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CARBON NANOTUBE-REINFORCED HOLLOW FIBER MEMBRANE FOR EXTRACTION OF
METAL OXYANION

Miss Khanitta Janput



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

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ชินชฐา จันทร์พุ่ม : เมมเบรนเส้นใยกลวงเสริมแรงด้วยท่อานาโนคาร์บอนสำหรับการสกัดออกซีแอนไอออนโลหะ (CARBON NANOTUBE-REINFORCED HOLLOW FIBER MEMBRANE FOR EXTRACTION OF METAL OXYANION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ปกรณ วรานุศุกกุล, 49 หน้า.

เทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวง (hollow fiber liquid phase microextraction) เป็นเทคนิคที่สามารถช่วยเพิ่มความเข้มข้นให้กับสารที่สนใจได้อย่างดีเยี่ยม แต่กระนั้นประสิทธิภาพของการสกัดกลับมีข้อจำกัดบางอย่าง ดังนั้นเพื่อเพิ่มประสิทธิภาพของการสกัดวิธีหนึ่งคือการประยุกต์นำสนามไฟฟ้าเข้าสู่ระบบของการสกัด เรียกเทคนิคนี้ว่า การสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้า (electro-enhanced hollow fiber liquid phase microextraction) เพื่อกระตุ้นการเคลื่อนที่ของสารที่สนใจที่อยู่ในรูปของไอออนด้วยไฟฟ้า ส่วนอีกวิธีหนึ่งคือการใส่ท่อานาโนคาร์บอนเข้าไปในรูพรุนของเมมเบรนเส้นใยกลวงเพื่อเพิ่มอันตรกิริยาระหว่างสารที่สนใจกับท่อานาโนคาร์บอน ซึ่งจะช่วยให้เพิ่มการเคลื่อนที่ของสารที่สนใจได้อีกทางหนึ่ง ในการศึกษาครั้งนี้ ท่อานาโนคาร์บอนได้ถูกนำมาประยุกต์ใช้กับเทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้าสำหรับใช้สกัดโครเมตไอออน จากนั้นศึกษาถึงผลของท่อานาโนคาร์บอนที่มีต่อการเคลื่อนที่ผ่านเมมเบรนของโครเมตไอออน โดยศึกษา 2 ระบบ ได้แก่ เทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้าที่เสริมและไม่เสริมแรงด้วยท่อานาโนคาร์บอนควบคู่กัน จากการศึกษาพบว่าเทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้าที่เสริมแรงด้วยท่อานาโนคาร์บอนแสดงประสิทธิภาพของการสกัดที่สูงกว่าประสิทธิภาพของการสกัดของเทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้าธรรมดา ต่อมาปัจจัยหลักต่างๆที่มีผลต่อระบบการสกัดได้ถูกศึกษาเพื่อที่จะหาสภาวะที่เหมาะสมที่สุดของเทคนิค สภาวะที่เหมาะสมที่ได้ ได้แก่ ความเข้มข้นของท่อานาโนคาร์บอนที่กระจายตัวในตัวทำละลายอินทรีย์ก่อนจะนำไปใช้เสริมในรูพรุนของเมมเบรนเส้นใยกลวงเป็น 3 mg/mL, ศักย์ไฟฟ้าที่ใช้เท่ากับ 50 โวลต์ และเวลาที่ใช้ในการสกัดเป็น 10 นาที ภายใต้สภาวะที่เหมาะสมที่สุดสำหรับการสกัด เทคนิคการสกัดระดับจุลภาคด้วยวัฏภาคของเหลวพองด้วยเมมเบรนเส้นใยกลวงกระตุ้นด้วยไฟฟ้าที่เสริมแรงด้วยท่อานาโนคาร์บอนได้แสดงค่าความเข้มข้นต่ำสุดที่สามารถวิเคราะห์ได้เท่ากับ 1.3 µg/L, ความเป็นเส้นตรง 0.9965, enrichment factor 133-134 และเปอร์เซ็นต์การคืนกลับเท่ากับ 112-113%

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KHANITTA JANPUT: CARBON NANOTUBE-REINFORCED HOLLOW FIBER MEMBRANE FOR EXTRACTION OF METAL OXYANION. ADVISOR: ASST. PROF. PAKORN VARANUSUPAKUL, Ph.D., 49 pp.

Hollow fiber liquid phase microextraction (HF-LPME) is an excellent preconcentration technique, which provides high enrichment factor. Nevertheless, the extraction efficiency is limited. To improve the extraction efficiency, one is an application of electrical field so called electro-enhanced HF-LPME to enhance the transportation of ionic analyte; the other one is a reinforcement of nanoparticles to the hollow fiber membrane to provide interaction between nanoparticles and analytes. In this study, carbon nanotubes (CNTs) were combined with electro-enhanced HF-LPME for extraction of chromate ion. The effects of CNTs on the transportation of chromate ion across membrane were studied. The comparative study between CNTs-reinforced and conventional electro-enhanced HF-LPME was explored. CNTs-reinforced with electro-enhanced HF-LPME showed improved extraction efficiency compared to the conventional electro-enhanced HF-LPME. In order to obtain high extraction efficiency of CNTs-reinforced with electro-enhanced HF-LPME method, main parameters were optimized. Optimal extractions were accomplished with 3 mg/mL of CNTs/octanol as the organic solvent membrane. Applied voltage was 50 V, extraction time of 10 min. Under the optimized conditions, carbon nanotubes-reinforced with electro-enhanced HF-LPME method presented low limit of detection (1.3 $\mu\text{g/L}$), good linear of regression (0.9965) and high enrichment factor 133-134. The recoveries were in acceptable value of 112 and 113% for 20 and 50 ppb Cr(VI), respectively.

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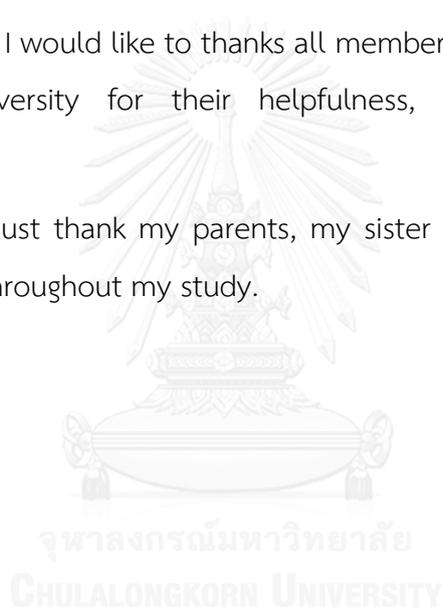
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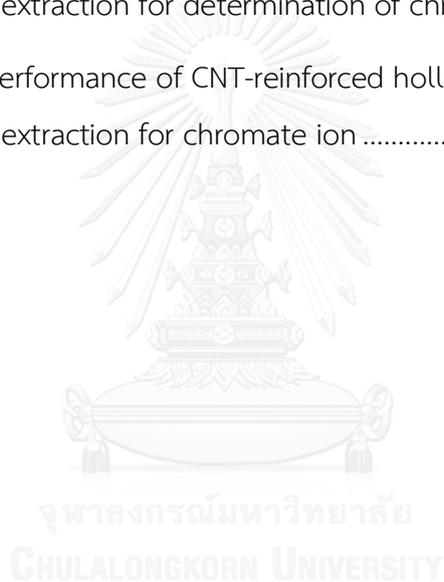
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LIST OF ABBREVIATION AND SYMBOLS

HF-LPME	Hollow fiber liquid phase microextraction
CNTs	Carbon nanotubes
O-CNTs	Oxidized carbon nanotubes
SPE	Solid phase extraction
SPME	Solid phase microextraction
SD-LPME	Single-drop liquid phase microextraction
DPC	1,5-diphenylcarbazide
mL	Milliliter
μ L	Microliter
OCT	Octanol
NPOE	Nitrophenyl octyl ether
HEPT	Heptanol

CHAPTER I

INTRODUCTION

1.1 Problem definition

Liquid phase microextraction (LPME) is an extraction technique that uses very small volume of extracting phase. Typically, LPME is a non-exhaustive extraction technique; i.e. analytes are partially extracted. LPME offers such a high enrichment factor; i.e. the ratio of the analytes concentration after extraction to its initial concentration. LPME techniques are available in several formats. Hollow fiber membrane liquid phase microextraction introduced by Pedersen-Bjergaard and Rasmussen in 1999. That has been widely used today.

In conventional HF-LPME, the analytes are extracted by being transferred from the donor solution across the organic solvent impregnated in the pores of the membrane into the acceptor phase/solution inside the lumen of the membrane. The analytes that are organic compounds or non-dissociated compounds transfers across the organic solvent membrane via partitioning process, which depends on the distribution constant of the analytes between the organic solvent membrane and the donor phase [1]. In addition, the analytes that are ionizable compounds can transfer across the organic solvent membrane with the assistance of an ionic carrier via ion exchanged process or coupled transport process. Therefore, the extraction efficiency of HF-LPME mainly depends on the diffusion rate or transportation rate of the analytes, which can be driven by the concentration gradient. For these reasons, the extraction efficiency of HF-LPME technique is limited; besides, it takes relatively long extraction time.

To improve the extraction efficiency of HF-LPME in the short extraction time, one method is an application of electrical field to the HF-LPME system so called electromembrane extraction (EME) or electro-enhanced HF-LPME [2, 3]. The electrodes are placed in the donor solution and the acceptor solution (inside the lumen of the membrane). When the electric field is applied, the analytes, especially

charged analytes will be driven across the organic solvent membrane towards the opposite charged electrode into the acceptor phase. For example, if analytes to be extracted are anion analytes, the negative and positive electrodes are placed in the donor and acceptor phase, respectively. The extraction efficiency can be improved due to the addition of electromigration mechanism. Recently, another method that can improve the HF-LPME performance is the reinforcement of nanoparticle sorbents into the pores of hollow fiber membrane in order to provide an additional sorption mechanism into the system.

Carbon nanotubes (CNTs) are types of nanomaterials popularly used as sorbents to improve the extraction efficiency because they are excellent thermally, electrically and structurally materials. CNTs have high surface area and they can interact with analytes by various mechanisms such as pi-pi interaction, hydrogen bonding and electrostatic attraction. CNTs have been mostly applied as a solid adsorbent in solid phase extraction (SPE) and solid phase microextraction (SPME) techniques for organic and inorganic analytes. Some works are summarized in Table 1.1. It indicates that CNTs are excellent solid adsorbent. CNTs can provide low limit of detection (LOD) and high %recovery. Recently, CNTs have been reinforced into the hollow fiber membrane pores in HF-LPME and electro-enhanced HF-LPME techniques in order to add adsorption mechanism and increase the transportation of analytes. Some works are summarized in Table 1.2

Table 1.1 Application of CNTs as solid adsorbents in SPE and SPME techniques

Analytes	PAHs	p-hydroxy benzoates	Estrogens	Pb ²⁺	Se ⁴⁺	Cr ⁶⁺
Matrix	Edible oils	Beverage	Milk	Waste water, Khoshk river water, rice, black tea, green tea, onion, potato	Tab water, lake water	Aqueous solution
CNTs	MWCNTs	MWCNTs	MWCNTs	MWCNTs	MWCNTs	MWCNTs, O-MWCNTs
Method	GC-MS	HPLC-DAD	HPLC-FLD	FAAS	HG-AFS	ASV
LOD	0.10-0.88 ng/g	0.01-0.02 ng/mL	1.21-2.35 µg/L	0.5 ng/mL	0.013 µg/L	-
%recovery	87.8-122.3	-	93-107.2	97-104.5	96.3-102.3	98
Ref.	[4]	[5]	[6]	[7]	[8]	[9]

Table 1.2 CNTs-reinforced hollow fiber membrane extraction methods

Analytes	caffeic acid	Ibuprofen, naproxen	Buprenorphine	Plant hormones
Matrix	Echinacea purpure herb	Spiked plasma, urine, breast milk, wastewater	urine	tomato
CNTs	MWCNTs	O-MWCNTs	O-MWCNTs	O-MWCNTs
Technique	HF-SLPME	EME	EME	EME
Method	HPLC-UV/Vis	CE	CE	HPLC/PDA
LOD	0.05 ng/L	1-3 ng/mL	1 ng/mL	1.5-2.0 ng/g
EF	1208	180-188	185	85-126
Ref.	[10]	[11]	[12]	[13]

All researches in Table 1.2 are CNTs-reinforced hollow fiber membrane extraction methods for organic analytes. They have successfully improved the enrichment factor (EF), which is higher than that without CNTs extraction system. Moreover, a higher EF can be obtained with a shorter extraction time. Most researchers have claimed that CNTs provide pi electron so that they can interact the organic analytes with pi-pi interaction. This mechanism can enhance the transportation of organic analytes crossing the membrane. Since CNTs can interact with analytes both organic and inorganic analytes by various mechanisms. They can interact with metal ions in SPE and SPME techniques with the electrostatic attraction. In addition, hollow fiber membrane extraction method for metal ions was being of interest and developed continuously to improve extraction efficiency. Therefore, in this work, we used CNTs to apply with the electro-enhanced HF-LPME methods for extraction and preconcentration of metal ion. Effects of CNTs (in membrane) on transportation of metal ion were studied. We hope that CNTs can increase the transportation of metal ion with their excellent mechanism.

1.2 Aim and scope of the research

The CNTs-reinforced and conventional electro-enhanced HF-LPME for metal ion has been comparative studied. Chromium (VI) in form of chromate ion was chosen as a model. The parameters that can affect in the transportation of chromate ion in the extraction performances including types of organic liquid membrane, types and concentration of CNTs, applied voltage and extraction time were studied.

CHAPTER II

THEORY

2.1 Development of liquid phase microextraction

The sample pretreatment is an important step in analytical method. In some analytical techniques, the real samples cannot be directly analyzed because of the matrix interferences. In this sample pretreatment step, the analyte will be isolated from matrices before analysis by an analytical instrument. The common sample pretreatment is liquid-liquid extraction (LLE) technique. This technique has some disadvantages such as its tediousness, cost and using large volume of toxic organic solvent. To overcome those problems, liquid-liquid phase microextraction (LPME) technique has been developed. In LPME technique, the organic solvent is minimized to use in microliter level so that LPME technique is not only isolate analyte from impurities but preconcentrate analyte in such microliter level. Nevertheless, LPME technique has some problems. For example, the single-drop microextraction (SDME), one format of LPME, has some problems that it is the unstable of organic solvent droplet which is hanged at syringe needle as showed in Fig.2.1. Under the extreme stirring condition, the droplet may loss during the extraction process. To solve this unstable of organic solvent droplet problem, recently, Pedersen-Bjergaard and Rasmussen have introduced hollow fiber liquid phase microextraction technique, where small volumes of organic solvent are supported by the porous hollow fiber membrane for extraction and preconcentration of some analytes.

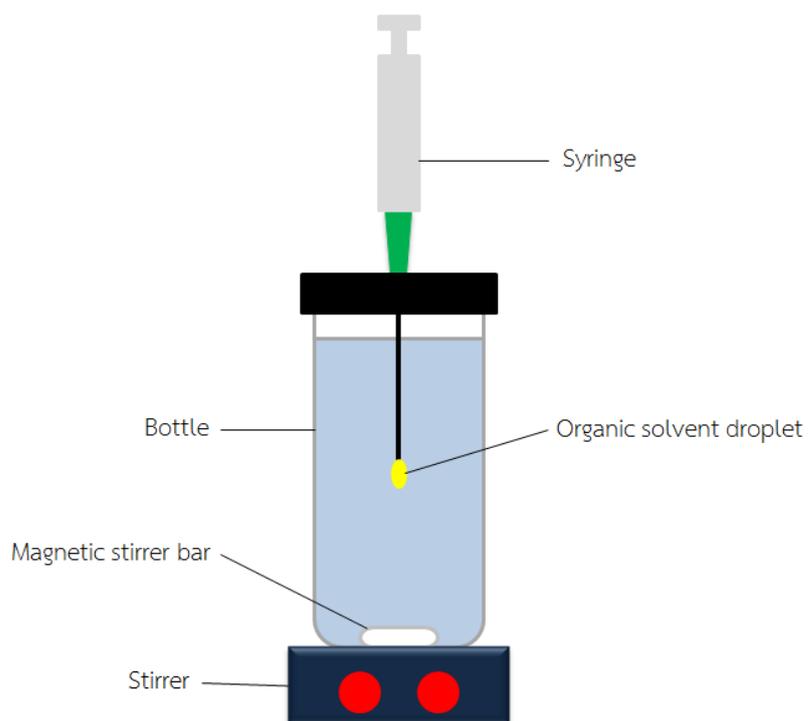


Figure 2.1 Hanging organic solvent droplet in SDME setup

2.2 Hollow fiber liquid phase microextraction

Hollow fiber liquid phase microextraction (HF-LPME) is a technique which has been developed to solve the instability of organic solvent droplets in SDME. Organic solvent is sustained in porous polypropylene hollow fiber. The HF-LPME setup is shown in Fig. 2.2. Aqueous sample solution is contained in a glass bottle. A porous hollow fiber membrane is immersed into the sample solution directly. In the membrane preparation, a hollow fiber membrane is soaked in an organic solvent. The pores are filled with the organic solvent. Then the excess of organic solvent is removed with air blow. The thin solvent membrane within the wall of hollow fiber is obtained. An acceptor solution is filled in the lumen of the hollow fiber membrane. The acceptor solution may be an organic solvent in case of two-phase HF-LPME system or an aqueous solution in three-phase HF-LPME system.

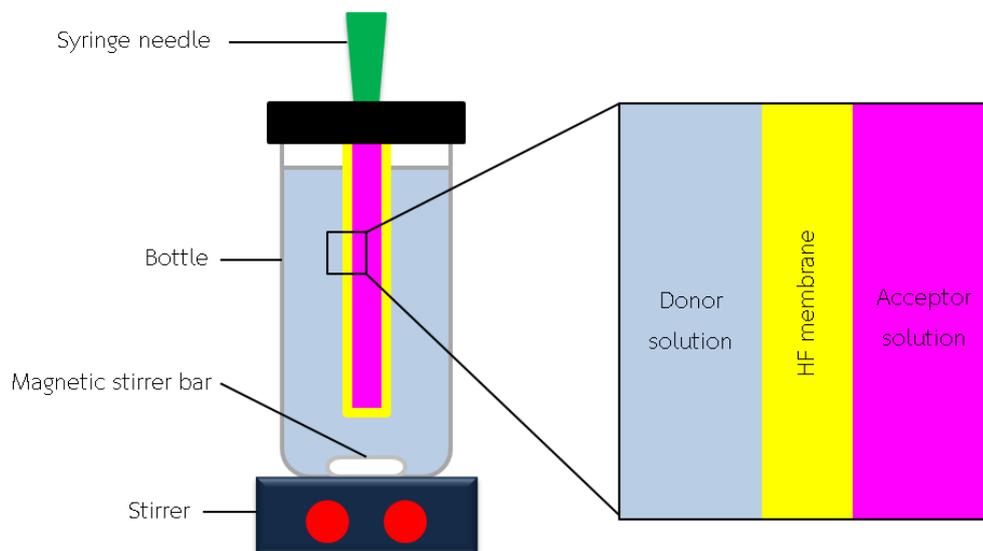


Figure 2.2 HF-LPME setup

For two-phase HF-LPME system, the organic solvent in the porous wall of hollow fiber and the acceptor solution are the same. The extraction efficiency depends mainly on the distribution constant of the analyte between the organic solvent membrane and the donor phase. The analyte diffuses from the sample solution to the organic solvent membrane and to the acceptor solution by concentration gradient. This two-phase system is favorably applied for organic compounds. When the extraction is completed, the acceptor solution is collected and analyzed.

For three-phase HF-LPME, the acceptor solution is an aqueous solution. It is favorably applied for ionizable compounds. The analytes diffuse from the sample solution to the organic solvent membrane and to the acceptor solution by concentration gradient. The analytes will ionize into an ionic form [14]. That cause analytes cannot be back extracted to organic solvent membrane again. When the extraction is completed, the aqueous acceptor solution is collected and analyzed.

In both HF-LPME systems, the transportation of analyte from the sample to the acceptor solution is diffusion mechanism. The extraction efficiency depends on

distribution coefficient. HF-LPME is typically applied for organic compounds. However, application of HF-LPME for inorganic metal ion analytes requires additional driving forces for transportation of the analytes. Several formats of HF-LPME have been introduced as follows.

2.3 Formats of HF-LPME and their mechanisms for transportation of ionic analytes through the organic solvent membrane

2.3.1 Carrier-mediated HF-LPME

Carrier is a substance added into the membrane to assist the transportation of ionic analytes across the membrane. The carrier is usually a hydrophobic reagent having a property of ion exchanger either anionic or cationic exchanger for anionic or cationic metal analytes, respectively. Carrier-mediated HF-LPME can transport ionic analytes to the acceptor solution via a couple transport mechanism as shown in Fig. 2.3. The ionic analytes are moved from the bulk solution to the membrane interface by convection, transported into the membrane by ion-exchange mechanism and; they diffuse from donor/membrane interface to membrane/acceptor interface by the action of concentration gradient; they are released to acceptor phase by ion-exchange mechanism between them and counter ion in acceptor phase [15].

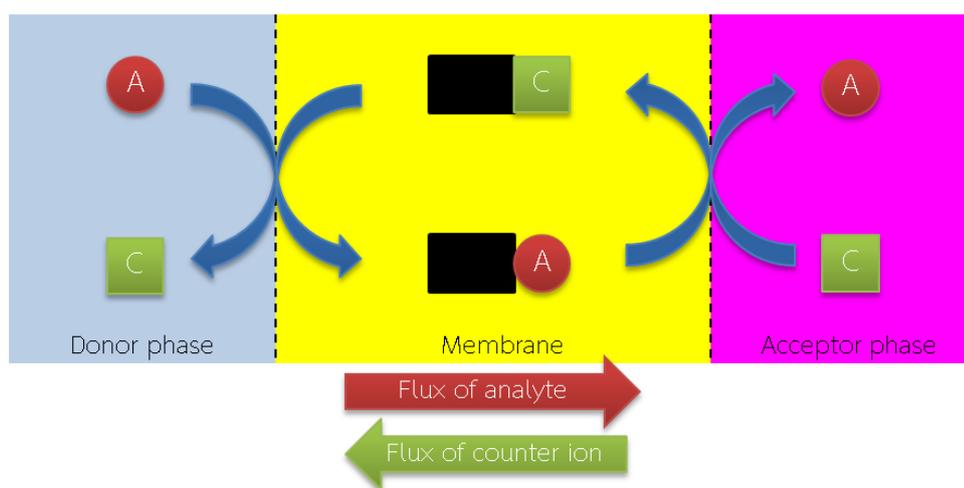


Figure 2.3 Transportation of ionic analyte through membrane in carrier-mediated HF-LPME format

Extraction efficiency of carrier-mediated HF-LPME format depends on diffusion rate of analyte. It is considered to be a passive mechanism. Therefore, extraction efficiency is limited. It usually takes long time for extraction. To improve the extraction efficiency, one method is an addition of electrical field to the HF-LPME system. This format is called “electromembrane extraction” or “electro-enhanced HF-LPME”

2.3.2 Electro-enhanced HF-LPME

Fig. 2.4 shows setup of electro-enhanced HF-LPME system. Two electrodes are placed in the donor and the acceptor solution (inside the lumen). Then an electric potential is applied. The electrokinetic migration mechanism is added to the system. The ionic analytes are transported from the donor towards the acceptor solution in the opposite charged direction through the membrane. The addition of electrokinetic migration mechanism can successfully improve the extraction efficiency in shorter extraction time [16].

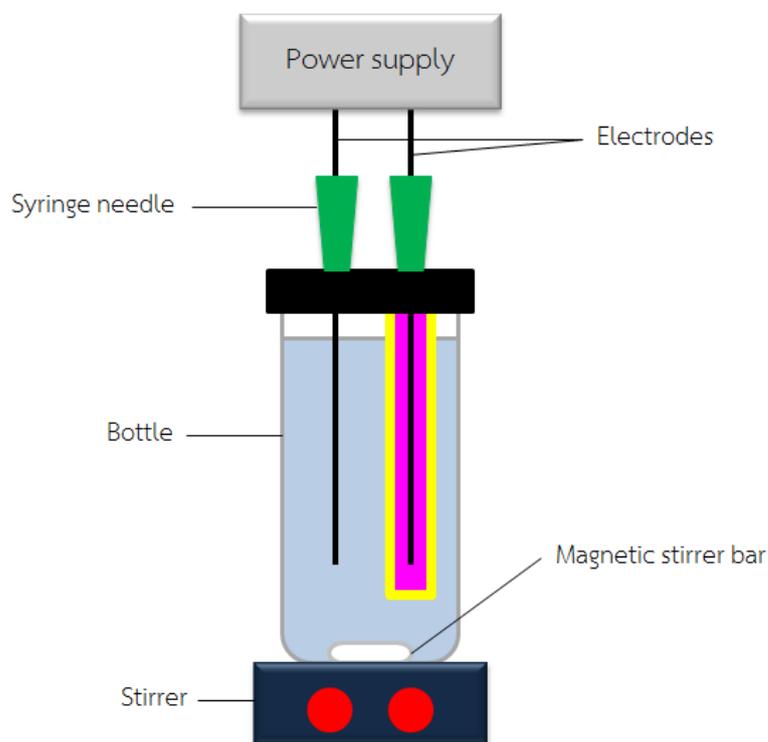


Figure 2.4 Electro-enhanced HF-LPME setup

2.3.3 Nanoparticle-reinforced with electro-enhanced HF-LPME

Recently, researchers have developed another technique to improve extraction efficiency of HF-LPME by reinforcement of nanoparticles into the pores of the membrane so called nanoparticles-reinforced with electro-enhanced HF-LPME. This technique introduced an additional adsorption mechanism to the electro-enhanced HF-LPME system. The interactions between the solid nanoparticle sorbents and the analytes can increase the transportation of the analyte through the membrane.

All HF-LPME formats, their transfer mechanisms and typical types of analytes are summarized in Table 2.1.

Table 2.1 Characteristics of various formats of HF-LPME

Formats of HF-LPME	Analyte	Mechanisms
Two-phase HF-LPME	Non-ionic organic compounds	Passive diffusion
Three-phase HF-LPME	Dissociated/ionizable compounds	Passive diffusion, pH gradient control
Carrier-mediated HF-LPME	Metal ion, ionic compounds	Passive diffusion, ion exchange
Electro-enhanced HF-LPME	Metal ion, ionic compounds	Electrokinetic migration
Nano-reinforced with electro-enhanced HF-LPME	Metal ion, ionic compounds	Electrokinetic migration, adsorption

2.4 Carbon nanotubes

Carbon nanotubes are nanomaterials consisting of graphene sheet rolled up into the tubular form [17]. Carbon nanotubes can be characterized into two types that are single-walled and multi-walled carbon nanotube as shown in Fig. 2.5.

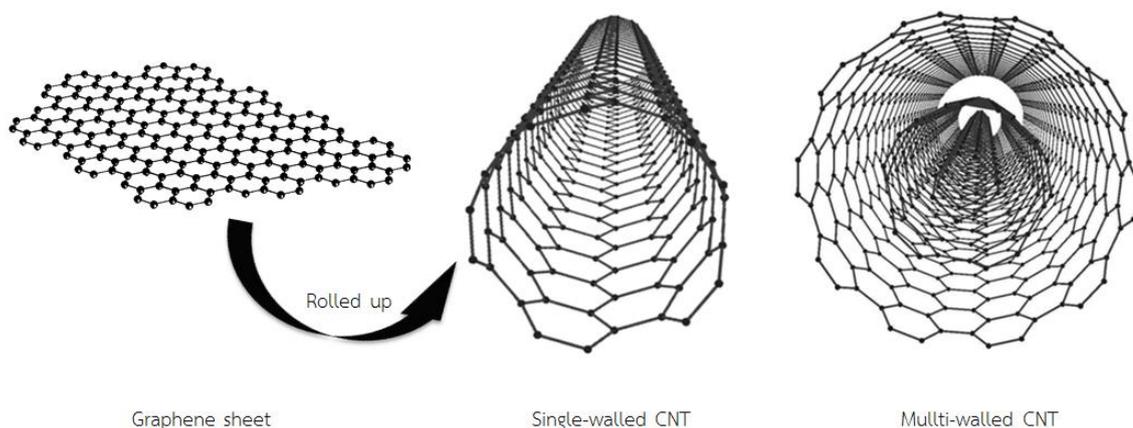


Figure 2.5 Structures of graphene and two types of carbon nanotubes

Carbon nanotubes are popular materials used as solid sorbents in extraction works because they offer excellent physical and chemical properties [18]. Carbon nanotubes usually contain high surface area and they can interact with various organic and inorganic analytes by various mechanisms such as pi-pi interaction and electrostatic attraction. Both pi-pi and electrostatic interactions of carbon nanotubes play important roles in improvement of extraction efficiency of nanoparticles-reinforced with electro-enhanced HF-LPME for organic and metal ion analytes, respectively. Two mechanisms are explained briefly as followed:

2.4.1 Mechanisms between carbon nanotubes and analytes

2.4.1.1 Pi-pi stacking between carbon nanotubes and organic analytes

Pi-pi stacking is interaction between substances containing pi electrons, and pi electrons of carbon nanotubes. This interaction can be applied in nanoparticles-reinforced HF-LPME technique for organic analytes in several researches. The transportation of analyte can be increased and the extraction efficiency can be improved successfully.

2.4.1.2 Electrostatic attraction between carbon nanotubes and metal ion analytes

The adsorption ability of carbon nanotubes with metal ions depends on the isoelectric point of the carbon nanotubes and the pH of solution [19, 20]. At $\text{pH} > \text{isoelectric point}$, the carbon nanotube surface is negatively charged. So this surface can interact with cationic metal by electrostatic attraction mechanism. In contrast, at $\text{pH} < \text{isoelectric point}$, the carbon nanotube surface is positively charged. So this positive charge surface can interact with anionic metal by electrostatic attraction mechanism and repel cationic metal. This controlled total charge ability has made carbon nanotubes excellent solid sorbents in solid-phase extraction for metal ions.

2.4 Chromium

2.4.1 Species of chromium

Most chromium existing in environment are trivalent [Cr(III)] and hexavalent [Cr(VI)] states. Trivalent chromium is not significant health risk. In contrast, hexavalent chromium is more toxic than trivalent chromium about 10-100 times with high mobility in soil and ground water [21]. The World Health Organization (WHO) has set the maximum contaminant level of hexavalent chromium in water at 50 $\mu\text{g/L}$ [22]. Chromium is usually released from the industrial processes such as dyes, paints, inks, plastics, surface coatings and alloy steels. Hexavalent chromium is found in the three forms including chromate anion (CrO_4^{2-}), dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) and hydro chromate anion (HCrO_4^-). All chemical structures are shown in Fig. 2.6. Chromium species depend on the pH of solutions [23]. According to the review [24], Fig. 2.7 shows that in an alkaline solution, chromate ion is the predominant species while in an acidic solution, dichromate and hydro chromate ion are the predominant species. In addition, the dichromate/hydro chromate ion ratio depends on the total concentration of Cr(VI), where HCrO_4^- is the predominant form when the total concentration of Cr(VI) is lower than $(1.26-1.74) \times 10^{-2}$ mol/L, $\text{Cr}_2\text{O}_7^{2-}$ changes to HCrO_4^- forms while $\text{Cr}_2\text{O}_7^{2-}$ is the predominant form at higher concentration of Cr(VI).

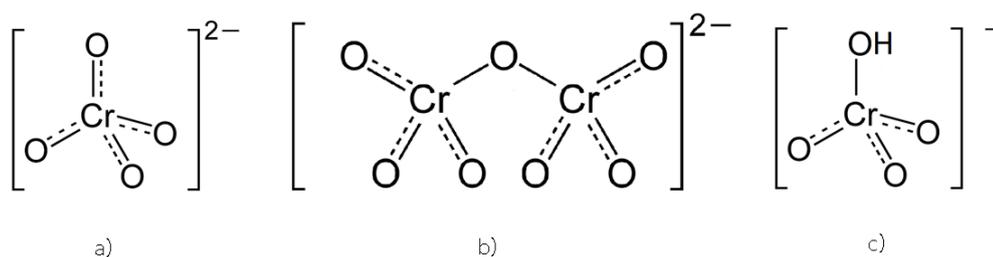


Figure 2.6 Chemical structures of hexavalent chromium species: a) chromate anion (CrO_4^{2-}), b) dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) and c) hydro chromate anion (HCrO_4^-)

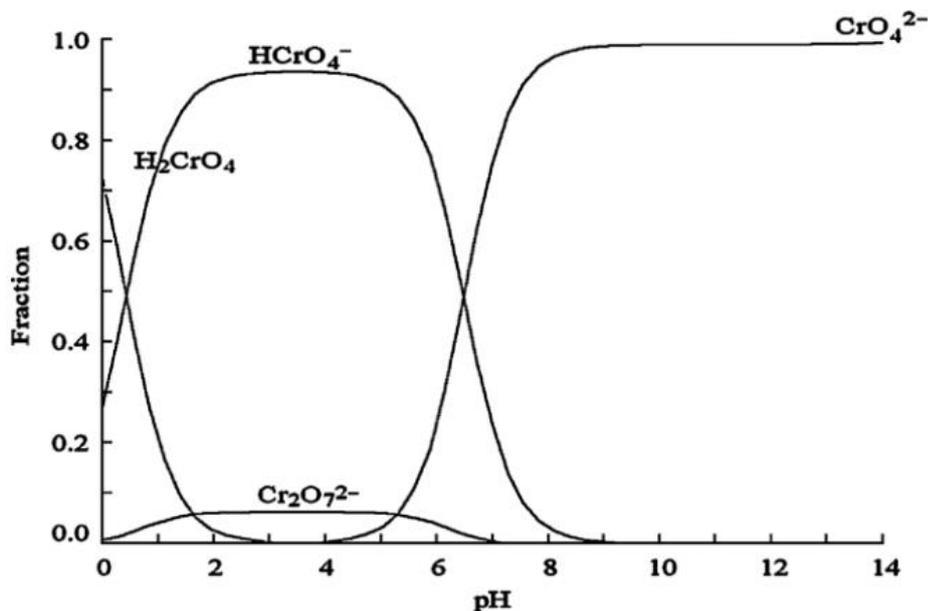


Figure 2.7 Speciation diagram of hexavalent chromium versus pH [24]

2.4.2 Colorimetric method for determination of chromium (VI)

In this study, the colorimetric method of Cr-DPC complex is used for determination of chromate ion. A 1,5-diphenylcarbazine or DPC is used as a colorimetric reagent. The chromate ion is reacted with DPC in acidic solution. Firstly, the chromate ion is reduced to Cr(III) by 1,5-diphenylcarbazine as shown in Fig. 2.8. Then the Cr(III) will react with 1,5-diphenylcarbazine (oxidized form of 1,5-diphenylcarbazine) forming Cr(III)-1,5-diphenylcarbazine (Cr-DPC) complex as shown in Fig 2.9. This complex is red-violet color that can absorb the visible light at 540 nm.

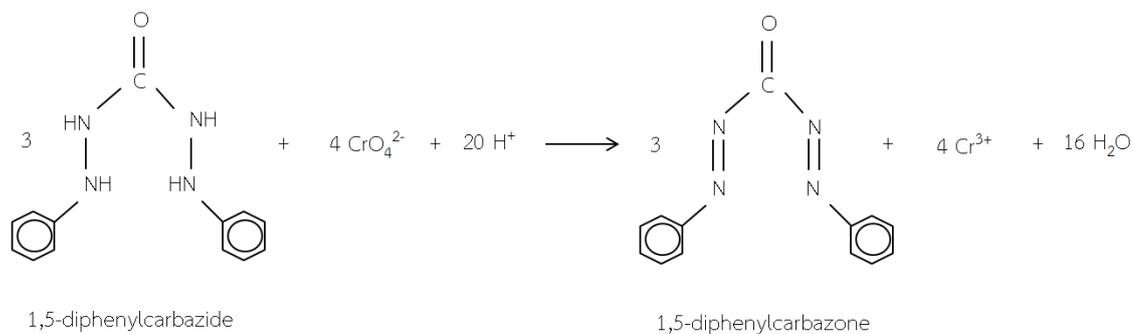


Figure 2.8 Reaction between chromate and DPC

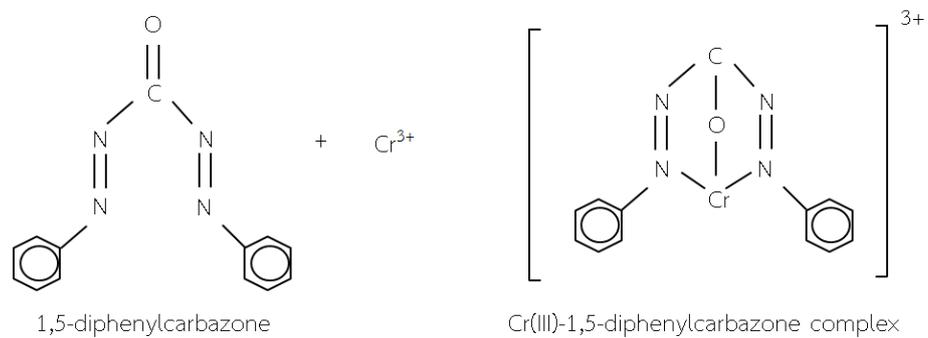


Figure 2.9 Reaction between trivalent chromium and 1,5-diphenylcarbazone



CHAPTER III

EXPERIMENTAL

3.1 Instrumentals and materials

1. DC power supply 375 W, 0-60 V, 0-3 A (GPC-6030): Electronics Source Co., Ltd. (Bangkok, Thailand)
2. Conductivity meter (CM-115): Kyoto Electronics (Kyoto, Japan)
3. Fiber optic UV-Vis spectrometer (USB4000) with Z-flow cell: Ocean Optics (Dunedin, FL, USA)
4. Milli-Q ultra-pure water system: model Millipore ZMQS5V00 (Massachusetts, USA)
5. Multi-station magnetic stirrer: model RCT basic IKAMAG®, IKA® Werke GmbH & Co. KG (Staufen, Germany)
6. Multimeter (UNI-T UT55): Transfer Multisort Elektronik Sp. z o. o. (Lodz, Poland)
7. Magnetic stirring bars: Spinbar (Wayne, NJ, USA)
8. Ultrasonicate: model crest575d, Crest Ultrasonic Corporation (New York, USA)
9. pH meter: METTLER TOLEDO (Greifensee, Switzerland)
10. Micro-porous polypropylene hollow fiber membrane Accurel® PP Q3/2, 600 μm i.d., 200 μm thickness, and 0.2 μm pore size: Membrana (Wuppertal, Germany)
11. Platinum wire, 0.20 mm diam., $\geq 99.99\%$ metals basis: Sigma-Aldrich (St. Louis, MO, USA)
12. Microsyringe, 50 μL : Hamilton Company (Nevada, USA)

13. Medical syringes, 3 mL: Becton Dickinson Medical (S) (Tuas, Singapore)
14. Medical syringe needles, 500 μm O.D.: Becton Dickinson Medical (S) (Tuas, Singapore)
15. EPA vial Kit, 30 mL: vertical chromatography (Bangkok, Thailand)
16. Insert glass vial, 300 μL : vertical chromatography (Bangkok, Thailand)
17. Micropipettes, 10-100 μL , 100-1000 μL and 1-10 mL: Eppendorf (Hamburg, Germany)

3.2 Chemicals and reagents

1. Potassium dichromate: BDH Chemicals (Poole, England)
2. Multi-walled carbon nanotubes: Nanogeneration (Thailand)
3. Sodium chloride (99.5%): Carlo erba (Rodano, Italy)
4. Sodium hydroxide ($\geq 99\%$): Merck (Darmstadt, Germany)
5. 1,5-diphenylcarbazide: Sigma-Aldrich (St. Louis, MO, USA)
6. 1-heptanol (99%): Sigma-Aldrich (St. Louis, MO, USA)
7. 1-octanol (99%): Sigma-Aldrich (St. Louis, MO, USA)
8. 2-Nitrophenyl octyl ether: Sigma-Aldrich (St. Louis, MO, USA)
9. Ethanol: Merck (Darmstadt, Germany)
10. Sulfuric acid 100%: J.T. Baker (Deventer, Netherlands)
11. Nitric acid 65%: Merck (Darmstadt, Germany)

3.3 Preparation of chemical solutions

3.3.1 Stock potassium dichromate ($K_2Cr_2O_7$) solution

A 1000 mg/L standard solution of Cr(VI) was prepared by dissolving 0.0707 g of $K_2Cr_2O_7$ in 25 mL volumetric flask with milli-Q water. The stock solution was stored in polypropylene vial at 4 °C until use.

3.3.2 Sodium chloride (NaCl) solution; 0.5 M

A 0.5 M solution of NaCl was prepared by dissolving 7.3125 g of NaCl in 250.00 mL volumetric flask with milli-Q water. The solution was stored in polypropylene vial in a refrigerator.

3.3.3 1,5-diphenylcarbazide (DPC) solution; 6.6 mM

A 6.6 mM solution of DPC was prepared by dissolving 0.0080 g of DPC in 5.00 mL volumetric flask with ethanol. The solution was stored in amber glass vial.

3.3.4 Sulfuric acid (H_2SO_4) solution; 100 mM

A 100 mM solution of H_2SO_4 was prepared by pipetting 250 μ L of a stock 4 M H_2SO_4 solution into 10.00 mL volumetric flask and diluting with milli-Q water.

3.4 Experimental

3.4.1 Preparation of CNT-HF membrane

The polypropylene hollow fiber membrane was cut into 5 cm segments. The membrane was soaked in the dispersed CNTs/OCT and sonicated for 1 h. The CNTs/OCT should be completely filled in the pores of the membrane. Fig. 3.1 shows the SEM images of cross section of the hollow fiber membrane with and without CNTs filled in the pores.

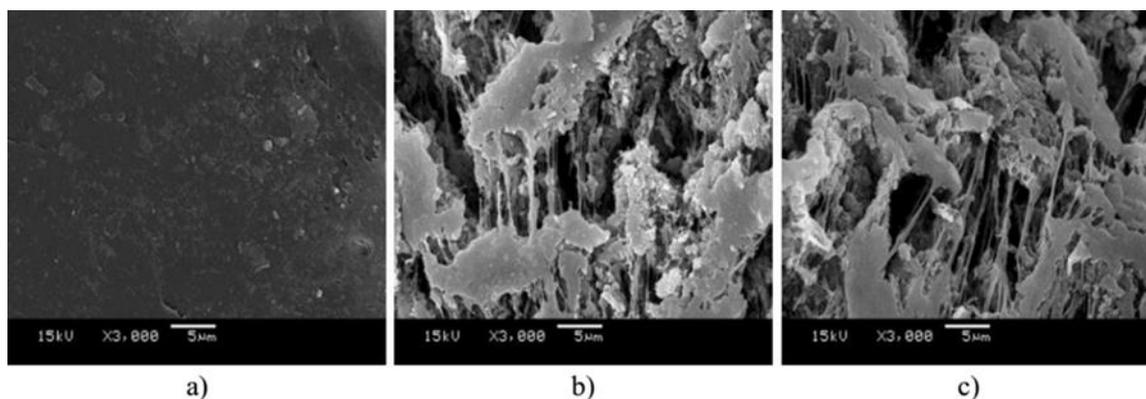


Figure 3.1 SEM images of HF membrane pores; a) without CNTs, b) with CNTs and c) with Oxidized-carbon nanotubes (O-CNTs)

3.4.2 Oxidation of CNTs

To study the effect of functionalized surface of CNTs such as carboxyl (-COOH), carbonyl (-CO) and hydroxyl (-OH) groups, the CNTs were oxidized. The CNTs were ultrasonicated in concentrated HNO_3 for 24 h at 40-50 °C. Then, the mixture was washed to pH 6-7, filtered using a 0.22 μm filter and kept at 80 °C for 12 h. Finally, the obtained oxidized-CNTs (O-CNTs) were dispersed in OCT by sonication for 15 min.

3.4.3 CNTs-reinforced with electro-enhanced hollow fiber membrane extraction of chromate anion

The CNTs/OCT loaded hollow fiber membrane was setup for CNTs-reinforced with electro-enhanced hollow fiber membrane extraction as illustrated in Fig. 3.2. A 12 μL of acceptor solution (0.5 M NaCl) was introduced into the lumen of the hollow fiber membrane using a microsyringe and the end of the membrane was thermally sealed. Then, the membrane containing CNTs/OCT and the acceptor solution was placed in 28 mL donor solution (standard Cr(VI) solutions or samples). Two platinum electrodes were connected to a DC power supply. The negatively charge electrode was placed in the donor and the opposite charge electrode was

placed in the acceptor solutions (in the lumen of the membrane). After extraction, a 10 μL of acceptor solution was collected and transferred into an insert glass vial with a microsyringe for analysis.

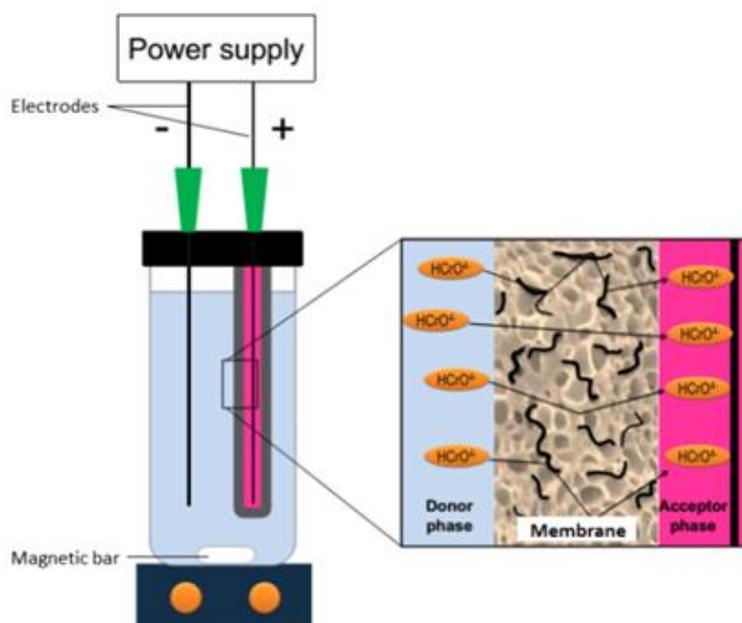


Figure 3.2 Schematic illustration of the CNTs-reinforced with electro-enhanced hollow fiber membrane extraction for chromate ion

3.4.4 Cr-DPC colorimetric method

When the extraction was complete, the acceptor solution was collected and transferred into an insert vial. The extract was mixed with 10 μL of 100 mM H_2SO_4 and 30 μL of 6.6 mM DPC and measured for the Cr-DPC complex by a fiber optic UV-Vis spectrometer at 540 nm.

3.4.5 Study of parameters affecting the transportation of chromate ion in CNTs-reinforced with electro-enhanced hollow fiber membrane extraction

3.4.5.1 Effect of CNTs on transportation of chromate ion in CNTs-reinforced membrane system

The effect of CNTs on transportation of chromate ion in CNTs-reinforced membrane system was studied compared to that in conventional pure organic solvent membrane system. The organic solvents for this study were 1-octanol, 1-heptanol and NPOE chosen according to the previous works on the electro-enhanced hollow fiber membrane extraction for metal ion [28,29]. Some properties of organic solvents such as the viscosity and dielectric constant might affect the extraction efficiency. Three organic solvents with different viscosity and dielectric constant are shown in Table 3.1 including 2-nitrophenyl octyl ether (NPOE), 1-octanol (OCT) and 1-heptanol (HEPT). They were selected as an organic solvent membrane for extracting chromate ion. Then the enrichment factors (EF) of each were studied.

Table 3.1 Properties of organic solvents using as organic solvent membrane

SLM	NPOE	OCT	HEPT
Viscosity (centipoise)	12.80 ^A	7.59 ^B	5.97 ^B
Dielectric constant	23.10 ^A	10.30 ^C	12.10 ^C

Reference A [25] B [26] C [27]

3.4.5.2 Effect of CNTs and O-CNTs on transportation of chromate ion

CNTs was oxidized in concentrated HNO₃ for attracts the polar groups such as -COOH, -OH and -CO. The polar groups may afford the additional interaction of chromate ion and it may cause the transportation of chromate ion increased from original CNTs. Therefore, CNTs and O-CNTs were comparative studies.

3.4.5.3 Different amounts of CNTs in HF-membrane

In order to provide an additional CNTs interaction into the system, the proper amounts of CNTs loaded hollow fiber membrane were studied. The hollow fiber membranes were soaked in various concentrations of CNTs of 0, 1, 3, 5, 7 and 9 mg/mL and used as the membrane in extraction system of chromate ion. Then the enrichment factors were calculated. The membrane that can provide the highest enrichment factor of the extraction system was used in subsequent experimental.

3.4.5.4 Applied electrical potential

According to Nernst-Planck equation, the flux of ionic analytes depends on the applied voltage. For the optimization, voltages of 0, 10, 30 and 50 V were used to apply the extraction system of chromate ion. The enrichment factors were calculated and plotted with the function of applied voltages.

3.4.5.5 Extraction time

The total amounts of analytes that transport from donor to acceptor phase are unequal if the extraction time is changed. So the extraction times in the ranges of 1-20 min are studied. For selection of the optimum extraction time, the enrichment factors of the extraction of chromate ion were plotted with the different time.

3.4.6 Method validation

3.4.6.1 Accuracy

The accuracy is the degree of the closeness of agreement between the measured value and the true value, which can be determined by the recovery study. The analytes spiked in blank sample was extracted using optimum condition and calculated for %recovery. In this work, %recovery was derived from eight replicates at two spiked concentration levels including: 20 and 50 $\mu\text{g/L}$, the %recovery was calculated with Equation 3.1. Observed value was determined from

the calibration curve. Blank value is the value obtained from the sample without Cr(VI). And True value is the spiked concentration of Cr(VI) in sample.

$$\% \text{recovery} = \frac{\text{Observed value} - \text{Blank value}}{\text{True value}} \times 100 \quad \text{Equation 3.1}$$

3.4.6.2 Precision

The precision is the closeness of results in replicated determination, which can be expressed as relative standard deviation (RSD). The precision of the method includes repeatability and reproducibility. In repeatability, it is the degree of closeness of results in replicated determination of the same laboratory, instrumental and researcher. In this work, intra-day precision was obtained from eight replicate analyses of spiked 50 µg/mL Cr(VI) in blank samples. Inter-day precision was obtained from total fifteen replicates (five replicates per day) of spiked 50 µg/mL Cr(VI) in blank samples. Then the RSD of the enrichment factors were reported.

3.4.6.3 Linearity

Linearity was determined by five concentration levels of spiked Cr(VI) in milli-Q water and extracted with CNT-reinforced hollow fiber electro-membrane extraction under optimized conditions. Each level of concentration was determined in three replicates. The calibration curve was obtained. The absorbance value and the spiked Cr(VI) concentration were plotted at Y- and X-axis, respectively. The linearity was determined by the coefficient of determination (R^2).

3.4.6.4 Limit of detection (LOD) and limit of quantitation (LOQ)

LOD is the lowest concentration of analytes that can be detected, while LOQ is the lowest concentration of analytes that can be detected with acceptable accuracy and precision. In this work, the concentration of Cr(VI) at 50 µg/L was used to study. Then LOD and LOQ were calculated with Equation 3.2 and 3.3, respectively.

$$\text{LOD} = 3 \text{ SD} \quad \text{Equation 3.2}$$

$$\text{LOQ} = 10 \text{ SD} \quad \text{Equation 3.3}$$

SD is the standard deviation of regression line. It is calculated with the Equation 3.4.

$$\text{SD} = \sqrt{\frac{\sum(y_i - Y_i)^2}{n-2}} \quad \text{Equation 3.4}$$

Where y_i is the signal of the analytes obtained from method, Y_i is the signal of the analytes obtained from linear regression equation and n is the level concentration number of linear regression line.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Optimization

4.1.1 Effect of CNTs on transportation of Chromate ion in CNTs-reinforced membrane system

The effect of CNTs on transportation of chromate ion in CNTs-reinforced membrane system was studied compared to that in conventional pure organic solvent membrane system. The organic solvents for this study were 1-octanol, 1-heptanol and NPOE chosen according to the previous works on electro-enhanced HF-LPME for metal ion [28, 29].

The results in Fig. 4.1 showed that the reinforcement of CNTs into both NPOE- and octanol-based system can improve the enrichment factor of extraction system. The improvement of extraction efficiency in CNTs-reinforced system may be resulted from the electrostatic attraction between chromate ion analytes and positive surfaces of CNTs, which will be described later in 4.1.2. Moreover, the electrical current pattern in Fig. 4.2 showed that the electrical current of system when using CNTs-reinforced as membrane was higher than using pure organic solvent (without CNTs). It was possible that the reinforcement of electrical conduct CNTs to both systems might reduce the amount of organic solvent by replacing. So the electrical resistance of organic solvent membrane was reduced and the analytes could pass through the organic solvent membrane more easily as well.

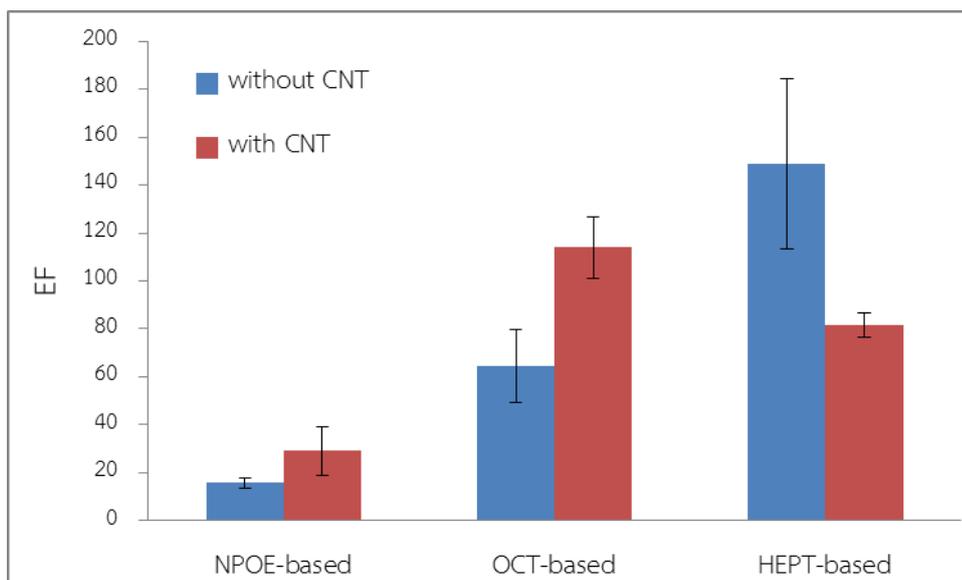


Figure 4.1 Comparison of extraction performance of chromate ion using organic solvent with CNTs and without CNTs. Donor solution adjusted to pH 7; Chromate ion: 50 $\mu\text{g/L}$; acceptor solution: 0.5 M NaCl; applied voltage: 50 V; extraction time: 7 min (n=3 each)

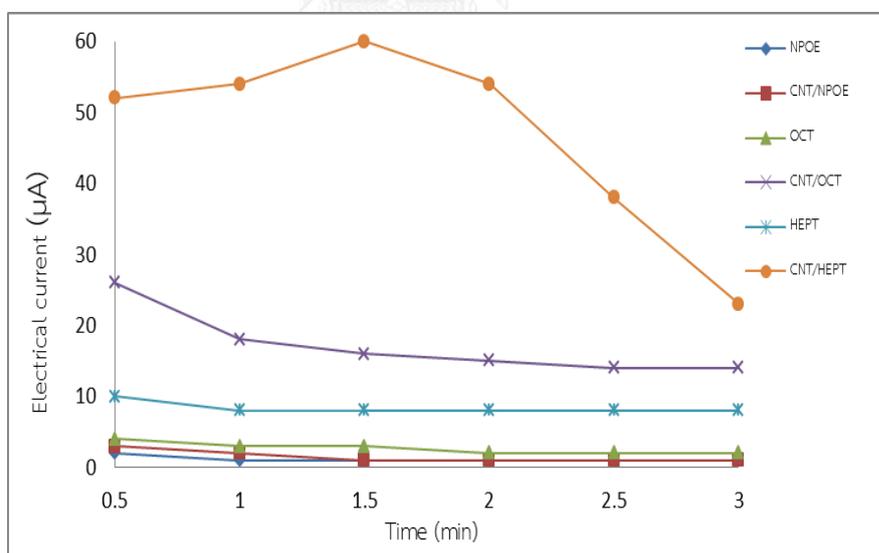


Figure 4.2 The electrical current patterns of extraction of chromate ion using organic solvent with CNTs and without CNTs

In contrast, the reinforcement of CNTs into heptanol-based system did not improve the extraction performance as previous two solvents did. The enrichment factor was even declined. Since heptanol is lowest viscous solvent compared to NPOE and octanol, the analytes might have passed through it easier than the other two organic solvents. Besides, when CNTs was reinforced into heptanol-based system, it reduced the resistance of the system causing the system unstable due to the occurrence of bubbles or electrolysis reaction at the electrodes. The high and inconstant electrical current was observed in Fig 4.2. Because electro-enhanced HF-LPME system with reinforcement of CNTs into octanol provides higher enrichment factor and gives stable extraction system with a stable electrical current pattern, it was selected for further studies.

4.1.2 Effect of CNTs and O-CNTs on transportation of chromate ion

Because the analytes in this study is ionic analyte, modifying the surface of CNTs by oxidizing the surfaces to be more polar functional group molecules was studied. CNTs were treated with concentrated hydrochloric acid to generate $-\text{COOH}$, $-\text{OH}$ and $-\text{CO}$ polar groups on the CNTs surfaces. Polar groups on O-CNTs surfaces may afford additional interactions and promote better transportation of chromate ion than the original CNTs. The surfaces of functional groups on O-CNTs are partially charged due to uneven bonding between different electronegative atoms. The oxygen atom on the surface is highly electronegative, it is partially negative and makes other atoms which are bonded to it partially positive. For this reason, the chromate ion may be attracted to these positive sites on the surfaces of O-CNTs as shown in Fig. 4.3. Like the solvation of water around NaCl that the Cl^- will be attract with partially positive H-atom of water molecule as show in Fig. 4.3

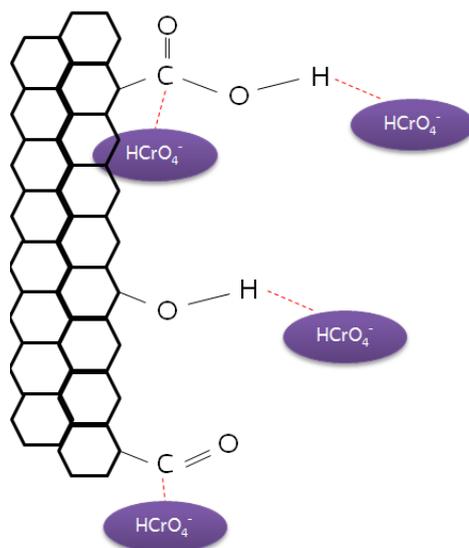


Figure 4.3 Expected interaction between chromate ion and partially positive site on the surface of O-CNTs

The success of oxidizing process was confirmed by FT-IR spectrum in Fig. 4.4. The peaks at 3445, 1741 and 1250 cm^{-1} were attributed to the characteristic absorptions of O-H, C=O and C-O stretching.

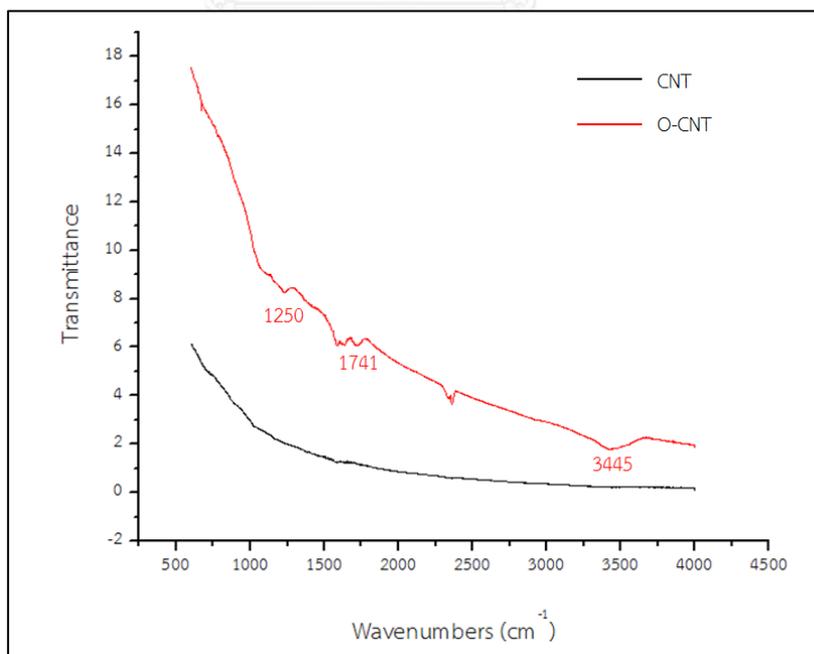


Figure 4.4 FT-IR spectrum of CNTs (black line) and O-CNTs (red line)

Moreover, dispersive ability of O-CNTs and CNTs in octanol were different. Fig. 4.5 shows dispersive ability of CNTs and O-CNTs within 2 days. The CNT could be still dispersed in octanol but O-CNTs could not. Otherwise, O-CNTs are aggregated and settled to the bottom. Since octanol is relatively less polar organic solvent, the less polar CNTs could have more adhesive force (the force between the CNTs and octanol) than cohesive force (the force between the CNTs and CNTs). Therefore, CNTs particles can be dispersed in octanol. In contrast, O-CNTs are more hydrophilic than CNTs. In a case, O-CNTs can not completely disperse in OCT. Cohesive force is stronger than adhesive force. So the O-CNTs particles will aggregate and fall to the bottom.



Figure 4.5 The difference of dispersive ability between CNT (left) and O-CNT (right) in octanol within 2 days

The results of using electro-enhanced HF-LPME with CNTs and O-CNTs reinforced membrane for extraction of chromate ion were shown in Fig. 4.6. The enrichment factor when using electro-enhanced HF-LPME with CNTs reinforced membrane was significantly improved compared to using electro-enhanced HF-LPME

with pure octanol as membrane but the extraction efficiency when using electro-enhanced HF-LPME with O-CNTs reinforced membrane was not much improved. The explanation might be attributed to the isoelectric point of the CNTs and O-CNTs. This isoelectric point indicates that the pH of donor solution might affect the total charges on the surfaces of CNTs and O-CNTs, which might affect the transportation of chromate ion.

Pillay et al. reported the isoelectric point of CNTs be around 8.5 [9]. The pH of the solution in this experiment was around 6.9. It suggests that the surfaces of CNTs would be relatively positive from protonation reaction on the CNTs surface. For this reason, the transportation of negatively charged chromate ions can be enhanced by an additional electrostatic adsorption of the positively charged surfaces of CNTs. The electrical current pattern in Fig. 4.7 showed that the electrical current of electro-enhanced HF-LPME system with CNTs reinforced membrane was higher than that with pure octanol membrane. In contrast, electro-enhanced HF-LPME system with O-CNTs reinforced membrane did not provide that kind of attraction to chromate ions as we expected. The explanation may be that despite the partially positive charge of C- and H-atom on O-CNTs surface can provide electrostatic attraction to the chromate ion, the partially negative charge of oxygen can also provide electrostatic repulsion to the chromate anion. Therefore, using electro-enhanced HF-LPME system with O-CNTs reinforced membrane could not significantly improve transportation of chromate ion. Moreover, the isoelectric point of O-CNTs reported by the same researcher was around 7, which was the same level as the pH of donor solution in this experiment resulting in no charges on the surfaces of O-CNTs. Therefore, there was no effect of electrostatic attraction to promote the transportation of chromate ion.

To prove this hypothesis, the pH of the donor solution was adjusted to lower than the isoelectric point of O-CNTs so that the total charge of O-CNTs surface would be positive so that O-CNTs could provide the electrostatic effect to the system.

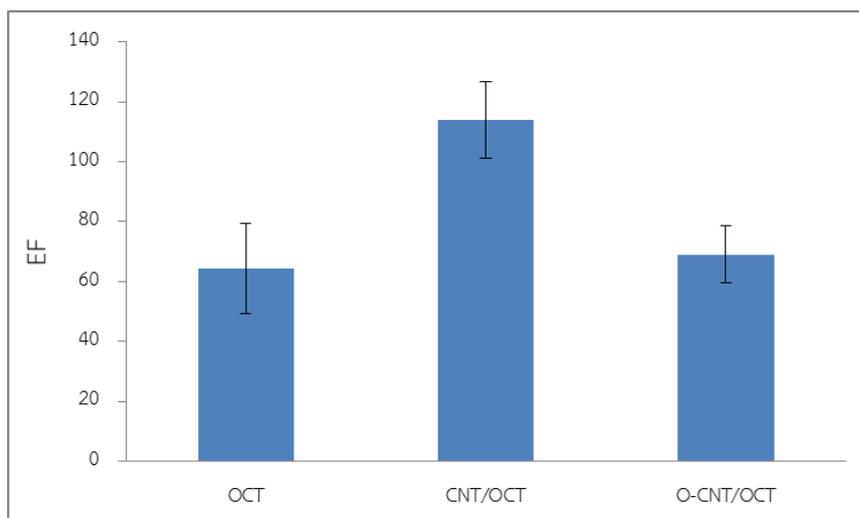


Figure 4.6 Extraction performance of chromate ion using CNTs and O-CNTs reinforced membrane. Donor solution adjusted to pH 7; Chromate ion: 50 $\mu\text{g/L}$; acceptor solution: 0.5 M NaCl; applied voltage: 50 V; extraction time: 7 min ($n=3$ each)

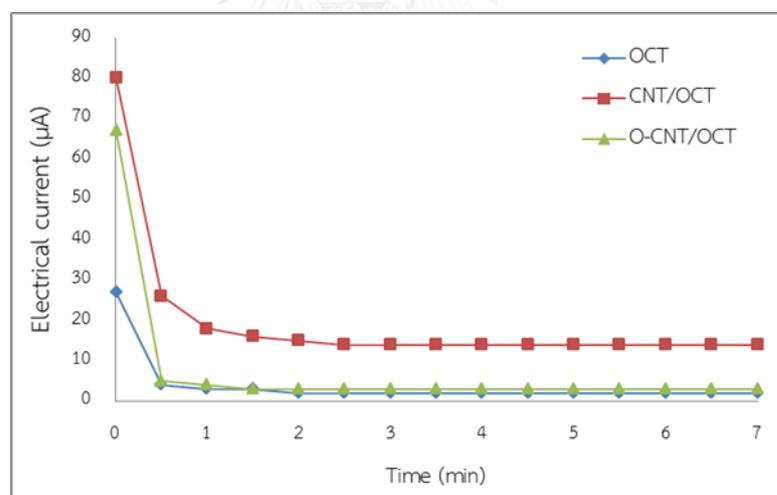


Figure 4.7 The electrical current patterns of electro-enhanced HF-LPME of chromate ion using CNTs and O-CNTs reinforced membrane

4.1.3 Effect of pH solution

To study the effect of pH solution, the pH of donor solution was adjusted to 4 with concentrated HCl acid. The experiment on electro-enhanced HF-LPME system with octanol-based SLM at donor adjusted to pH 4 was not successful. This problem can be explained that chloride ion is small so that it can better move under electric field than chromate ion. According to the principles of electrophoresis [30], the mobility of the ion is given by the equation 4.1 and 4.2:

$$\eta = \frac{v}{E} \quad \text{Equation 4.1}$$

$$v = \frac{E \times q}{f} \quad \text{Equation 4.2}$$

Where η is the mobility of ion, v is the velocity, E is the electrical field, q is net charge on the ion and f is coefficient of friction. Two equations show that the mobility of ion depends on charge and size of ion. Chloride ion has smaller size than chromate ion. It causes the friction coefficient, which depends on mass of ion, of chloride ion is lower than chromate ion.

Therefore, the excess of chloride ion cause the electrical current is unstable and increased to the range of 65-150 μA . Moreover, the occurrence of electrolysis was observed with bubble formation at the electrodes.

To study the effect of pH solution, it was necessary to select other organic solvent. From the previous work, NPOE was appropriate organic solvent to be used as membrane for high ionic content solution [29]. Since NPOE has high viscosity and high dielectric constant, it can well control the migration of ionic species across membrane and can delay the occurrence of electrolysis and bubble formation at the electrodes. Therefore, NPOE-based system including pure NPOE, CNTs/NPOE and O-CNTs/NPOE were used to study. Fig. 4.8 shows much improved extraction efficiency of chromate ions when using electro-enhanced HF-LPME system with O-CNTs reinforced NPOE as the membrane from the donor solution adjusted to pH 4. The electrical current pattern in Fig. 4.9 confirmed that the electrical current of electro-enhanced HF-LPME system with O-CNTs reinforced NPOE increased from 0 in pH7

solution to 1 μA in pH4 solution. The explanation may be that the surfaces of O-CNTs in pH4 solution would show positively charged so that it can provide the electrostatic attraction as CNTs would do so. The highly positive surfaces of O-CNTs are due to protonation on functionalized surfaces forming dihydrogen cations such as $-\text{COOH}_2^+$ and $-\text{OH}_2^+$. So electro-enhanced HF-LPME system with O-CNTs reinforced NPOE can increase the transportation of hydro chromate anion (HCrO_4^- , the predominant species of Cr(VI) in acidic solution). In comparison between O-CNTs reinforced NPOE and CNTs reinforced octanol, the CNTs reinforced octanol can provide higher EF. Therefore, CNTs reinforced octanol was used as a membrane to study other parameters.



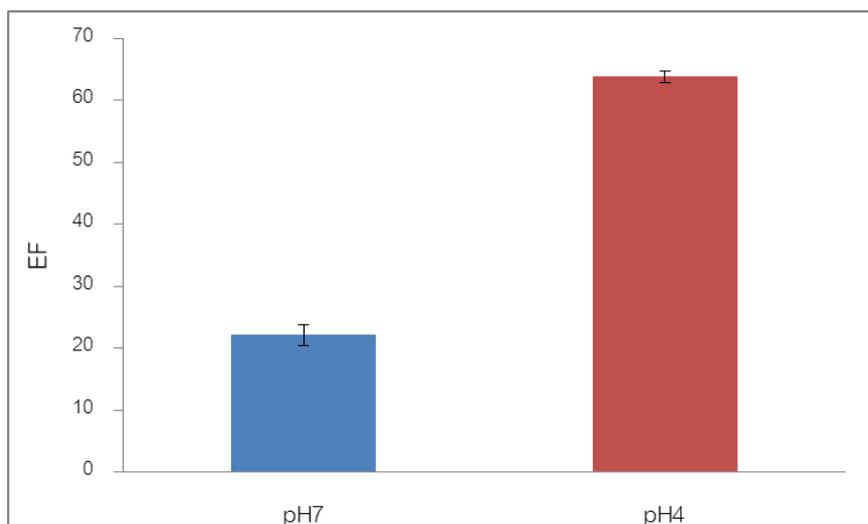


Figure 4.8 Extraction performance of chromate ion using electro-enhanced HF-LPME system with O-CNTs reinforced NPOE from donor solution adjusted to pH 7 and pH 4; Chromate ion: 50 $\mu\text{g/L}$; acceptor solution: 0.5 M NaCl; applied voltage: 50 V; extraction time: 7 min (n=3 each)

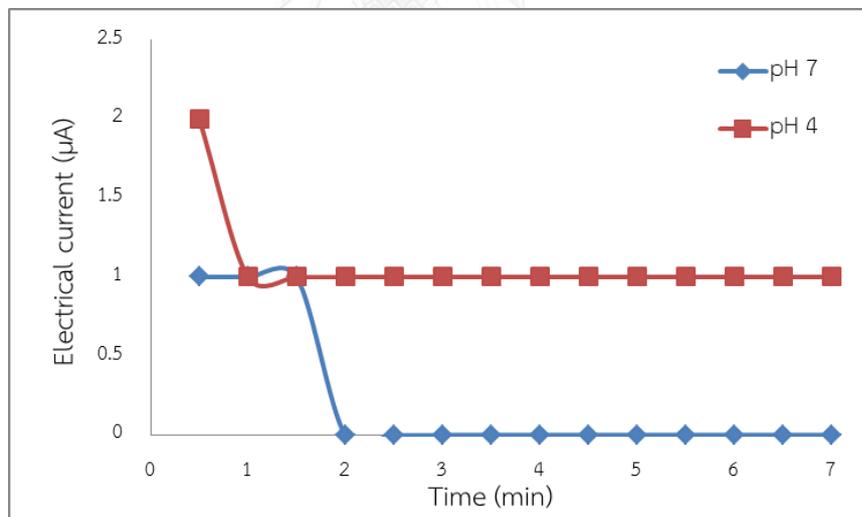


Figure 4.9 The electrical current patterns of electro-enhanced HF-LPME of chromate ion using O-CNTs reinforced NPOE from donor solution adjusted to pH 7 and pH 4

4.1.4 Different amounts of CNTs in HF membrane

The reinforcement of CNTs to electro-enhanced HF-LPME system is like the addition of electrostatic attraction to the system, which increases the transportation of analytes across the membrane. However, the excess of CNTs might cause membrane losing the electrical resistance. The electrical conductive CNTs may reduce the amount of octanol solvent by replacing. This happening can make the system unstable. Therefore, the different concentrations of CNTs in octanol in the range of 0-9 mg/mL were studied. The results in Fig. 4.10 show that the optimal concentration of CNTs in octanol was 3 mg/mL. The electrical current in Fig. 4.11 shows that CNTs reinforced octanol yielded high and stable electrical current pattern (14 μA) while the electrical current of pure octanol system was 1 μA . This electrical current pattern confirms that the transportation of chromate ion through the membrane is increased. At the higher CNTs concentration (5-9 mg/mL), not only the extraction efficiency was not improved but also it was worse. The excess CNTs might cause the amount of octanol in the membrane decreased. Since CNTs is high electrical conduct material, the electrical resistance of membrane may be reduced leading to unstable system. So the electrical current patterns were higher and more fluctuate. Besides, the reinforcement of the excess CNTs in membrane was not physically homogeneous. It appears that there were clusters of CNTs in some areas observed with the naked eyes. Therefore, the optimal CNTs concentration of 3 mg/mL was used for reinforcement in the hollow fiber membrane.

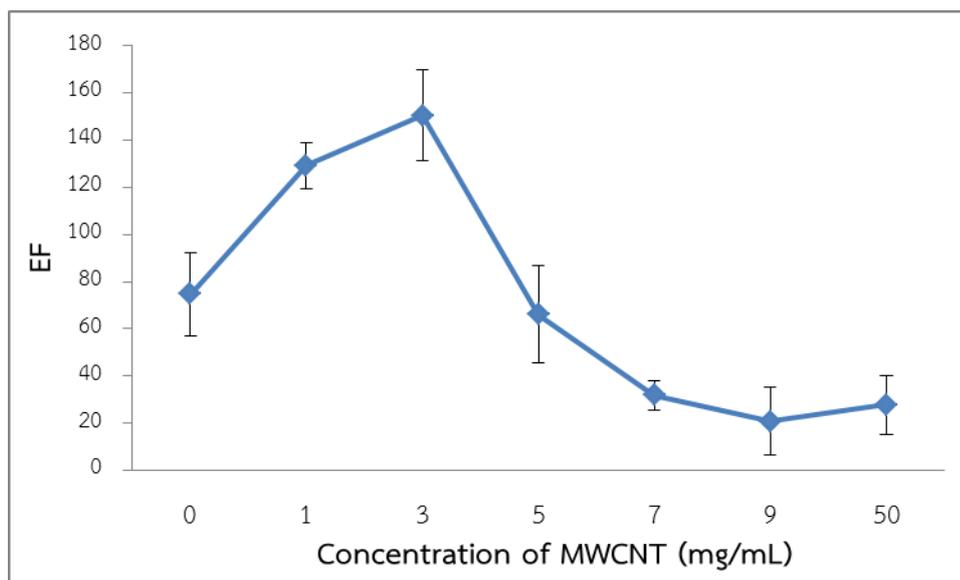


Figure 4.10 Extraction performance of chromate ion using different amounts of CNTs reinforced membrane. Donor solution adjusted to pH 7; Chromate ion: 50 $\mu\text{g/L}$; acceptor solution: 0.5 M NaCl; applied voltage: 50 V; extraction time: 10 min (n=3 each)

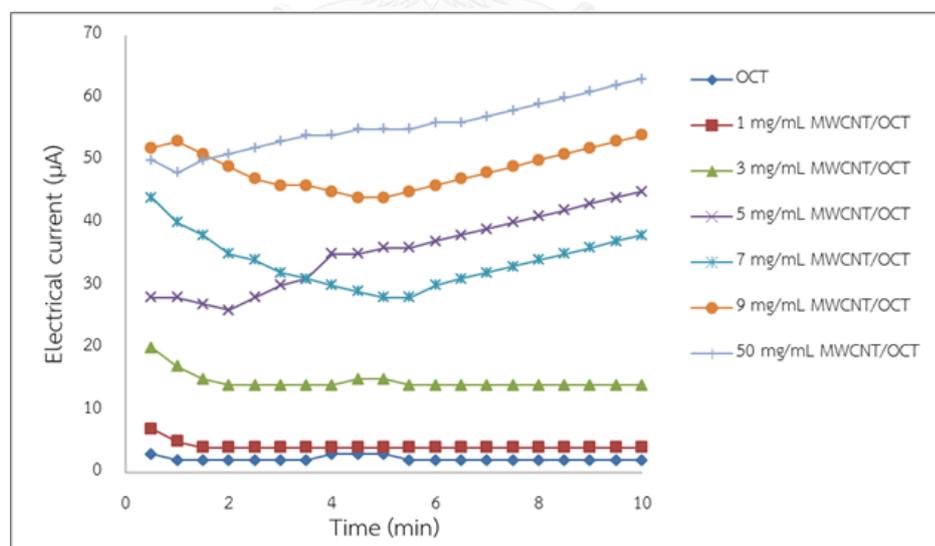


Figure 4.11 The electrical current patterns of electro-enhanced HF-LPME of chromate ion using different amounts of CNTs reinforced membrane

4.1.5 Applied electrical potential

The applied voltage influences the flux of ionic analytes according to the Nernst-Planck equation.

$$J_i = \frac{D_i}{h} \left(1 + \frac{v}{\ln x}\right) \left(\frac{x-1}{x - \exp(-v)}\right) (C_{ih} - C_{io} \exp(-v)) \quad \text{Equation 4.3}$$

where J_i is the flux of the ionic analyte; D_i is the diffusion coefficient; h is the thickness of membrane; C_{ih} is the concentration of analyte at the membrane/donor interface; C_{io} is the concentration of analyte at the acceptor/membrane interface; x is the ion balance, which is the ratio of total ionic concentration in donor solution to total ionic concentration in acceptor solution; and v is the function of applied voltage. The flux of ionic analyte depends on the applied voltage. Fig. 4.12 shows the effect of applied voltage on extraction efficiency of chromate ion. When no applied voltage, no chromate ion was found in the acceptor solution. So chromate ion could not transport across the membrane via passive diffusion. Thus there was no electrical current observed. The transportation of chromate ion was increased proportionally to the increasing applied voltages. Therefore, the applied voltage of 50 V was used in subsequent experimental.

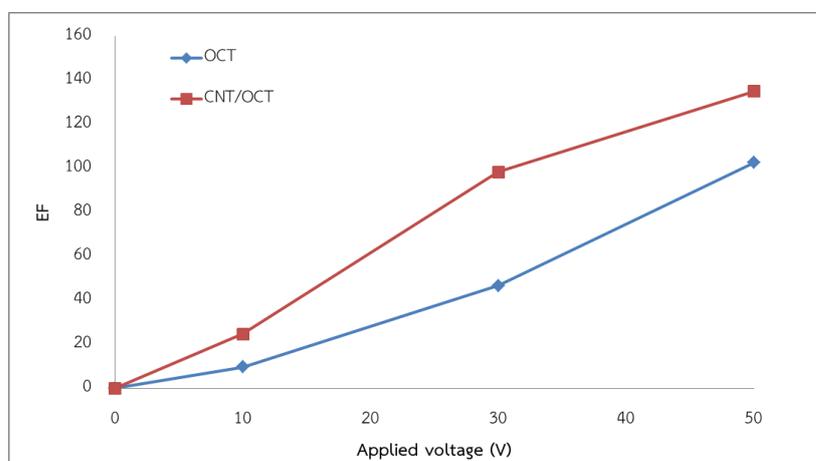


Figure 4.12 Extraction performance of chromate ion using different applied voltages.

Donor solution adjusted to pH 7; Chromate ion $50 \mu\text{g/L}$; acceptor solution: 0.5 M

NaCl ; extraction time: 10 min ($n=3$ each)

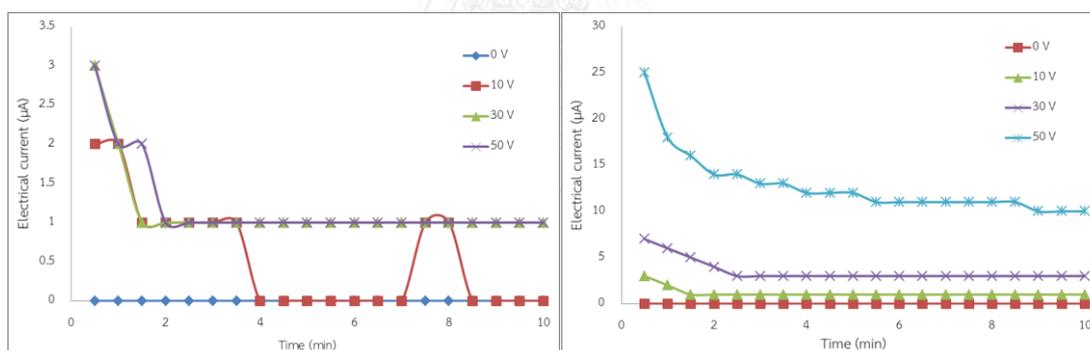


Figure 4.13 The electrical current patterns of electro-enhanced HF-LPME of chromate ion at different applied voltage in pure octanol membrane (left) and CNT reinforced octanol membrane (right)

4.1.6 Extraction time

Extraction time is one important parameter. If extraction time is changed, the total amounts of analytes that transport from donor to acceptor phase also change. Different extraction times in the range of 1-20 min using CNTs reinforced octanol as the membrane were studied and compared with using pure octanol membrane. Fig. 4.14 shows the extraction time profiles of electro-enhanced HF-LPME system with CNTs reinforced octanol and that with pure octanol. The optimal extraction times were 10 and 15 min, respectively. The electrical current patterns of CNTs reinforced octanol in Fig. 4.15 shows that the current could remain stable about 14 μA until 12 min. After that the current continue increased. It indicates the extraction process could be run with stable system within only 12 min. The longer extraction time may cause the thickness of organic solvent membrane reduced resulting in unstable electrical current. Moreover, the bubbles were formed at the electrodes so the extraction efficiency was also reduced. For pure octanol SLM, the extraction process can be run with stable system longer than CNT reinforced octanol (about 17 min) yielding lower electrical current. We can conclude that the CNTs reinforced octanol membrane can provide the same EF with shorter time than the pure octanol membrane.

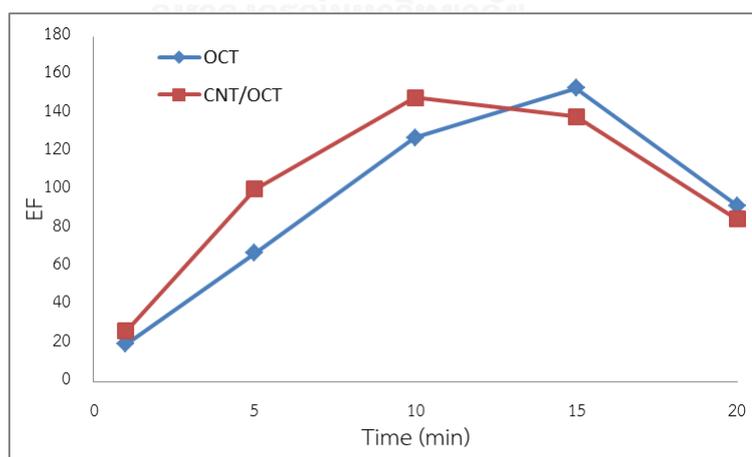


Figure 4.14 Extraction profiles of chromate ion using CNTs reinforced octanol and pure octanol membrane. Donor solution adjusted to pH 7; Chromate ion 50 $\mu\text{g/L}$; acceptor solution: 0.5 M NaCl; applied voltage: 50 V; extraction time: 10 min (n=3 each)

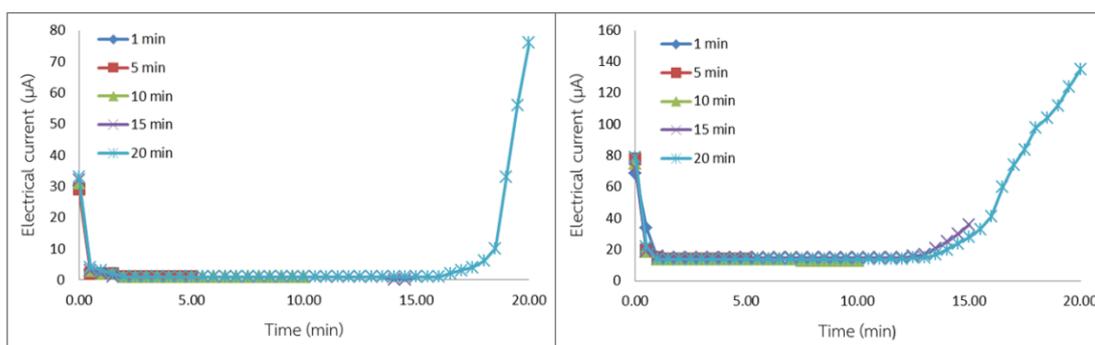


Figure 4.15 The electrical current patterns of electro-enhanced HF-LPME of chromate ion at different extraction time in pure octanol (left) and CNTs reinforced octanol (right) membrane

From this study, the optimal conditions of CNTs-reinforced hollow fiber electro-membrane extraction for determination of chromate ion are summarized in Table 4.1.

Table 4.1 The optimum conditions of CNTs-reinforced hollow fiber electro-membrane extraction for determination of chromate ion

Extraction parameters	Optimum condition
Hollow fiber length	5 cm
Membrane	3 mg/mL CNTs/OCT
Donor solution volume	28 mL
Acceptor solution	0.5 M NaCl
Acceptor solution volume	12 μ L
Applied voltage	50 V
Extraction time	10 min
Stirring rate	750 rpm

4.2 Method validation

4.2.1 Calibration curve

The calibration curve of the method was obtained using standard Cr(VI) at various concentrations in the range of 10-80 $\mu\text{g/L}$ in milli-Q water. This range cover the maximum contamination level of Cr(VI) in drinking water and tap water (WHO recommend). The linear working range was plotted between absorbance and spiked standard concentration as show in Fig 4.16.

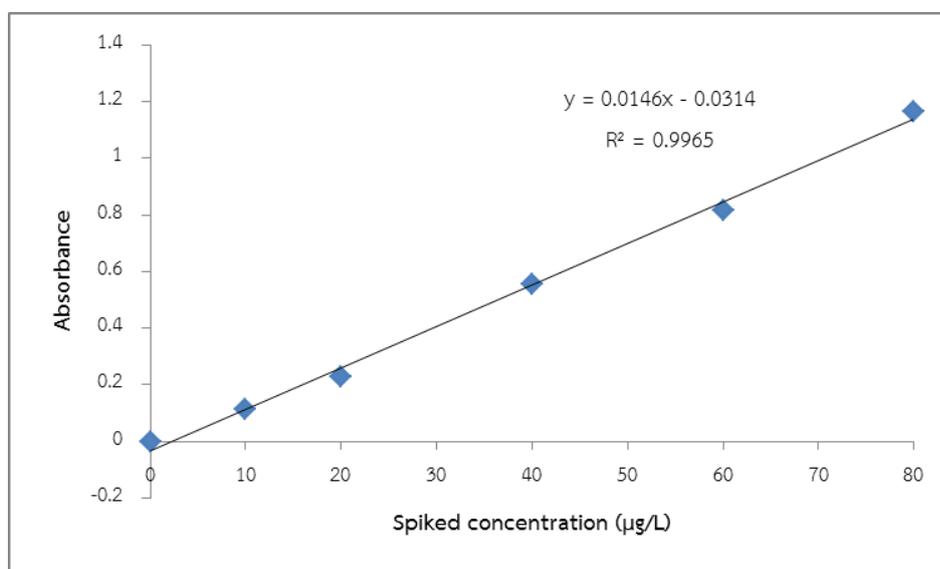


Figure 4.16 Calibration curve of CNT-reinforced electro-enhanced HF-LPME method for determination of Cr(VI) in milli-Q water

4.2.2 Accuracy

The method accuracy was evaluated using recovery study. The %recovery was derived from three replicates at two spiked concentration levels including: 20 and 50 $\mu\text{g/L}$, and calculated with Equation 3.1. The results were summarized in Table 4.2.

4.2.3 Precision

The method repeatability was evaluated from RSD of EF. For intra-day precision was obtained from eight replicate analyses of spiked 50 µg/L Cr(VI) in blank samples. Inter-day precision was obtained from total five replicates of spiked 50 µg/L Cr(VI) in blank samples. Then the RSD of the enrichment factors were calculated and reported in Table 4.2.

4.2.4 LOD and LOQ

The LOD and LOQ of this CNT-reinforced hollow fiber electro-membrane extraction method were calculated based on standard deviation of regression line. Both LOD and LOQ were reported in Table 4.2.

Table 4.2 Analytical performance of CNT-reinforced hollow fiber electro-membrane extraction for chromate ion

Linear equation		$y = 0.0146x - 0.0314$
R^2		0.9965
Linearity		10 – 80 µg/L
%recovery (n=3)	20 µg/L	112%
	50 µg/L	114%
Intra-day precision (n=8)	Average EF ± SD	133 ± 2.2
	RSD	1.7
Inter-day precision (n=5)	Average EF ± SD	134 ± 0.3
	RSD	0.3
LOD		1.3 µg/L
LOQ		4.5 µg/L

CHAPTER V

CONCLUSION

Carbon nanotubes-reinforced with electro-enhanced HF-LPME was developed to improve the extraction efficiency of the conventional electro-enhanced HF-LPME. CNTs were added to the organic solvent membrane for additional mechanism to improve transportation of analyte.

From this study, we found that CNTs significantly affect the transportation of chromate ion probably due to two reasons. One was the electrostatic attraction between CNTs and chromate ion. The other one was that CNTs could reduce the resistance of the organic solvent membrane because CNTs are conductive materials. Chromate ion transported across the organic solvent membrane easier under an electric field. O-CNTs exhibited much improved extraction efficiency in acidic solution providing an additional electrostatic attraction to the extraction system. However, acidic solution contained lots of ionic content, the excess of ion causes the electrical current is unstable and the occurrence of electrolysis was observed with bubble formation at the electrodes. The higher dielectric constant solvent such as NPOE may be required.

In comparison to the conventional electro-enhanced HF-LPME method, carbon nanotubes-reinforced with electro-enhanced HF-LPME method showed higher enrichment factor in shorter extraction time. Optimal extractions were accomplished with 3 mg/mL of CNTs/octanol as the organic solvent membrane. Applied voltage is 50 V, extraction time of 10 min. Under the optimized conditions, carbon nanotubes-reinforced with electro-enhanced HF-LPME method provided low limit of detection (1.3 $\mu\text{g/L}$), good linear of regression (0.9965), enrichment factor (133-134) and recovery (112 and 113% for 20 and 50 $\mu\text{g/L}$ Cr(III), respectively).

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Poster presentation and proceedings

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