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2016

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UNIVERSITY OF CALIFORNIA,
IRVINE

Copper and Mercury Ions Adsorption on Ion Exchangers

THESIS

submitted in partial satisfaction of the requirements
for the degree of

MASTER OF SCIENCE

in Chemical and Biochemical Engineering

by

Milan Wang

Thesis Committee:
Professor Mikael Nilsson, Chair
Professor Frank G. Shi
Professor Hung Duc Nguyen

2016

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

I would like to express the deepest appreciation to my committee chair, Professor Mikael Nilsson, who has the attitude and the substance of a genius: he continually and convincingly conveyed a spirit of adventure in regard to research, and an excitement in regard to teaching. Without his guidance and persistent help this dissertation would not have been possible.

I would like to thank my committee members, Professor Frank G. Shi and Professor Hung Duc Nguyen, who taught me two core courses, thermodynamic and reaction engineering. Due to their courses, I have a strong background in chemical engineering, which has allow me to finish this dissertation.

ABSTRACT OF THE THESIS

Copper and Mercury Ions Adsorption on Ion Exchangers

By

Milan Wang

Master of Science in Chemical and Biochemical Engineering

University of California, Irvine, 2016

Professor Mikael Nilsson, Chair

In this thesis, the treatments of mercury and copper were studied because these heavy metals can be found in certain contaminated water. They accumulate in the food chain and damage the health of humans. Two exchange resins, Dowex 50W, a strong acid cation exchanger with sulfonic acid functional group, and Amberlite IRA-67, a weak basic anion exchanger with amino group, were compared to determine which resin was more effective for removing heavy metals from water. In this work, neutron activation analysis was used to determine the concentrations in aqueous solutions. Under certain concentrations, the adsorption percentages of copper were 97.6% ± 0.2% of Dowex 50W and 81.2% ± 2% of Amberlite IRA-67, and those of mercury were 81.5% ± 9% of Dowex 50W and 37.7% ± 9% of Amberlite IRA-67. The adsorption capacities of Dowex 50W were found to be 0.988 and 4.167, and those of Amberlite IRA-67 were found to be 0.606 and 9.462 for copper and mercury, respectively. Therefore, this paper recommends that Dowex 50W is used for the removal of heavy metals.

INTRODUCTION

Finding a way to treat low concentrations of heavy metals in river water is a serious industrial problem.[1] The presence of these heavy metals is a result of the extraction and processing of metals, the surface disposal of oil paints and pigments, and the production of batteries, etc.[2] Today, scientists realize that it is extremely important to extract and recycle these heavy metals from contaminated water. Thus, many methods have been introduced to pull the heavy metals out of the water, but the lower concentrations of certain heavy metals, like mercury, are still overwhelmingly difficult to process and filter efficiently. Here, using drinking water as the standard (shown in Table 1), if heavy metal concentrations go beyond established health standards, this will lead to inestimable public health consequences.

Table 1 Standard of heavy metals for surface water[3]

Categories	Standards	Designated uses	Heavy Metals	
			Cu	Hg
Surface water[a], mg/l	Grade II	Habitat for aquatic animals	1.0	0.05
	Grade III	Aquaculture and swimming area	1.0	0.1
	Grade IV	Industrial use and recreation use	1.0	1
	Grade V	Agriculture and landscape use	1.0	1
Sea water[b], mg/l	Grade I	Marine fish, shellfish and wildlife habitat	0.005	0.05
Drinking water[c], mg/l	WHO	Drinking water	1.3	0.006
	EPA	Drinking water	1.3	0.002

a China SEPA (2002). Environmental quality standards for surface water (GB3838-2002).
b China SEPA (1997). Sea water quality standard (GB3097-1997).
c WHO (1996). Guidelines for drinking water quality 2, 940-949.
   EPA (2015). The national primary drinking water regulations (NPDWRs or primary standards).

In certain areas, due to a history of inattention and neglect, heavy metals have been discharged from industrial plants located near rivers and oceans for decades, and thus, the concentrations of these heavy metals in water systems have increased. Little by little, the heavy metals have accumulated in the ecological system of many rivers and oceans, leading to a build-up of these heavy metals in organisms living in these waters, from phytoplankton

to small carnivorous fish. Humans are at the highest level of nature's food chain, and because mercury salts have high solubility, these salts are easily absorbed and thus heavy metals can accumulate in the human body. Furthermore, the human body will not eliminate certain heavy metals such as mercury, which is one of the most serious and toxic heavy metals found in nature, if it has inadvertently entered the human body through inhalation or ingestion. The accumulation of mercury can destroy the function of various parts of the body, including the adipose tissue, gonad, pituitary gland, and hypothalamus. More seriously, it can influence the transmission of the nervous system and the production of hormones.[4] Mercury poisoning can result in several diseases, including acrodynia (pink) disease, Hunter-Russell syndrome and Minamata disease. For example, in 1956 in Japan, Minamata disease broke out and rapidly became widespread. After that disaster, people began to focus on extracting heavy metals from water sources. Hence, the removal of heavy metals from industrial wastewater is of practical interest. According to a report by Guo and Yan[3] regarding heavy metals in the environment, concentrations of copper from the surface water were 2.4 to 131 times to the standard in Table 1. The vital need to extract heavy metals like copper and mercury from river water provided the impetus for this research.

There are a great number of methods that have been researched to extract heavy metals from water. They include solvent extraction, ion exchange, membrane processes, adsorption and precipitation. Although all of these methods can achieve the goal of eliminating heavy metals, each has its own advantages and disadvantages,[6] which are listed in Table 2.

In this paper, mercury and copper are used as representative heavy metals in view of the fact that they are commonly distributed in natural water in China[5] and other regions of the

world. In this research, two exchange resins, Dowex 50W and Amberlite IRA-67, were used to remove mercury and copper from water. The method of neutron activation analysis was used to determine the concentration in aqueous solutions. This method is different from the methods used in previous articles. This method will be introduced in the following chapters.

Table 2 The methods of eliminating heavy metals

Method	Principle	Advantages	Disadvantages
Ion exchange	Heavy metal ions can be exchanged with the ions in the resins.	Large capacity and high efficiency. Better chemical, thermal and mechanical stability. Macroporous can be improved. Specific functions. Inexpensive and easy recycling.	Popular and wildly used but lots of kinds of resins that have different specific ability to exchange.[6]
Membrane filtration	Permeable membranes can separate the particles with large sizes.	High efficiency. Easy operation. Space saving.[6]	The product is demineralized water (not necessary for water supply industry)[5] High cost and problem of reuse. Complex for permeation flux.
Coagulation	Coagulation aims to bind hydrophobic colloids and suspended particles into large insoluble particles and sediment them. [6]	Simple operation. Quick sedimentation.	Incomplete removal of the metal ions. Chemical consumption involved in the process. Harmful for health.
Flocculation	Flocculation can form bridges between the flocs and bind the particles into large agglomerates or clumps.[6]	Simple operation. Quick sedimentation.	Incomplete removal of the metal ions. Chemical consumption involved in the process. Harmful for health.
Precipitation	Chemicals react with heavy metals to form insoluble precipitates, and then separate the production by sedimentation and filtration.[6]	Simple and inexpensive operation.	Low recovery of metal value and low selectivity. Large volumes of sludge should be treated after the process. Not economical.
Adsorption (e.g. Active carbon and cross-linked chitosan)	A process whereby a solid can remove soluble substances from the water by selectivity.	High adsorption capacity. Materials can be modeled in different shapes, microspheres.	Insoluble with water and organic solvents. Poisonous effects[5] on human health. Many kinds of adsorbents.[16]

Chapter 1 Study of Ion Exchange

1.1 Introduction

One of the most common methods to remove metal ions from water is known as ion exchange using synthetic resins. It is an inexpensive and effective method; however, the ideal ion exchange materials have not yet been determined. According to the paper by Erol and Altun[1], styrene-divinylbenzene copolymers can be a good ion exchange material because of their sulfonic acid function.

Adsorption and ion exchange are two different, but simultaneous reactions that occur in resins.[7] Using ion exchange as an example, positively charged ions can exchange with hydrogen ions on the resins special functional groups. The ion exchange material consists of different functional groups with opposite charge types.[1] Therefore, the selection of the most optimum resin for a particular situation requires a prudent balance of the resin's physical and chemical properties.
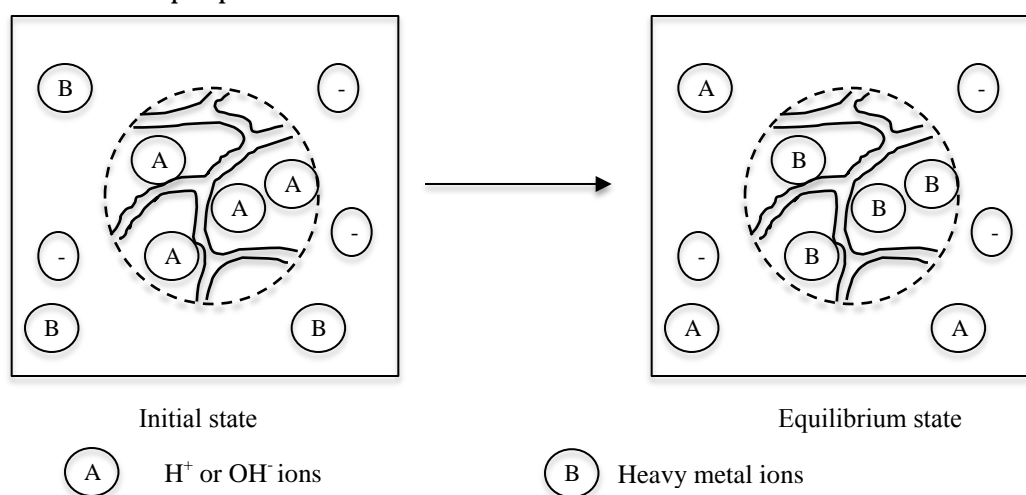

Figure 1.1 Ion exchange between a solution with a resin[19]

Based on the selective extraction of ion exchangers by LEWIS-base-acid, the process of ion exchange occurs not only on the surface, but also in the interior.[1] The trace heavy

metal ions move toward the ion exchangers, and, in the interface interaction, the diffusion of heavy metal ions from the liquid to the solid phase can be described in three stages: film diffusion, particle diffusion, and chemical adsorption reaction, occurring at the functional sites.[5] This process is illustrated in Figure 1.1.

In this research, Dowex 50W resin was chosen due to its high efficiency in removing toxic and harmful heavy metal ions because of its durable, compatible, and insoluble properties. Because of the backbone of Dowex 50W (which is composed of styrene cross-linked with divinylbenzene combined with the functional group), the ion exchange site has great properties, such as high selectivity, great exchangeability, and great reversibility.[4-5] Exchange reaction equation 1.1 illustrates the exchange process of the strong acid cation exchanger, Dowex 50W, whereby metal ions replace the hydrogen ions in the sulfonic group[6]:

$$\overline{nR - SO_3H} + M^{n+} \rightarrow \overline{(R - SO_3^-)_n M^{n+}} + nH^+ \tag{1.1}$$
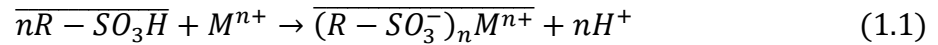
where the over-barred symbols refer to the resin phase.

Another alternative choice for this experiment is Amberlite IRA-67; it is approved by Food and Drug Administration, and used for food production.[8] The LEWIS-base properties of nitrogen atoms can coordinate to cations such as heavy metal ions, and result in high selectivity of the materials.[5] In an aqueous solution, the electron donor atoms of the amino groups of Amberlite IRA-67 can offer unshared electron pairs and act as the LEWIS base, but only when they are not protonated.

However, many heavy metal ions such as mercury (Hg^{2+}) can offer unsaturated vacant orbits because of their incomplete (n-1)d- or (n-2)f- half sublevel of the last energy level,

$$Me^{q+} + L^{p-} \rightarrow [Me(L)_n]^{q-np} \tag{1.2}$$

Me is a heavy metal and L is the ligand in the water; p is the valence of Me and q is valence of L.

Consequently, as a result of the LEWIS-acid-base interaction, heavy metal ions undergo coordination with the amino ligands of weak basic anion exchange resins.[5]

$$\overline{R-NH_2} + [Me(L)_n]^{q-np} + Y^{s-} \overset{k}{\Leftrightarrow} \overline{R-NH_2\{Me^{q+},L^{p-},Y^{s-}\}} + L^{p-} \qquad (1.3)$$
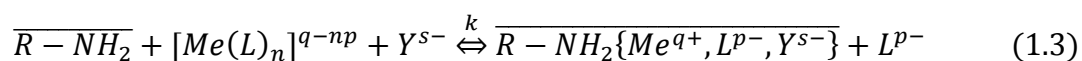
where R is the matrix of resin, and Y^{s-} is an anion of strong acids with the valence of s^-.

1.2 Experimental

1.2.1 Materials

Synthetic Dowex 50W was from ACROS ORGANICS Company and Amberlite IRA-67 was from Aldrich Chemistry Company. The properties of the resins are given in Table 3.

Table 3 Characteristic data of tested Dowex 50W and Amberlite IRA-67

Type	Dowex 50W	Amberlite IRA-67
Active Group	Sulfonic Acid	Tertiary amine
Matrix	Gel(microporous)-syrene divinylbenzene	Poly-acrylamide
Type	Strong acid cation exchanger	Weak basic anion exchanger

1.2.2 Apparatus

An analytical balance was made in the USA from SARTORIUS Company. The maximum weight was 120 g and the readability is 0.1 mg. The vacuum pump was made in the USA from Gast manufacturing Inc.

1.2.3 General procedures of purification of exchange resins

First, a 5 g resin was weighed and added to a beaker full of a solution of 5 ml of 50% NaOH and 5 ml of 30% H_2O_2. The solution was stirred with a glass rod for approximately 5 minutes and then 5 ml of ultrapure water was added. The solution was stirred for another 5 minutes with a stir bar, and the resin was filtered through a vacuum filtration unit washed

3-4 times with ultrapure water. The reaction was extremely violent and the researcher needed to be carefully protected. Next, the materials were placed into a fresh beaker with a new stir bar and an excess of ultrapure water, and then stirred for 1 hour to remove any traces of NaOH and H_2O_2. Finally, water was filtered off the resins and the resins were stored in plastic containers.

1.3 Results and discussion

1.3.1 Determine conditions for ion exchange process

1.3.1.1 Initial concentration of heavy metals

The ion exchange experiments could be carried out with varying conditions such as initial concentrations, different pH and temperature ranges. Equilibrium states are determined by exposing different amounts of resin to equal volumes of a solution containing 10^{-3} M of the metal at a constant temperature.[1] As the study by Erol and Altun's paper[1] mentioned, this experiment was designed with 10^{-3} M solutions of copper and mercury with the same volumes. The initial concentrations were 2.03×10^{-3} M and 2.99×10^{-3} M respectively. In that case, the concentration of copper was 100 times higher than the drinking water standard, in Table 1; mercury was 100,000 times higher than the standard, which is similar to the concentration in most rivers in Southeastern China. In ideal conditions, if resins had more than 99% efficiency, these concentrations could reach the drinking water standard. However, most resins cannot meet this optimum efficiency rate, but resins can easily reach the more lenient discharging water standard. This paper will discuss the efficiency, capacity and kinetics of two different resins, Dowex 50W and Amberlite IRA-67, a strong acid cation exchanger with sulfonic acid functional group and a

weak basic anion exchanger with amino group respectively. It will provide a strong foundation for future multistage process studies.

1.3.1.2 Contact time of solution and resins

Erol and Altun[1] used Dowex 50W synthesis from a different company than the one used in this study. Therefore, their plateau value at 70 minutes can only be used as a reference time for reaction in this study. In this experiment, the contact time will be 3 hours, which is enough time to observe the adsorption equilibrium state of the resins. Samples were taken every 5 minutes at the beginning of the experiment, and then were taken every 10 minutes for the following half hour, and during the remaining 2 hours, a sample was taken every 30 minutes. Samples taken from the experiment were determined by neutron activation analysis.

1.3.1.3 Amount of resins and solutions

By increasing the resin amount in the range of 0.01 to 0.13 g, the equilibrium concentration of heavy metal decreased with increasing resin doses for a given initial concentration, because increasing adsorbent amount provided greater surface area and sorption sites. In conclusion, the retention of metals increased with the increasing amount of resin up to 0.10 g. In order to make the adsorption capacity reach the highest level, 5 ml of solutions were placed into an approximately 6 ml vessel to fully allow heavy metal ions access to the resins. In addition, a sample was taken of approximately 0.15 ml each time from the top of the solution, which occupied only 3% of volume of the total amount of solutions. Therefore, extracting samples should not influence the result of adsorption.

1.3.1.4 pH effect

The concentration of hydronium ion is another important parameter affecting the ion exchange process. The resins exhibit the highest uptake at neutral or base solutions.[5] The solution of heavy metal in this experiment, cupric nitrate and mercuric nitrate were in a neutral pH without any adjustment. If necessary, potassium hydrogen phthalate-HCl and potassium dihydrogen phosphate-NaOH could be added to the solutions to make them neutral.

1.3.1.5 Temperature

The experiment from Erol and Altun[1] showed that the temperature was at 25 °C. At this temperature, it is convenient for the researcher to do the experiment in the laboratory. When the experiment is conducted in the plant instead of a laboratory, the temperature should be easier to control, if needed.

1.3.2 Batch reactor for equilibrium

To evaluate the performance of the ion exchange process, batch reactors can obtain the liquid-solid exchange without influence of pH, temperature, weight of resins, etc.[1] In this experiment, the solutions were in vessels and mixed with resins by using the vortex mixer, and the samples were taken in each interval mentioned above. Vessels, as batch reactors, were simple containers that enable easy evaluation of the performance and exactly fit in the vortex mixer.

Chapter 2 Heavy Metals Determination by Neutron Activation Analysis

2.1 Introduction

Neutron activation analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast range of different materials. In this paper, this method was used to measure the concentrations of copper and mercury in solutions. The process is shown in Figure 2.1 below.
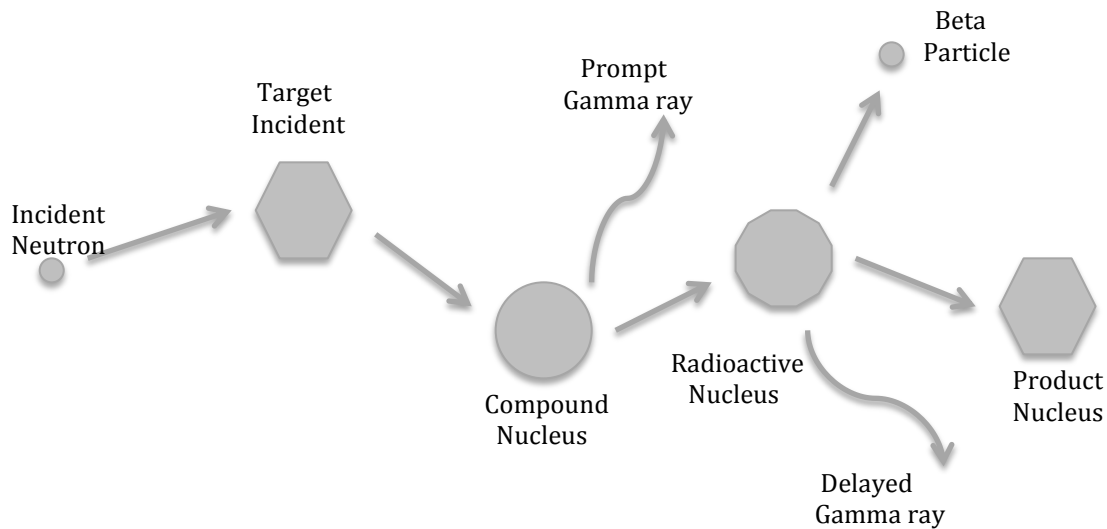

Figure 2.1 The process of neutron capture[18]

First, several neutrons had appropriate velocities to enter the target nucleus. Then the neutron blended into the target nucleus and changed it into a compound nucleus. The compound nucleus has one neutron more than the original nucleus. After the compound nucleus emits a gamma ray, a new nucleus is formed, which is often radioactive and can be measured by the semiconductor detector, an HPGe detector, operated at liquid nitrogen temperatures. By analyzing the spectra of the emission, the concentrations of different samples were obtained.

Gamma ray spectra can be measured with very high precision using semiconductor detectors. The higher the density of the material, the more efficient the semiconductor

material is in absorbing the energy.[13] First, a reference of irradiation is created, using several standard solutions. After irradiation of the samples, the concentration of each sample was determined by using the reference.

In this paper, because the irradiation time of mercury is quite long, we use a rotary sample rack, which is also named Lazy Susan, to determine the concentration in solutions, and finally find out the adsorption curve of the resins. Furthermore, the produced isotope ^{66}Cu has a very short decay time of 5.1 minutes, the researcher had to detect the samples within one minute after the irradiation. The pneumatic transfer system was used for short time irradiation in the research reactor. It is used in irradiation of target materials for neutron activation analysis in the TRIGA reactor, which works by sending the capsules from a NAA laboratory into the core of the reactor and back, after which the researcher can retrieve the samples.[12]

Copper is a common element but it is toxic: it harms plants, damages the environment and has a negative effect on the human body.[6,10] Even though there are many methods to remove copper ions from water, and these methods have been used in many plants, wastewater and river water still have large amounts of copper that contaminate them.

Mercury is one of the most hazardous contaminants in the natural environment because it spreads easily and accumulates in living organisms. In wastewater, mercury occurs in the form of metallic, dissociated molecules, Hg^{2+} as well as complex ions.[10]

This chapter describes how the ion exchange method was used with two different resins to extract copper and mercury ions from laboratory solutions.

2.2 Experimental

2.2.1 Materials

The mercuric nitrate ($Hg(NO_3)_2 \cdot H_2O$) and the Cupric Nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) were obtained from Fisher Scientific Company, with M_w = 342.62 g/mol and M_w = 241.60 g/mol respectively. Prepared resins were mentioned in chapter 1.

2.2.2 Apparatus

An analytical balance from SARTORIUS Company was used. The maximum weight of the balance was 120 g and the readability is 0.1 mg. A vortex mixer was used from Fisher Scientific Company, which was made in the USA.

2.2.3 Procedure

Weighted 0.0245 g $Cu(NO_3)_2$ (or 0.0512 g $Hg(NO_3)_2$) was used to make a 50 ml solution. Then, 0.1 g of resin materials of Dowex 50W and Amberlite IRA-67 and 5 ml of a metal solution were placed into a vessel. After mixing, the resin was allowed to reach equilibrium for 3 hours under static conditions in a thermostated room (25±1 °C) using a vortex mixer. The samples for analysis were taken by pipette from the top of the vessel at different time intervals at a constant temperature, and the concentration of samples were determined by the neutron activation analysis.

2.3 Analysis

2.3.1 General Consideration[13]

Equipment, such as particle accelerators and nuclear reactors, can produce radioactive nuclides. The processes of these facilities use neutron irradiation, which causes the target atoms to absorb the neutron and turn into a radioactive nucleus, which can emit γ-rays that can be sensed by a detector.

2.3.1.1 Copper isotopes

The chart below shows copper isotopes. Copper has only two kinds of stable isotopes, ^{63}Cu and ^{65}Cu, which are shown in the shaded square boxes in Figure 2.2. Typical reactions of copper are

$$^{63}\text{Cu (n, γ)} \; ^{64}\text{Cu} \; \& \; ^{65}\text{Cu (n, γ)} \; ^{66}\text{Cu} \tag{2.1}$$
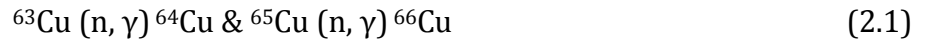
which yield two other important isotopes, ^{64}Cu ($t_{1/2}$ 12.7 h) and ^{66}Cu ($t_{1/2}$ 5.1 m), that are diluted by the ^{63}Cu and ^{65}Cu target atoms.

Cu 63 69.15 σ 4.5	Cu 64 12.7004 h ε β-0.6 β+0.8 γ(1346) σ 270	Cu 65 30.85 σ 2.17	Cu 66 5.1 m β-0.2.6… γ 1039, (834) σ 140

	Stable nuclide	ε :Electron capture β- :Negatron decay β+ :Positron decay γ :Energy (keV) σ :Cross section
	Unstable nuclide	

Figure 2.2 The nuclides of copper[9]

2.3.1.2 Mercury isotopes

Based on the chart of the nuclides[9], mercury has seven stable isotopes, four of them can be irradiated to unstable isotopes. ^{198}Hg and ^{204}Hg are low in abundance and cross section, thus the amount of production of their isotopes after irradiation will be small, and cannot be examined by the detector. Even though ^{196}Hg naturally has 0.15% of mercury, the high cross section can make up for its low abundance, the amount of production, radioactive isotope irradiating from ^{202}Hg will be more easily detected than other isotopes. The isotopes of mercury are shown in the below boxes.

A typical reaction of mercury is

$$^{196}Hg\ (n,\gamma)\ ^{197}Hg\ \&\ ^{202}Hg\ (n,\gamma)\ ^{203}Hg \tag{2.2}$$
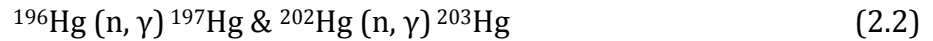
which yields other important radioactive nuclei, ^{197}Hg ($t_{1/2}$ 64.1 h) and ^{203}Hg ($t_{1/2}$ 46.59 d), that are diluted by all other mercury isotopes.

Hg 196 0.15 σ 3000	Hg 197 64.1 h ε γ 77, 191... e- g	Hg 198 9.97 σ 0.017	Hg 199 42.6 m Iγ 158, 374... e-
Hg 202 29.86 σ 4.9	Hg 203 46.59 d β-0.2 γ 279	Hg 204 6.87 σ 0.4	Hg 205 5.2 m β- 1.5... γ 204

g : Ground state of the daughter nuclide is populated
e- :Conversion electron
Iγ : Isomeric transition

Figure 2.3 The nuclides of mercury[9]

2.3.2 Irradiation yield

2.3.2.1 Production by activation [13]

The rate of production (dN'/dt) depends on the number of target nuclei in the samples (Equation 2.3) and the number of neutrons bombarding an area per second.

$$N_t = \frac{m_{element} \times f_{abundance} \times 6.022 \times 10^{23}}{M_{element}} \tag{2.3}$$

The final equation is simple

$$\frac{dN'}{dt} = N_t \times \sigma \times \Phi \tag{2.4}$$

Φ is the neutron flux in neutrons per area and per second.

σ is the section area in cm^2.

However, the product of the reaction is radioactive; in other words, the moment radioactive atoms are produced they can also decay. A decay term (equation 2.5) is thus added into equation 2.4, combining production and decay to get

$$Rate\ of\ decay = -\frac{dN'}{dt} = \lambda N' \tag{2.5}$$

$$\frac{dN'}{dt} = N_t \times \sigma \times \Phi - \lambda N' \tag{2.6}$$

Integrating the equation will yield

$$N'(t) = \frac{N_t \times \sigma \times \Phi \times (1 - \exp(-\lambda t))}{\lambda} \tag{2.7}$$

Equation 2.8, gives the activity in Bq (dps)

$$A(t)=\lambda N' \tag{2.8}$$

$$A(t) = N_t \times \sigma \times \Phi \times (1 - \exp(-\lambda t)) \tag{2.9}$$

$$\lambda = \frac{0.693}{t_{1/2}} \tag{2.10}$$

where $t_{1/2}$ is the product nuclide half-life.

The consecutive irradiated production of a radioactive nuclide is

$$X_{target} \xrightarrow{k} X_1 \xrightarrow{\lambda_1} X_2 \tag{2.11}$$

When producing radioactive X_1 (produced at rate k), X_1 is decaying to the stable nucleus X_2. N_1 presents the number of radioactive atoms of X_1 at any time t. For the consecutive process, the number of atoms changes:

$$dN_1 = kdt - \lambda_1 N_1 dt \tag{2.12}$$

Integrating the above equation and combining the initial concentration (this assumes that at t_{irr}, $N_1 = 0$), the equation will be

$$N_1 = \left(\frac{k}{\lambda_1}\right)(1 - \exp(-\lambda_1 t_{irr})) \tag{2.13}$$

Adding the decay term, after the end of irradiation (termed the cooling time) as t_{cool},

$$N_1 = \left(\frac{k}{\lambda_1}\right)\left(\left(1 - \exp\left(-\frac{0.693 t_{irr}}{t_{\frac{1}{2}}}\right)\right)\exp\left(-\frac{0.693 t_{cool}}{t_{\frac{1}{2}}}\right)\right) \tag{2.14}$$

The production rate k is

$$k = \Phi\, \sigma\, N_t \tag{2.15}$$

2.3.2.2 Change in activity of ^{64}Cu and ^{66}Cu during and after irradiation
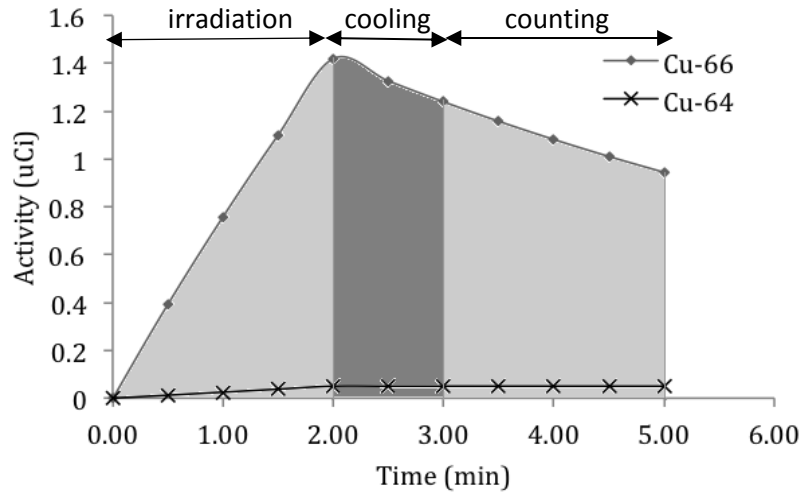
Figure 2.4 Change in activity of ^{64}Cu and ^{66}Cu during and after irradiation
(irradiation time 120 s, cooling time 60 s, counting time 120 s)

Cu(NO$_3$)$_2\cdot$3H$_2$O (M = 241.6) is irradiated in a reactor to produce ^{64}Cu and ^{66}Cu, which have half-lives of 12.7 h and 5.1 m respectively, and emit β- and γ-rays. The reaction cross section of ^{63}Cu (69.15% in the nature copper) is 4.5 barns for thermal neutrons and for ^{65}Cu (30.85% in the nature copper) is 2.17 barns for thermal neutrons. For a 0.13 g/L (2.03×10^{-3} M) sample, a 120 s irradiation time, and a thermal flux of 1.8×10^{12} n cm^{-2} s^{-1}, a cooling time of 60 s and a counting time of 120 s, the irradiation yields will be as shown in Figure 2.4.

Using the highest concentration ($2.03×10^{-3}$ M) as an example, according to Figure 2.4, the activity of ^{66}Cu has a rapid increase during the irradiation time, and reaches 1.5 uCi, which can be sensed by the detector. At that time, the graph displays a noticeable decrease in activity during the cooling time. In contrast, the activity of ^{64}Cu grows marginally at the beginning, and a decline can't be clearly illustrated. Thus, ^{66}Cu was the target atom when directly determining the concentration in samples. The abundance in nature of ^{63}Cu and ^{65}Cu, cross section of ^{64}Cu and ^{66}Cu are in the same order of magnitude, and the only difference between two isotopes is their half-lives, shown in Figure 2.2. Equation 2.9 illustrates that the shorter the half-life, the higher the activity.
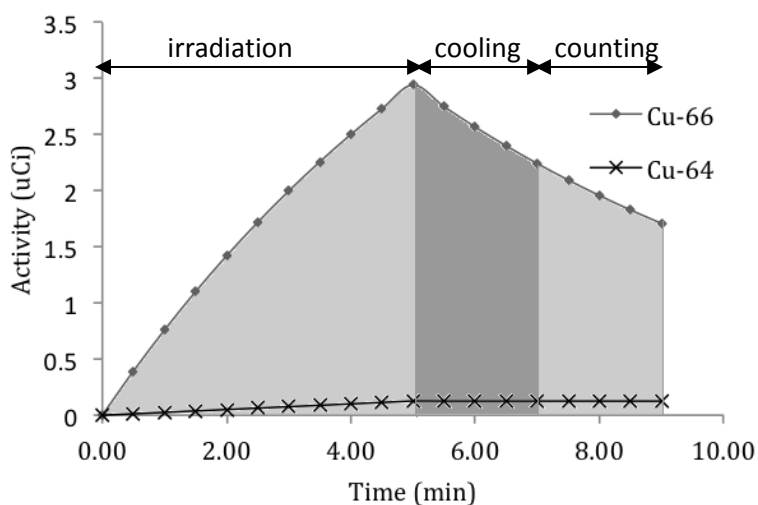

Figure 2.5 Change in activity of ^{64}Cu and ^{66}Cu during and after irradiation
(irradiation time 300 s, cooling time 120 s, counting time 120 s)

The adsorption of Amberlite IRA-67 was obtained by the above irradiation and cooling time. However, some of the samples, which were reacted by Dowex 50W cannot be detected. At lower sample concentrations, most of the high concentration samples could appear as obvious peaks in detected spectra. For even lower concentrations, the detected areas were relatively small, so that the samples required a longer irradiation time.

Therefore, for a 0.13 g/L (2.03×10^{-3} M) sample, a 300 s irradiation time, and a thermal flux of 1.8×10^{12} n cm^{-2} s^{-1}, a cooling time of 120 s and a counting time of 120 s, the irradiation yields will be as shown in Figure 2.5.

From the above graph, the activity of ^{66}Cu has obvious uptrend and downtrend. Therefore, the concentrations of samples can be successfully determined by neutron activation analysis, even at low concentrations of samples.

2.3.2.3 Change in activity of ^{196}Hg and ^{202}Hg during and after irradiation

Hg(NO$_3$)$_2 \cdot$H$_2$O (M=324.59 g/mol) is irradiated to produce ^{197}Hg and ^{203}Hg, which have half-lives of 64.1 h and 46.59 d, respectively. The reaction cross section of ^{196}Hg (0.15% of mercury) is 3000 barns for thermal neutrons and that of ^{202}Hg (46.59% of mercury) is 5 barns for thermal neutrons. For a 60 mg/L (2.99×10^{-3} M) sample, a 4 h irradiation time, a thermal flux of 8×10^{11} n cm^{-2} s^{-1}, a cooling time of 24 h and a counting time of 120 s, the irradiation yields will be as shown in Figure 2.6.
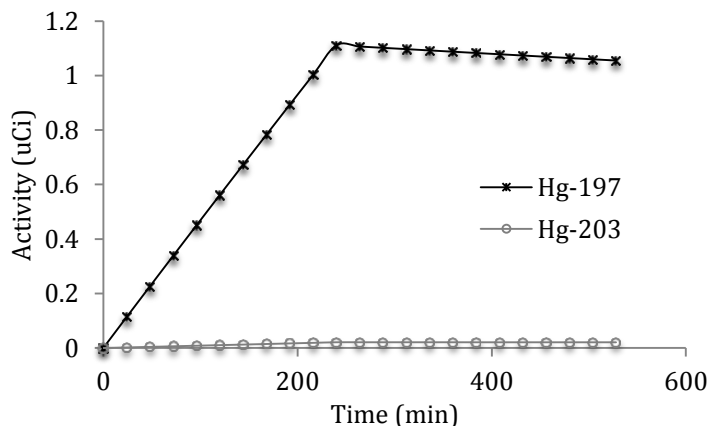

Figure 2.6 Change in activity of ^{197}Hg and ^{203}Hg during and after irradiation
(irradiation time 4 h, cooling time 24 h)

Using the sample with the highest concentration (2.99×10^{-3} M) as an example as shown in Figure 2.6, the activity of ^{197}Hg increases during the 4-hour irradiation, and reaches 1.1 uCi, which can be sensed by the detector. After that point, the graph decreases because of

the decaying of the target atoms. In contrast, the graph of irradiation yield of ^{203}Hg also cannot clearly illustrate the decline, and the maximum of activity is 0.1 uCi, so that it cannot be examined by the detector. Thus, ^{197}Hg was the target atom to directly determine the concentration in samples.

Therefore, the samples can appear as obvious peaks in the detected spectra. After detecting the area of the known concentration of samples, the standard curve is obtained. The area of unknown concentration samples can be found from the standard curve. Finally, the adsorption curve depending on time will be drawn in the following chapter.

Chapter 3 Results and Discussions

3.1 Spectrum

3.1.1 Copper spectrum

Figure 3.2 shows such a spectrum for the decay of various excited states of ^{66}Cu.[13] There are three main peaks in the spectrum between 0 and 3000 keV, which are distributed at 1039 keV, 1294 keV and 1778.9 keV. Spectra were obtained after 2 minutes of cooling time.

Ar 40 99.6035	Ar 41 1.83 h		Al 27 100	Al 28 2.246 m
σ 0.64	β- 1.2, 2.5… γ 1294 σ 0.5		σ 0.230	β- 2.9 γ 1779

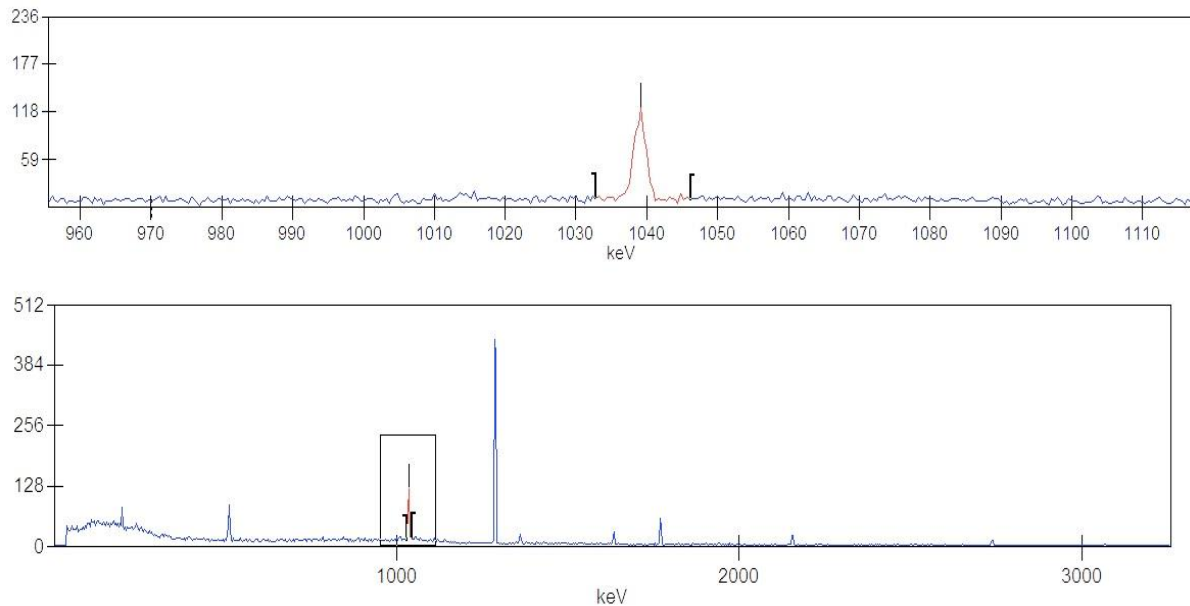**Figure 3.1** The nuclides of Argon and Aluminum[9]

Figure 3.2 Gamma spectrum for ^{66}Cu

The first peak is the target isotope, ^{66}Cu, at 1039 keV. After obtaining the area of the peak, the concentration of the copper sample can be found in the reference.

There is a large portion of air remaining in the capsules, and air naturally has a high level of argon. Because ^{41}Ar is a radioactive isotope with a long half-life (i.e. longer than 2 minutes) a significant amount of it remains in the air. Therefore, the second peak is ^{41}Ar at energy 1294 keV.

The third peak at 1778.9 keV is ^{28}Al. For the same reason as ^{41}Ar, ^{28}Al is naturally highly abundant in nature and thus has not decayed completely in 2 minutes, so the detector can sense ^{28}Al.

At low energy, there are background noises induced by impurities from air measured in the chamber.

3.1.2 Mercury spectrum

Figure 3.3 shows the spectrum for the target atoms, ^{197}Hg.
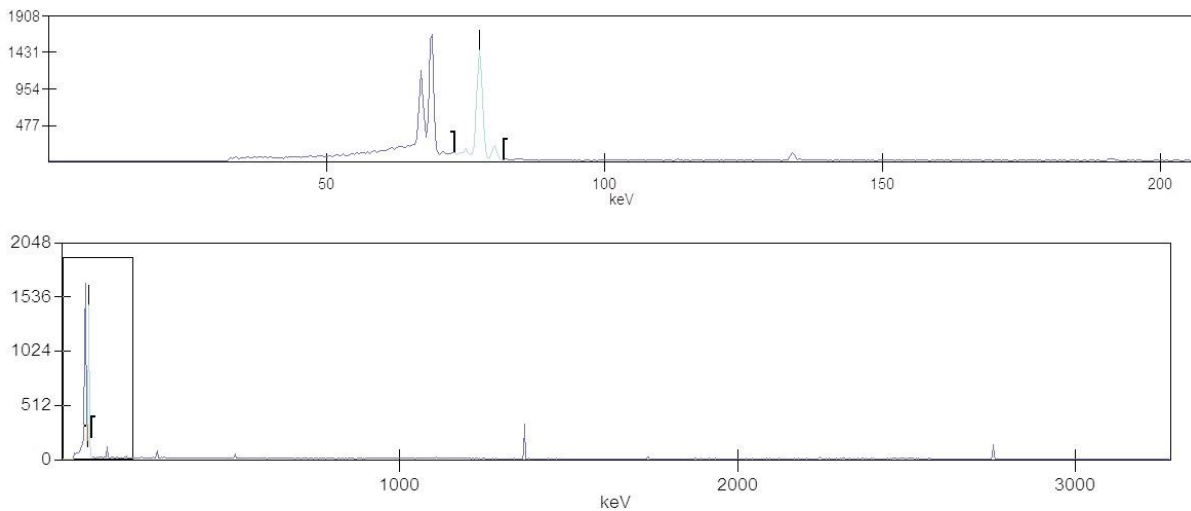

Figure 3.3 Gamma spectrum for ^{197}Hg

There are four noticeable peaks in the spectrum, which are distributed at 67 keV, 69 keV, 77 keV and 1368.4 keV. Spectra were obtained after a 24-hour cooling time. The peaks at 67 keV and 69 keV are X-ray noise.

The third peak is the target isotope, ^{197}Hg, at 77 keV. As discussed above, ^{197}Hg was the target atom for determining the concentration of the mercury.

The fourth peak at 1368.4 keV is ^{24}Na. For the same reason that ^{28}Al remained after the cooling time as mentioned above, and ^{24}Na had not decayed completely after 24 hours, so that ^{24}Na can be sensed by the detector.

Na 23 100	Na 24 14.96 h
σ 0.1	β- 1.4… γ 2754 1369…

Figure 3.4 The nuclides of Sodium[9]

3.2 Sorption of different resins

3.2.1 Copper sorption

The data show that, the adsorption percentages were 97.6% ± 0.2% of Dowex 50W and 81.2% ± 2% of Amberlite IRA-67. The unit mass efficiency of Dowex 50W is higher than Amberlite IRA-67.
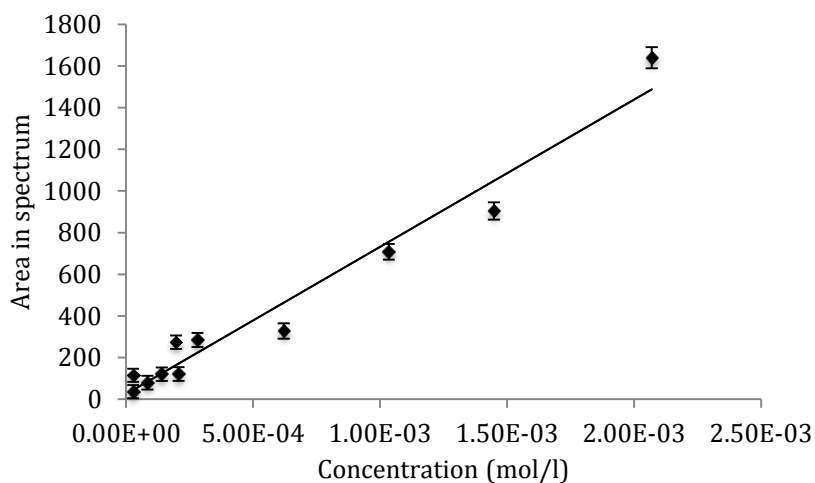

Figure 3.5 Standard curve of known concentration samples
(irradiation time 300 s, cooling time 120 s)

23

As mentioned above, the adsorption of Dowex 50W was obtained by 300 s irradiation and 120 s cooling. The known concentration of samples increased with the area in linear fashion. After regression analysis, the linear line was followed along the equation:

$$Area = 707097 * concentration + 24.605 \qquad (3.1)$$

After finding the area of the unknown concentration of solutions, the concentration was obtained from equation 3.1. The concentrations of samples at different intervals are drawn in the following graph, Figure 3.6.
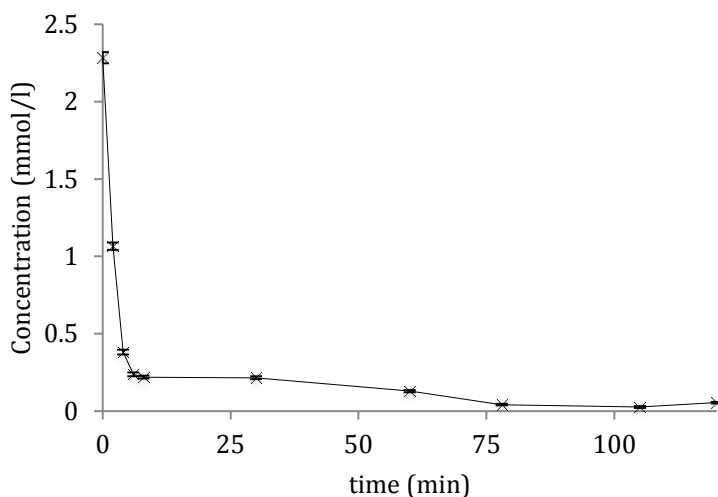

Figure 3.6 The concentration change of copper due to the sorption
by Dowex 50W at different contact times
(initial concentration of metals, 2.03×10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 5 ml; temperature, 25 ± 1 °C; stirring rate, speed at 3 in vortex mixer.)

As can be seen from Figure 3.6, great changes took place at the beginning of the adsorption. The Cu^{2+} extraction rate was extremely high for the Dowex 50W resin in the first 10 minutes of the process. This can be explained by the copper ions' easy access to sulfonic acid functional groups for ion exchange. At 70 minutes, the reaction of Dowex 50W resin and solutions reached the equilibrium state. This timing was mentioned in chapter 1. The adsorption curve can be fit into an exponential function trend line,

$$Concentration(mol/l) = 0.0021 \exp(-0.224t) \tag{3.2}$$

which indicates that the ion exchange process followed a first order reaction and finally approached 0 mmol/l. The reason why it was a first order reaction will be discussed in the following section.
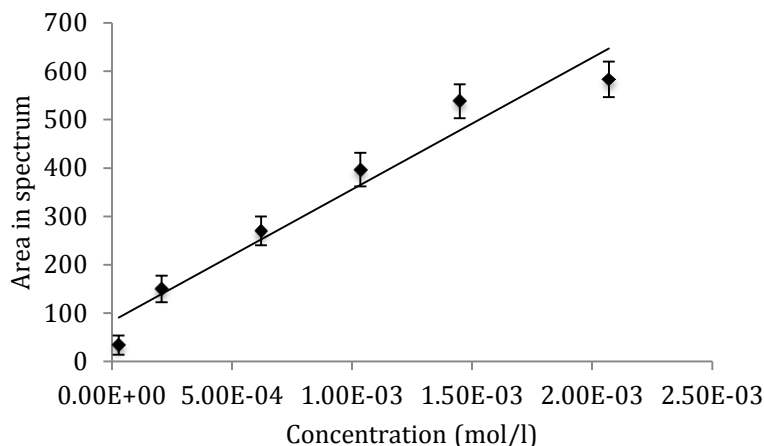

Figure 3.7 Standard curve of known concentration samples
(irradiation time 120 s, cooling time 60 s)

After 120 s irradiation and 120 s cooling time, the adsorption curve of Amberlite IRA-67 was obtained. The standard curve is different from Dowex 50W because different irradiation times resulted in different maximum activities. However, both standard curves show that the relationship of concentration and area in spectra can be linear. In Figure 3.7, a straight line follows the equation 3.3,

$$Area = 272387 * concentration + 83.112 \tag{3.3}$$

Following the same method as mentioned above, when the researcher knew the area of spectra, the concentrations of samples can be found through equation 3.3.

Figure 3.8 shows the change of concentration in the copper solution for Amberlite IRA-67 at different contact times. There is a downward trend in the graph, which indicates that the Amberlite IRA-67 resin had the anticipated adsorption capacity. The graph shows a slight

decrease from the beginning of the process to the end. The trend line is fitted to the graph, and does not exceed the area of the error bar. The equation of trend line is:

$$Concentration(mol/l) = 0.0018 \exp(-0.00486t) \tag{3.4}$$

This is also an exponential equation. The equation suggests that the ion exchange process of Amberlite IRA-67 was with a first order reaction. This will be discussed in the following section.
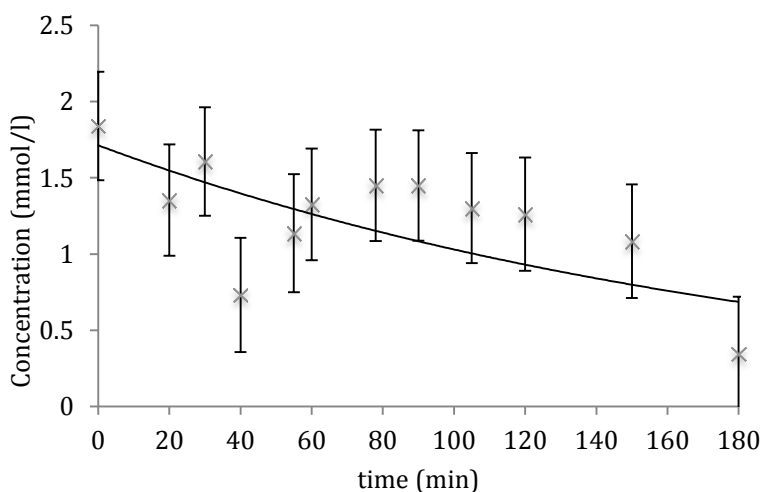

Figure 3.8 The concentration change of copper due to the sorption
by Amberlite IRA-67 at different contact times
(initial concentration of metals, 2.03×10⁻³ M; amount of resin, 0.1 g; volume of sorption
medium, 5 ml; temperature, 25±1 °C; stirring rate, speed at 3 in vortex mixer.)

However, there is an obvious difference between the resins; Amberlite IRA-67 cannot reach 0 mmol/l equilibrium state. On one hand, the error bars of this graph are large; at 180 minutes, the concentration had a range from 0 mmol/l to 0.75 mmol/l. The trend line is fitted to the graph to match the large error bars. If the samples were irradiated as long as Dowex 50W (300 s irradiation time), it is possible to find out whether Amberlite IRA-67 can reach 0 mmol/l at equilibrium state.

On the other hand, weak basic anion exchange resins (Amberlite IRA-67) have the ability to remove the trace amounts of heavy metals from water. However, the strong acid cation exchangers (Dowex 50W) have fast kinetics in the uptake of transition metals and their operation cost is cheaper compared with the other synthetic resins. Compared with the adsorption curve of weak basic anion exchanger, the property of Amberlite IRA-67 is obviously worse than Dowex 50W.

3.2.2 Mercury sorption

The adsorption percentage was 81.5% ± 9% of Dowex 50W and 37.7% ± 9% of Amberlite IRA-67. The adsorption curves of resins were obtained by 4 hours of irradiating and 24 hours of cooling. There is a linear increase in the area with the known concentration of samples. After regression analysis, the following equation was calculated for the line:

$$Area = 3287.4 * concentration(mmol/l) - 786.9 \tag{3.5}$$

After the area of unknown concentration of solutions was obtained, the concentration can be calculated from equation 3.5. The concentrations of samples at different intervals can then be drawn.

In Figure 3.10, the change of mercury concentration decreased obviously at the first 40 minutes of the process due to sulfonic functional groups of Dowex 50W. The contact time of Dowex 50W resin and solutions was about 120 minutes, which is longer than the time mentioned in chapter 1. After these 120 minutes, the reaction reached the equilibrium state. An exponential function trend line is

$$Concentration(mol/l) = 0.003 \exp(-0.0343t) \tag{3.6}$$

which also specifies that the ion exchange process followed a first order reaction.

However, compared with the adsorption of copper, the Dowex 50W does not show great adsorption capacity and efficiency. At the equilibrium state, the final concentration reached approximately 0.5 mmol/l in the solutions.
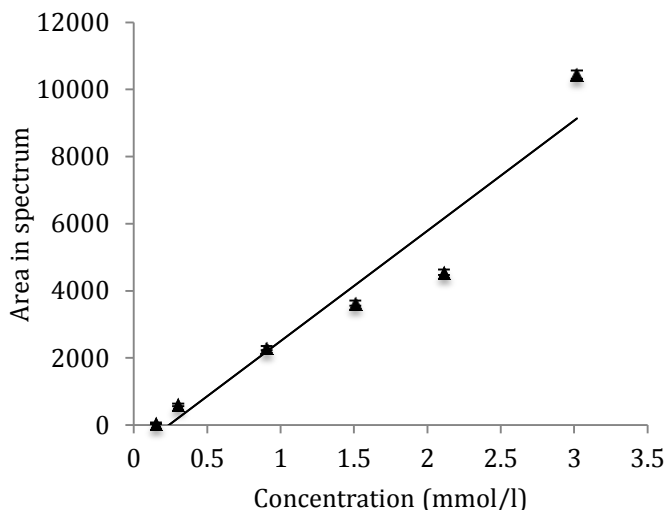

Figure 3.9 Standard curve of known concentration samples
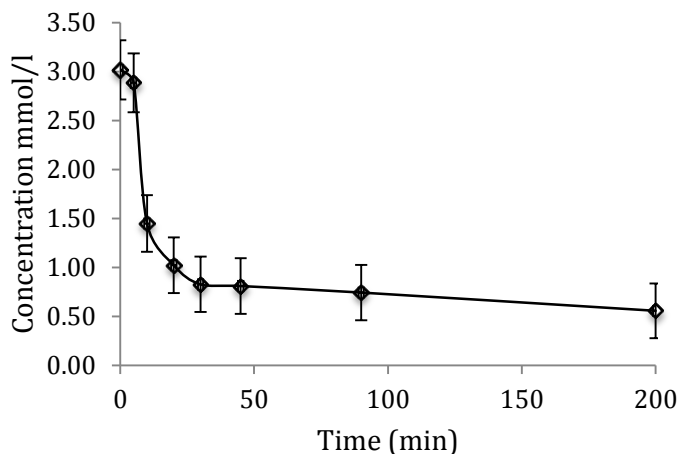(irradiation time 4 h, cooling time 24 h)

Figure 3.10 The concentration change of mercury due to the sorption
by Dowex 50W at different contact times
(initial concentration of metals, 2.99×10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 5 ml; temperature, 25 ± 1 °C; stirring rate, speed at 3 in vortex mixer.)

There is a downward trend in the adsorption curve of Amberlite IRA-67. Figure 3.11 indicates that the Amberlite IRA-67 resin can adsorb heavy metals in solutions as expected by the researcher. Although the resin adsorbed quickly during the first 10 minutes and then

reached the equilibrium, the capacity was not shown well in this graph. The error bar in both the standard curve and the adsorption curve of Amberlite IRA-67 are the same because of similar irradiation operations. The trend line was fitted in the graph by ignoring the concentration change after 10 minutes, and the equation of trend line is:

$$Concentration(mol/l) = 0.003\exp(-0.303t) \tag{3.7}$$

which is also an exponential equation. It describes that the ion exchange process of Amberlite IRA-67 was the same as Dowex 50W, and both of them follow first order reactions.
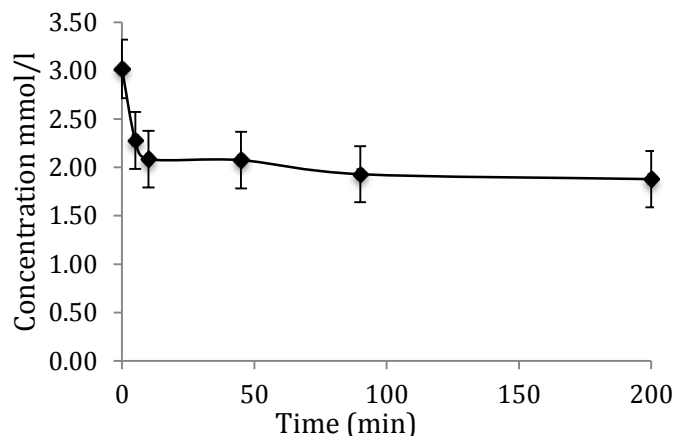

Figure 3.11 The concentration change of mercury due to the sorption
by Amberlite IRA-67 at different contact times
(initial concentration of metals, 2.99×10^{-3} M; amount of resin, 0.1 g; volume of sorption medium, 5 ml; temperature, 25±1 °C; stirring rate, speed at 3 in vortex mixer).

3.3 Adsorption kinetics

3.3.1 General Consideration[17]

The ion exchange obeys a reversible first-order kinetics in aqueous systems.[1] From the liquid to solid phase, the expression of the metal sorption is

$$A \overset{k}{\leftrightarrow} B \tag{3.8}$$

k is the overall reaction rate constant.

The rate of the sorption is,

$$\frac{dx}{dt} = \frac{-d(a - x)}{dt} = k(a - x) \tag{3.9}$$

Here, a is the initial concentration of heavy metals in solutions, which is also called C_0, and x is the amount transferred from solution to resin at any time t. Since k_1 and k_2, the forward reaction rate constant and the backward reaction rate constant respectively, are for the reversible process, the rate can be expressed as

$$\frac{dx}{dt} = k_1(a - x) - k_2 x \tag{3.10}$$

At equilibrium,

$$\frac{dx_e}{dt} = k_1(a - x_e) - k_2 x_e = 0 \tag{3.11}$$

x_e represents the concentration of heavy metal adsorbed at equilibrium. Combining equations 3.10 and 3.11 eliminates a, giving the equation,

$$\frac{dx}{dt} = (k_1 + k_2)(x_e - x) \tag{3.12}$$

After integrating the above equation and using the initial condition (at t = 0, x = 0), the equation is

$$-ln(x_e - x) + \ln(x_e) = (k_1 + k_2)t \tag{3.13}$$

$$K_C = \frac{x_e}{a - x_e} = \frac{k_1}{k_2} \tag{3.14}$$

Combining equation 3.14, the relation between k and x(t) can be demonstrated as

$$ln\left(\frac{x_e}{x_e - x}\right) = k't \tag{3.15}$$

Further,

$$k' = k_1 + k_2 = k_2(1 + K_C) \tag{3.16}$$

Simplifying 3.16, the equation is,

$$ln\left(1 - \frac{x}{x_e}\right) = -k't \tag{3.17}$$

Here, x_e equals C_0-C_e, x equals C_0-C, C is the concentration in solutions at any time, and C_e is the concentration of heavy metal in solutions at equilibrium.

Finally, the equation can change as follows,

$$ln(1 - U_t) = -k't \tag{3.18}$$

In this equation,

$$U_t = \frac{C_0 - C}{C_0 - C_e} \tag{3.19}$$

It can be easily shown that ln(1-U_t) is linearly proportional to time, and thus the overall reaction coefficient k' can be determined by the slope of plot ln(1-U_t) vs. t through trend line fit.

3.3.2 Kinetic fits for copper

The graph (Figure 3.12) illustrates that ln(1-U_t) is linearly proportional to time. The equation of the line of the kinetic adsorption of copper on Dowex 50W is

$$-\ln(1 - U_t) = 0.23t + 0.9252 \tag{3.20}$$

The parameter before the time (0.23) in equation 3.20 is very similar to that of the parameter (0.224) in the adsorption curve trend line, equation 3.2. The fact that the parameters are similar proves that the reaction of the ion exchange is a first order reversible reaction for the kinetics.

In other words, exchanging the U_t into concentration terms, equation 3.18 will be,

$$\ln\left(\frac{C - C_e}{C_0 - C_e}\right) = -k't \tag{3.21}$$

$$\ln(C - C_e) = -k't + \ln(C_0 - C_e) \tag{3.22}$$

$$C - C_e = (C_0 - C_e)\exp(-k't) \tag{3.23}$$

Here, Ce is approximately equal to 0, and so equation 3.23 has the same form as the adsorption curve trend line.
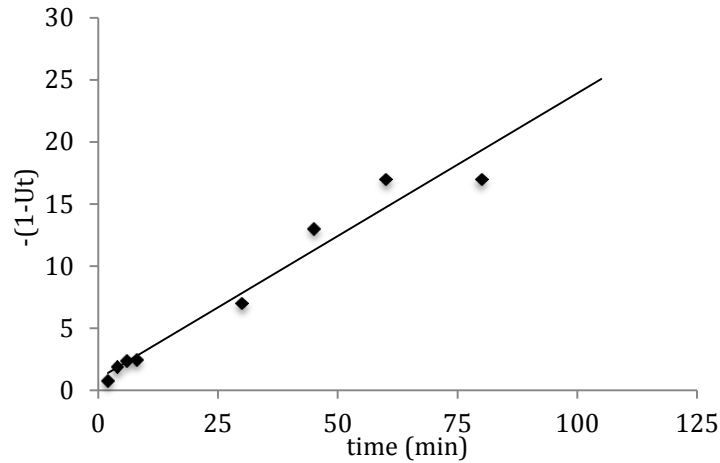

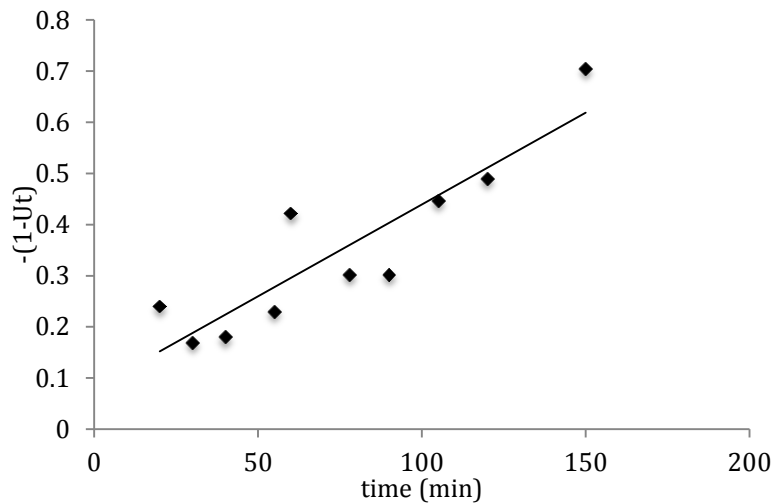**Figure 3.12** Kinetic fits for the adsorption of copper on Dowex 50W

Figure 3.13 Kinetic fits for the adsorption of copper on Amberlite IRA-67

The kinetic fits for the adsorption of Amberlite IRA-67 are also linearly proportional to the time. The equation of the line in Figure 3.13 is

$$-\ln(1 - U_t) = 0.0036t + 0.08 \tag{3.24}$$

The parameter before the time (0.0036) in equation 3.24 is close to the parameter (0.00486) in equation 3.4.

3.3.3 Kinetic fits for mercury

Figure 3.14 shows that -ln(1-U_t) is linearly proportional to time. The linear fit equation of kinetic adsorption for mercury on Dowex 50W is

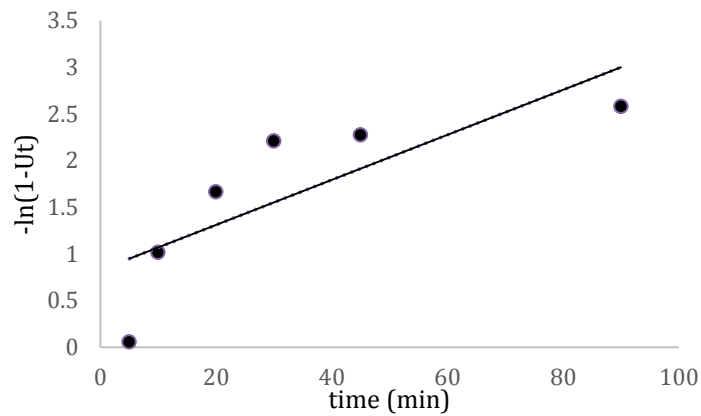$$-\ln(1 - U_t) = 0.0241t + 0.82 \tag{3.25}$$

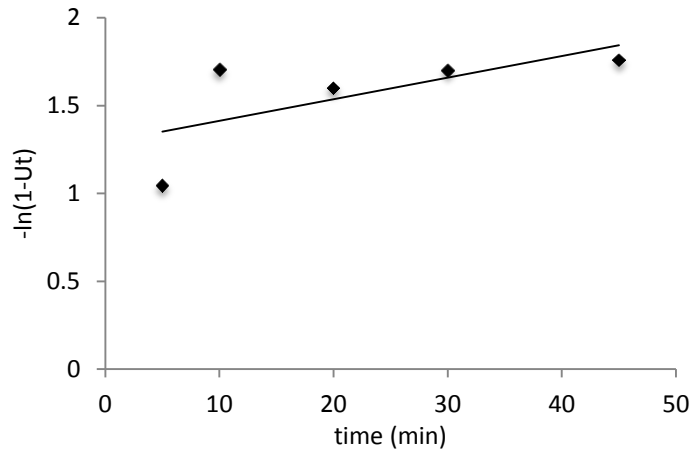**Figure 3.14** Kinetic fits for the adsorption of mercury on Dowex 50W

Figure 3.15 Kinetic fits for the adsorption of mercury on Amberlite IRA-67

The parameter 0.0241 in equation 3.25 is similar to that (0.0343) in the equation of the adsorption curve trend line, which proves that the reaction obeys a first order reversible reaction for the kinetics.

The kinetic fits for Amberlite IRA-67 is approximately linear to the time and the equation of the line in Figure 3.15 is

$$-\ln(1 - U_t) = 0.0123t + 1.2911 \tag{3.26}$$

The parameter 0.0123 in equation 3.26 is much lower than the parameter (0.303) in equation 3.7. However, these parameters are so small that the impact of the difference between them is negligible, furthermore, uncertainties are large.

3.4 Adsorption isotherms

3.4.1 General Consideration[3]

The results obtained from the adsorption of heavy metals on two different ion exchange resins at optimum conditions, room temperature (25±1 °C) and contact time, when using 0.1 g of the adsorbent, follow the Freundlich adsorption isotherm.

$$\frac{x}{m} = kC_e^{1/n} \tag{3.27}$$

where x is the amount of copper removed (mg), m is the amount of resin(g), C_e is the equilibrium concentration and k and n are Freundlich constants.

The logarithmic form of the equation is

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_e \tag{3.28}$$

Here k and n are constants representing the adsorption capacity and intensity of adsorption, respectively.

3.4.2 Copper adsorption isotherms

The data obtained in this study agree with the Freundlich adsorption isotherm, as shown in Figure 3.16.

The plot of $\log(x/m)$ versus $\log C_e$ for various initial concentrations is found to be linear. The equation of Freundlich adsorption isotherm on Dowex 50W is

$$\log\left(\frac{x}{m}\right) = -0.1335 \log C_e + 2.9949 \tag{3.29}$$

and the equation of Freundlich adsorption isotherm on Amberlite IRA-67 is

$$\log\left(\frac{x}{m}\right) = -2.2813 \log C_e + 2.7826 \tag{3.30}$$

The adsorption capacities (k) were found to be 0.988 and 0.606 for Dowex 50W and Amberlite IRA-67, respectively. In this experiment, the total mass of copper in the 5 ml solution is 0.65 mg, which is far less than the mass of both resins used in the experiment. Therefore, the adsorption capacities of both resins were not reached.
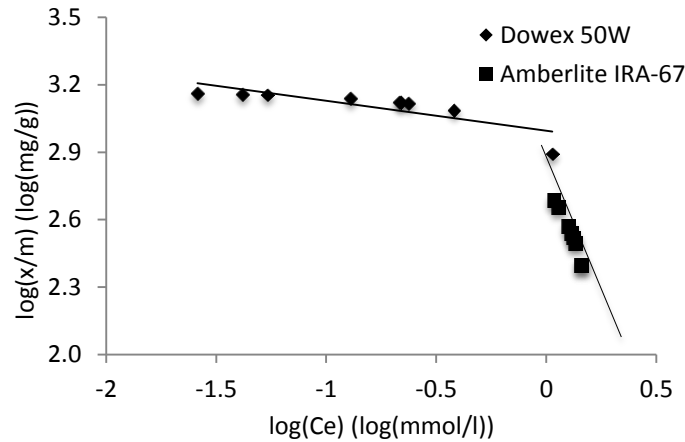
Figure 3.16 Freundlich adsorption isotherm for copper
on Dowex 50W and Amberlite IRA-67

3.4.3 Mercury adsorption isotherms

The data obtained in this study were as shown in Figure 3.17. The equation for Freundlich adsorption isotherm on Dowex 50W is

$$\log\left(\frac{x}{m}\right) = -0.2916 \log C_e + 3.6199 \tag{3.31}$$

and the equation for Freundlich adsorption isotherm on Amberlite IRA-67 is

$$\log\left(\frac{x}{m}\right) = -2.2286 \log C_e + 3.976 \qquad (3.32)$$

The adsorption capacities (k) were found to be 4.167 and 9.462 for Dowex 50W and Amberlite IRA-67, respectively. In this experiment, the total mass of mercury in this solution is 3 mg, which is far less than the mass of both resins used in the experiment. Therefore, the absorption capacities of both resins were not reached. However, in this experiment, the final concentrations of Dowex 50W and Amberlite IRA-67 were approximately 0.5 mmol/l (0.1 mg/l) which was lower than the standard of Grade III in table 1 and 2.0 mmol/l (0.4 mg/l) which was lower than the standard of Grade IV in table 1), respectively. They reach the equilibrium state and therefore could not decrease further. Thus, even though the final concentrations could not reach the standard of drinking water levels, the results achieve the goal of reaching other, lower standards.
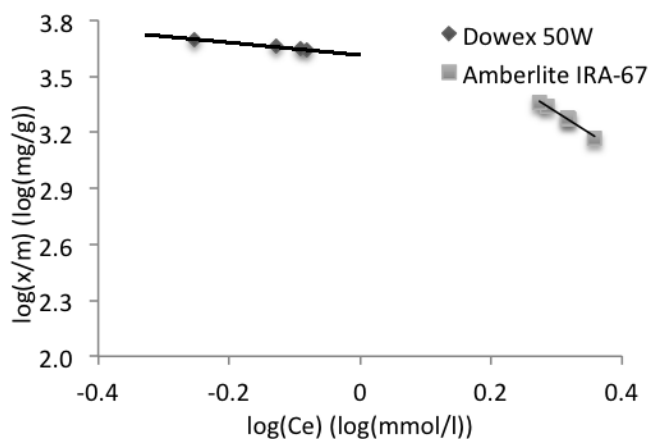

Figure 3.17 Freundlich adsorption isotherm for mercury
on Dowex 50W and Amberlite IRA-67

Chapter 4 General Conclusions and Future Work

4.1 Conclusions

4.1.1 Neutron activation analysis

In this work, neutron activation analysis was used to determine the concentrations of heavy metals in solutions. Under the following condition, 300 s irradiation and 120 s cooling, the samples of copper can be accurately measured by the counter. The best operation to detect mercury samples is irradiating for 4 hours and cooling for 24 hours.

The graph of adsorption curves provides some interesting data. The error bars in the adsorption curve of Amberlite IRA-67 for copper is larger than the curve of Dowex 50W, because of the different operations. In conclusion, the optimal condition for detecting copper is 300 s irradiation time. Furthermore, the adsorption curves of mercury have the same large error bar due to the same operation of determination.

4.1.2 Properties of resins

Two exchange resins—Dowex 50W, a strong acid cation exchanger with sulfonic acid functional group, and Amberlite IRA-67, a weak basic anion exchanger with amino group— were compared for removing heavy metals from water. The results are listed in the below tables 4 and 5.

The reaction rate constant k', the parameter before the time in the following tables, can determine the adsorption rate. From the results, the rate constants k' of two different resins in mercury experiments are approximately near each other and the adsorption rates (the slope of adsorption curve) seem like each other. However, in the copper experiment, the rate constant for Dowex 50W is extremely high (0.23), 10 times higher than the rate

constants obtained from the mercury experiment, so that it is obvious from the curve, Dowex 50W can adsorb copper ions in an efficient way.

Table 4 Two different resins adsorption on copper

	Dowex 50W	Amberlite IRA-67
Adsorption Percentage	97.6%±0.2%	81.2%±2%
Contact Time	70min	180min
Equilibrium State	reach 0mmol/l	reach 0-0.75mmol/l
Trend line of adsorption curve Concentration(mol/l) =	$0.0021\exp(-0.224t)$	$0.0018\exp(-0.0048t)$
Adsorption Kinetics $-\ln(1-U_t) =$	$0.23t + 0.9252$	$0.0036t + 0.08$
Freundlich Adsorption Isotherms $\log\left(\frac{x}{m}\right) =$	$-0.1335\log C_e + 2.9949$	$-2.2813\log C_e + 2.7826$
Adsorption Capacity	0.988	0.606

Table 5 Two different resins adsorption on mercury

	Dowex 50W	Amberlite IRA-67
Adsorption Percentage	81.5%±9%	37.7%±9%
Contact Time	120min	90min
Equilibrium State	reach 0.5mmol/l	reach 1.8mmol/l
Trend line of adsorption curve Concentration(mol/l) =	$0.003\exp(-0.0343t)$	$0.003\exp(-0.303t)$
Adsorption Kinetics $-\ln(1-U_t) =$	$0.0241t + 0.829$	$0.0205t + 1.1348$
Freundlich Adsorption Isotherms $\log\left(\frac{x}{m}\right) =$	$-0.2916\log C_e + 3.6199$	$-2.2286\log C_e + 3.976$
Adsorption Capacity	4.167	9.462

The adsorption capacities of copper are above 10 times less than the adsorption capacities of mercury on mass base unit. However, by transferring the mass base unit into mole base unit, dividing by the atomic mass (atomic mass of mercury is 200.6 g/mol and

atomic mass of copper is 64 g/mol), the opposite results will be obtained. Therefore, this paper recommends that Dowex 50W is used for the removal of heavy metals.

4.2 Future Work

4.2.1 Heavy metals and resins studies

In this work, two heavy metals were studied. However, other metals, e.g. nickel, zinc, cadmium and arsenic, reported in the paper from Guo and Yan[3], can be followed by using the same steps in future studies. The determination methods do not only include neutron activation analysis, but also other alternative methods, such as ICP-MS and flame atomic absorption spectroscopy. For example, zinc cannot be detected by neutron activation analysis because of low activity by irradiating it for 24 hours after calculation.

Two resins, which are studied in this work, show they can achieve the initial goal that, even though the final concentrations cannot reach the standard of drinking water levels, it can reach other standards. In the future, the researcher can find two other resins that can reach the goals. In that way, it is convenient for researchers to do the next steps.

Table 6 Alternative Resins Recommended

Name	Manufacturer	Matrix	Functional Group	Prefer
Dowex 50W[1]	Fluka Co.	Gel(microporous)-styrene divinylbenzene	Sulfonic acid	in lab
Amberlite IRA- 67[21]	ROHM & HAAS	Poly-acrylamide	Tertiary amine	in lab
Duolite A7[5,21]	ROHM & HAAS	Phenol-formaldehyde Copolymer	Secondary amine	
Purolite A832[5,21]	Purolite International	Polystyrene	Secondary amine	
Duolite A365[21]	ROHM & HAAS	Polystyrene	Secondary amine	
Purolite A830[21]	Purolite International	Polystyrene	Secondary amine	
Purolite A845[21]	Purolite International	Poly-acrylamide	Tertiary amine	
Fuji Pei CS[21]	Fuji Comp.	Chitosan	Secondary amine	

4.2.2 Multistage process

Using two or more resins in a series can enhance the efficiency of the resins to remove heavy metals, compared with the single-stage process.[10]
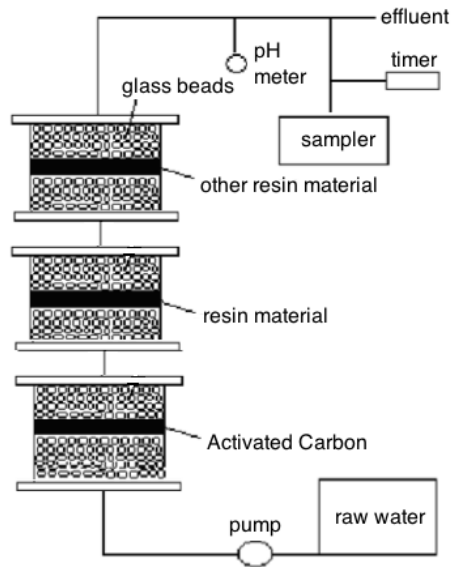

Figure 4.1 Example of multiple stage process[5]

If the studies mentioned above were finished, the multistage process can be carried out.

References:

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