensional lumber, round wood size reduction, composites, and remediation (Clausen, 2003). Remediation managements include chemical extraction, bioleaching, chelation, and liquefaction or a combination of these techniques. To reduce the re-pollution of remediation, chelation is a better method than others because it uses some biodegradable chelating agents to extract heavy metals. And chelating agents can separate heavy metals from their substrates.

This study uses three types of chelating agents, [S,S]-ethylenediaminedisuccinic acid (EDDS), nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). EDTA is one of the most common biodegradable chelating agents used to bind the metal ions to very stable complexes in heavy metal contaminated soils and water, and EDTA can remediate such substrates. However, EDDS and NTA are more biodegradable than EDTA (Cao *et al.*, 2007). The purpose of this study is to compares the extraction efficiencies with EDDS, NTA and EDTA, and the extraction efficiencies are changed with different conditions, including pH, chelating concentration, temperature, and chelating duration.

Extraction of CCA treated wood with EDDS solution was also evaluated at various solution to wood ratios and EDDS-CCA stoichiometric ratios. Various solution to wood ratios and EDDS-CCA stoichiometric ratios effect the extraction efficiency of chelating CCA treated wood. Solution to wood ratios present the use of solution in the industry, and they are important factors. EDDS-CCA stoichiometric ratios demonstrate how the concentration of EDDS affects the extraction efficiency. And EDDS-CCA stoichiometric ratios give the information to explain different extraction efficiencies between chromium, copper, and arsenic. Mobility of metals in the samples is evaluated by using the sequential extraction scheme. The results of sequential extraction scheme mention what bonds EDDS breaks at pH 4.0 and pH 9.0, respectively.

Therefore, this study will compare extraction efficiencies with three different chelating agents: EDDS, NTA, and EDTA.

Chapter 2 Literature review

2.1 Chromated copper arsenate (CCA)

The wood preservation process involves impregnating the wood with chemicals that protect the wood from biological deterioration and to delay fire development. The most common process includes pressurized-treatment in which the chemicals were carried into the wood by a carrier fluid. Treatment chemicals utilized during the wood preserving process are categorized into four major categories (AWPA, 1994). These categories include: waterborne preservatives including CCA, oilborne preservatives including pentachlorophenol, creosote and fire-retardants. Most common use for creosote treated wood includes railroad and bridge ties. Pentachlorophenol is used to treat utility poles and cross-arms (Milton, 1995). Both pentachlorophenol and creosote impart a dark color to the wood, have an odor, and result in an oily surface that is difficult to paint. In addition, wood treated with either chemical is flammable and skin contact may cause irritation. Neither pentachlorophenol treated wood nor creosote treated wood should be used in indoor.

Waterborne preservatives use water as the carrier fluid during the treatment. The water is evaporated shortly from the wood after treatment, which leaves behind the treatment chemicals. The most common waterborne chemicals are metal oxides. These chemicals include chromated copper arsenate (CCA), acid copper chromate (ACC), ammoniacal copper arsenate (ACA), chromated zinc chloride (CZC), and ammoniacal copper zinc arsenate (ACZA). The most common of these waterborne preservatives is CCA, which represents over 90% of the U. S. waterborne preservative market (AWPA, 1996).

Chromated copper arsenate (CCA) is one of the most widely used wood preservative to protect the wood which is attacked by fungi, wood attacking insects and a lot of types of marine organisms. CCA also improves the weather-resistance of treated timber, and it can assist paint adherence in the long term (Hingston J. A. *et al*., 2000). CCA is a mix of copper, chromium, and arsenic formulated as oxides or salts. Since the 1930s, CCA has been used to pressure treated lumber used for decks, playgrounds (play-sets), and other outdoor uses. As the 1970s, the majority of the wood used in residential settings was CCA treated wood.

CCA has been prohibited from using in house use wood such as furniture and outdoor desks by U.S. Environment Protection Agency (USEPA) in 2004, because the volume of CCA treated wood increased with the grand use of CCA in the United States. However, CCA treated wood was still used in building materials or materials of the groundwork. In Taiwan, the government prohibited CCA from house-use wood and materials, which may contact human skin in 2007. Around the world, CCA is not all prohibited, CCA and CCA treated wood are only used less than before in some areas. Though some users may use other preservatives like alkaline copper quaternary (ACQ) to replace CCA,

CCA treated wood is still a used material.

In general, CCA treated wood can be utilized more than 50 years. The waste of CCA treated wood would be a big problem in waste disposal, because CCA treated wood waste, which is not treated by any pretreatment, will cause the diffusion of toxins into the atmosphere or into the soil and groundwater. Options for recycling and reusing CCA treated wood waste include dimensional lumber, round wood size reduction, composites, and remediation (Clausen, 2003). Size reduction by re-milling, shaving, or re-sawing CCA treated wood waste reduces the volume of landfilled waste material and provides more choices for reusing used CCA treated wood. Manufacturing composite products from CCA treated wood waste combined with untreated wood, plastic, or cement.

CCA is stabilized in the wood by means of chemical reaction called fixation (Kartal and Lebow, 2001). The leach-resistance of CCA is a result of the chemical fixation, which renders the toxic ingredients insoluble in water (Kartal, 2003). The essence of CCA fixation is the reduction of chromium from hexavalent to the trivalent state, and then is the subsequent precipitation or absorption of copper, chromium, and arsenic complexes in the wood (Lebow and Kartal, 1999). The reaction that takes place in the wood during fixation of CCA has a great effect on the metal species that are emitted from the wood, and the subsequent toxicity of these leachates is presented (Kartal, 2003). The toxicity of copper, chromium and arsenic is highly dependent on the specific form present.

Hexavalent chromium, for instance, is known to be carcinogenic and mutagenic, but if it is reduced to trivalent chromium during the fixation process, it may be significantly less harmful (Kartal, 2003). Copper in the free ionic state above trace levels is toxic, but copper is one of the most important fungicides and forms a major fungi-toxic component of CCA. As a toxicant, copper is also believed to have a variety of broad-spectrum effects on microorganisms (Morrell, 1989). Pentavalent arsenic, in turn, is thought to be more prevalent and less toxic than trivalent arsenic. In CCA treated wood, the chromium fixes the copper and arsenic to the wood, and arsenic can protect the wood against insects.

2.2 Characterization of CCA treated wood

One of the most important preserved woods in United State as well as in Canada is CCA treated wood, which is used in outdoor decks, playgrounds and fences. CCA treated wood is the green-tinged lumber sold in almost every home center and lumberyard in America. The primary advantage in the use of CCA treated wood is that it produces no odor or vapor. CCA has been favored for lumber treatment because it is inexpensive, leaves a dry, paintable surface, and has relatively great leach-resistant (Moghaddam and Mulligan, 2008), and CCA treated wood has the indisputable benefit of being highly resistant to rot and insects. CCA is used to treat primarily lumber, timbers, posts and plywood. Its use in treating other products, such as poles and pilings, has seen relative increases as well.

However, there is increasing interest and attention about potential environmental contamination from the leaching of copper, chromium and arsenic from CCA treated wood when CCA treated wood placed in landfills in North America. The life cycle of CCA treated wood is estimated to be more than 50 years, and then the wood are discarded as waste. By 1995, more then 90% of 67 million kg of utilized waterborne preservatives was CCA and the quantity of removed treated wood from service is estimated to increase to 12 million m^3 by the year 2004 and to 16 million m^3 by 2020 in the United State (Moghaddam and Mulligan, 2008).

In CCA treated wood, the amount of chromium, copper and arsenic was calculated as CrO_3, CuO and As_2O_3 (Moghaddam and Mulligan, 2008). The America Wood Perservers' Association (AWPA) defined three formulations for CCA. The differences of the A, B and C types were in the relative ratio of chromium, copper and arsenic. Comparison of the analysis results with the three types of CCA treated wood in Figure 1 (AWPA, 1996).

The major difference between the three types of CCA treated wood is the amount of chromium and arsenic, whereas copper does not vary a lot. The relative proportions range from 35~65%, 16~45%, 18~20% for chromium, arsenic, and copper, respectively. Type A is high in chromium and type B is rich in arsenic (Figure 1), but type C is by far the most common type, which has been used as it is the most leach resistant (Ibach, 1999).

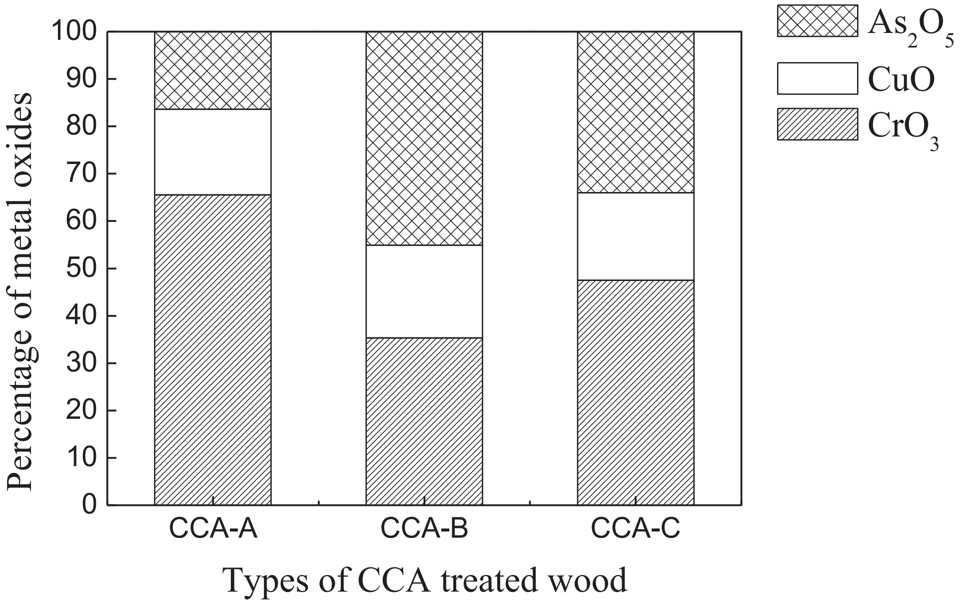


Figure 1. Three types of CCA treated wood (AWPA, 1996)

According to Pizzi (1982), the ratio of As/Cu determines the fixation rate; increasing arsenic slows the fixation reaction and increasing copper stimulates them. With increased arsenic, more chromium arsenate is formed, and less hexavalent chromium as H_2CrO_4 is available for rapid complexation with lignin, but increased copper increases the hexavalent chromium as $CuCrO_4$ (Moghaddam and Mulligan, 2008).

As a consequence of this variation in different formulations, early leaching studies generated variable results, with arsenic often proving to leach the most, presumably due to insufficient chromium available for fixation (Moghaddam and Mulligan, 2008). As CCA-C treated wood offered the best combination of performance and leach resistance, most of the produced CCA wood was treated with type C of CCA (Tom, 2001). And type

C was chosen by the AWPA technical committees to encourage a single standard for CCA (Ibach, 1999). The use of CCA-B was currently confined to field and remedial treatments, and relatively few people used CCA-A (Moghaddam and Mulligan, 2008).

In Table 1 (AWPA, 1996), the amount of CCA utilized to treat the wood or retention level depends upon the particular application for the wood product. Low retention values (0.25 lb/ft^3) are permissible for plywood, lumber, and timbers if the wood is used for above ground applications. Higher retention values are required for load bearing wood components such as pilings, structural poles, and columns. The highest retention levels (0.8 and 2.5 lb/ft^3) are required for wood components which are used for foundations or saltwater applications.

Table 1. Retention requirements for CCA treated wood (AWPA, 1996)

Application	Retention value (lb/ft^3)
Above ground: lumber, timbers, and plywood	0.25
Ground/Freshwater contact: lumber, timbers, plywood	0.40
Salt water splash, wood foundations: lumber, timbers, and plywood	0.60
Structural poles	0.60
Foundation/Freshwater: pilings and columns	0.80
Salt water immersion: pilings and columns	2.50

Nevertheless, these metals may be leached from CCA treated wood. According to Kartal (2003), copper that may loss from CCA treated wood causes certain primary concerns due to its potential to contaminate the environment. And Moghaddam and Mulligan (2008) indicated that the leached metals during rain polluted ground and surface water used for drinking water. As the leachate of CCA treated wood in landfills is genotoxic and carcinogenic, the contaminated water is dangerous for human beings and animals, and the investigation of leaching and biodegradation of CCA treated wood are important. Land-filling of existing CCA treated wood and its related environmental problems will continue to be problematic due to leaching heavy metals (Jambeck *et al.*, 2006). It is very important to use better waste disposal to decrease the pollution of toxic metals.

2.3 Waste disposal of CCA treated wood

With the extensive use of CCA, a large amount of CCA treated wood waste has already caused worldwide attention and environmental consciousness. Disposing of CCA treated wood waste would be necessary to reduce the pollution produced by landfilling or incineration. In United States, Canada and Australia, the method of disposal most used for CCA treated wood is landfilling without any pretreatment (Moghaddam and Mulligan, 2008). Countries such as Germany ban landfill disposal, but the ash of incinerated CCA treated wood is regarded as hazardous since heavy metals concentrate in the ash (Solo-Gabriele *et al*., 2002), and for this reason, proper air pollution control is required (Iida *et al.*, 2004).

When CCA treated wood waste is disposed, the heavy metals should be separated from CCA treated wood waste in order to prevent the diffusion of toxics into the atmosphere (as in the case of incineration) or into the soil and groundwater (as in the case of land-filling) (Kakitani *et al*., 2006). Figure 2 (Clausen, 2003) shows some options for disposing of or reusing CCA treated wood waste.

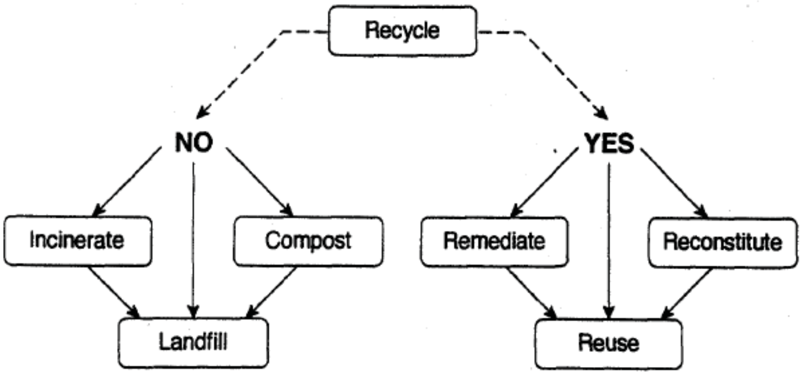


Figure 2. Options for disposing of or reusing CCA treated wood (Clausen, 2003)

These options are divided into recycling options or non-recycling options (Clausen, 2003). Conventional methods of disposing CCA treated wood waste are incineration and land-filling, but in Figure 2, some lightly polluted CCA treated wood waste will be reused by certain processes including remediate, reconstitute or reuse. Before incineration or land-filling, CCA treated wood waste which is remediated by chemicals or with heavy metals removed would decrease the damage to the environment.

After disposal of CCA treated wood waste, the remediated CCA treated wood waste is able to reuse for composite or paper products (Clausen, 2003). In Table 2 (Clausen, 2003), the technology of reusing CCA treated wood has been developed since the middle 1990s, but few have gained wide acceptance.

Table 2. Tangible products from reused CCA treated wood categorized by method (Clausen, 2003)

Method	Products
Size reduction	
Shaving, resawing, remilling	Decking, poles, posts
Reconstituted composites	
Wood-Wood composites	Flakeboard, OSB[a], particleboard, MDF[a], glulam
Wood-cement composites	Sound baeeiers, structural forms
Thermoplastic composites	Specialty products
Remediation	
Chemical extraction, bioleaching, chelation	Composite products, paper products
Liquefaction	Polyurethane products

[a] OSB, oriented strandboard; MDF, medium-density fiberboard.

Clausen (2003) indicated that CCA treated wood waste was not classified as a hazardous waste before, because chromium and arsenic were strongly fixed to the lignin component of wood. Therefore, the disposal of CCA treated wood waste was not seemly important in the country where human has used CCA in 1960s ago. Incineration or land-filling of CCA treated wood waste still has potential diffusion of toxic metals. Accurate disposal of CCA treated wood waste would decrease these risks.

There are many methods to remediate CCA treated wood waste. Solution extraction is the most useful method to remediate CCA treated wood waste. Solution extraction techniques for the purpose of removing heavy metals have been discussed extensively in the field of purification of CCA treated wood waste, because heavy metals have strong fixation with CCA treated wood. It is difficult for CCA treated wood to extract chromium, copper and arsenic. When solution impregnated with CCA reagents, the elements in the solution form slightly soluble salts, primarily $CuCrO_4$ or $CrAsO_4$, which are fixed strongly with the wood components for a long time period (Kakitani *et al.*, 2006). Traditional solution extraction is usually used strong acid solution like H_2SO_4 or HNO_3, but the efficiency is only about 50% (Clausen, 2003). By using some solution like ethylenediaminetetraacetic acid (EDTA), [S,S]-ethylenediaminedisuccinic acid (EDDS), and oxalate (OA), the effect of extraction can raise to 60% ~ 90% (Kartal and Kose, 2003).

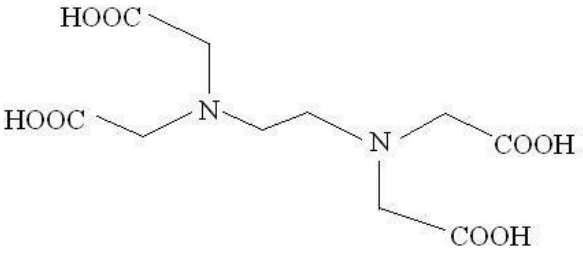
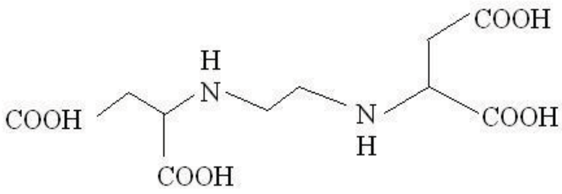
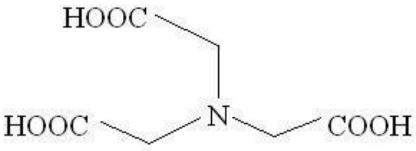
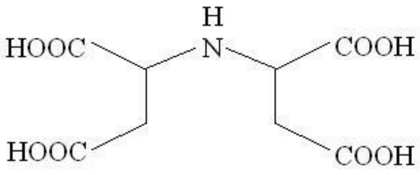
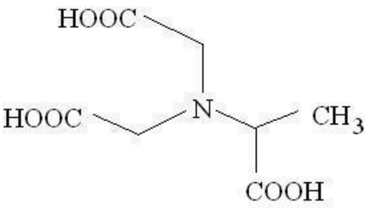
High efficiency in the removal of heavy metals from CCA treated wood by solution extraction has been achieved with various chelating agents (Kakitani *et al*., 2006). As the heavy metals of CCA is connected with lignin, the mechanism of chelating extraction from CCA-treated wood can be assumed as

Lignin-CCA + Ligand-H ←→ Lignin-H + Ligand-CCA (Kakitani *et al*., 2006)

2.4 Chelating agents

To realize chelating agents in solution extraction, it is important to design a solution extraction process and take notice for the characteristic behavior of CCA elements; these behaviors include substitution, solvation, complexation and precipitation (Kakitani *et al*., 2006). Most of the solutions for extracting heavy metals are acid that include strong acid, weak acid, oxidative acid, non-oxidative acid, organic acid, and inorganic acid. There are many other studies, which use strong acid such as dilute sulphurous acid, dilute sulfuric acid, and nitric acid (Moghaddam and Mulligan, 2008). Chelating agents are organic and inorganic chemicals reacting with polyvalent metal ions and can sequester metal ions to form water-soluble complexes (Kartal and Kose, 2003), like [S,S]-ethylenediaminedisuccinic acid ([S, S]-EDDS, in this article referred to as EDDS), nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Table 3 (Tandy *et al*., 2004) shows certain common use chelating agents.

Table 3. Abbreviation and structure for metal complexation of the used chelating agents (Tandy *et al*., 2004)

Abbreviation	Structure
EDTA (ethylenediaminetetracetic acid)	
EDDS ([S,S]-ethylenediaminedisuccinic acid)	
NTA (nitrilotriacetic acid)	
IDSA (iminodisuccinic acid)	
MGDA (methylglycinediacetic acid)	

Chelation is a chemical combination with a metal in complexes in which the metal is part of a ring. Organic ligand is called chelator or chelating agent, the chelate is a metal complex. The larger number of ring closures to a metal atom is the more stable compound. This phenomenon is called the chelate effect, and it is generally attributed to an increase in the thermodynamic quantity called entropy that accompanies chelation (http://chemicalland21.com/specialtychem/perchem/CHELATING%20AGENTS.htm).

The stability of a chelate is also related to the number of atoms in the chelate ring. Monodentate ligands which have one coordinating atom like H_2O or NH_3 are easily broken apart by other chemical processes. On the other hand, polydentate chelators, donating multiple binds to metal ion, provide more stable complexes. Chelation is applied in metal complex chemistry, organic and inorganic chemistry, biochemistry, and environment protection. Chelating agents offers a wide range of sequestrants to detoxify metal ions in aqueous systems. By forming stable water soluble complexes with multivalent metal ions, chelating agents prevent undesired interaction by blocking normal reactivity of metal ions.

Chelating agents are also important in the field of soap, detergents, textile dyeing, water softening, metal finishing and plating, pulp and paper, enzyme deactivation, photo chemistry, and bacteriocides. For instance, EDTA (ethylenediaminetetracetic acid) is a good example of a common chelating agent which has nitrogen atoms and short chain carboxylic groups. The sodium salt of EDTA is used as an antidote for metal poisoning, an anticoagulant, and an ingredient in a variety of detergents. (http://chemicalland21.com/specialtychem/perchem/CHELATING%20AGENTS.htm).

In recent studies, chelating agents such as ethylenediaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA) are great extractive agents for the remediation of metal-polluted soils (Kartal and Kose, 2003). EDTA extraction is able to mobilize copper from heavily polluted soil. Using this method, copper was either the most mobile metal or one of the most mobile metals (Kartal and Kose, 2003). According to Kartal (2003), EDTA extraction of copper, chromium, and arsenic from CCA-C treated wood was studied by using batch-leaching experiments. The study showed that EDTA could be a viable agent for the enhanced removal of copper from CCA treated wood waste.

About the properties of Ethylenediaminetetraacetic acid (EDTA), EDTA is a widely-used chemical compound. EDTA refers to the chelating agent with the formula $C_{10}H_{16}N_2O_8$. This amino acid is widely used to sequester divalent and trivalent metal ions. EDTA binds to metals via four carboxylate and two amine groups. EDTA forms especially strong complexes with Mn(II), Cu(II), Fe(III), and Co(III) (Holleman and Wiberg, 2001). EDTA becomes two forms, $EDTA^{4-}$, the conjugate base that is the ligand, and H_4EDTA, the precursor to that ligand. H_4EDTA forms highly stable coordination compounds that are soluble in water. In these complexes, the ligand is usually either hexadentate or pentadentate, EDTA^{4-} or HEDTA^{3-}, respectively. Such complexes are chiral, and [Co(EDTA)]$^{-}$ has been resolved into enantiomers (Kirchner and Barium, 1957). The most important uses of EDTA are industrial cleaning, reduction of water hardness, as a good oxidizing agent in photography, pulp and paper industry, and added into agrochemicals.

EDTA is also added in food as a preservative to prevent catalytic oxidation by metal ions, and EDTA can be applied for recovery of lead from used lead acid batteries. Figure 3 shows EDTA molecular structure, and Figure 4 shows EDTA coordinating an ion (Nowack and VanBriesen, 2005). EDTA is a useful biodegradable chemical under environmental conditions, so it was widely applied in many fields to assist other chemical reactions. However, when the use volume of EDTA is too much, EDTA still produces some environmental problems and risks.

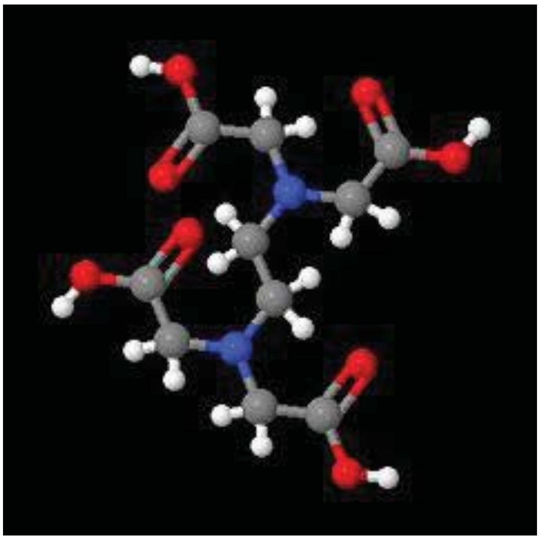


Figure 3. EDTA molecular structure

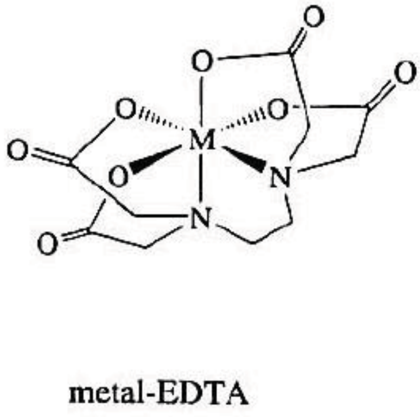


Figure 4. EDTA coordinating an ion (Nowack and VanBriesen, 2005)

Nitrilotriacetic acid (NTA) is another useful biodegradable chelating agent. Its structure is showed in Figure 5(a). NTA has been used as a chelating agent with its sodium salt form for more than 50 years. The main use of the chelating properties of NTA is to control metal ions activity. Typical applications of NTA are scale control in cleaners, water softening (because NTA can decrease water hardness with removal of calcium or magnesium), and as a builder in laundry detergents (European amino-carboxylates producers committee (EAC)). Figure 5(b) (Nowack and VanBriesen, 2005) is the ideal structure of metal-NTA complex, which is formed with NTA binding to metal ions.

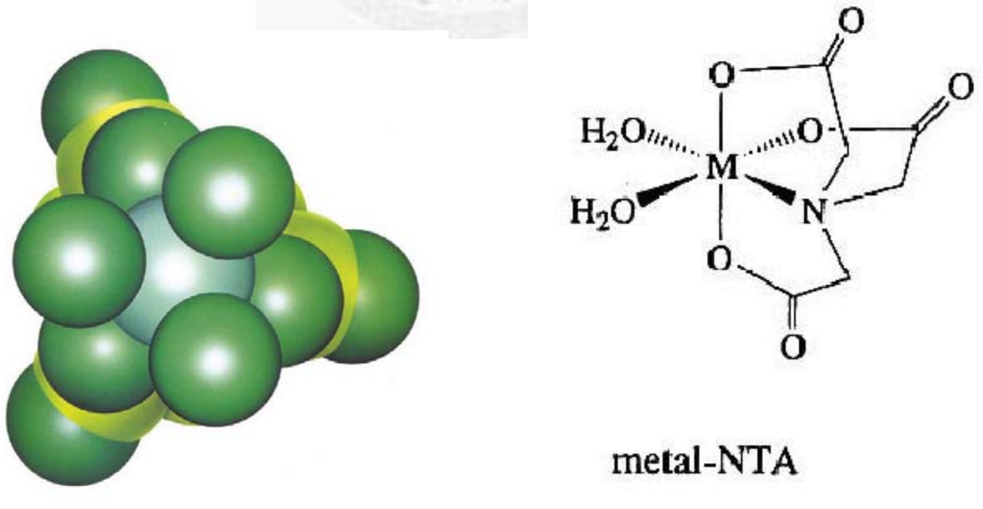

(a) (b)

Figure 5. (a) The structure of NTA (European amino-carboxylates producers committee (EAC)) (b) Ideal octahedral structure of metal-NTA complex (Nowack and VanBriesen, 2005)

NTA is readily biodegraded under environmental conditions and thus does not accumulate in the environment. NTA breaks down into carbon dioxide, water and inorganic substances without forming residual metabolites (European amino-carboxylates producers committee (EAC)).

[S,S]-ethylenediaminedisuccinic acid (EDDS) is also a biodegradable chelating agent. EDDS is an isomer of EDTA, so the formula of EDDS is also $C_{10}H_{16}N_2O_8$, but the sites of acetic acids of EDDS are different with EDTA (Table 3). In recent studies, EDDS was determined a potential alternative with EDTA. Tandy *et al.* (2004) reported that the aim of their study was to investigated the biodegradable chelating agent [S,S]-ethylenediaminedisuccinic acid (EDDS) and nitrilotriacetic acid (NTA) as potential alternatives and compare them with EDTA for effectiveness. Their results indicated that for copper at pH 7, the order of extraction efficiency was EDDS > NTA> EDTA, and for Zn it was NTA > EDDS > EDTA. Kos and Lestan (2003) reported that EDDS was introduced as an ingredient of industrial detergents. The toxicity of EDDS to fish and daphnia is low (E_{50} > 1000 mg/L). Besides, EDDS is readily biodegradable; Cao *et al.* (2007) stated that EDDS demonstrated a far higher biodegradability with respect to EDTA: 90% of EDDS can be degraded in 20 days while no EDTA was degraded in 30 days.

2.5 Condition of extraction

According to recent studies, researchers generalized certain parameters of chelating extraction and results. They reported the effect of pH, chelating concentration, temperature, extraction duration, and liquid to solid ratio. These studies also indicated the results for their experiments.

2.5.1 Effect of pH

The pH of extraction solution is an important factor. The pH of EDTA, NTA, and OA solutions in the study of Kartal and Kose (2003) provided acid conditions which facilitate remediation and removal of copper. Exposure of CCA treated wood may reverse the CCA fixation process under high acidity conditions and pH plays an important role in removal of elements (Clausen and Smith, 1998). Kartal (2003) found that 1% EDTA extraction (pH = 2.19) for 24 hr caused 93% copper, 36% chromium, and 38% arsenic removal from CCA treated sawdust.

Kakitani *et al*. (2009) showed the effect of solution pH of copper, chromium and arsenic extract from CCA treated wood chips with 0.125 M oxalate at 75°C in Figure 6. Figure 6 indicated chromium and arsenic is removed >85% in higher acidic condition (pH = 1~3). However, copper is removed >80% in lower acidic condition (pH = 3~5). It is concluded that more acidic condition preferred the extraction for chelating agents than less acidic condition.

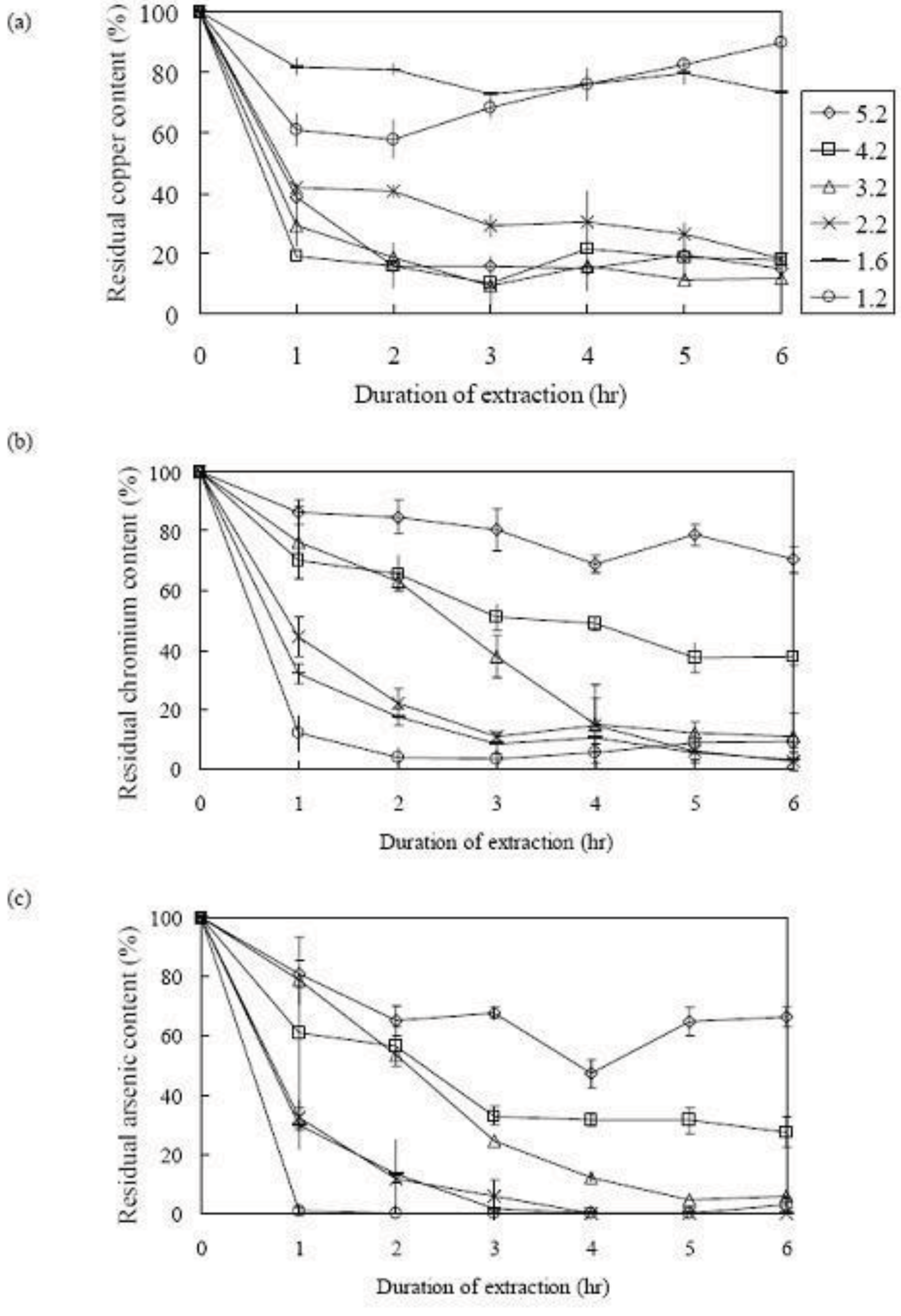


Figure 6. Effect of solution pH of copper, chromium and arsenic from CCA treated wood chips with 0.125 M oxalate at 75°C (a) Extractability of copper (b) Extractability of chromium (c) Extractability of arsenic (Kakitani *et al*., 2009)

2.5.2 Effect of chelating concentration

Chelating concentration is a considerable factor because it directly affects the effect of removing metals in extraction. According to Kartal (2003), the percentage removal of elements increased as EDTA concentration from 0.00% increased to 1.00% (Figure 7). 1.0% EDTA extraction for 24 hr removed about 62.86% copper, 12.73% chromium and 24.64% arsenic from CCA treated wood chips. From sawdust of CCA treated wood, 1.0% EDTA extraction for 24hr removed about 93.16% copper, 36.43% chromium and 38.12% arsenic.

The result also showed that the effect of extraction by using CCA treated wood chips was lower than CCA treated wood sawdust. Because the particle size of the sawdust was smaller than the chips, the effects of extraction were different. In the experiment, the size of particles is 10-17×0.20-0.35×0.15-0.35 mm, and the sawdust is passed a US standard 40-mesh screen (420 μ m).

When Kartal (2003) used the larger size of CCA treated wood blocks, which the size was 19×19×19 mm, the effect of extraction was indicated in Figure 8. The result of extraction was lower effect than above results, but it can be used in outdoor and long time experiments.

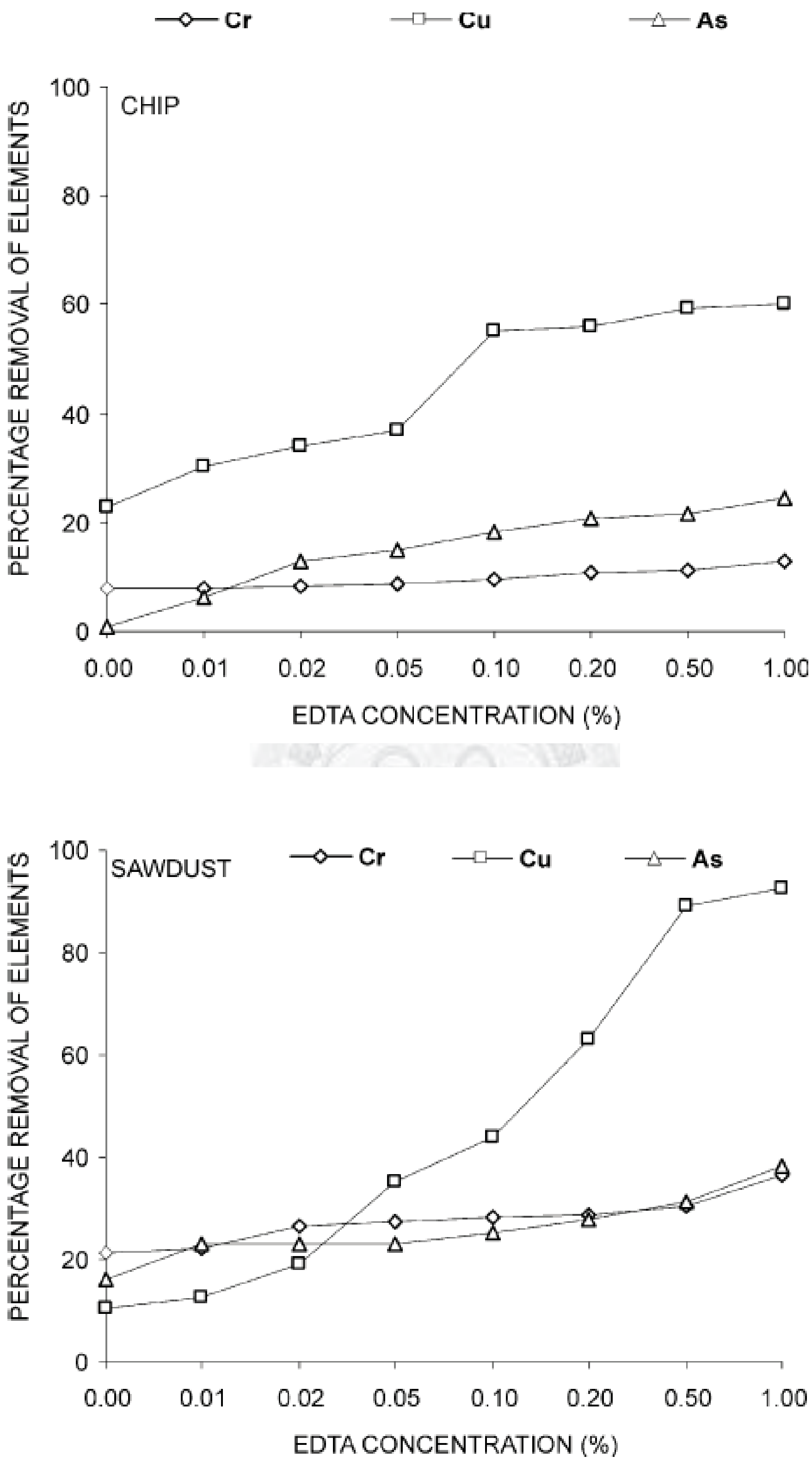


Figure 7. Percentage removal of elements from CCA treated chips and sawdust following EDTA extraction at various concentrations for 24 hr (Kartal, 2003)

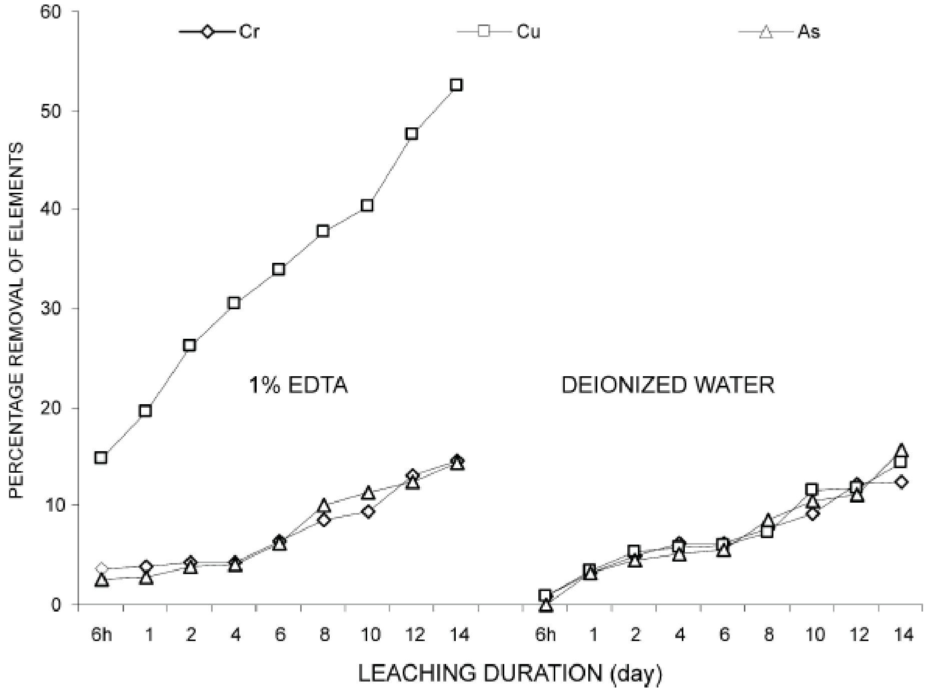


Figure 8. Percentage of total copper, chromium and arsenic extracted from CCA treated blocks using 1% EDTA and deionized water (Kartal, 2003)

2.5.3 Effect of temperature

Temperature is another factor that may affect the extraction efficiency of heavy metals from CCA treated wood. Kakitani *et al.* (2009) reported the extraction efficiencies of copper, chromium and arsenic on different temperature from CCA treated wood chips with 0.125 M oxalate at pH 3.2 (Figure 9). In Figure 9, the extraction efficiencies of copper, chromium and arsenic increased as temperature increased. The extraction efficiencies for chromium and arsenic after 6 hr of treatment were 10.8% and 29.3 % at 25°C, 50.9% and 67.6% at 50°C, and 89.4% and 94.1% at 75°C.

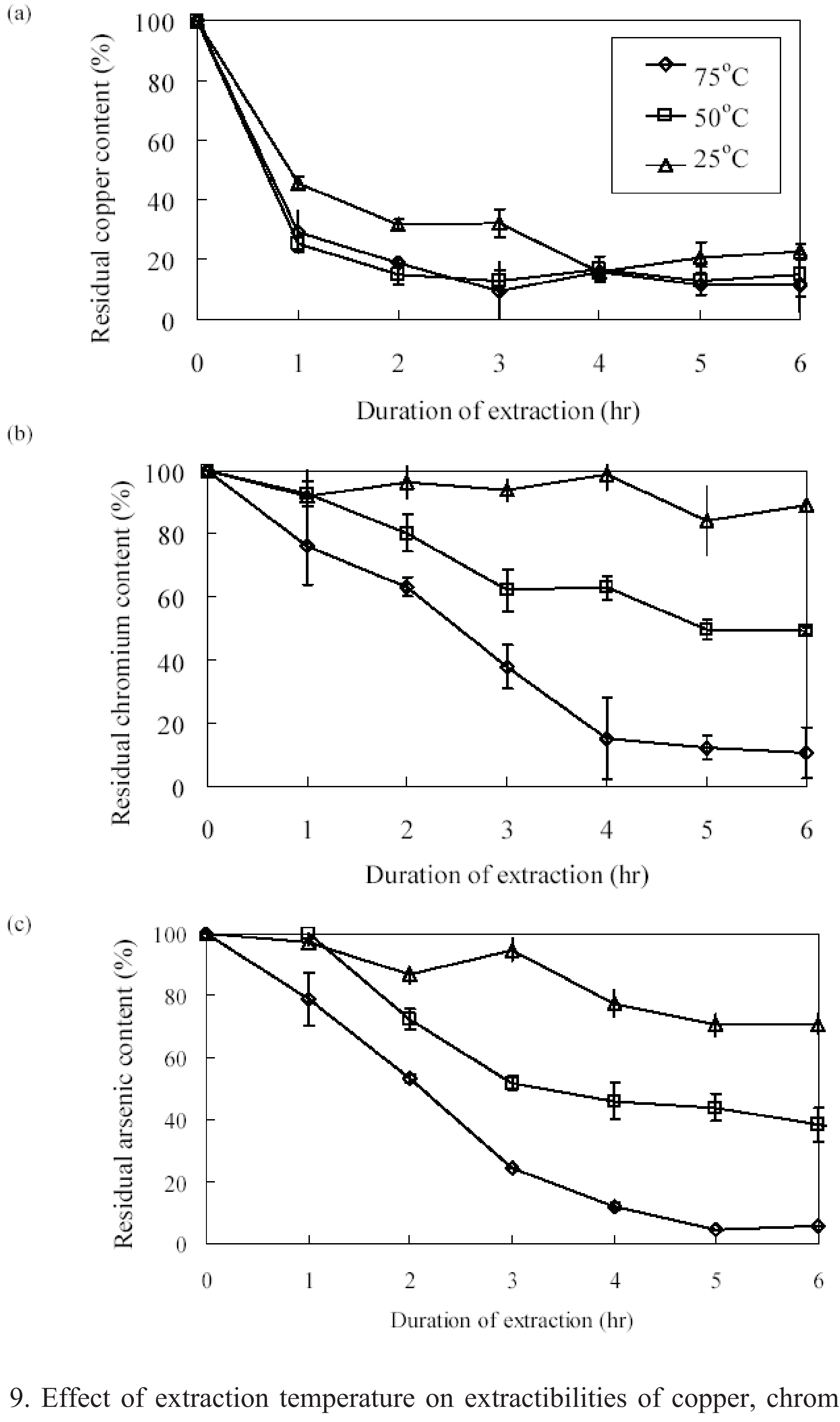


Figure 9. Effect of extraction temperature on extractibilities of copper, chromium and arsenic from CCA treated wood chips with 0.125 M oxalate at pH 3.2. (a) Extractability of copper. (b) Extractability of chromium. (c) Extractability of arsenic (Kakitani *et al*., 2009)

Chromium and arsenic were removed mostly in 75°C, and in lower temperature, the removal of chromium and arsenic was much less. The removal of copper was similar between three temperatures, but after 6 hr of treatment, extraction efficiency reached 77.4%, 85.1% and 88.2% at 25°C, 50°C and 75°C, respectively.

2.5.4 Effect of chelating duration

When the duration of extracting is changed, the effects of extraction are different. The percentage removal of elements increased as extraction duration increased, because extraction duration is the duration of contact. Figure 10 (Kartal, 2003) showed the variation with 1% EDTA for extraction time was 4, 8, 18 and 24 hr from CCA treated samples.

There were two types of sample sizes, one was chips, which the size was 10-17×0.20-0.35×0.15-0.35 mm, and the other was sawdust, which was passed a US standard 40-mesh screen (420 μm). Comparing the different duration and particle sizes, long term duration usually got better results of extraction. On the other hand, there were different results between chips and sawdust. Since the sawdust had larger particle sizes, it had been extracted better than the chips.

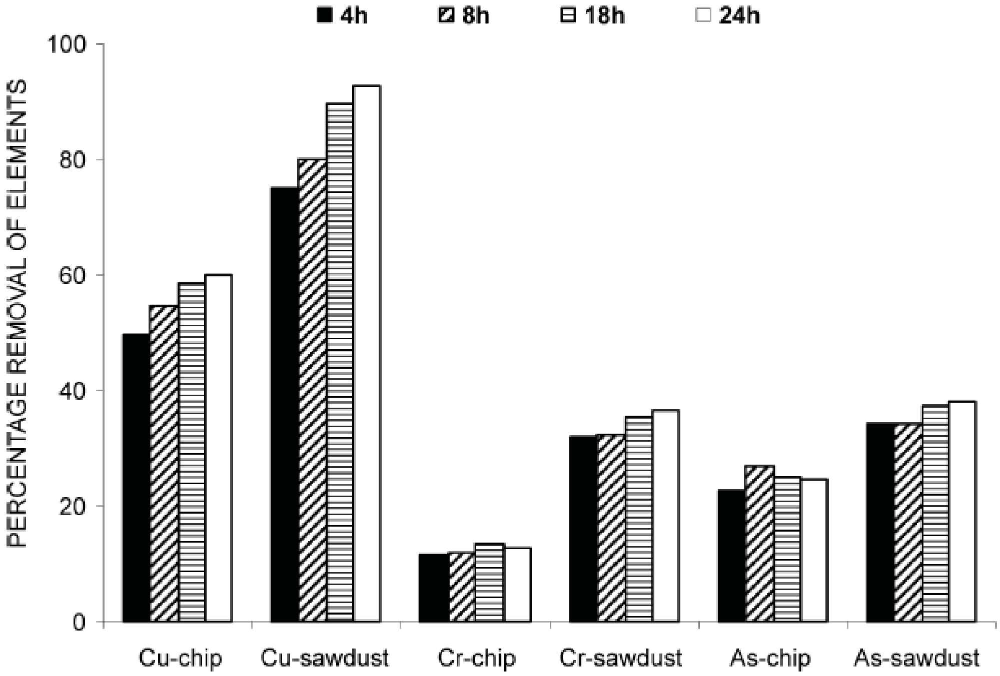


Figure 10. Percentage of copper, chromium and arsenic released following 1% EDTA extraction of CCA treated chips and sawdust for varying extraction duration (Kartal, 2003)

In Figure 10, after 24 hr, the percentage removals of three elements from CCA treated sawdust for 1% EDTA extraction were 91.8% copper, 19.2% chromium, and 26.4% arsenic.

2.5.5 Effect of liquid to solid ratio

Liquid to solid ratio is an important factor to consider some condition of experiments. Kakitani *et al.* (2009) indicated that the use of chemical solutions or post-treatment of waste water in sequential processes should be minimized.

In Figures 11(a), (b) and (c) (Kakitani *et al*., 2009), pH, concentration and temperature of oxalate solution were fixed at 3.2, 0.125 M and 75°C. The extraction efficiency for copper, chromium and arsenic was a function of solution to wood chip ratio, which were 20:1, 15:1 and 10:1 (ml:g), during extraction. At 10:1, the extraction efficiencies were 68.4% for arsenic, 75.5% for copper and 62.0% for chromium, while at 20:1, these were 94.1%, 88.2% and 89.4%, respectively, after 6 hr duration.

However, the lower ratio (10:1) resulted in insufficient extraction, while allowing metal re-adsorption onto the wood surface during and after extraction (Kakitani *et al*., 2009). This ratio also caused problems during the washing process. A liquid to solid ratio of 10:1 was apparently ineffective due to difficulties in stirring and re-absorption of CCA metals (Kakitani *et al*., 2009). Therefore, the ideal ratio of liquid to solid was determined to be 20:1 for extraction of CCA metals (Kakitani *et al*., 2009).

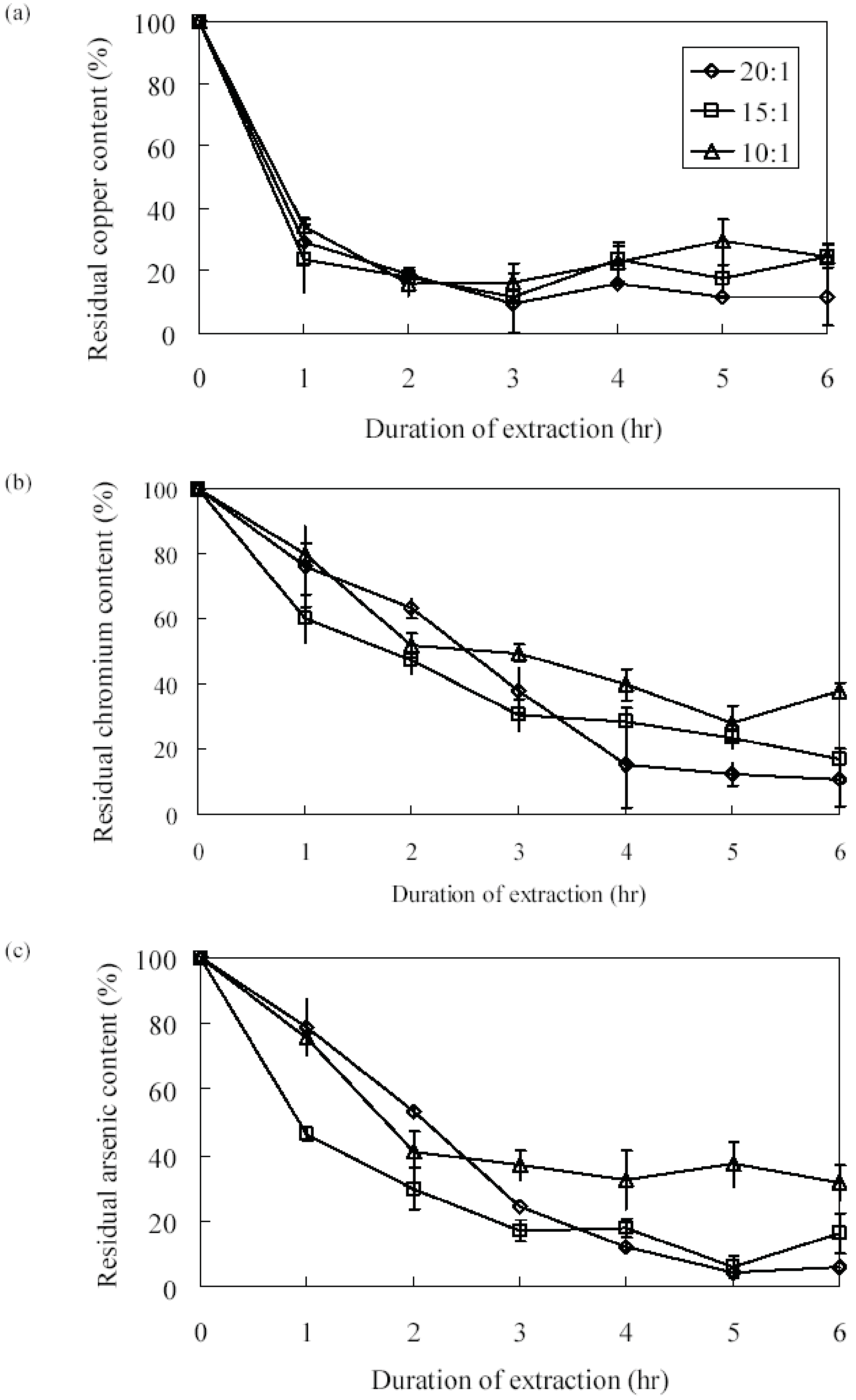


Figure 11. Effect of liquid to solid ratio on extractibilities of copper, chromium and arsenic from CCA treated wood chips with 0.125 M oxalate at pH 3.2 and 75°C (a) Extractability of copper (b) Extractability of chromium (c) Extractability of arsenic (Kakitani *et al*., 2009)

Chapter 3 Materials and methods

3.1 Preparation of CCA treated wood

Southern pine (*Pinus taeda*) that was treated with CCA-C preservative (hexavalent chromium as CrO_3, 47.5%; copper as CuO, 18.5%; arsenic as As_2O_5, 34.0%) that was supplied by Tai Jing Co. was used in the study. The sizes of wood samples were 2×2×30 cm^3. Wood samples were commercially treated by using a full cell process which included 30 min vacuum treatment (0.10 MPa) that was followed by a 4 hr pressure period (1.47 MPa). Samples were removed from the tank and drained of excessive solution (30 min). They were allowed to cure at room temperature for 3 months in order to assure fixation of metals in the wood. Then, CCA treated samples were cut into small chips (length, 30 mm) and were dried at 60°C for two weeks in order to achieve complete fixation of CCA reagents. Then these small chips were grinded into wood powders, and wood powders were mixed evenly. Finally, CCA treated wood powders were passed a US standard 40-mesh screen (420 μm)

Southern pine is composed of 30.4% of lignin, 15.5% of hemicellulose, 51.6% of cellulose, and the others are extractives and ash. The density of the sample was approximately 0.51 g/cm^3. Hot water (according to ASTM Standard D1110-84, ASTM 2007 and ASTM Standard D1105-96, ASTM 2007) and ethanol-benzene extractives were 2.60% and 2.51%, respectively.

3.2 Experiment

Chelating agents ethylenediaminetetracetic acid (EDTA, Sigma, St. Louis, MO) and nitrilotriacetic acid (NTA, Sigma) were used as received. [S, S]-ethylenediaminedisuccinic acid (EDDS), was obtained from Procter & Gamble. All aqueous solutions were made in water purified with a Milli-Q™ system (18.2 MΩ cm^{-1}). All flasks were sealed with stoppers to reduce gas exchange with the atmosphere during experiments. All pH adjustments were performed by addition of either a 1 M HNO_3 or 1 M NaOH solution.

Three parts of extraction experiments were conducted to assess the effects. First, chelating extraction uses vary conditions that include pH, chelating concentration, temperature, and chelating duration on chromium, copper, and arsenic extraction efficiencies. Second, various liquid to solid ratios (ml:g) also affect the extraction efficiencies of EDDS, NTA, and EDTA. Third, it is important to understand the metal associations in CCA treated woods before and to know the metal associations in CCA treated woods after chelating extractive decontamination.

Each test was performed three times: the results obtained, reported in the following figures, always represent the mean value obtained from three simultaneous tests. The amounts of chromium, copper, and arsenic extracted from CCA treated wood were determined based on differences between the initial concentrations in wood and the concentration in wood after extraction. The initial metal content in the CCA treated wood was 5.72 mg/g for chromium, 3.61 mg/g for copper, and 5.07 mg/g for arsenic.

3.2.1 Chelating extraction

A typical extraction procedure consists of placing 2.0 g of CCA treated wood with a measured volume of chelating solution in a 50 ml polypropylene centrifuge tube. The slurry was then shaken with a reciprocal shaker for up to 6 hr. Flowchart is showed in Figure 12. The pH were set in 2.0-10.0, and concentration of chelating agents were 0.01–0.1 M. Extraction temperature was set at 25, 50, 75, or 90°C by using a water bath heating system. The samples were centrifuged for 10 min at 8000 rpm, and then were followed by filtration using Whatman no. 42 filter to remove particulates in the solution.

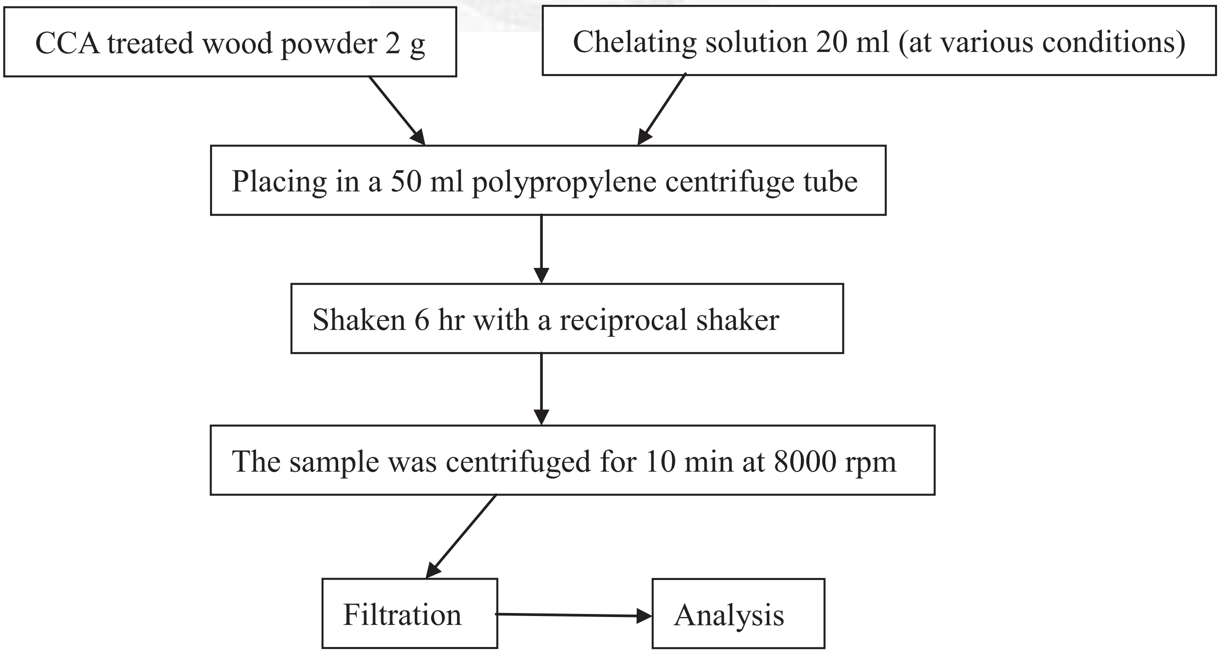


Figure 12. Flowchart of chelating extraction

3.2.2 The ratio of solution to CCA treated wood

The solution: CCA treated wood mass ratio on chromium, copper, and arsenic extraction efficiencies were assessed by using chelating agents. The volumes of chelating solution used were 5 and 10 ml giving chelating solution: CCA treated wood mass ratios of 5 and 10, respectively while the mass of CCA treated wood used was 1.0 g.

Stoichiometry is the calculation of quantitative (measurable) relationships of the reactants and products in a balanced chemical reaction (chemicals). In general, chemical reactions combine in definite ratios of chemicals. Since chemical reactions can neither create nor destroy matter, nor transmute one element into another, the amount of each element must be the same throughout the overall reaction. To study the effects of EDDS–CCA stoichiometric ratio, applied EDDS concentration varied from 0.0025 to 2.5 M giving an EDDS–CCA stoichiometric ratio of 0.1 to 100. In the results, the impact of EDDS–CCA stoichiometric ratio on chromium, copper and arsenic extraction efficiencies is discussed. The extraction time was 6 hr for the above experiments.

3.2.3 Sequential extraction

Following Chang *et al*. (2007), five-step sequential extraction scheme is modified the original Tessier *et al*. (1979) to examine the composition of toxic metal elements in the

CCA treated wood before extracted and after being extracted in different pH. Figure 13 is the flowchart summarizing the six-step sequential extraction method basically modified from the method proposed by Tessier *et al*. (1979), but the residual fraction was particularly digested by $HNO_3/H_2O_2/HF$ acid mixture.

Steps 1–5 were conducted in the same 15 ml polyethylene centrifuge tube with the same extraction process by shaking at a speed of 150 rpm for 3 hr at different temperatures. The extract was then separated from the solid residue by centrifugation for 5 minutes. The supernatant was removed with the pipette and stored in a polyethylene tube at 4^oC for analysis. Solid residue obtained after solid–liquid separation was to be used in the subsequent extraction process, thus, between each step, care had to be taken not to discard any such residue. In Step 6, after high-pressure bomb digestion, the sample solution was transferred into a PTFE beaker and heated gently (< 90^oC) on a hot plate to allow the residual acid to evaporate. The final residue was diluted to 50 ml for instrumental analysis.

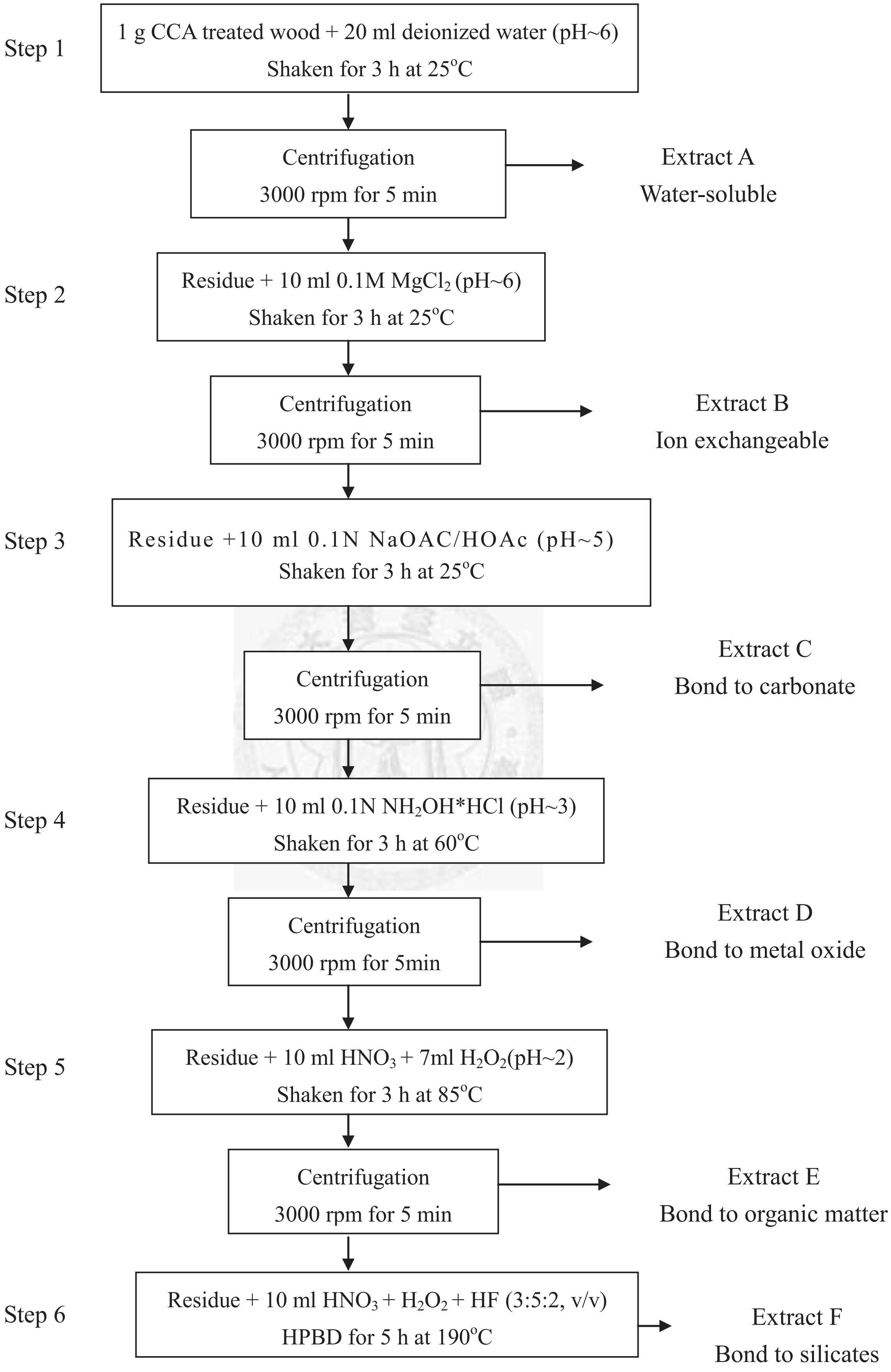


Figure 13. Flowchart of sequential extraction procedure (Tessier *et al*., 1979)

3.3 Analysis

3.3.1 Chelating extraction

After filtering the samples by Whatman no. 42 filter, the concentrations of chromium, copper, and arsenic were determined by Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon—JY24), following acid digestion (USEPA, 1996).

3.3.2 Ratio of solution to CCA treated wood

After the liquid to solid ratio experiment of extraction, filtering the samples by Whatman no. 42 filter, the concentrations of chromium, copper, and arsenic were determined by ICP-AES.

3.3.3 Sequential extraction

After the samples of respective steps were diluted to 50 ml, the concentrations of major components (such as chromium, copper, and arsenic) in the different extracts were measured by ICP-AES.

3.3.4 Inductively coupled plasma atomic emission spectrometry (ICP-AES)

The sample will be collected into sample bottles. Detecting the concentration of chromium, copper and arsenic by inductively coupled plasma atomic emission spectrometry (ICP-AES). The equipment of ICP-AES includes nebulizer, atomizer and detector.

The principle of ICP-AES is atomization the sample from ground state to excited state by plasma. Nebulizer is concentric nebulizer of pneumatic nebulizer. Atomizers is use inductively coupled argon plasma whose temperature can reach 6000^{o}C, and the temperature of radio-frequency induction coil that in inductively coupled argon plasma even can reach 10,000^{o}C. The detector is set above inductively coupled argon plasma to detect atoms.

Finally, detector transforms the information to computer and shows the results. According to the data, graphs are plotted to show the results.

Chapter 4 Results and discussion

Recent research reported generalized the factors of chelating extraction and results. This study discusses the effect of changing chelating extraction factors, and discusses the effect of ratio of solution to sample. Then, the study also analyzes the mobility of metals when they are extracted.

There are some chelating extraction factors that affect the percentage removal of elements from CCA treated wood. In chelating extraction, the pH, chelating concentration, temperature, and chelating duration affect the results. In liquid to solid ratio, different ratios affect the extraction efficiencies. In sequential extraction, it is necessary to discuss the mobility of three metals.

Different factors may affect extraction efficiency of heavy metals. And then the results of pH, chelating concentration, temperature, chelating duration, solution: CCA treated wood ratios, and sequential extraction are individually discussed. In the same condition, the effect of EDDS, NTA, and EDTA are compared. Finally, the percentage removal of chromium, copper and arsenic in different conditions are illustrated.

4.1 Effect of pH

In general, the lower pH of the chelating solution, the greater extraction efficiency of the toxic metals. According to Kakitani *et al.* (2009), the pH of chelating solution has an effect on extraction efficiency for chromium, copper and arsenic. In this section, effects of pH on extraction efficiency for CCA metals are studied. Throughout the experiments of this section, reaction temperature was 75°C, duration of extraction was 4 hr, and chelating concentration was 0.1 M.

The extraction efficiency of the CCA treated wood at different chelating agents and pH was shown in Figure 14. At studied pH range, extraction efficiency of chromium was EDDS ≥ NTA > EDTA (Figure 14(a)). The extraction efficiency of EDDS for chromium was much closer to that of NTA. It indicates that the best pH is 3.0-5.0 for chromium, which yielded an extraction efficiency of 59-66% using EDDS or NTA and 44-53% using EDTA (Table 4).

Table 4. Extraction efficiency of three metals in the optimal pH condition

	Extraction efficiency in the beest pH condition (%) (Concentration in 0.1 M, 75°C, 6 hr extraction period)			
	The best pH range	EDDS	NTA	EDTA
Cr	3.0-5.0	59-66	59-66	44-53
Cu	3.0-5.0	85-93	79-84	85-93
As	2.0-4.0	58-62	50-60	47-55

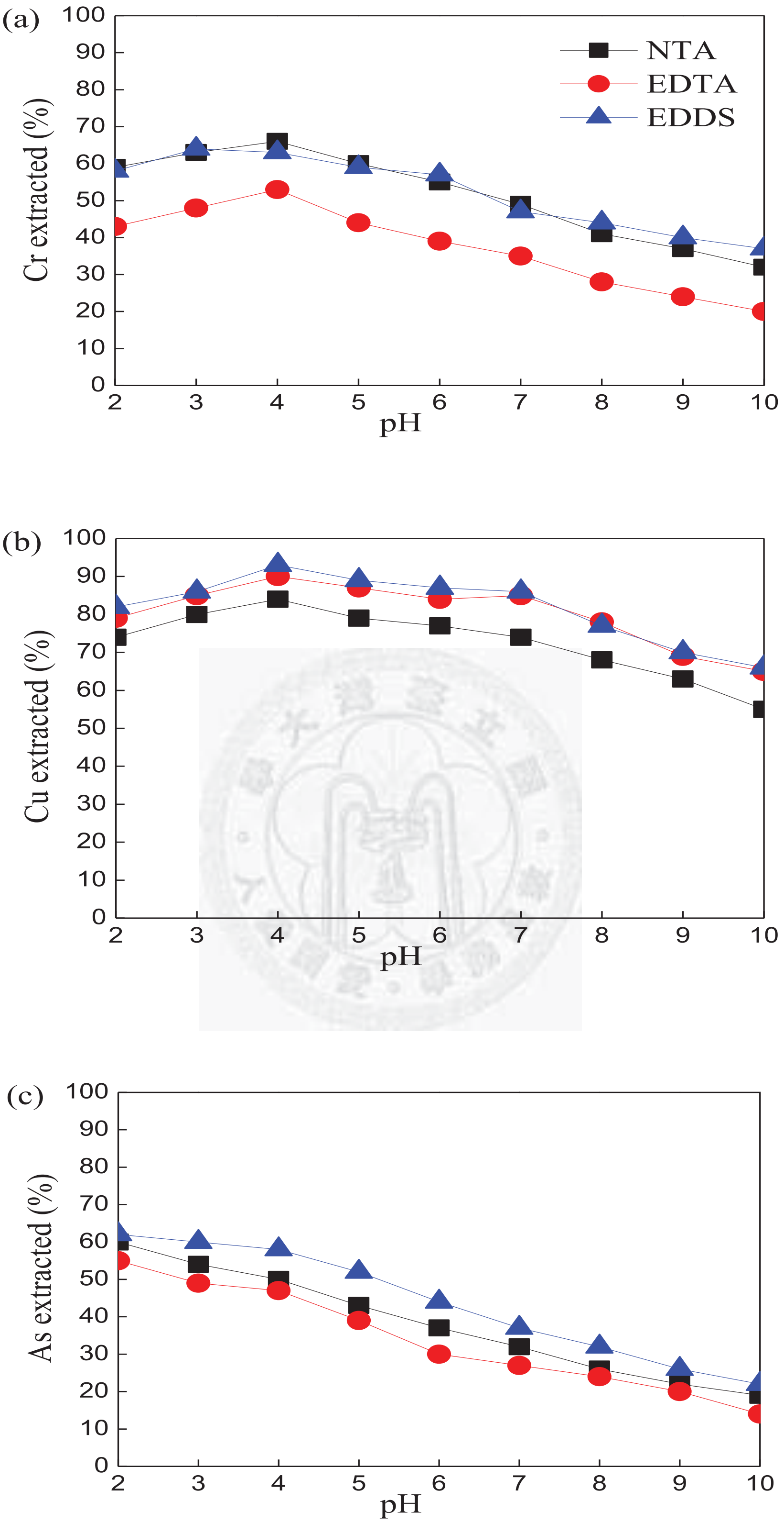


Figure 14. Effects of pH on chromium, copper, and arsenic extraction for CCA treated wood with 0.1 M chelating agents at 75°C (6 hr extraction period). (a) Cr extracted. (b) Cu extracted. (c) As extracted.

Chromium reportedly has the highest resistance to leaching (Kakitani *et al*., 2004) with the strong bonding between chromium and wood components in CCA treated wood. Extraction efficiency drastically changed between pH 4.0 and 7.0. The pH of chelating agents was controlled by addition of NaOH to chelating solution. The increased pH and hydroxide ion conditions (possible chromium hydration) restrain the extraction efficiency of chromium in the present experiment. At higher pH level, chelating solution was unable to effectively break the wood-metal bonds, and to form a soluble complex. Thus, lower pH conditions (pH 3.0-5.0) were more effective than higher pH conditions for extraction of chromium with EDDS or NTA solutions (Figure 14 and Table 4).

Figure 14(b) shows the extraction efficiency for copper from CCA treated wood as a function of pH and the kinds of chelating agents. At studied pH range, the order of the copper extraction efficiency was EDDS ≥ EDTA > NTA, but copper extraction was progressively enhanced by all tested chelating agents. The extraction efficiency of copper using EDDS was similar with EDTA, irrespective of pH. It shows that the best pH is 3.0-5.0 for copper, yielding an extraction efficiency of 85-93% using EDDS or EDTA and 79-84% using NTA (Table 4). Higher pH was determined to be unsuitable for extraction of copper. The extraction efficiency of copper at pH 2.0 was lower than that at relatively higher pH level (3.0, 4.0, and 5.0). The pH of chelating agents was controlled by addition of HNO_3 to chelating solution. The decreased pH and increased nitric ion conditions enhanced the crystallization of copper nitrate in the present experiment. Because there is an accumulation of insoluble copper nitrate, and insoluble copper nitrate decreases the extraction efficiency of copper. Thus, copper was readily extracted with EDDS or EDTA solution at pH level between 3.0-5.0 (Figure 14 and Table 4).

The extraction efficiency of arsenic from the CCA treated wood at different chelating agents and pH was shown in Figure 14(c). The effectiveness of arsenic extraction from CCA treated wood using different pH levels of chelating solution decreases greatly to the level, which is expected for pH 10.0. At studied pH range the order of the arsenic extraction efficiency was EDDS > NTA > EDTA. The best pH is 2.0-4.0 for arsenic, and extraction efficiencies are 58-62% using EDDS, 50-60% using NTA, and 47-55% using EDTA (in Table 4). Thus, lower pH conditions were more effective than higher pH conditions for extraction of arsenic.

When the results of EDTA are discussed with literature, extraction efficiency of chromium, copper, and arsenic is similar with Kartal (2003). In this study, chelating duration is only 6 hr then extraction efficiency of three metals has been higher than Kartal (2003). The similar is that copper is extracted most, and over 90%. Chromium and arsenic are extracted much lower than copper, and extraction efficiency of chromium is near to arsenic. Besides, EDDS and NTA approach a higher extraction efficiency of three metals than EDTA.

4.2 Effect of chelating concentration

From the research of Kartal (2003), concentration of chelating solution may affect the extraction efficiency of CCA metals. In general, EDTA may react with metal ions other than CCA metals, because each metal ion has different reactivity with EDTA. The competition between CCA metal ions and other metal ions is dependent on the dissolved concentration of the specific metal ion, dissolved anions, pH and the stability constant between the specific metal ion and EDTA. Thus, higher chelating ligand is required for efficient extraction of CCA metals. The extraction efficiency for CCA metals as a function of concentration at pH 6.0 was thus studied. The molar ratios of chromium, copper, and arsenic to 0.1 M chelating solution were calculated to be approximately 1:9.1 (chromium: chelant), 1:17.6 (copper: chelant), and 1:14.8 (arsenic: chelant).

The effectiveness of chromium, copper, and arsenic extraction from CCA treated wood using different concentrations of chelant increased progressively to the level expected for 0.1 M EDTA, EDDS, or NTA (Figure 15).

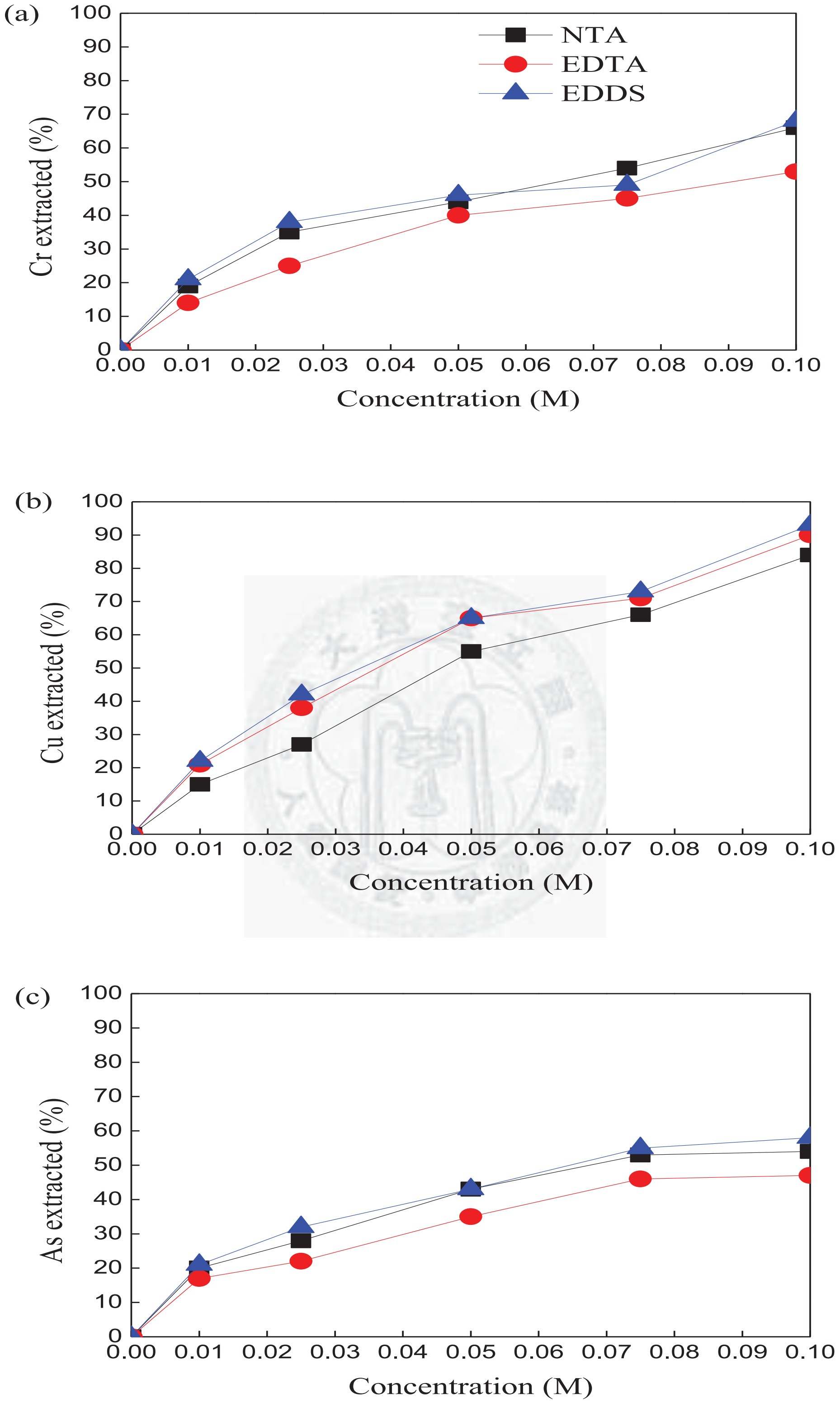


Figure 15. Solution concentration effects on chromium, copper, and arsenic extraction for CCA treated wood with chelating agents at 75°C and pH 4.0 (6 hr extraction period). (a) Cr extracted. (b) Cu extracted. (c) As extracted.

Extraction efficiency using different concentrations of chelating agents exhibited a similar trend as using different pH of chelating agents. Figure 15(a) shows the extraction efficiency of chromium during chelating extraction at concentration between 0.01 M and 0.1 M. The extraction efficiencies of chromium from CCA treated wood were 68% by EDDS, 66% by NTA, and 53% by EDTA for 0.1 M. The highest extraction efficiency was obtained at 0.1 M EDDS.

The extraction efficiency for copper during chelating extraction is shown in Figure 15(b). At studied concentration range, the extraction efficiency for copper was EDDS ≥ EDTA > NTA. The extraction efficiencies of copper from CCA treated wood were 93% by EDDS, 90% by EDTA, and 84% by NTA for 0.1 M. The chelating extraction of CCA treated wood using EDDS, EDTA, or NTA resulted in lesser chromium and arsenic removal than copper. The highest extraction efficiency was obtained at 0.1 M EDTA.

Figure 15(c) shows the effects of concentration on extraction efficiency of arsenic. At studied concentration range the order of the arsenic extraction efficiency was EDDS ≥ NTA > EDTA. And, the extraction efficiency of arsenic was similar to that of chromium. The extraction efficiencies of arsenic from CCA treated wood were 58% by EDDS, 54% by NTA, and 47% by EDTA for 0.1 M (Table 5). The highest extraction efficiency was also obtained at 0.1 M EDDS.

Table 5. Optimal extraction efficiency of concentration 0.01M to 0.1M

	Extraction efficiency of 0.1 M chelting solution (%) (pH=4.0, 75°C, 6 hr extraction period)		
	EDDS	NTA	EDTA
Cr	68	66	53
Cu	93	84	90
As	58	54	47

In literature review, Kartal (2003) showed similar results of EDTA with the results of this study, extraction efficiency of chromium, copper, and arsenic is similar with concentration increasing. In this study, chelating duration is only 6 hr then extraction efficiency of three metals has been higher than Kartal (2003) that chelating duration was 24 hr. The similar is that copper is extracted most, and over 90%. Chromium and arsenic are extracted much lower than copper, and extraction efficiency of chromium is near to arsenic. Besides, EDDS and NTA approach a higher extraction efficiency of three metals than EDTA in chromium and arsenic. Copper is extracted more by EDDS than by EDTA.

4.3 Effect of temperature

Extraction temperature would affect the extraction efficiency of heavy metals from CCA treated wood, as the solubility of weakly soluble salts mostly depends on solution temperature (Kakitani *et al*., 2009). Thus, higher reaction temperatures resulted in higher extraction efficiency. According to the section 4.1 and 4.2, pH and concentration of chelating solution were set at 4.0 and 0.1 M, and the effects of reaction temperature on extraction efficiency for CCA metals was evaluated at 25°C, 50°C, 75°C, and 90°C in order to determine the influence of temperature.

As shown in Figure 16, increased temperature significantly enhanced the extraction efficiency of CCA metals, especially chromium and arsenic.

In Figure 16, extraction efficiency using different temperature exhibited a similar trend as using different pH or concentrations of chelating agents. The extraction efficiencies of chromium were 32-36% at 25^{o}C, 36-45% at 50^{o}C, 50-65% at 75^{o}C, and 54-66% at 90^{o}C. The extraction efficiencies of copper were 65-80% at 25^{o}C, 76-90% at 50^{o}C, 84-92% at 75^{o}C, and 85-95% at 90^{o}C. The extraction efficiencies of arsenic were 22-29% at 25^{o}C, 39-52% at 50^{o}C, 55-62% at 75^{o}C, and 57-64% at 90^{o}C.

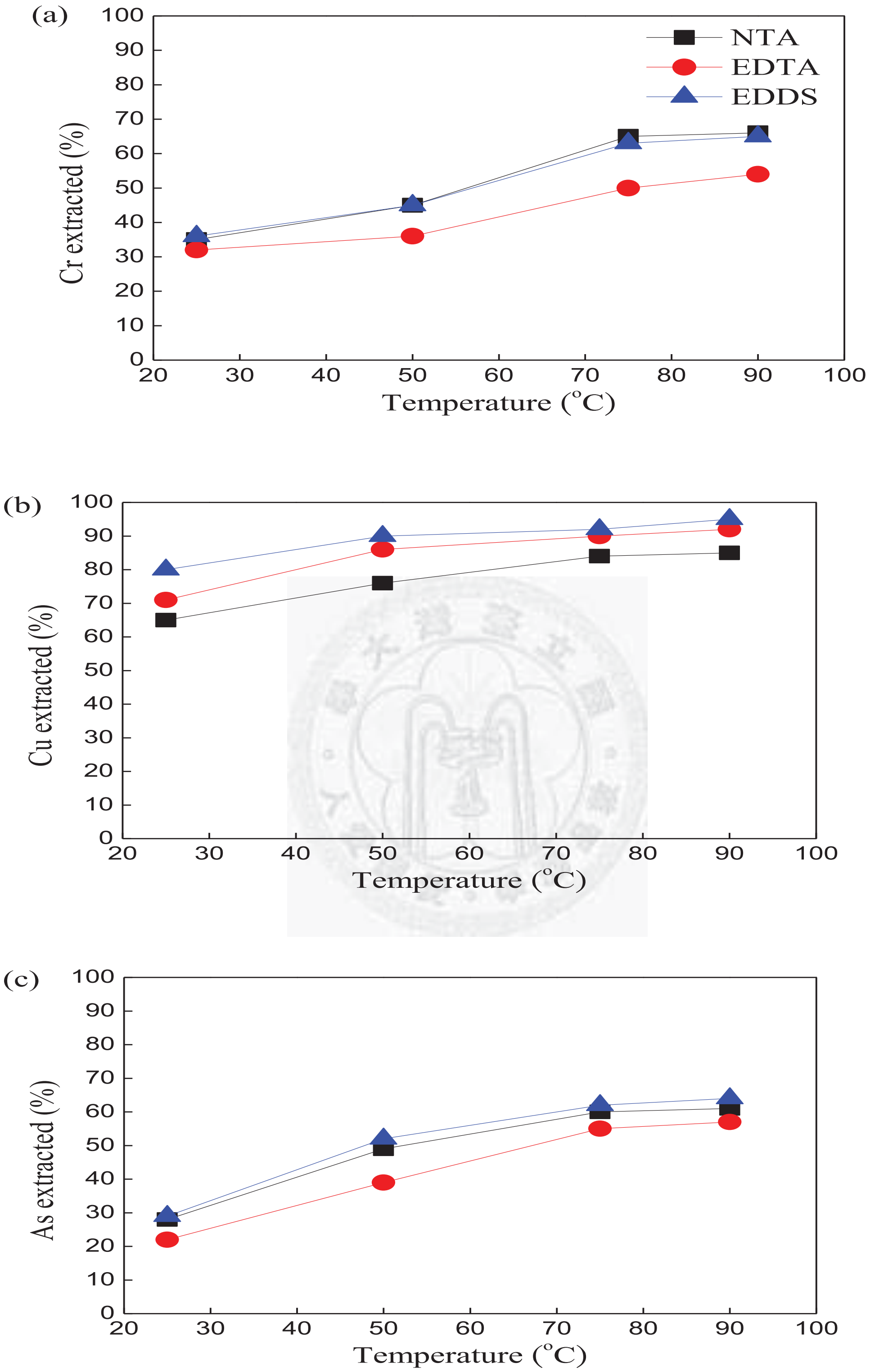


Figure 16. Effect of temperature on extraction of chromium, copper, and arsenic from CCA treated wood with 0.1 M chelating agents and pH 4.0 (6 hr extraction period). (a) Cr extracted. (b) Cu extracted. (c) As extracted.

The increased extraction efficiency of CCA metals was insignificant when reaction temperature increased from 75^{o}C to 90^{o}C, but the extraction efficiency of chromium and arsenic strongly depends on extraction temperature. On the other hand, copper was easily extractive under both high and low temperature conditions. Therefore, reaction temperature plays an important role in solubility of chromium and arsenic in waste management of CCA treated wood, as was expected before the experiment. The ideal extraction temperature for CCA metals was determined 75^{o}C.

When the results of changing temperature are discussed with literature, extraction efficiency of chromium, copper, and arsenic by EDTA, EDDS, and NTA form low temperature to high temperature is similar with Kakitani *et al*. (2009) by oxalate. In this study, chelating agent is different from Kakitani *et al*. (2009), so extraction efficiency of chromium and arsenic is lower. But extraction efficiency of copper is high than Kakitani *et al*. (2009). If chromium and arsenic are needed to extracted more, oxalate will be mixed with EDDS or NTA to enhance the extraction efficiency.

4.4 Effect of chelating duration

In literature review, Kartal (2003) indicated that the duration of extraction would affect the percentage removal of CCA metals. In Figure 17, the results of chelating duration are showed that long term extraction has better efficiency of CCA metals than short term extraction.

Figure 17(a) and (c) indicate when duration of extraction is 5 or 6 hr, the percentages of extracted chromium and arsenic are most. But in Figure 17(b), copper is extracted up to 90% when duration is only 2 hr. These results present different extracting rates of chromium, copper, and arsenic. According to Figure 17, the extracting rate of copper is faster than chromium and arsenic; for chromium and arsenic, the chelating durations easily affect the results of extraction. There is great difference between 4 and 6 hr extraction, about 5~10%.

When the results of EDTA are discussed with literature, extraction efficiency of chromium, copper, and arsenic is similar with Kartal (2003). In this study, chelating duration is only 6 hr then extraction efficiency of three metals has been higher than Kartal (2003) that chelating duration is only 8 hr. The similar is that copper is extracted most, and over 90%. Chromium and arsenic are extracted much lower than copper, and extraction efficiency of chromium is near to arsenic. Besides, EDDS and NTA approach a higher extraction efficiency of three metals than EDTA.

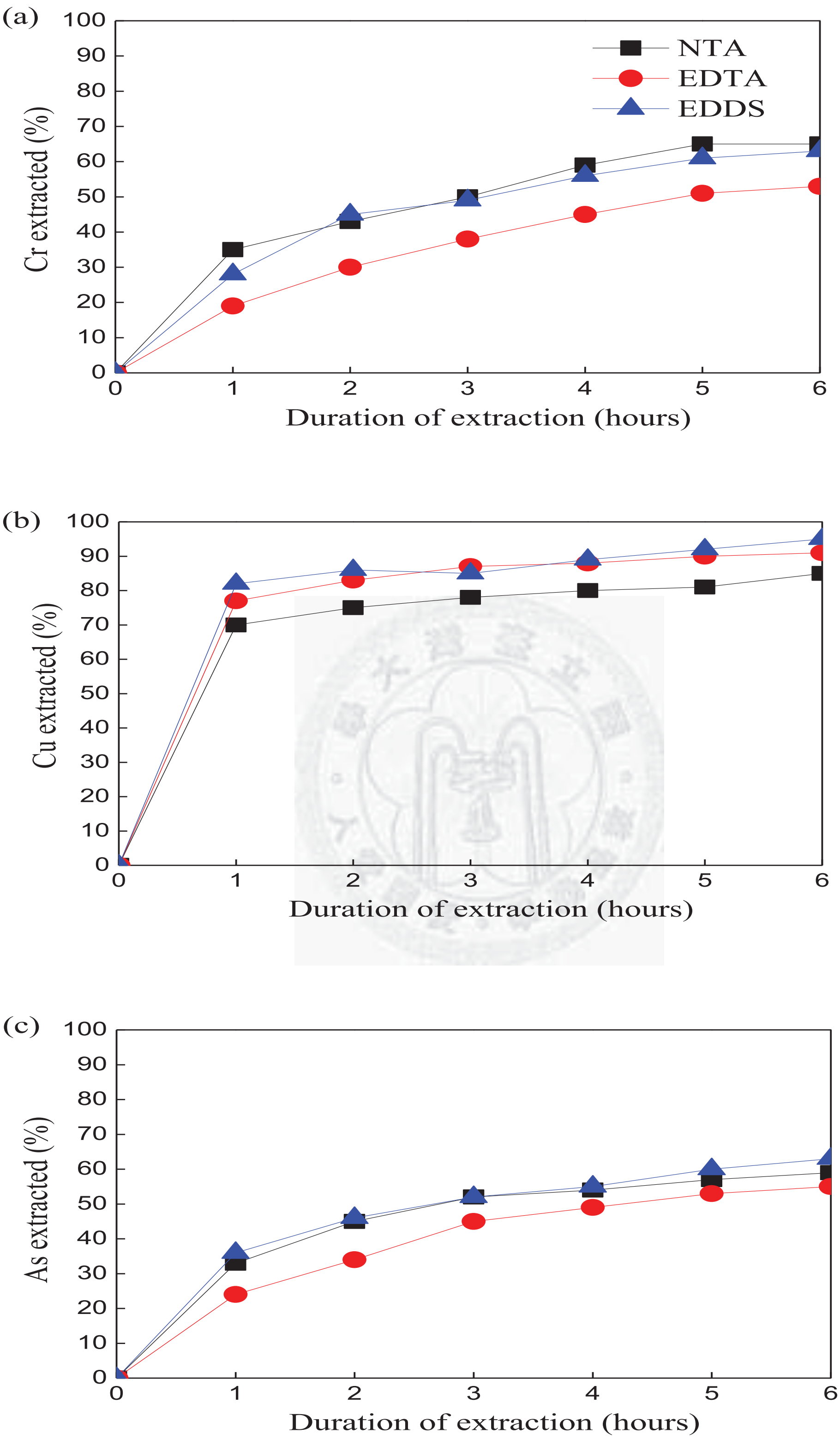


Figure 17. Effect of chelating duration of chromium, copper, and arsenic from CCA treated wood with 0.1 M chelating agents at 75°C and pH 4.0. (a) Cr extracted. (b) Cu extracted. (c) As extracted.

4.5 EDDS-CCA stoichiometric ratios

According to Kakitani *et al.* (2009), the ratio of solution to wood chips with factors for practical use is studied. The use of chemical solutions or post-treatment of waste waser in sequential processes should be minimized. However, decreasing the ratio of solution to wood chips may decrease reaction efficiency or cause problems, such as a clogging, during the stirring process (Kakitani *et al*., 2009).

In this study, chromium, copper and arsenic extraction efficiencies for different EDDS-CCA metals stoichiometric ratios and solution: wood ratios for CCA treated wood are presented in Figure 18. Chelating duration for these experiments was 6 hr without pH adjustment.

Figure 18 demonstrates that chromium, copper, and arsenic extraction efficiencies for CCA treated wood were different, and chromium, copper, and arsenic extraction was a function of the stoichiometric ratio of the applied EDDS concentration to the total CCA metals concentration in the wood sample. Figure 18 shows that the extraction with solution: wood ratio as low as 5:1 on a mass basis were lower than that of a solution: wood ratio of 10:1 for those chelating agents. The extraction efficiencies were found to be dependent on the quantity of EDDS present.

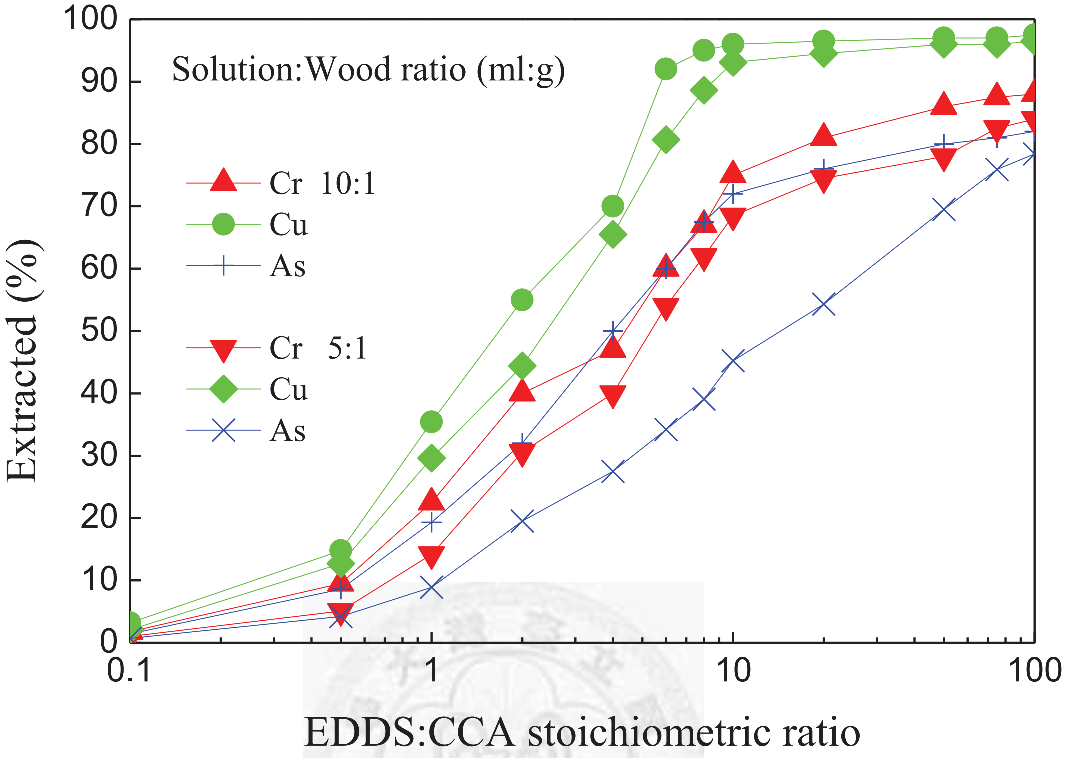


Figure 18. Stoichiometric ratios and solution to wood ratios effects on chromium, copper, and arsenic extraction for CCA treated wood at 75°C (6 hr extraction period without pH adjustment).

Since the wastewater generated from the extraction process should be treated before disposal, reducing the volume of wastewater would reduce the treatment costs and provide additional savings for the application of CCA treated wood extracting technology. It is interesting to find that the extraction efficiencies for chromium and arsenic were gradual for higher EDDS–CCA metals stoichiometric ratio while for copper, the change in extraction efficiencies seemed to be quite steep for a small change in EDDS–CCA metals stoichiometric ratio. However, if sufficiently large amount of

EDDS was applied, almost all the copper is extracted for CCA treated wood.

Figure 18 also shows that for a unit stoichiometric ratio of EDDS to total CCA metals concentration, approximately 35.4% of copper, 22.5% of chromium, and 19.3% of arsenic which was extracted from is extracted at solution: wood ratio of 10:1. 29.6% of copper, 14.2% of chromium, and 8.9% of arsenic are extracted from CCA treated wood at solution: wood ratio of 5:1. The different CCA metals extraction efficiencies for CCA treated wood at unit stoichiometric ratio may be due to the solution properties such metal species present in the wood sample. EDDS concentrations above unit stoichiometric requirement were needed for CCA treated wood to maximize CCA metals extraction. For example, an EDDS–CCA metals stoichiometric ratio of at least 8 is needed to achieve the maximum extraction efficiency of copper while an EDDS–CCA metals ratio of at least 20 is needed for the extraction of chromium.

When the results of EDDS are discussed with the results of oxalate (Kakitani *et al*., 2009), extraction efficiency of chromium, copper, and arsenic in solution to wood ratio is similar. In this study, is only 10:1 then extraction efficiency of copper has been higher than Kakitani *et al*. (2009). And it is similar that solution to wood ratio increase, extraction efficiency of three metals increase. Extraction efficiency in different solution to wood ratios are 10>5.

4.6 Influence of solid-phase speciation on extraction yield

Sequential extractions give the information needed to explain different extraction efficiencies for different metals. Figure 19 shows the distribution of chromium, copper, and arsenic fractions in CCA treated wood before and after the extraction with EDDS.

In the results of control, chromium was mainly found in the organic and residual fractions (85.6%), while about 83.9% of the copper was found in exchangeable, Fe/Mn-oxide, and residual fractions, and about 90.7% of the arsenic was found in Fe/Mn-oxide, organic, and residual fractions.

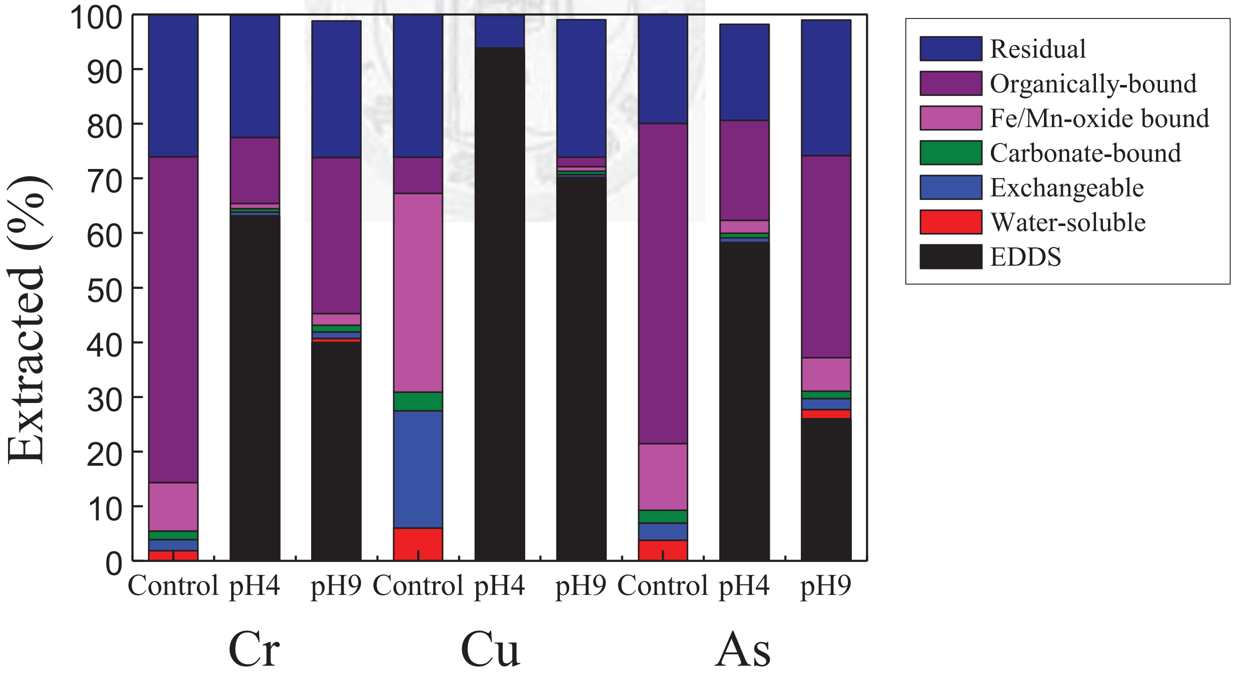


Figure 19. Mobility of Cr, Cu, and As in CCA treated wood before and after extraction with EDDS given as percentage of heavy metals concentration.

The applied EDDS solution extracted these metals mainly from the first five fractions, the water-soluble, exchangeable, carbonate, Fe/Mn-oxide, and organic fraction. Therefore, the much better extractability of copper compared to chromium and arsenic by chelating agents can be explained by the presence of larger weakly bound fractions.

The maximum extraction efficiency (pH 4.0) for CCA treated wood using EDDS was 63% for chromium, 93% for copper, and 58% for arsenic, while the first five fractions of the sequential extraction amounted to 74% for chromium, 74% for copper, and 80% for arsenic. So, in the results of pH 4.0, EDDS could break more organically-bond than other bonds for chromium and arsenic. For copper, EDDS could break almost every kind of bonds because the extraction efficiency was 93%. The results of pH 9.0 indicated that the extraction efficiencies of EDDS are less than pH 4.0, because in the section 4.1, we know the extraction of EDDS is more suitable at acid condition than alkaline. In the results of pH 9.0, we could compare about different pH conditions to affect the results of breaking bonds.

Chapter 5 Conclusion

For above results, the solubility of chromium, copper and arsenic depends on pH of the chelating solution. Decreased pH clearly increases the solubility of chromium, copper, and arsenic. Higher concentration like 0.1 M of chelating solution has good extraction efficiency of chromium, copper, and arsenic than lower concentration. Higher temperatures also increased the solubility of chromium, copper, and arsenic, so at high temperature such as 75°C or 90°C, chromium, copper, and arsenic are removed most. From the results of chelating duration, copper is extracted quickly, but chromium and arsenic are extracted slower than copper. When chromium and arsenic are extracted, it is different results between 4 hr and 6 hr periods. So the results indicate that chelating duration can affect the extraction efficiency of metals. Based on the present data, the recommended extraction conditions are pH 4.0 adjusted with 1 M HNO_3 or 1 M NaOH, chelating agent concentration of 0.1 M, 75°C and duration of 6hr. Discussion indicates some results that are similar with literatures under these conditional factors.

The results of EDDS-CCA stoichiometric ratios demonstrate that chromium, copper and arsenic extraction is a function of the stoichiometric ratio of the applied EDDS concentration to the total CCA metals concentration in the wood sample. The different CCA metals extraction efficiencies for CCA treated wood at unit stoichiometric ratio may be caused the solution properties. Then, EDDS concentrations above unit stoichiometric requirement are needed for CCA treated wood to remove maximize CCA metals.

Before EDDS extraction, the results of sequential extractions show that chromium is mainly found in the organic and residual fractions; copper is mainly found in exchangeable, Fe/Mn-oxide, and residual fractions; arsenic is mainly found in Fe/Mn-oxide, organic, and residual fractions. After EDDS extraction, the results of sequential extractions indicate that EDDS extractions break most of weakly bonds for chromium, copper, and arsenic, respectively.

This study discusses the effect of solution extraction, which is one of remediation for CCA treated wood by using chelating agents. These chelating agents, EDTA, EDDS and NTA are biodegradable chelating agents, but EDDS and NTA are more effective and biodegradable. They will be greater chelating agents than EDTA, and they even can replace EDTA in the further. Therefore, pretreatment or remediation for CCA treated wood waste is necessary for waste management to prevent the pollution of CCA metals from CCA treated wood.

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