DETERMINATION OF TRACE LEVEL PERCHLORATE IN WATER AND SEAFOOD SAMPLES USING LAYERED DOUBLE HYDROXIDES AND BIOSYNTHESIZED SILVER NANOPARTICLES

BY

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A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

MAY 2015

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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This thesis is dedicated

To:

Spirit of my father

My beloved mother for her prayers and my brother and sisters

ACKNOWLEDGMENTS

Praise is to almighty Allah who gave me the ability, strength and success to complete this work. Acknowledgment is due to King Fahd University of Petroleum & Minerals for giving me this opportunity to complete the MSc. degree. I gratefully acknowledge the Deanship of Scientific Research of KFUPM for the financial support given to this project (Project no. IN121021).

I wish to express my appreciation to *Dr.Basheer Chanbasha* who served as my major advisor and devoted his time for this research. I also wish to thank the other members of my thesis/dissertation committee; *Dr Thaer Ali Barri,* and *Dr. Abdul Malik Peedikakkal* for their valuable comments and advices.

I acknowledge, with deep appreciation, all faculty members, Colleagues and staff in chemistry department for their help and support through my course and research work.

Last but not the least; I would like to thank my friends at KFUPM, and everywhere for their support and love.

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LIST OF ABBREVIATIONS

LDHs: Layered double hydroxides

EME: Electromembrane extraction

SLM: Supported liquid membrane

SPE: Solid phase extraction

US EPA: United States Environmental Protection Agency

NRC: The National Research Council (NRC)

AgNPs: Silver nanoparticles

NIS: Sodium-Iodide Symporter

IQ: Intelligence quotient

LLE: Liquid liquid extraction

MAE: Microwave assisted extraction

COD: Chemical oxygen demand

OER: Oxygen evolution reaction

CNTs: Carbon nanotubes

MWCNT: Multiwall carbon nanotubes

FT-IR: Fourier transform infra-red sperctroscopy

SEM: Scanning electron microscope

XRD: X-ray diffraction

IC: Ion chromatography

LOD: Limit of detection

LOQ: Limit of Quantitation

S/N: Signal to noise ratio

ppm: Parts per million (10^{-6})

µg/ L: Microgram per litre(10^{-6})

µg /g: Microgram per gram (10^{-6})

µL :Micro liter (10^{-6})

ABSTRACT

Full Name : MOHANAD MUBASHAR BUSHRA ABDULLAH

Thesis Title : Determination of trace level perchlorate in water and seafood samples using layered double hydroxides and biosynthesized silver nanoparticles

Major Field : CHEMISTRY

Date of Degree : MAY 2015

Perchlorate, a known thyroid endocrine disruptor, originates as a contaminant in the environment from the use of solid salts in the manufacture of solid rocket fuels and munitions. Knowing this, it is very important to monitor these contaminants and take appropriate measures to eliminate risks of such water and food contaminants in different locations.

Due to the intricate nature of food and biological matrices, complex, time consuming sample preparation steps are required in order to quantify contaminants such as perchlorate. Hence conventional sample preparation methods such as solid-liquid extraction and soxhlet extraction are multistep procedures and prone to source of errors or not suitable for trace level monitoring applications. In this research, independent methods for the extraction of perchlorate from water and complex seafood matrices samples were developed. For seafood samples, a microwave-assisted extraction (MAE) followed by biosynthesized silver nanoparticles coated electro-membrane extraction (EME) was developed. Whereas for water samples, layered double hydroxides extraction was developed. Both methods were optimized to improve the extraction efficiency that includes the determination of linearity, recoveries, and precision and matrix interferences.

The proposed methods were applied to real samples to determine the concentrations of perchlorate

ملخص الرسالة

الإسم الكامل: مهند مبشر بشرى عبدالله

عنوان الرسالة: تقدير الكميات الضئيلة من البيركلورات في عينات من المياه والمأكولات البحرية بإستخدام الهيدروكسيدات مزدوجة الطبقات و جسيمات الفضة النانوية المصنعة حيوياً

التخصص: الكيمياء

تاريخ الدرجة العلمية: مايو 2015

تشتهر البيركلورات بأنها أحد مسببات إختلال الغدة الدرقية والتي تنشأ كملوث للبيئة نتيجة لإستخدام أملاحها الصلبة في صناعة وقود الصواريخ والذخيرة. وبمعرفة ذلك فإنه من المهم مراقبة هذه الملوثات وأخذ التدابير المناسبة للحد من خطورتها كملوث للماء والطعام في مختلف المواقع.

نسبة للطبيعة المعقدة لبيئة العينات الحيوية وعينات الطعام فإن ذلك يتطلب خطوات تحضير عينات معقدة ومستهلكة للزمن وذلك من أجل التحديد الكمي للملوثات مثل البيركلورات.من هذا المنطلق فإن طرق تحضير العينات التقليدية مثل إستخلاص السائل-السائل والإستخلاص بواسطة السوكسلت لربما تكون مصدر للأخطاء أو غير مناسبة لتطبيقات مراقبة الكميات الضئيلة من المواد.

في هذا البحث تم إقتراح تطوير طرق مستقلة لإستخلاص البيركلورات من عينات المياه وعينات المأكولات البحرية معقدة البيئة. لعينات المأكولات البحرية تم تطوير طريقة الإستخلاص المساعد بالمايكرويف متبوعة بالإستخلاص بواسطة غشاء مزود بالكهرباء مطلي بجسيمات الفضة النانوية المصنعة حيوياً. بينما لعينات المياه تم تطوير طريقة الإستخلاص بواسطة الهيدروكسيدات مزدوجة الطبقات. تم تحسين كلتا الطريقتين وذلك لترقية كفاءة الإستخلاص والتي تتضمن تقدير التناسب الخطي والإسترداد والدقة وتداخلات بيئة التحليل.

الطرق المقترحة تم تطبيقها علي عينات حقيقية وذلك من تقدير تراكيز البيركلورات في هذه العينات.

CHAPTER 1

INTRODUCTION

1.1 Historical background

The determination of endocrine disrupter contaminants to an analytical chemist has reached a great concern. Perchlorate represents an important group of these contaminants. The use of perchlorate in making rocket fuel, explosive materials, and pyrotechnics for decades leads to common occurrence of these contaminants in drinking and surface water, soil, and food stocks in the United States as well as several other countries [1].

The sources of perchlorate are mainly anthropogenic; with its only natural source coming from evaporate deposits in extremely arid regions. Chilean saltpetre, a commonly used fertilizer, for example, contains a significant amount of perchlorate [2]. Potassium perchlorate is used extensively in the manufacture of firework products and as substituent for black powder gun propellants. Generally, fireworks manufacturers encase their chemical compounds in cardboard cylinders or spheres called “shells”. Black powder usually used as one of the major components of the lofting charge or propellant, and also it is one of the components of the buster. At the time that fireworks have a loud crackle and a glimmering of the white light, they are described as “photoflash” or a “flash and sound” effect. The previous named effect is generated using a mixture of potassium perchlorate and fine aluminum or magnesium powder. Popular implementations involve distinctive impacts for roman candles, rock concerts, illuminations for night photography

[3]. Furthermore it is used historically as a therapeutic agent in the treatment of thyrotoxicosis (e.g., Graves disease) [4]. Ammonium perchlorate is utilized as an oxidant in solid propellants for missiles, rockets, and fire-works [5]. The usage of perchlorate salts has also been noticed in nuclear reactors, additives for oil lubricants, air bag inflators, refining of aluminum, finishing and tanning, gild and paint production, and in fabrication of matches [6].

Perchlorate has also been used by electrochemists as an inert electrolyte. The inertness of perchlorate is due to its non-complexing nature, and kinetic inertness to oxidation and reduction. Perchlorate has one of the lowest hydration energies among inorganic anions, and maybe due to the delocalization of the negative charge over its four oxygen atoms. Its high polarizability and low charge density results in interactions that are similar to hydrophobic interactions [7].

The detrimental health effects of perchlorate are significant. The similarity in size between perchlorate ion and the iodide ion particularized the ability of perchlorate ion to be taken up in place of iodine ion by the mammalian thyroid gland. As a result of this, perchlorate can disrupt thyroid hormones production and thus disorganize the metabolism. As an extra factor or circumstance , other physiologic systems may be affected indirectly [8].

The possible existence of perchlorate in breast milk may lead to the exposure of infants to harmful perchlorate. This exposure to perchlorate may intervene with the growth of both the central and skeletal nervous systems of infants by lowering the amount of iodine uptake into the thyroid and thus decreasing the synthesis of thyroid hormones [9].

In view of the possible risks to the health of humans, ''Environmental Protection Agency in the United States" (US EPA) Office of Water inserted perchlorate in the Contaminant Candidate List in 1998 and to the Rule of Unregulated Contaminants Monitoring in 1999. In general, for a person who weighs 70 kg and drinks 2L of water a day, 24 µg/L concentration of perchlorate in water for drinking would come with an outcome of estimated daily exposure commensurate to "the National Research Council (NRC)" recommended reference dose (RfD) of 0.0007 mg/kg/day.

1.2 Problem statement

The fact that there is a low number of identified contaminated sites is probably limited by the fact that widespread observations for this contaminant has not been achieved. This is confused by the lack of knowledge with regard to the fate in environmental, toxicokinetics, transport bioavailability, and the impact done by this compound on the quality of water in aquatic systems. Furthermore, because of the frequent consumption of seafood by humans, this could represent a potential pathway of exposure to a certain number of human populations living in close vicinity to a contaminated perchlorate site. Thus, the effort asked is to evaluate the exposure of various food kinds to perchlorate as well as to assess the potential exposure for perchlorate in humans through using the resource of contaminated food and water samples [10].

The improvement and optimization of sensitive, fast and unsophisticated analytical methods is essential for perchlorate monitoring in seafood samples, better recognition of how it can be formed and it can be removed in distribution systems. With this realization it is possible to assess human exposure to perchlorate and optimize present treatment

practices with having a complete picture to decrease the pollution by perchlorate in water seafood samples, minimizing health risks as far as possible.

Hence; the determination of perchlorate in water and seafood samples using layered double hydroxides (LDHs) as sorbents and biosynthesized silver nanoparticles coated electromembrane extraction (EME) respectively has attracted significant research efforts.

1.3 Study objectives

The overall objective is to assess the potential determination of perchlorate in water and seafood samples using dissolvable layered double hydroxides (LDHs) as sorbents and biosynthesized silver nanoparticles coated electromembrane extraction (EME) respectively. The overall objective will be achieved by the following specific objectives

i. Developing and optimizing the analytical techniques for extraction and determination of perchlorate.
ii. Application of developed methods for the quantitation of perchlorate in seafood and water samples from different locations.

1.4 Significance of the study

In spite of the fact that the use of perchlorate has come up with the production of some useful materials and other benefits, but the contrast effects on human health and environment by perchlorate is possible [11]. The greatest unintended impact for perchlorate can be seen among the pollution of the earth water systems, which originate aquatic life and their food chains, and considered as a source of drinking water, surface water, and ground water [12]-[13].

CHAPTER 2

LITERATURE RIVIEW

2.1 Perchlorate contamination and health risk

The environmental existence of perchlorate is considered as a possible health risk for people who ingest or consume water or food that contains perchlorate [14]. Environmental exposure of perchlorate may be resulted from the solid rocket fuel production and other devices, through its combination with water and food supplies, aggregated groundwater, and other sources. Some of the studies have expressed the relationship between concentrations of perchorate in human urine (as a biomarker of environmental perchlorate exposure) and thyroid abnormality. So the argue still exists , US legislation has been proposed to adjust drinking water perchlorate content [15].

An increasing number of noticeable scientific researches pointed out that industrial chemicals and pesticides which are made by the hand of humans might conflict with the normal functioning of endocrine systems in human and wildlife. The essential task of hormones, or the endocrine system, is to preserve the stability of environment within the body; this is often well known as homeostasis. The reproduction and growth are also controlled by the endocrine system [16] . In addition, the endocrine disrupting nature of these compounds and their biological activity is noticed even when they are present at very low concentrations such as 10^{-9} mol [16] . Therefore one of the major concerns is monitoring the level of these contaminants in the food chain. Several reports are available on pesticide residue analyses in water, seafood and food related products [17]-[19].

However, there are not many examples in the literature available from Saudi Arabia and Middle East on this subject. Therefore, there is a need to monitor and investigate the residues of toxic chemicals in water and seafood samples in these regions.

Perchlorate anion (ClO_4^-) is generated by the dissolution of solid salts of ammonium, potassium, and sodium perchlorate, and perchloric acid in water. Before 1997, the possibility of detecting perchlorate in groundwater could not be achieved at concentration <100 µg/L. Posteriorly, groundwater containing perchlorate was soon be faced in several Western states in the United States, and the level of contamination became prominent in Colorado Rivers water. This is due to the extensive use of ammonium perchlorate in defense purposes [20].

Most perchlorate salts have the ability to be water soluble; the densities of concentrated solutions are greater than water. The time it is dissolve, it move faster having high mobility, and required decades to degrade. For ClO_4^- ingestion from contaminated water, the only known mechanism of describing the toxicity of perchlorate is interfering with uptake of iodide at the Sodium-Iodide Symporter (NIS).Thus inhibiting the production of thyroid hormones. The thyroid situation of the embryo maternal and infant iodine absorption is risked by the exposure of each other to TH-disrupting chemicals. The high doses of perchlorate will lead to hypothyroidism – which results in low weight brain with densely packed neurons, thus affecting the baby and the brain development; low intelligence quotient (IQ), poor learning ability, reading and language deficits [20].

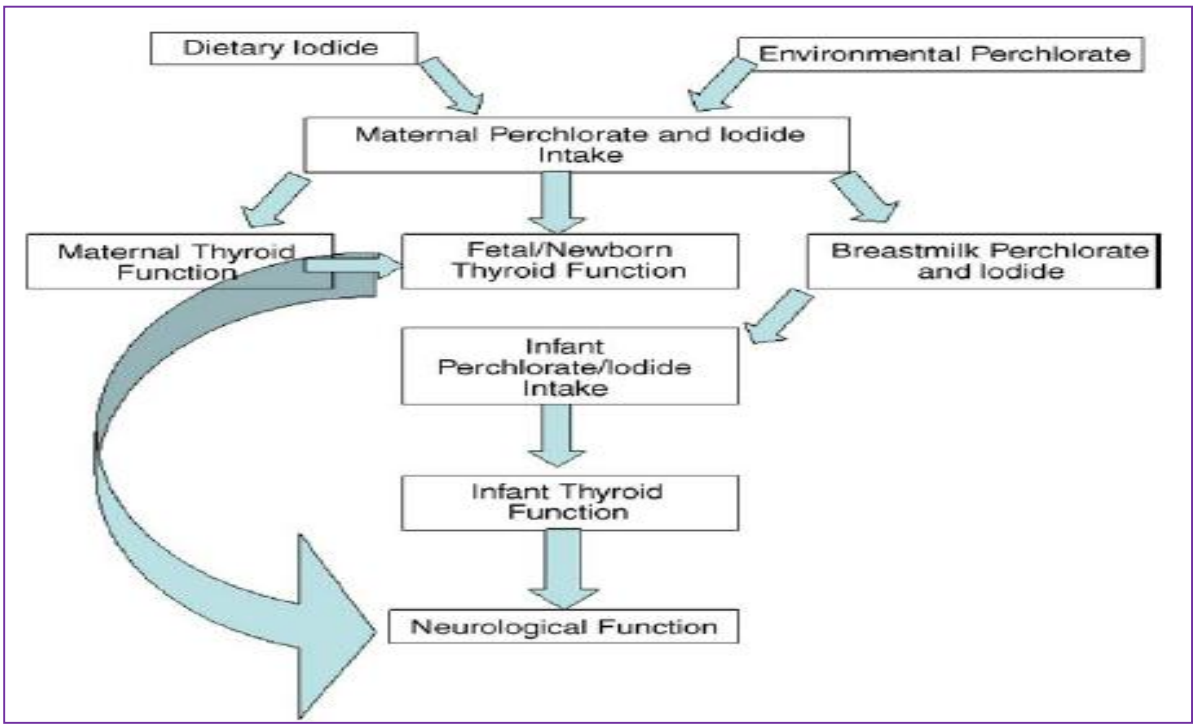

Figure 2.1 Effects of perchlorate on mother-fetus/infant system.

The fact that perchlorate anion is excessively water-soluble and stable in environment resulting in rapid mobility through surface and ground waters, is combined with the widespread usage of perchlorate in industrial and military applications, originates the potential for perchlorate pollution in the environment [21]. The highly soluble and mobile perchlorate can exist in the environment under the standard groundwater conditions for many decades. Perchlorate is known to have a strong oxidizing ability and it is kinetically a sluggish type [22].

One way to grasp and understand the environmental dilemmas and solutions commonly related with perchlorate is to check sites where the contaminant affected soil and ground water. The rate of detecting perchlorate in groundwater and drinking water sources has been steadily growing due to the more continual sampling and enhancement of more sensitive analytical techniques since the beginning of identifying it as a chemical contaminant concern in 1997 [23]. However not only water has been contaminated by perchlorate but also dust could be polluted. A considerable populations could be at risk when exposed to perchlorate from dust which used beyond the period of firworks activities due to resuspending of them on the air [24].

For better understanding for the contamination level of an area, checking the concentration of perchlorate in urine samples is performed. For example in Liuyang the largest fireworks production area in China a country that represents 90% of the international production of fireworks a study concluded that the local people near the production areas faced a greater exposure dose of perchlorate [25].

Recent studies show that the negative impacts of perchlorate are not only to thyroid function and its androgenic influence may not be just to humans as well. The expectation of" hermaphroditism" would not be just induced in any mammal, including humans, but other reproductive function can be disrupted [26]. It is determined that chronic exposure to perchlorate diminished developing the bony structures in young three spine stickleback (Gasterosteus aculeatus, hereafter: stickle- back) in a concentration-dependent manner. It is found that stick-leback exposed to greater than 12 mg/L perchlorate exhibited "phenotypic abnormalities". Of the measured 25 bony characters, 24 were significantly modified, and gross dysfunctionalities occurred such as losing lateral plates and skin pigments lacking. Exposed fish had reduced suitability with abnormal movement and reproduction [27].

2.2 Methods for determination

The rapid determination of trace level quantities of ionic species, by simple techniques, has attracted special attention in analytical chemistry. Perchlorate ions have been directly or indirectly determined by a sort of classical and traditional instrumental methods, including volumetric titrations, gravimetry, spectrophotometry, and chromatography. However most of them are rather complicated, or suffering from interferences from different ionic species, in addition to the high cost of them [28].

The determination of contamination in food and biological matrices is very complex. It often requires several processing steps, in which, analyte losses and new sources of contamination are major problems which must be taken into consideration [29].

Due to the low concentration of perchlorate present in the environment, a preconcentration step usually precedes analysis. The pre-concentration steps must be selective and sensitive, and allow for the minimization of the co-extraction of the matrix or other analytes present [30].

LLE and soxhlet and other conventional extraction techniques turn to have different disadvantages as follows [31]

- Involve tedious multi-step extraction procedures.
- Require sample clean up that may result in a loss of analytes.
- The large amounts of toxic solvents involved in LLE and soxhlet make these techniques very environmentally unfriendly.

Microwave assisted extraction is an emerging and attractive alternative to conventional extraction methods. It is used as a digestion method for various sample types such as, biological, environmental and geological matrices. MAE is now vastly having the acceptance in analytical laboratories. The major advantage of MAE resides in the effectiveness of the heating source. The high temperatures that could be attained by microwave heating decreases dramatically both the extraction time and the required solvent volume, in addition to the affordability of the instrument [32].

Another key advantage of MAE is in the potential reduction of organic solvents required for sample extraction. For instance, it was reported that the use of MAE with distilled water as the main solvent could successfully extract polysaccharides from Potentilla anserina L. The coupling of MAE with an analytical platform for plant metabolite profiling has already become one of its key applications [33].

2.2.1 Layered double hydroxides (LDHs)

A class of anionic clays of hydrotalcite-like compounds known as LDHs has been paid great attention in the field of scientific research. LDHs are sorbents showing signs for future success for anion enrichment with their outstanding anion exchangeability, considerable porosity, and they turn to have a high specific surface area. The previous usage of these materials as sorbents is noticed in traditional solid-phase extraction (SPE) to separate different kind of analytes. For instance fluoride, iodate and even polycyclic aromatic hydrocarbons could be extracted using the dissolution of the LDH sorbent immediately after extraction by pH control, thus "releasing" the adsorbed analytes into solution which drastically shortened the experimental time [34]. Also they prove that they can be a good choice of determination of trace levels of carbonate. The existence of carbonate ion in the interlayer space of MgAl-LDH has made the influence of its anion exchange capacity. This fact is directly related with the extent of drug-loading when the LDH is used as a transporter for drug delivery [35].

Beside to the considerable large surface area and high anion exchange capacity that LDHs have, they own flexible interlayer region that is attainable to a variety of anionic species as well as polar molecular species, and this is another important feature that could be added to their high removal efficiencies of contaminants [36], they demonstrate that they can be an alternative adsorbent for perchlorate-contaminated water. The so-called "memory effect" which is intercalation by reconstruction of calcined products appeared to play a significant role in adsorption of perchlorate ion [37].

The use of LDHs as adsorbents for removing toxic and hazardous anions from aqueous systems in water treatment is combined with taking into consideration that the long term exposure of these adsorbents could be both environmental and human health risk especially aluminum based ones [38]. However not only drinking water could be the target of these adsorbents but also removing color and chemical oxygen demand (COD) from textile industrial waste water. Adsorption studies with raw and biologically treated (activated sludge) textile effluent samples showed that the best conditions for color and COD removal were obtained at lower values of temperature (25 °C) and pH (7). Characterization analyses performed before and after each adsorption and regeneration experiment showed that the dye molecules and other anions were not intercalated in the interlayer region of LDH, indicating that the COD and color removal was due to the adsorption of organic pollutants onto the LDH surface [39].

The variable compositions and unique structural properties allows LDHs to be widely applied in catalysis, and as good examples of that is using LDHs derived catalysts for concurrent catalytic removing of soot and NO_x, Researchers have proven that the LDH derived mixed oxides can not only store NO_x but also oxidize soot to CO_2. By doping with certain noble metals, the stored NOx can be then converted into N_2 in the presence of reducing reagents [40]. Using the highly active cobalt manganese layered double hydroxide (CoMn LDH) as an effective catalyst in oxygen evolution reactions. Co or Mn-based oxide exhibits comparable activity to the best Ni or Fe-based oxide catalysts, which considerably expands the chemical space of earth-abundant OER catalysts [41].

2.2.2 Silver nanoparticles coated electromembrane extraction (EME)

Electromembrane extraction (EME) is an extraction technique where target analytes are extracted between donor and acceptor phase with the use of an organic solvent as a supported liquid membrane (SLM) and the electrical potential as a driving force [42]. It is first introduced in 2006 by using it in the preconcentration of charged analytes from biological samples [43].

EME is a simple and environmentally friendly technique due the less amounts of solvent used. And due to the rapid electrokinetic migration mechanism it is fast and effective sample preparation technique [44].With all these benefits EME has attracted a lot of attention and used in a lot of applications not only for extraction of pure aqueous samples but also from aqueous samples containing polar organic solvents [45].

Recently, EME method is developed to determine perchloarate and other organic acids from amniotic fluids samples. The porous membrane acted as a filtering device; only target analytes entered the acceptor phase. The interfering materials such as fat, larger size particles and unwanted debris were easily eliminated [46].

EME provides sensitivity and selectivity when it is used in the determination of uranium (VI) in real water samples [47]. EME has the ability to give very clean extracts from complex real samples like human plasma [48], whole blood [49], urine [50], saliva [51], breast milk [52], waste water [53], tap mineral and river water [54].

Recent studies were focused on improving the extraction efficiency and enhancing EME. One example is using nonionic surfactant in the donor phase which encourage ionic analytes to migrate to the acceptor phase [55]. Other strategy is using carbon nanotubes

(CNTs) with their large surface area and high adsorption capacity in the SLM could increase the analyte transport to the acceptor phase [56], Or decorating the micro porous hollow fibers with silver nanoparticles which rose the electrokinetick peregrination across the supported liquid membranes. These new nanometallic-decorated supports open a wide field of odds in electromembrane extraction due to the singular properties of nanometallic particles, including possible chemical fiber functionalization [57].

Silver nanoparticles are shown to have a significant influence on the transport properties of the membrane materials and they could increase their conductivity. Their conductivity decreases at low doping levels and rises at sufficiently high metal contents, whereas the activation energy for conduction decreases steadily with increasing metal content. It is believed that this is mainly due to the doping effect on the size of the pores and channels in the ion exchange membranes. At the same time, metal doping reduces the diffusion permeability of the membranes, which makes the transport processes in them more selective [58].

Ag NPs can participate with multiwall carbon nanotubes in reducing coated polymers resistivity. MWCNT act as a long unidirectional backbone that ensures percolation at low filler content. This helps to achieve a good dispersion of the Ag particles that are strongly bonded to the MWCNT [59].

One of the possible ways to obtain these silver nanoparticles is to synthesize them from plant extracts which can provide a controlled size and morphology nanoparticles and the method is inexpensive and environmentally friendly [60]. The beauty of the synthesized

nanoparticles is that they can act as a nanoadsorbent and can be utilized for the separation and preconcentration of various analytes [61].

AgNPs have attracted a great interest in research as they own special characteristics relying on their size and shape , beside their unique optical properties [62]. In addition to the variety of applications of these materials such as selective coating for solar energy [63] ,and as an inhibitor and antibacterial [64] ,anticancer and antiflammatory material [65].

The challenge in the synthesis of these materials motivate the scientific researchers to develop new methods[66]. Different approaches were introduced for the synthesis of AgNPs including chemical [67], electrochemical radiation [68], photochemical and biological technique ,etc. Among all of these methods for AgNPs preparation, plant-mediated green biomimetic synthesis of silver nanoparticles has gained a wide acceptance for the rapid production of the targeted nanoparticles and covered the significant need and current market demand and reduced the excessive risk of using hazardous substances to human health and the environment [69].

This literature review clearly suggests that monitoring of perchlorate in water and seafood samples is mandatory to improve the water and food safety issue at the locations under investigation.

CHAPTER 3

EXPERIMENTAL

3.1 Part A: Determination of trace level perchlorate in water using layered double hydroxides

3.1.1 Chemicals and Materials

Magnesium chloride hexahydrate, sodium carbonate, aluminum chloride anhydrous, magnesium nitrate hexahydrate, aluminum nitrate nonahydrate and sodium hydrate were purchased from J. T. Baker (Philipsburg, NJ). Solvents and trifluoroacetic acid (TFA) (99%) were purchased from Sigma Aldrich (Milwaukee, WI, USA).Water samples were collected from different locations in different provinces of Saudi Arabia.

3.1.2 LDHs Synthesis

Three different types of LDHs (LDH-CO_3^{2-}, LDH-NO_3^-, and LDH-Cl^-) were synthesized in accordance with Reichle proposed method [70]. For LDH-Cl, 15.25g $MgCl_2$•6H2O and 3.34 g $AlCl_3$ were dissolved in 100 mL deionized water under vigorous stirring at 30°C. The pH of the solution was adjusted to 11 by adding 3 mL of 1M NaOH solution. After 4 h, the solution was transferred into an autoclave and aged by hydrothermal

treatment at 180°C for 36 h. The obtained powder was filtered and dried at 70°C overnight.

For LDH-CO_3, 15.25g $MgCl_2$•6H2O and 7.95 g Na_2CO_3 were dissolved in 100 mL deionized water under vigorous stirring at 30°C. The pH of the solution was adjusted to 11 by adding 3 mL of 1M NaOH solution. After 4 h, the solution was transferred into an autoclave and aged by hydrothermal treatment at 180°C for 36 h. The obtained powder was filtered and dried at 70°C overnight. For LDH-NO_3 15.25g $MgCl_2$•6H2O and 28.13 g $AlNO_3$•9H2O were dissolved in 100 mL deionized water under vigorous stirring at 30°C. The pH of the solution was adjusted to 11 by adding 3 mL of 1M NaOH solution. After 4 h, the solution was transferred into an autoclave and aged by hydrothermal treatment at 180°C for 36 h. The obtained powder was filtered and dried at 70°C overnight.

In the same way that LDHs were synthesized, they were characterized, scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), and by X-ray diffraction (XRD)

3.1.3 Extraction Process

The two diverse extraction processes explained in figure 3.1.3. In dispersive solid phase extraction process, 3 milligrams of the sorbent combined by 10 milliliters of the sample were added together inside a centrifuge tube. The formed mixture was applied to sonication at 25 °C for 5 min and after that swirled to make sure that sorbents were distributed . The adjustment of the pH solution is done using sodium hydroxide to different pHs between 4−12. Thereafter, a water bath is used to condition the tubes at the

specified temperatures. When extraction achieved, centrifugation is applied to sedimentate the sorbents from the solution, and the supernatant was decanted. This process is then followed by dissolving the sorbent in 100 microliters of TFA 8% aqueous solution, and 25 microliters now containing our perchlorate, was injected into the IC.

In the co-precipitation extraction process, 3 milligrams of the sorbent combined with 10 milliliters of sample were placed together into a centrifuge tube. 35µL of TFA 99% is added to the solution for the dissolving LDHs. The pH of the sample solution was adapted with adding of sodium hydroxide 0.1M for the pH adjustment between8-12 to develop formation of a new intercalation (LDH). Through this time, and in a water bath, the tubes heated at the specified temperature. After extraction, the sorbent was dissolved in 100 microliters of TFA 8% aqueous solution, and 25 microliters now containing our perchlorate, was injected into the IC.

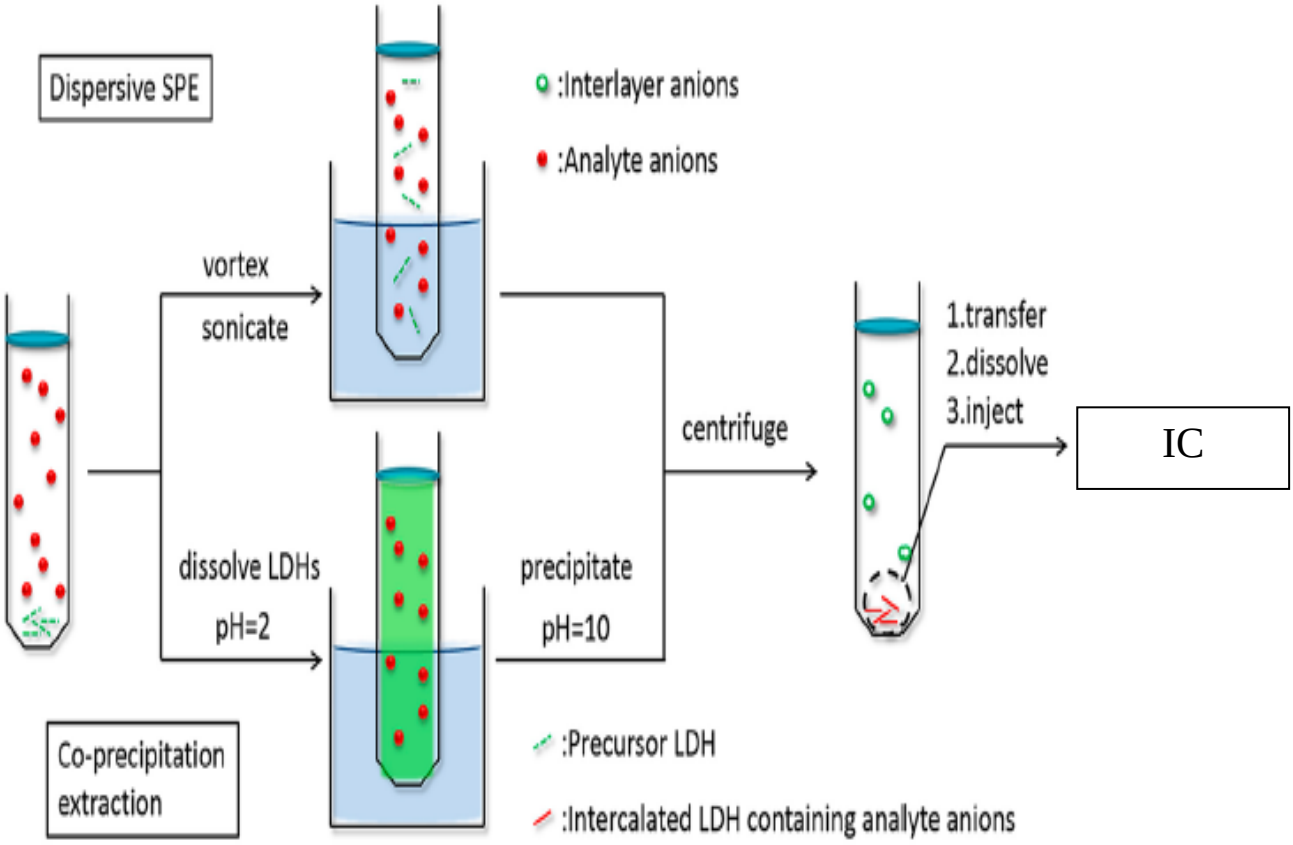

Figure 3.1 Schematic shows the dispersive SPE and co-precipitation extraction processes.

3.1.4 Ion chromatography system

Analysis was carried out using Dionex (Sunnyvale, CA, USA) ICS-2000 IC system equipped with a gradient pump, an eluent generator, an auto sampler, an LC 30 chromatography oven, a conductivity detector, a 2 mm anion self-regenerating suppressor, suppressor external reagent installation kit for external water mode and conductivity meter (Thermo orion). Dionex ion pac (AS16) guard analytical column was used for ion separation. System control was monitored using Chromeleon 7 chromatography workstation software (Dionex). The system conditions were set as: eluent = 35 mM sodium hydroxide; flow rate = 0.25 mL/min; injection volume =2.5 μL and temperature = 30°C. Suppressed conductivity in the external water mode was used for ion detection.

3.2 Part B: biosynthesized silver nanoparticles coated EME of perchlorate from seafood samples

3.2.1 Chemicals and Materials

All chemicals used were of reagent grade and ultrapure water of greater than 18MΩcm resistivity generated through a Milli-Q purification system (Millipore, MA, and USA) was used throughout the experiment. Sodium hydroxide, potassium hydroxide, sodium chloride, nitric acid were obtained from J. T. Baker (Philipsburg, NJ). HPLC-grade organic solvents for EME extractions were secured from Sigma Aldrich (Milwaukee, WI, USA) and Strem Chemicals (Newburyport, MA, USA), respectively. An ES 0300 with programmable voltage (0–300V) and with a current output in the range 0–450mA (Delta Elektronika BV, Zierikzee, The Netherlands) was used for power supply. The electrodes used were platinum wires of diameter 0.5mm (K.A. Rasmussen, Hamar, Norway). Polypropylene membrane Sheet (157μm thickness, 0.2μm pore size) (Membrana, Wuppertal, Germany) was used in the fabrication of EME membrane envelopes. Agitation during extraction was performed on a Vibramax 100 agitator (Heidolph, Kelheim, Germany). Standard stock solution of sodium perchlorate at 100 μg ml^{-1} and working standards were prepared in ultrapure water and refrigerated at 4°C.

3.2.2 Microwave assisted extraction (MAE) system

Multiwave 3000 (Anton Paar, Graz, Austria) with software version v1.52 was used for closed-vessel extractions. The system consisted of 16 high pressure

polytetrafluoroethylene (PTFE) vessels of capacity 100 mL (240◦C temperature, and 40 bars pressure). Before and after use, all plastic and glass wares were washed with concentrated nitric acid and copious amounts of ultrapure water.

3.2.3 Seafood sampling and digestion

Fresh seafood samples were purchased from local fish markets in different provinces of Saudi Arabia. The study attempted to include different seafood species within the community. A minimum of two specimens from each individual species were randomly selected, transported to the laboratory in an icebox for temporary storage and at -4^{o}C. The frozen samples were then thawed and allowed to reach room temperature, gutted and minced prior to microwave digestion.

3.2.4 MAE Procedure

3 grams seafood samples were weighed, rinsed with ultra pure water, air-dried and introduced into sealed PTFE vessels. 20 ml of 100 mM HNO_3 solution were added to the vessels. They were then sealed and put into the microwave extraction system. Extraction was performed at a temperature of 100 ^{o}C and irradiation power from 250W. Desired temperatures were obtained by dynamic extraction times ranging from 5 min followed by holding time of 10 min in the static mode. When vessels cooling finished they were opened and the solution transferred to EME extraction.

3.2.5 Biosynthesis of Silver Nanoparticles

Basil (*Ocimum basilicum*) plant extract was used for the biosynthesis of silver nanoparticles. The plant extract was responsible for the reduction of $AgNO_3$ to silver nanoparticles and the subsequent capping and stabilizing of the synthesized nanoparticles [71]. 20g of the plant leaves were obtained boiled in 150 mL of deionized water. The plant extract solution formed is filtered using whatmann filter paper and stored in the refrigerator at 4°C until further use. The plant extract was added to 2mM $AgNO_3$ in volume ratio 1:25 with the mixture adjusted to pH. The mixture was stirred for 2-hours at room temperature and subsequently centrifuged at 17, 000 rpm for 5 mins. After the addition of plant extract, the solution gradually turned from colorless to yellow and finally to dark brown confirms the existence of silver nanoparticles in the solution.

3.2.6 AgNPs coated EME

The transferred solution from the MAE part was put into an EME set up as a donor solution. The acceptor solution was constituted 1 ml of 100mM NaOH. A nanoparticle coated polypropylene membrane envelop was prepared as illustrated in figure 3.2.6 during the synthesis of silver nanoparticles via in-situ method. Coating the membrane is achieved by immersing the membrane for 30 min in the solution of the biosynthesized AgNPs with applying continuous sonication at 25 °C. The coated membrane was impregnated with n-hexanol for few seconds to get supported liquid membrane (SLM) and the EME was performed. Finally, the extracted analyte was injected into IC for analysis. The IC system is as described in the first part for LDHs extraction.

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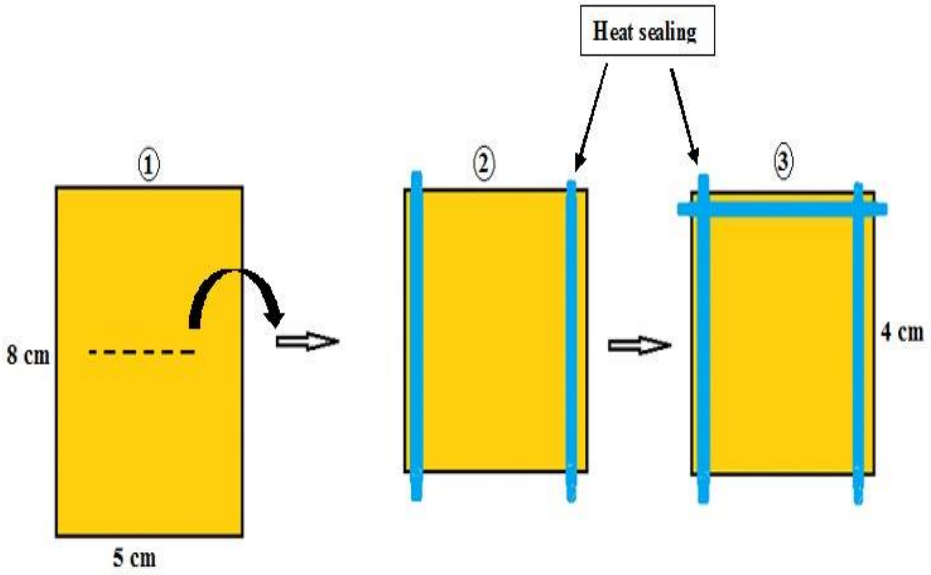


Figure 3.2 Fabrication of membrane bag used for biosynthesized EME procedure.

CHAPTER 4

RESULTS AND DISCUSSIONS

Part I: Determination of trace level perchlorate in water using layered double hydroxides

4.1 LDHs characterization

The LDHs were characterized using scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), and by X-ray diffraction (XRD).The results confirmed the success of the synthetic process of the three sorbents. With every individual technique, the feature of our target synthesized LDH is expressed.

4.1.1 FT-IR

The FT-IR spectra in Figure 4.1.1 show the characteristic absorption bands of each LDH. The broad band at 3480cm^{-1} could be assigned to the stretching vibration of hydrogen bonding and interlayer water molecules. The weak absorption band at 1640 cm^{-1} was attributed to the bending vibration of interlayer water molecules. The stretching vibration of NO_3^- and CO_3^{2-} was responsible for the strong peak at 1384cm^{-1}. The bands in the range of 500-800 cm^{-1} could be ascribed to metal-oxygen-metal stretching.

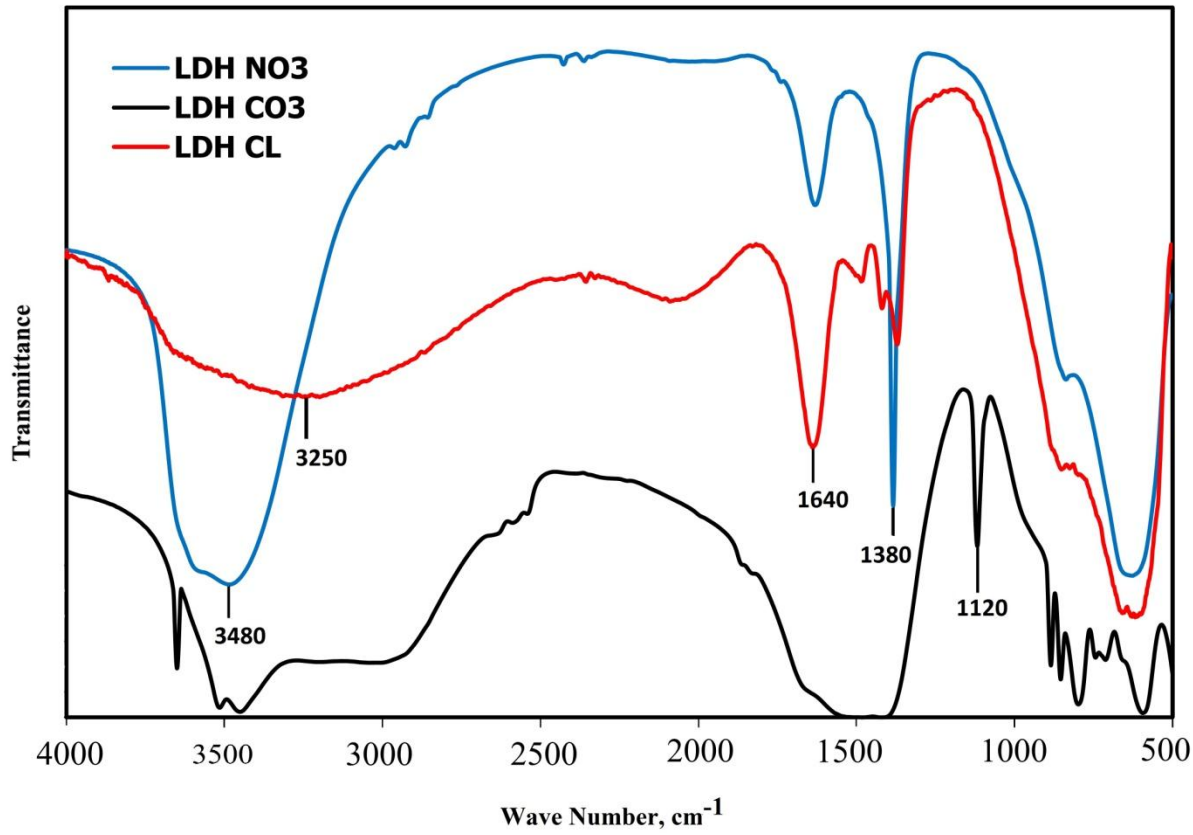


Figure 4.1 FT-IR spectra of three kinds of LDHs (NO_3^-,Cl^-, CO_3^{2-}).

4.1.2 SEM

Figure 4.1.2 a, b, c show the SEM images of LDH-Cl, LDH-CO3, and LDH-NO3 respectively, revealing that the sorbents consist of crystallites. Taking LDH-NO3 as an example (Figure d), the small crystallites were thin platelets with approximate sizes in the range of 200 nm and thickness of about 20 nm.

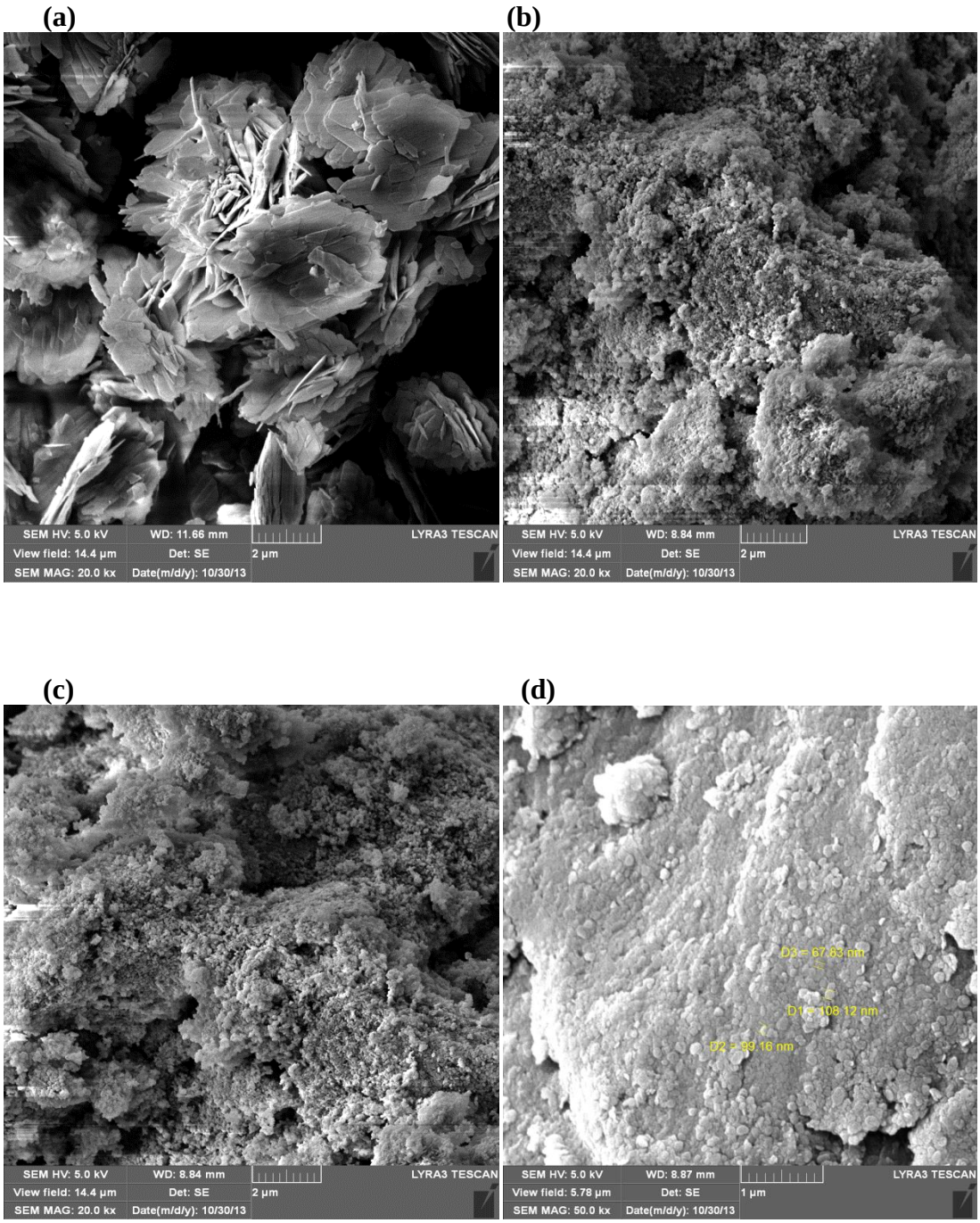


Figure 4.2 SEM images of (a) LDH-CO_3, (b) LDH-Cl, and (c) and (d) LDH-NO_3.

4.1.3 XRD

Figure 4.1.3 shows the XRD pattern of the three types of LDHs with different interlayer anions (NO_3^-, Cl^-, CO_3^{2-}). The sharp and intense diffraction peaks around 11°, 23°, 35°, 60°-62° corresponded to the (003), (006), (009)+(012), (110), (113) planes of the LDHs crystal structure. All the LDHs showed pure and well-crystallized LDH phase. Compared to LDH-Cl and LDH-CO3, LDH-NO3 had the strongest intensity both in planes (003) and (006). This indicated that the LDH-NO3 had the most perfect crystal structure in short range among these three kinds of LDHs.

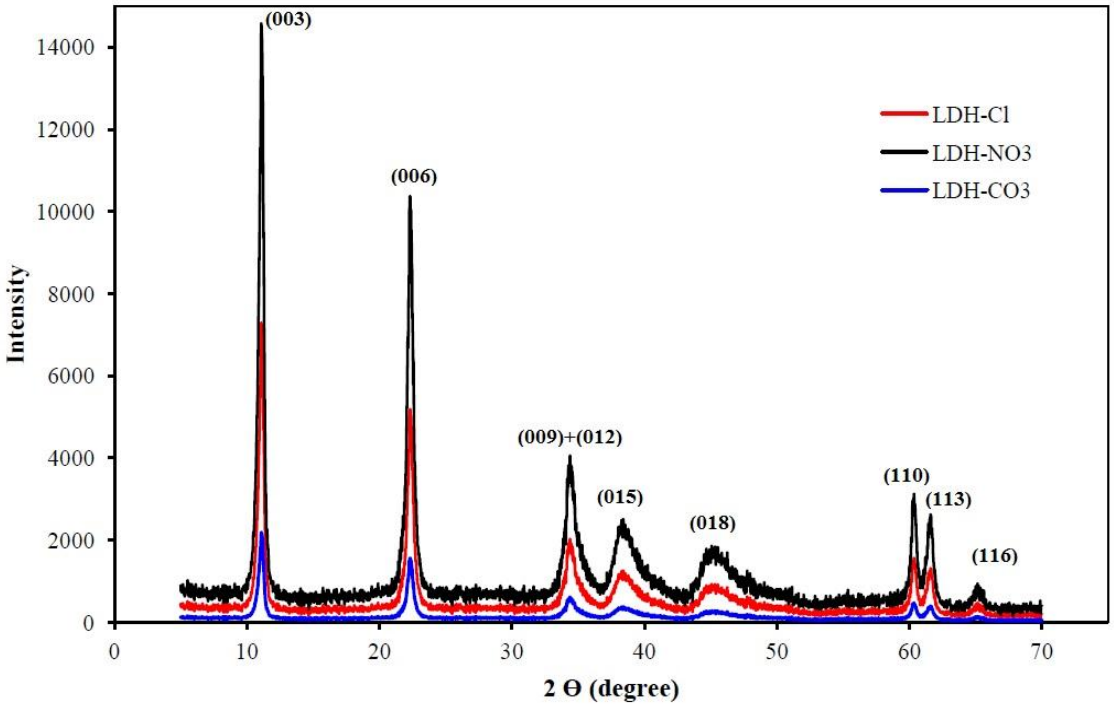


Figure 4.3 XRD patterns of three kinds of LDHs (NO_3^-,Cl^-, CO_3^{2-}).

4.2 Calibration

The calibration curve is established in the range of 0.1-50 µg/L of 7 standard solutions of our target analyte perchlorate.

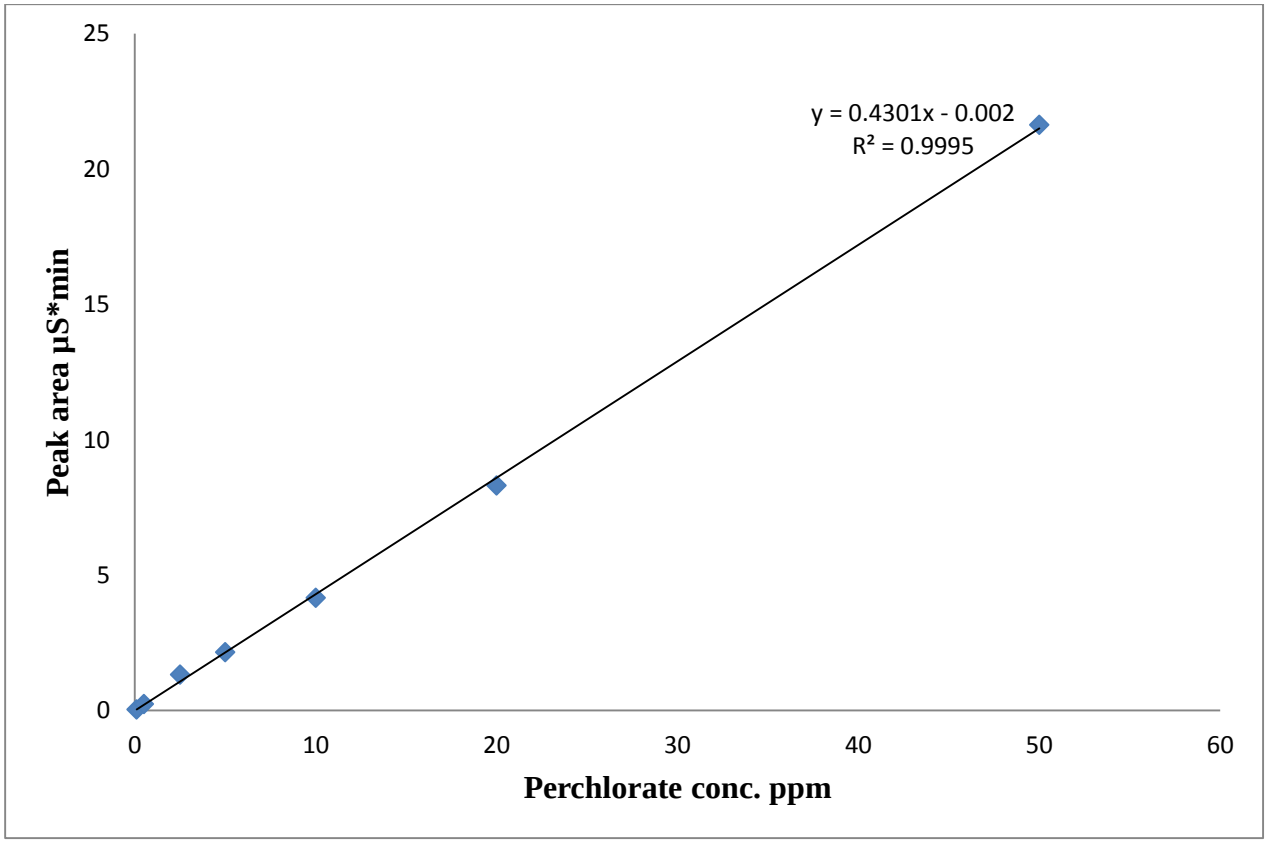
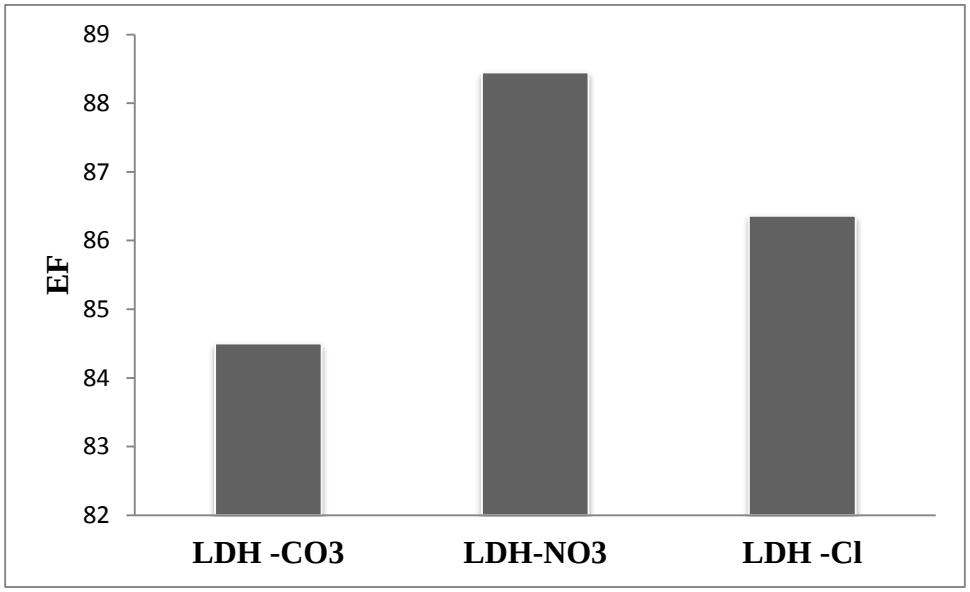


Fig 4.4 Calibration curve for perchlorate standards using ion chromatography.

4.3 Selection of sorbent

The efficacy of extraction by (LDHs) is influenced by the intera-ions sort. These interlayer anions have dissimilar capability of ion exchange to the LDHs [72]. The comparison between results of the three different LDHs (NO_3^-, Cl^-, and CO_3^{2-}) in co-precipitation extraction and dispersive SPE are expressed in Figure 4.3. It is clear that higher enrichment factors were accomplished by using (LDH− NO3) than the other two sorbents in the two methods. The enrichment factors of the sorbents were in the order NO_3^- > Cl^- > CO_3^{2-}. Having all these facts LDH−NO_3 was chosen to be the most appropriate sorbent for conducting the extraction experiments with it.

(A)



(B)

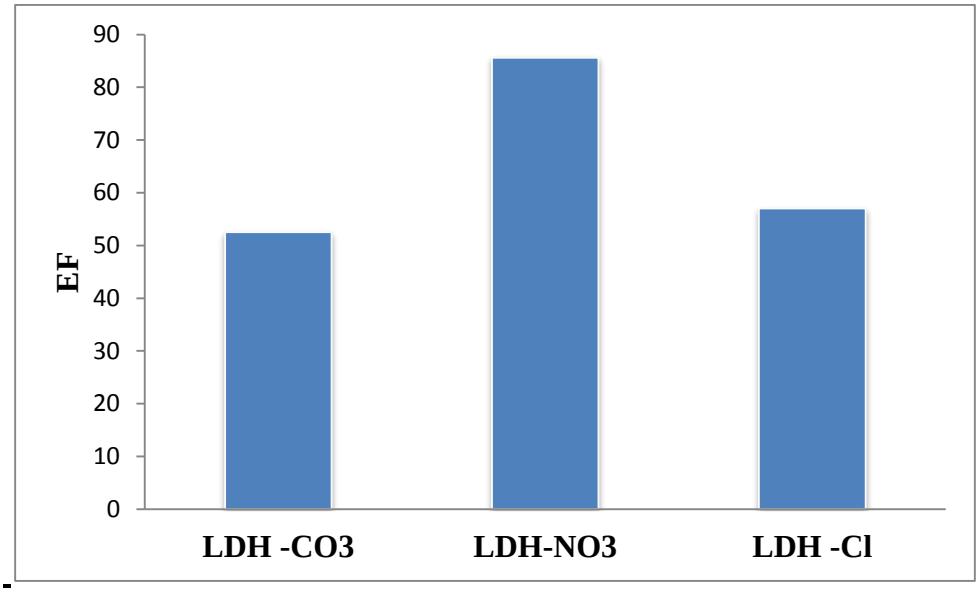


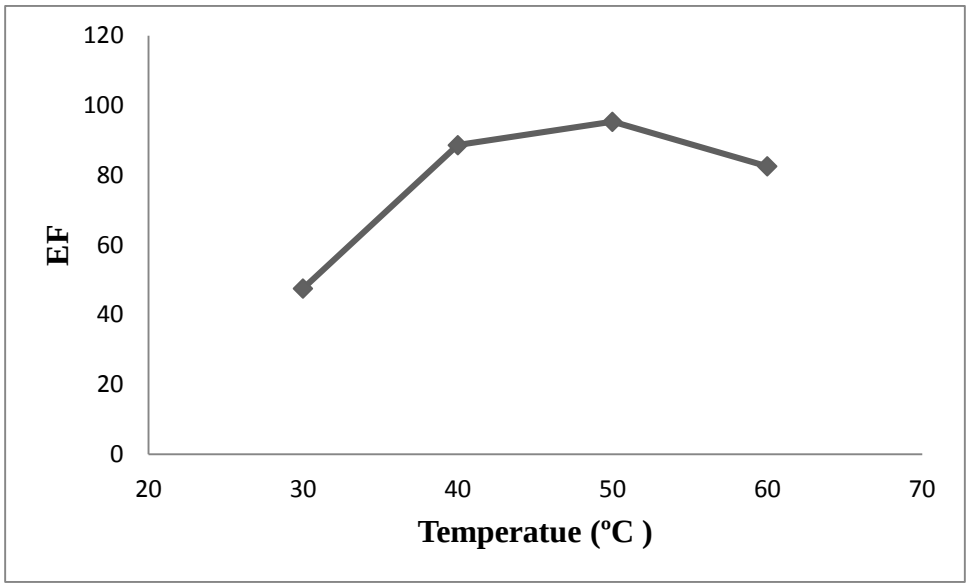
Figure 4.5 Comparison between enrichment factors of perchlorate extraction by three types of LDHs (CO_3^{2-}, NO_3^- and Cl^-) by (A) dispersive SPE (B) co-precipitation extraction.

4.4 Method optimization

4.4.1 Extraction Temperature

The experiments were done from between 30 and 80 °C to investigate the influence of temperature on extraction. Figure 4.4.1 shows that the enrichment factors is increasing with the increase of temperature until it reached the maximum value at 50 °C for dispersive SPE and 70 °C for co-precipitation extraction. Generally, the higher the temperature, the higher diffusion coefficients, and this motivate the migration of target analytes from the aqueous solution to the distributed sorbent particles.

(A)



(B)

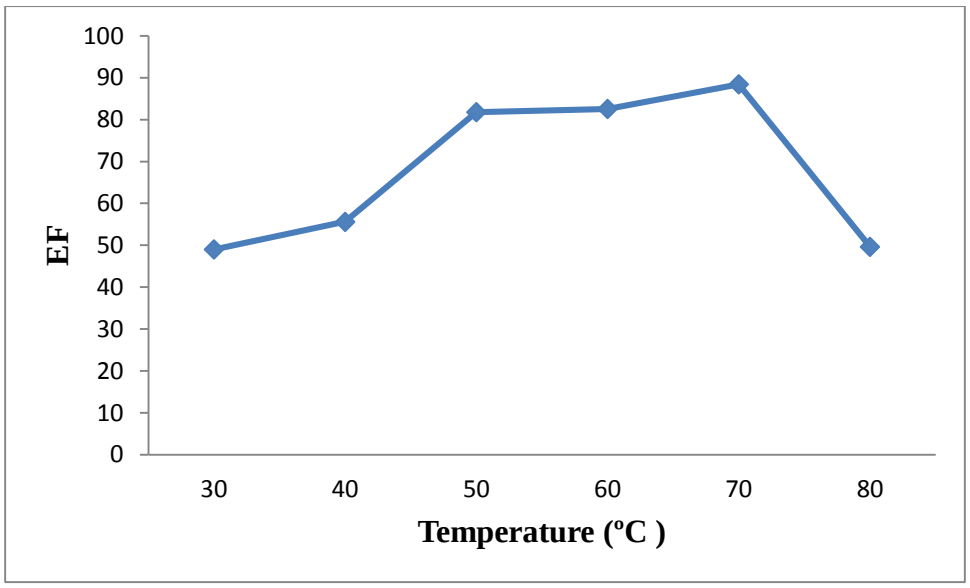
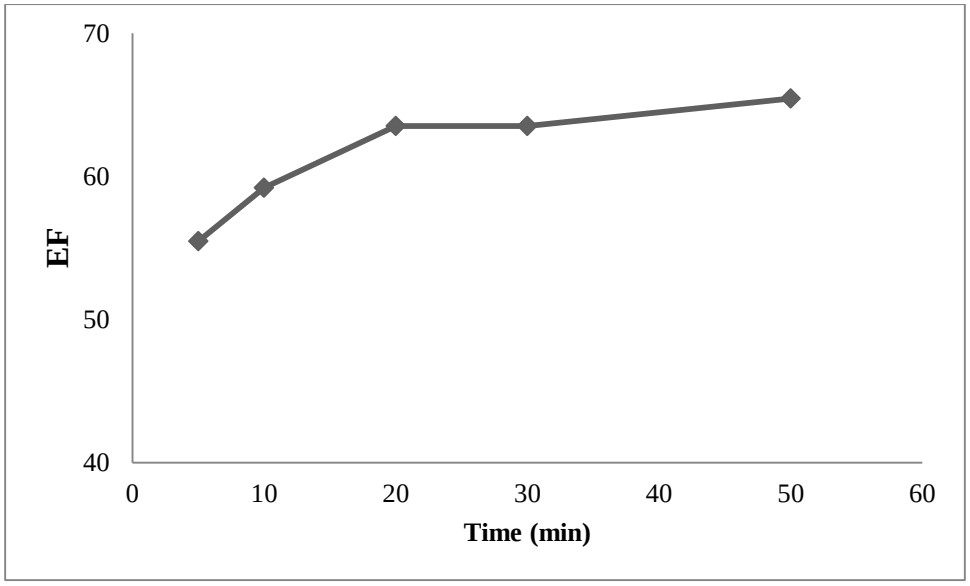


Figure 4.6 Extraction temperature optimization of (A) dispersive SPE and (B) co-precipitation extraction. The conditions: 50 µg/L perchlorate spiked solution; sample volume, 10 mL.

4.4.2 Extraction time

Different times of extraction from 5 to 60 min were put under study, and the results appear in Figure 4.4.2. It can be seen that enrichment factor values stabilized after 20 min in dispersive SPE. In previous studies, after 2−8 h using (LDH) as sorbent in conventional SPE equilibrium was accomplished [73]. It's clear that, the extraction process was accelerated by dispersive sorbent particles. The co-precipitation method achieved the highest enrichment factor values in 10 min and a decrease afterward. Over an extended duration of extraction, however, back extraction occurred because the high concentration of OH^- from the solution became competitive with the analytes[74]. With the above results taken into account, 20 min was selected as optimum time for the extraction for dispersive SPE and 10 min for co-precipitation extraction.

(A)



(B)

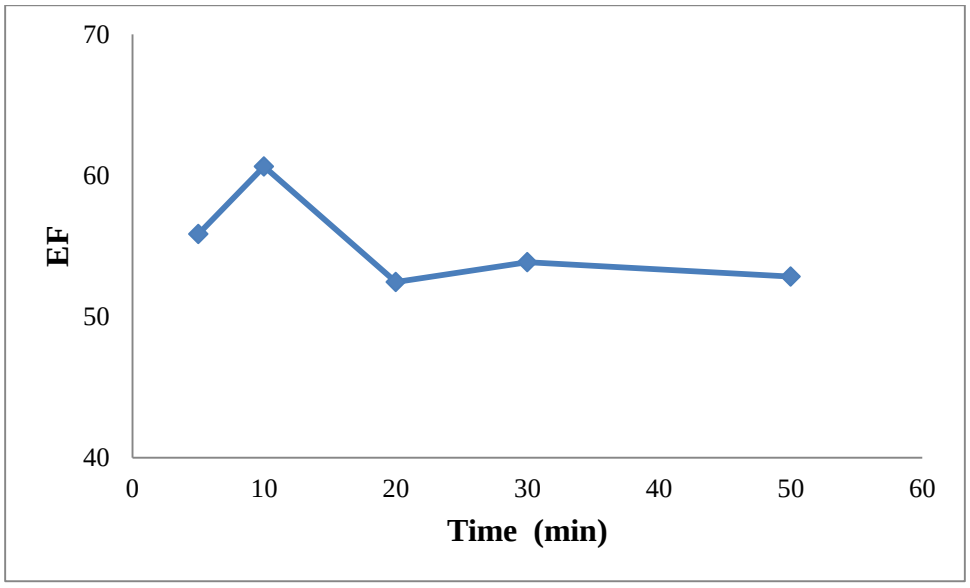
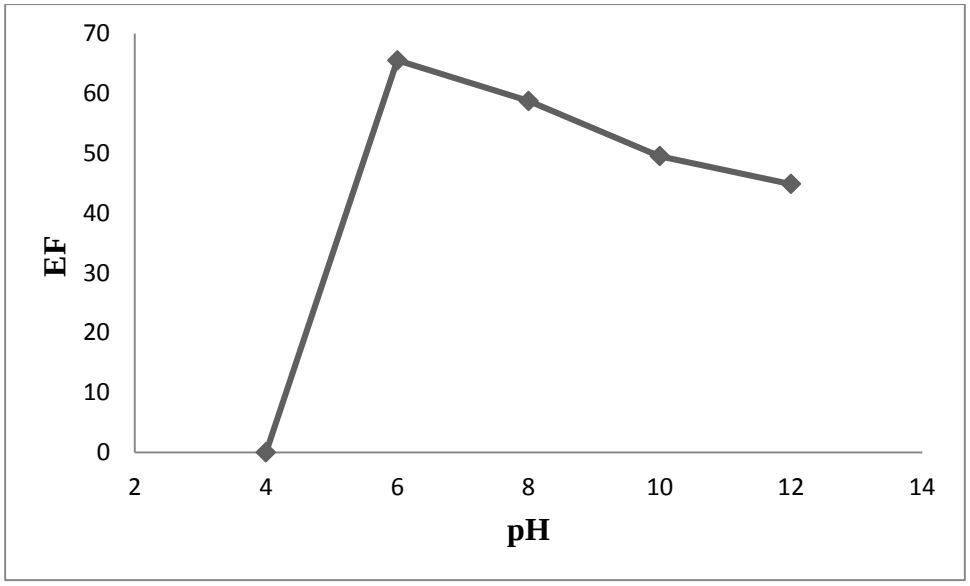


Figure 4.7 Extraction time optimization of (A) dispersive SPE and (B) co-precipitation extraction. The Conditions: 50 µg/L perchlorate spiked solution; sample volume, 10 mL.

4.4.3 Extraction pH

The pH effect on the extraction was investigated. Different pH were applied from 4-12 (dispersive SPE: 4−12; co-precipitation: 8−12). All these are demonstrated in Figure 4.4.3, at a pH value 6, by increasing of the pH the extraction was enhanced, probably due to two factors: (1) the enhancement of the analytes ionizations and (2) the solubility of (LDH) in strong acidic media. When pH was >6 EF values showed a drop. This can be due to the increase of concentration of competing hydroxide anions. Meanwhile, since the pH corresponded to the pH pzc (where pzc is the point of zero charge of surface) of LDH, the decrease of surface positive charge reduced the interaction between analytes and LDH [75]. To get high enrichment factors, a pH of 6 was selected to be optimum in dispersive SPE. For the co-precipitation method, since (LDH) can only precipitate in basic solution, the study of pH influence started from pH of 8. Figure 4.4.3 shows that EF values also decreased with the increase in pH. The explanation of that there was competition from hydroxide ions. After all these observations, a pH of 8 was adopted as most favorable in co-precipitation extraction.

(A)



(B)

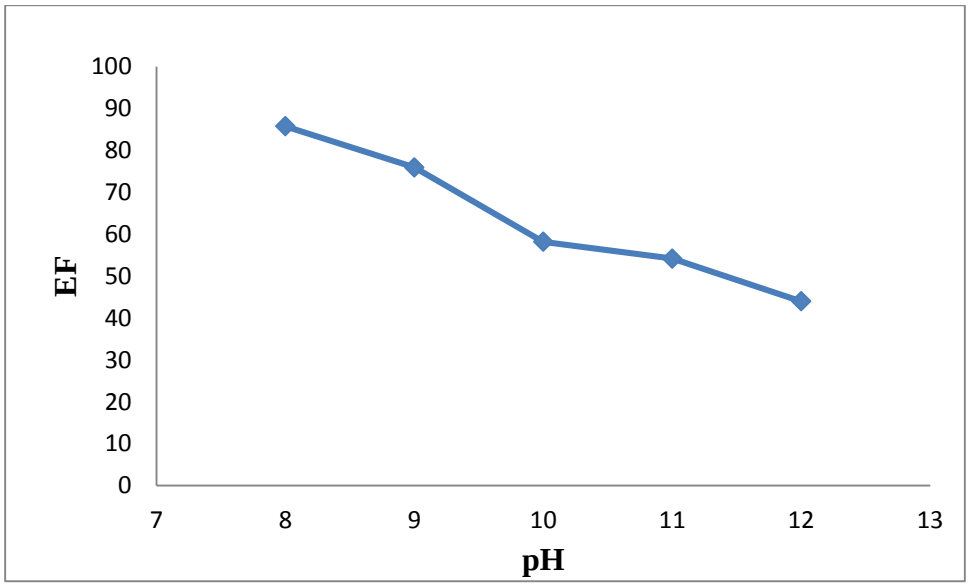


Figure 4.8 Extraction pH optimization of (A) dispersive SPE and (B) co-precipitation extraction. The pH values from 4 to 6 were adjusted with minimum volumes of 0.25 mol L^{-1} HCl solution, and from 8 to 12 with minimum volumes of 0.25 mol L^{-1} NaOH solution. The Conditions: 50 µg/L perchlorate spiked solution; sample volume, 10 mL.

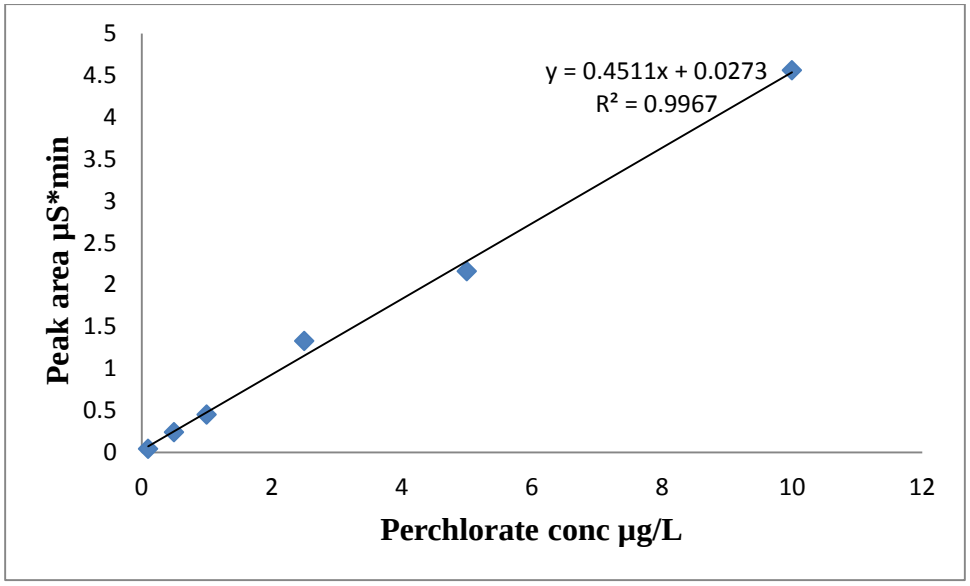
4.4.4 Method evaluation

To measure the effectiveness using LDH-NO_3 for both methods, linearity, quantitative parameters like limits of detection (LOD), and limits of quantitation (LOQ) were calculated. The limit of detection (LOD) for the perchlorate ion was determined on the basis of a signal/noise ratio (S/N) of 3 while LOQ was obtained on a signal/noise (S/N) ratio of 10.The two methods showed good linearity of the calibration plots. (RSD %) was calculated at 10 μg/L spike sample of perchlorate to assess the precision of the method.

Method	Linearity (μg/L)	coefficient of determination (r^2)	LOD (μg/L)	LOQ (μg/L)	RSD% (n=3)
Dispersive SPE	0.1-10	0.9967	0.061	0.203	0.92
Co-precipitation Extraction	0.1-10	0.9915	0.044	0.146	0.68

Table 4.1 Quantitative parameters of both dispersive SPE and co-precipitation extraction methods for perchlorate.

(A)



(B)

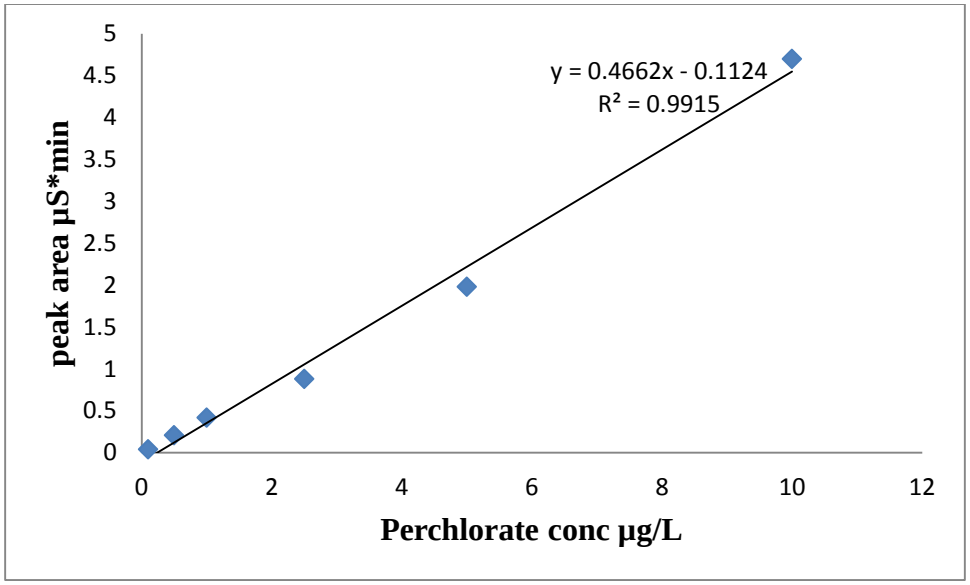


Figure 4.9 Calibration curve for perchlorate extraction by LDH-NO_3 (A) dispersive SPE and (B) co-precipitation extraction.

4.5 Real sea water sample Analysis

To estimate how these methods are applicable, the analysis of available water samples containing perchlorate was conducted. Perchlorate was detected with different concentrations from different locations.

Method	Location	Non spiked concentration(µg/L) (n=3)	Spiked 5 µg/L	
			Mean recovery% (n=3)	RSD% (n=3)
Dispersive SPE	Location1	2.86±0.09	91.2	2.9
	Location2	2.35±0.19	102.3	5.2
	Location3	2.33±0.17	89.5	6.1
	Location4	1.91±0.13	97.0	3.3
	Location5	0.66±0.03	93.1	2.0
Co-precipitation extraction	Location1	3.11±0.12	93	5.8
	Location2	2.27±0.17	99.8	1.7
	Location3	2.41±0.15	86	3.4
	Location4	2.17±0.07	92.6	2.2
	Location5	0.95±0.09	89.8	4.6

Table 4.2 Real sea water sample Analysis by both dispersive SPE and co-precipitation extraction of perchlorate anion.

Part II: biosynthesized silver nanoparticles coated EME of perchlorate from seafood samples

4.6 Characterization of AgNPs

The figure below is showing SEM images of AgNPs. SEM provided further insight into the morphology and size details of the biosynthesized AgNPs. The image shows that AgNPs are Colloids consist mainly of small nanoparticles having nearly spherical shape particles of size 7– 10 nm.

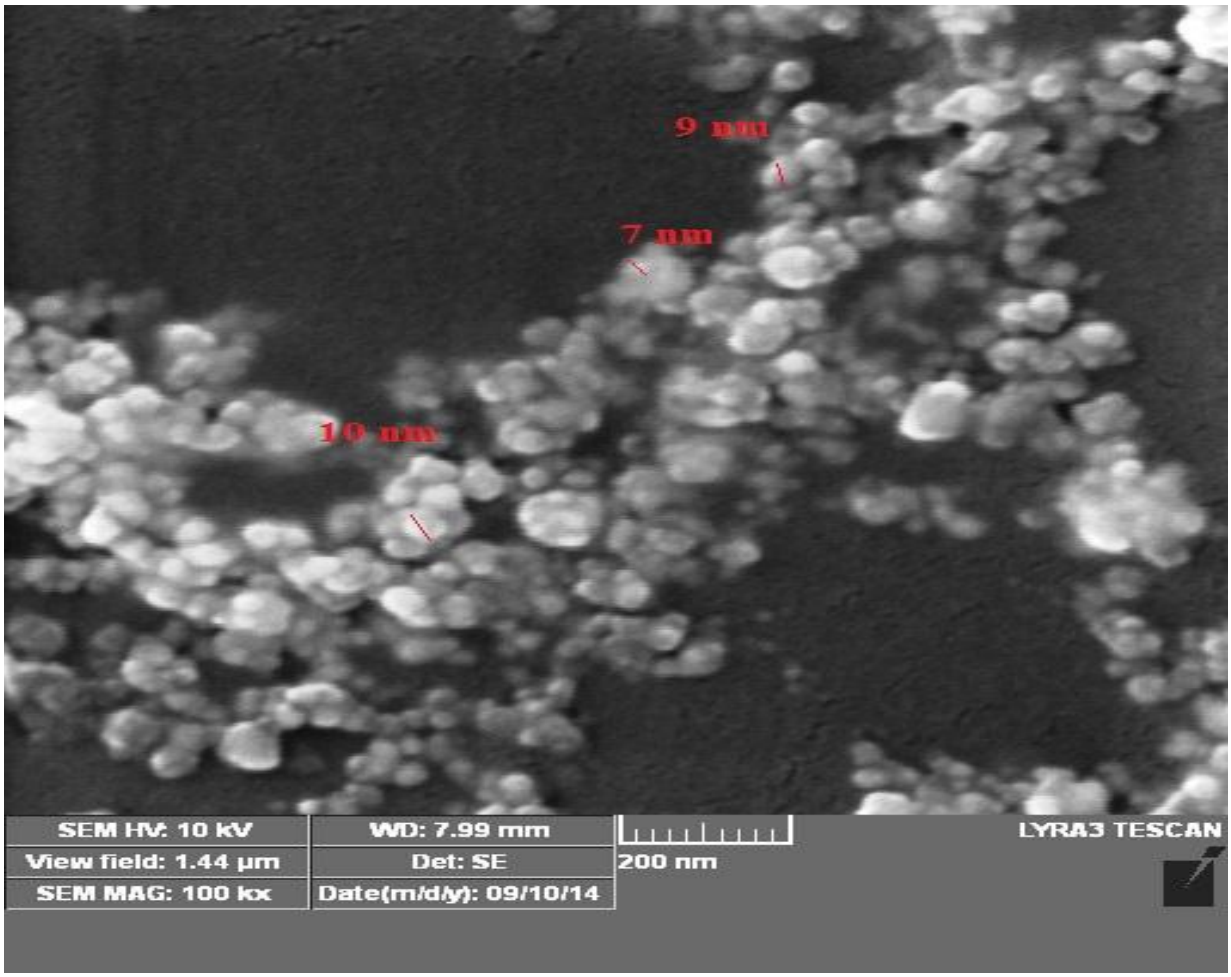
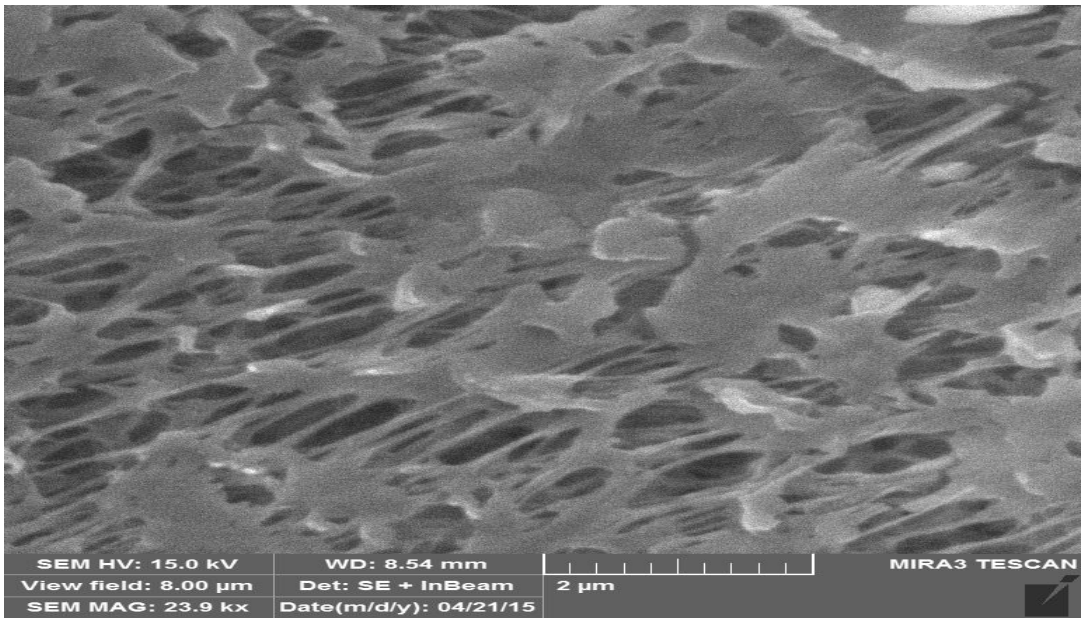


Figure 4.10 SEM image of the biosynthesized AgNPs.

4.7 Characterization of biosynthesized AgNPs coated membrane

The figure below shows the SEM images of the coated and uncoated polypropylene membrane with biosynthesized AgNPs. The first image shows our pure polypropylene membrane with pore size of about 0.2µm, where the second image reveals the successful dispersion of AgNPs within the polypropylene hollow fiber.

(a)



(b)

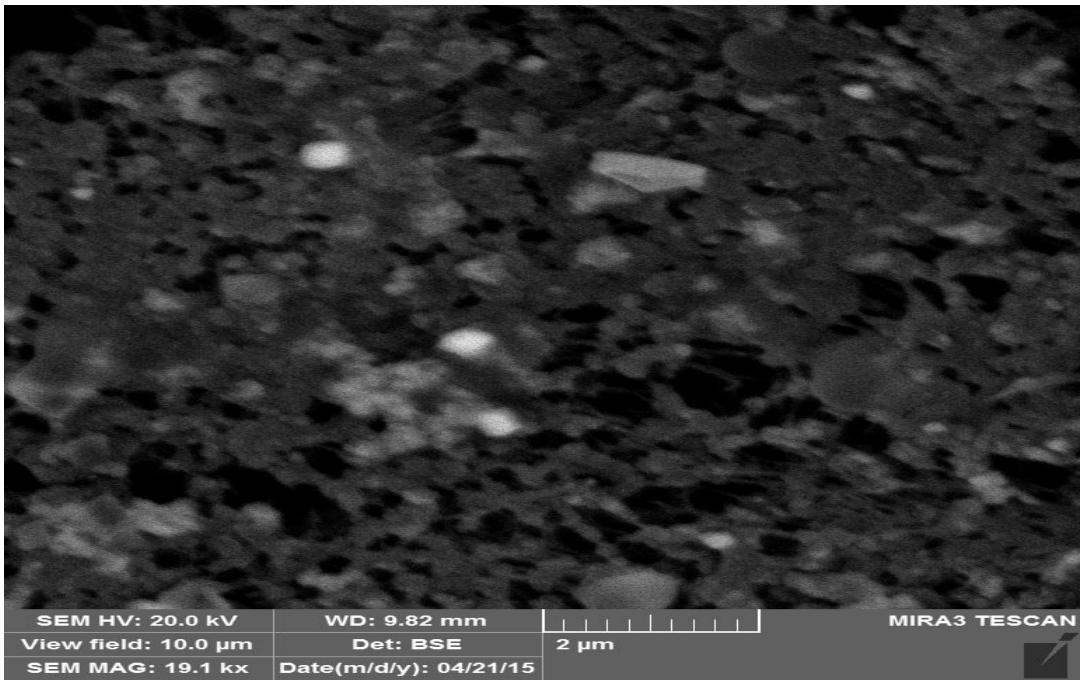


Figure 4.11 SEM images of (a) uncoated and (b) biosynthesized AgNPs coated membrane.

4.8 Biosynthesized silver nanoparticles coated EME method optimization

4.8.1 Extraction Time

The short extraction time is one of the major attribute of EME. In this study, the effect of extraction time (from 5 to 20 min) was investigated. Fig4.8.1 shows the change in trend of the peak area with the extraction time. EME is a charge driven extraction and as such was demonstrated to offer fast extractions in relation to liquid phase microextraction [76]. Initially, the peak area dramatically increased when the extraction time was increased from 5 to 10 min, then reached its maximum at 10 min. Then, it shows a very little increase with the continued increase in time. At this time, the system might have entered a steady state condition resulting in minimal gain in transfer. A similar trend has been observed in the previous research reports [77]. As a result min extraction time was adopted for further experiments.

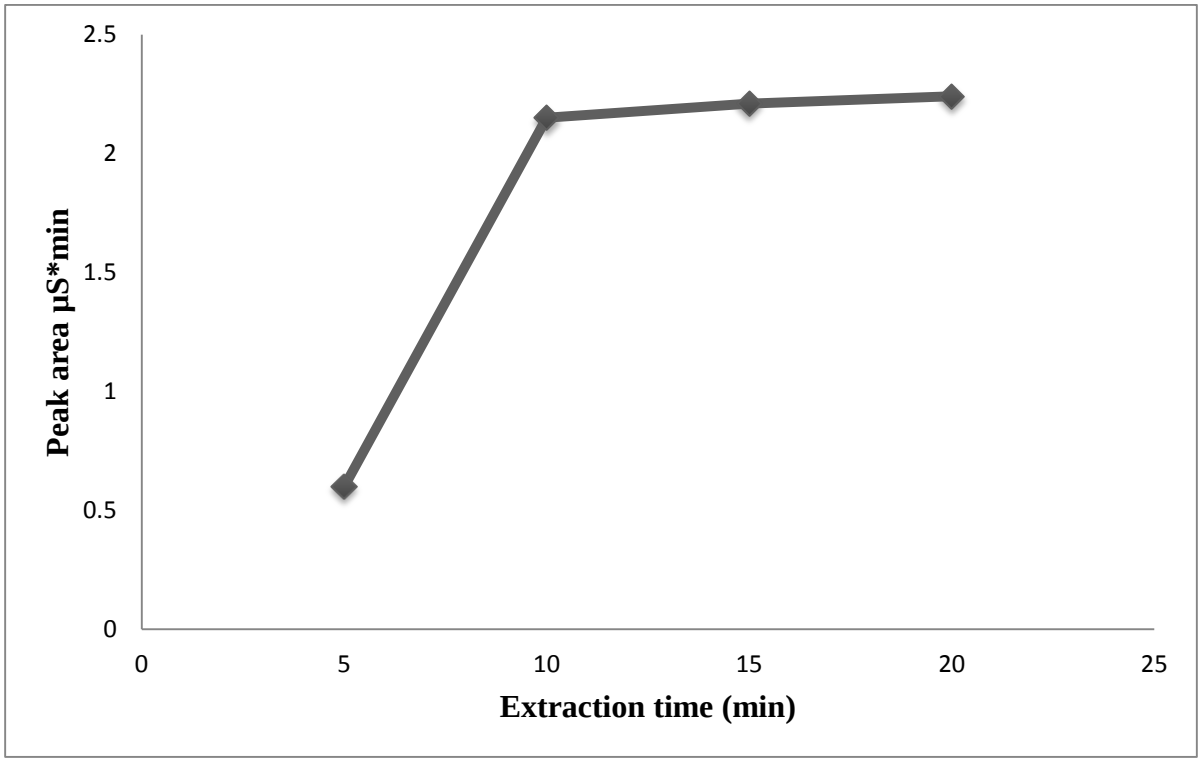


Figure 4.12 Extraction time optimization of biosynthesized silver nanoparticles coated EME.

4.8.2 Voltage optimization

The biosynthesized silver nanoparticles coated EME system was evaluated at potentials ranging from 0 to 40 V for 10 minutes as shown in Fig4.8.2 the peak area is increased as the voltage was increased from 0 to 20 V. As the voltage was further increased beyond 20 V, a decrease in the peak area was then observed. The results show that a lower voltage can provide higher peak areas. Precisely, the explanation for this observation is that the entire EME setup is an electric circuit, in which the SLM acts as an electric resistance and the charged analytes follow the path of the electric current. This current must therefore be kept small to prevent electrolysis that would otherwise affect the mass transfer and reduce ClO_4^- peak areas. Constant stirring of the donor solution ensures efficient replenishment and transfer of the ions into the acceptor phase. Voltages higher than 20 V generated current flow fluctuations. As a result, excessive bubble formation was witnessed at the electrodes, though this was not investigated. 20 V was selected for subsequent experiments.

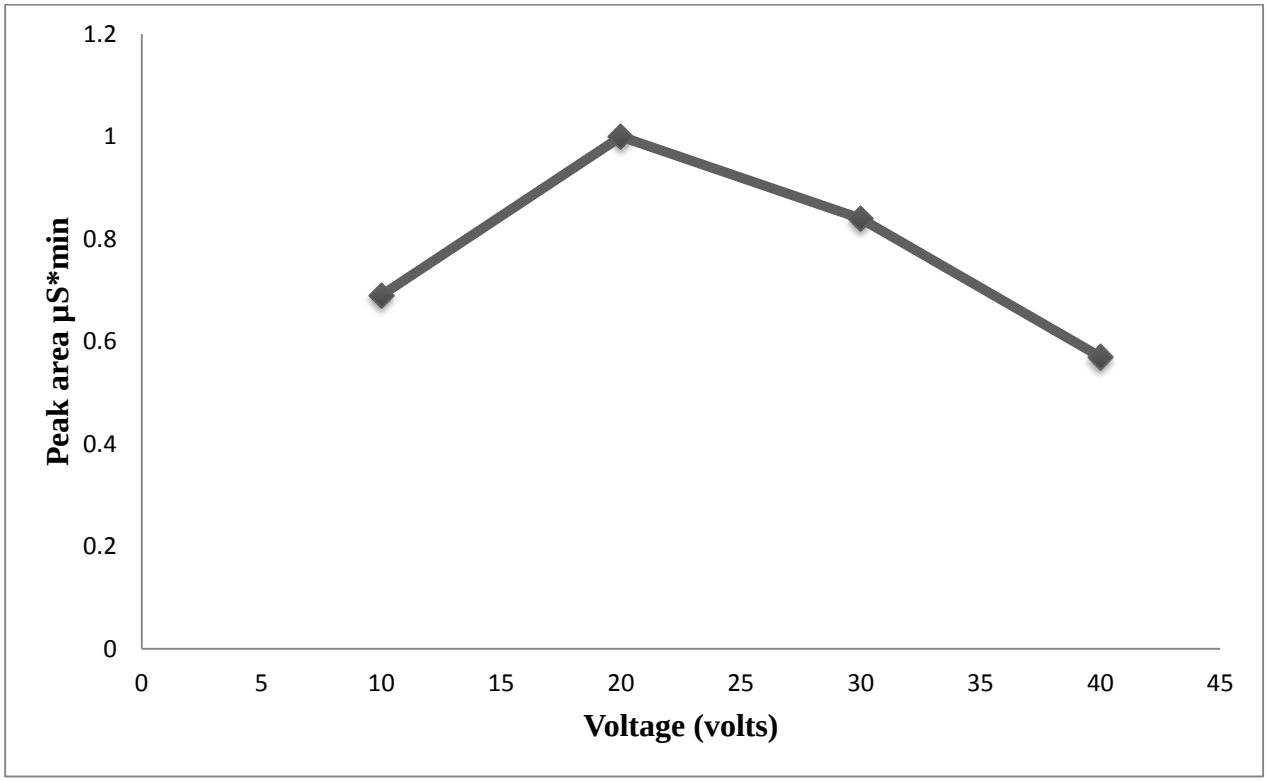


Figure 4.13 Extraction Voltage optimization of biosynthesized silver nanoparticles coated EME.

4.8.3 Method Evaluation

To assess the suitability and practicability of the developed biosynthesized silver nanoparticles coated EME method, parameters such as linearity, repeatability, limits of detection and quantification were investigated. The linearity of this method was evaluated at five spiking concentration levels ranging from 0.1 to 3 μg/g. Good linearity with coefficient of determination (r^2) of ≥0.991 was observed. Satisfactory reproducibility of relative standard deviations (RSD) 4.1% (n = 3) was obtained. The limit of detection (LOD) for the perchlorate ion was determined on the basis of a signal/noise ratio (S/N) of 3 and was found to be 0.04 μg/g while LOQ value of 0.1225 μg/g was obtained on a signal/noise (S/N) ratio of 10. The enrichment factor (EF) is obtained from the highest spiked concentration and its' value is 12.33. To evaluate the accuracy of the proposed method, the extraction recoveries were performed on ten seafood samples spiked with perchlorate standard at 3μg/g concentration and the results are shown in table 4.8.3.

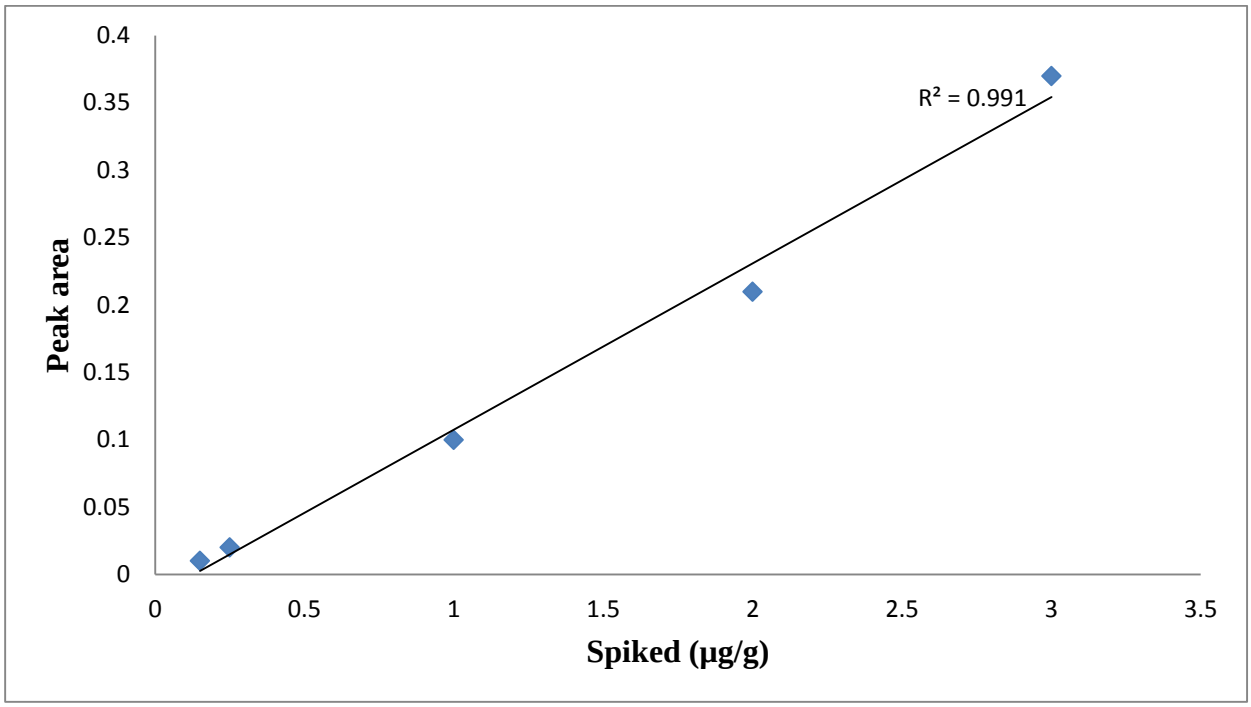


Figure 4.14 Extraction calibration curve of biosynthesized silver nanoparticles coated EME.

Fish name	Location	Mean Recovery % (n=3)	RSD% (n=3)
Tuna	Jeddah	93.8	2.6
Morgan	Jeddah	87.2	3.2
Mousa	Jeddah	103.4	2.7
Sardines	Riadh	106.2	1.1
Faskar	Riadh	90.7	0.9
Kumal	Riadh	94.1	3.5
Rabeeb	Jubail	100.9	1.9
Shiriwa	Jubail	96.2	2.5
Boori	Al-Hassa	95.9	3.7
Tamara	Al-Hassa	102	0.8

Table 4.3 Ten different spiked fish samples and their mean recovery percentages with the relative standard deviation percentage.

4.9 Extraction enhancement with AgNPs coating

The improvement of extractability is noted within the comparison of the peaks before and after AgNPs membrane coating when a spiked concentration of 5ppm of perchlorate is used for extraction enhancement check. The figure below shows enhancement of the peak area by 32.82%.

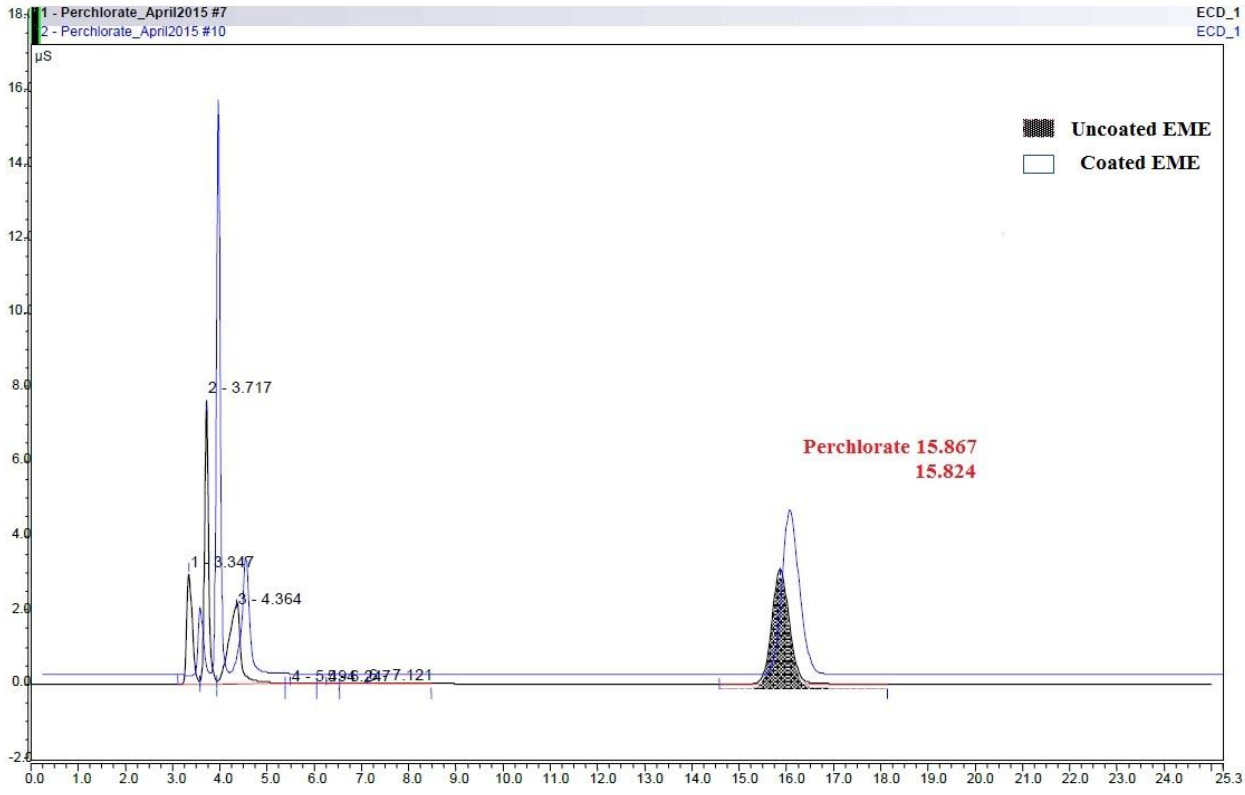


Figure 4.15 Chromatogram show the extraction enhancement by coated EME.

4.10 biosynthesized AgNPs coated membrane reusability

The reusability of the coated membrane was studied and the results in figure 4.10 indicate the validity of the coated membrane for more than one cycle of extraction.

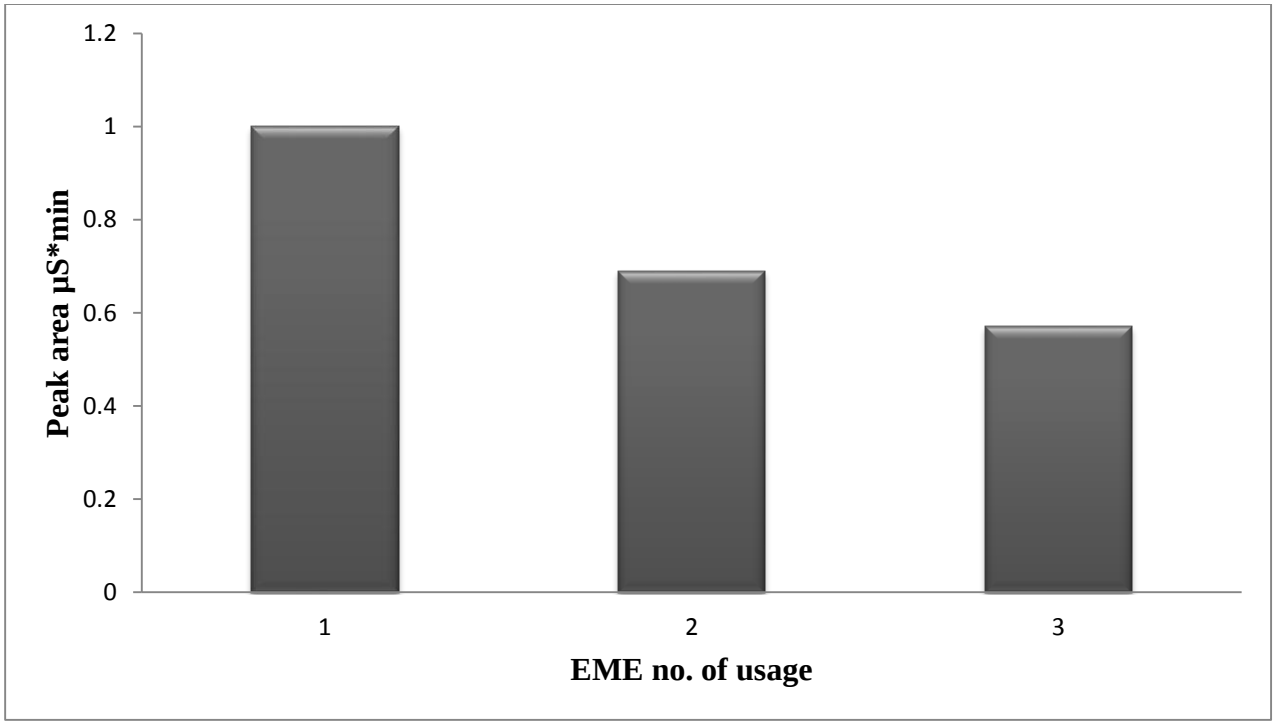


Figure 4.16 The reusability of biosynthesized silver nanoparticles coated EME.

4.11 Real sea food sample analysis

Different seafood samples which collected from different locations are listed with their names and abbreviations in the tables 4.11(a, b, c and d). Perchlorate concentrations were calculated after extraction process with coated EME with the utilization of the previous calibration curve.

Fish name	Location	Fish name	Perchlorate conc. µg/g
Shrimps	Jeddah	J-1	0.47±0.02
Parrot fish	Jeddah	J-2	2.35±0.21
Boori	Jeddah	J-3	1.12±0.13
Hamoor(spotted grouper) fish	Jeddah	J-4	1.07±0.05
Shaoor	Jeddah	J-5	0.62±0.01
Morgan (bream fish)	Jeddah	J-6	0.19±0.02
Harid	Jeddah	J-7	0.31±0.03
Tuna	Jeddah	J-8	2.96±0.22
Najel (Saddle Grouper	Jeddah	J-9	0.44±0.03
Sultan Ibrahim(Striped red mullet)	Jeddah	J-10	0.66±0.06
Biad(Jack fish)	Jeddah	J-11	2.23±0.21
Badah fish	Jeddah	J-12	1.42±0.04
Mousa(Sole fish)	Jeddah	J-13	0.70±0.03

Table 4.4 Fish samples from Jeddah and their perchlorate concentration in µg/g.

J-1 **J-2** **J-3**

J-4 **J-5** **J-6**

J-7 **J-8** **J-9**

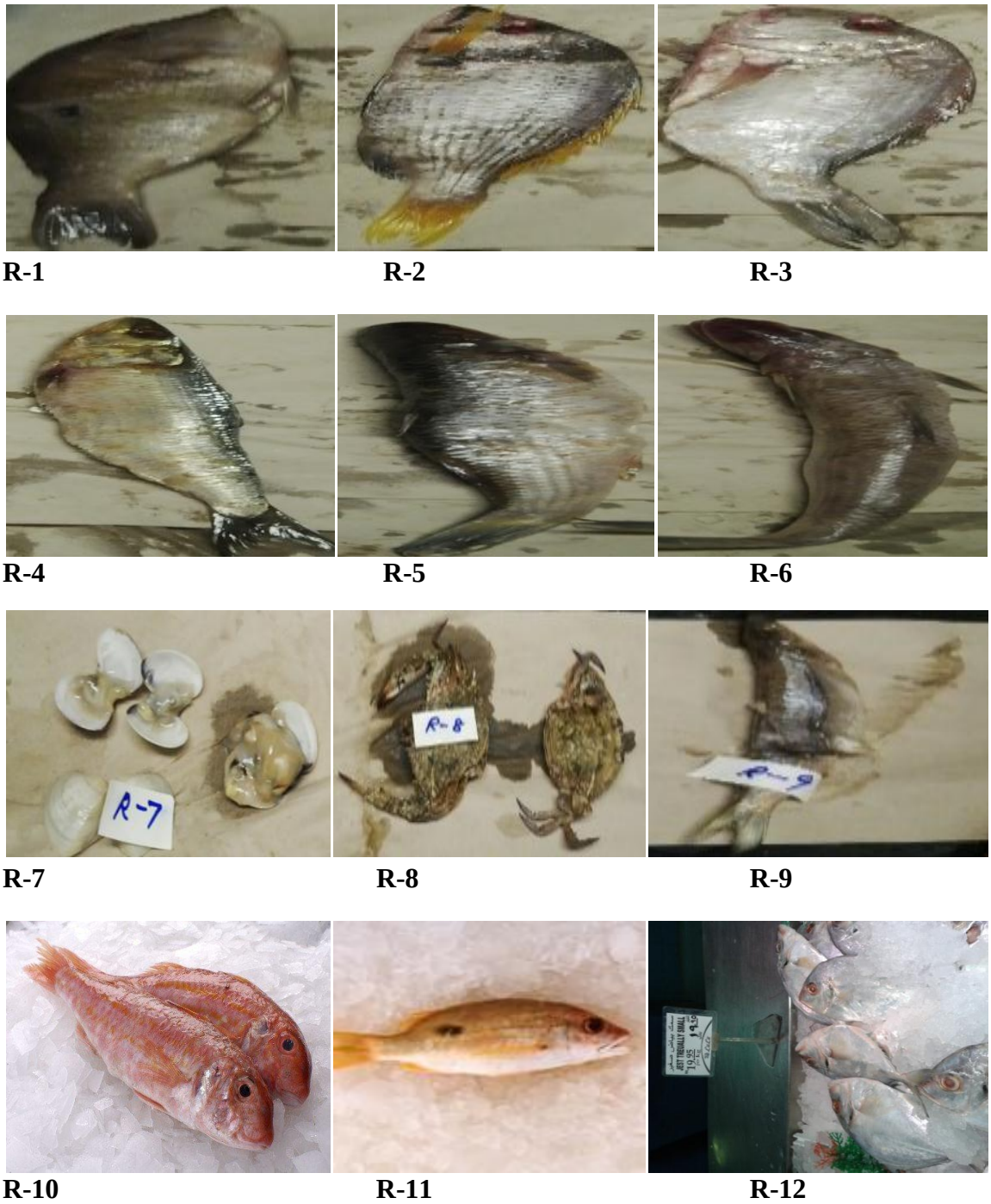
J-10 **J-11** **J-12**

J-13

Figure 4.17 Fish images of fish samples from Jeddah area.

Fish name	Location	Fish	Perchlorate conc. µg/g
Sal/gahash	Riyadh	R-1	0.13±0.03
Faskar	Riyadh	R-2	0.16±0.05
Thallah	Riyadh	R-3	0.21±0.08
Sardines	Riyadh	R-4	0.15±0.04
Ooma/alfa	Riyadh	R-5	0.53±0.03
Kumal/chimkhen	Riyadh	R-6	0.92±0.04
Clams	Riyadh	R-7	0.19±0.01
Gabgoob	Riyadh	R-8	0.20±0.04
Barriya	Riyadh	R-9	0.14±0.06
Sultan Ibrahim(Striped red mullet)	Riyadh	R-10	2.17±0.15
Naiser	Riyadh	R-11	0.95±0.06
Jest Trevally small	Riyadh	R-12	0.50±0.03

Table 4.5 Fish samples from Riadh and their perchlorate concentration in µg/g.



R-1 **R-2** **R-3**

R-4 **R-5** **R-6**

R-7 **R-8** **R-9**

R-10 **R-11** **R-12**

Figure 4.18 Fish images of fish samples from Riyadh area.

Fish name	Location	Fish	Perchlorate conc. µg/g
Hammour	Jubail	JU-1	1.00±0.10
Tamrah / biah	Jubail	JU-2	0.82±0.04
Faskar	Jubail	JU-3	0.15±0.06
Al sibin	Jubail	JU-4	0.37±0.02
Hamam	Jubail	JU-5	0.76±0.02
Sultan Ibrahim	Jubail	JU-6	1.92±0.07
Faskar	Jubail	JU-7	2.38±0.26
Anthallah	Jubail	JU-8	1.84±0.13
Rabeeb	Jubail	JU-9	0.93±0.14
Shiriwa	Jubail	JU-10	0.71±0.03

Table 4.6 Fish samples from Jubail and their perchlorate concentration in µg/g.

JU-1 **JU-2** **JU-3**

JU-4 **JU-5** **JU-6**

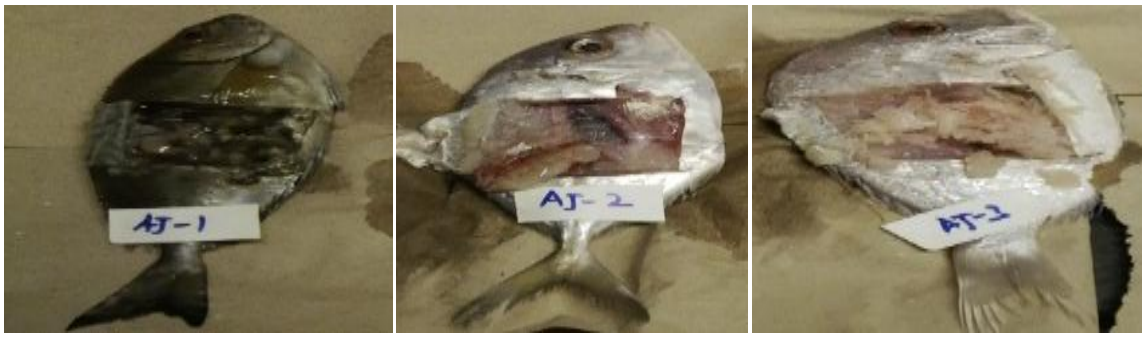
JU-7 **JU-8** **JU-9**

JU-10

Figure 4.19 Fish images of fish samples from Jubail area.

Fish name	Location	Fish	Perchlorate conc. µg/g
Shiriwa	Al-Hassa	AJ-1	0.13± 0.04
Antallah	Al-Hassa	AJ-2	0.65±0.03
Tallah	Al-Hassa	AJ-3	0.46±0.12
Faskar	Al-Hassa	AJ-4	0.15±0.02
Sarah/naisarah	Al-Hassa	AJ-5	0.24±0.06
Boori/bolty	Al-Hassa	AJ-6	0.21±0.05
Tamarah/biah	Al-Hassa	AJ-7	0.45±0.08
Sultan Ibrahim	Al-Hassa	AJ-8	0.19±0.02
Shaour	Al-Hassa	AJ-9	0.17±0.06

Table 4.7 Fish samples from Al-Hassa and their perchlorate concentration in µg/g.



AJ-1 **AJ-2** **AJ-3**

AJ-4 **AJ-5** **AJ-6**

AJ-7 **AJ-8** **AJ-9**

Figure 4.20 Fish images of fish samples from Al-Hassa area.

4.12 Discussions

Perchlorate ion (CIO^{-4}) which obtained from different perchlorate salts has been produced since the 1950s in various locations for the production of rocket fuel, fireworks and missiles. The concern of perchlorate as a thyroid disrupter is risen after detection of perchlorate in ground and surface water. The United States Environmental Protection Agency (USEPA) assigned perchlorate to the contaminant candidate list. Because of the high solubility of these compounds in water, once released to aqueous systems they can readily dissociate producing perchlorate anion.

The developed LDHs methods proved an applicable method which was utilized to effectively inspect perchlorate in sea waters. The selectivity and efficacy of various parameters that could have impact on the usage of the LDHs were estimated by studying and compromising different measurable factors as expressed in the previous results, when sorbent sort, pH of extraction, extraction temperatures and times were achieved with successful optimization .Afterward real water from the red sea and the gulf is analyzed after collection from different locations in the kingdom of Saudi Arabia. The detected concentration pictured that perchlorate contamination still exists and the highest amount of 3.11± 0.12µg/L were noted at Jeddah site, while lowest concentration was 0.66±0.03 µg/L near Dammam beach. The detection and quantitative measurment of perchlorate target analyte in the area of study was achieved.

A considerable existence of perchlorate could be seen in the area of study which shows most likely pollution by such kind of contaminants.

44 samples of sea food from different locations were analysed successfully detecting perchlorate in it. Sample Tuna from Jeddah region having a concentration of 2.96±0.22 µg/g marked is the highest one while the lowest concentration detected for Sal/gahash sample in Riyadh region with a concentration of 0.13±0.03 µg/g.

The complete picture comparison of perchlorate concentration showed Jeddah region has high concentration levels in comparison with other regions. The detected amounts are seem to be relatively high and perchlorate bioaccumulation in the tissue and body of sea foods shine the lights on its long term impact to human health and environment.

CHAPTER 5

CONCLUSION & RECOMENDATIONS

5.1 Conclusion

To monitor the widespread distribution of perchlorate in water and sea food samples, this necessitates the availability of rapid, effective and powerful analytical techniques. The awareness of contamination by perchlorate in water from different sites also has a significant role in the determination and monitoring the extent of contamination. The developed analytical methods for determination of perchlorate shows the efficient utilization of attainable chemicals and materials to construct a well-baved way of determination reducing the time and cost. The LDHs and biosynthesized EME methodologies are capable of performing rapid separation.

The differentiation between the uninteresting conventional methods and our developed methods explained that they produced better results, however the classical methods seem to be difficult and generating high amount of organic solvent.

The significant concentrations of perchlorate reported in this study are potential threats to the local community and ecosystems in proximity including the aquatic life. This perchlorate can be drained from areas of exposure into the nearby water bodies and reach the non-target organisms.

The problem might be intensified with the lack of education and awareness about the toxic effect of perchlorate exposure in the studied areas. Additionally, the ability of perchlorate to undergo long-range global transport poses an international concern about the residue detected at any corner of the globe.

The presence and detection of the target analyte perchlorate in the samples of sea foods signifies the danger and potential threat of perchlorate to the human consumption and subsequent bioaccumulation in the body.

5.2 Recommendations

Recommendation1

We recommend checking more LDHs as they prove their ability in perchlorate extraction. Furthermore the significant need for EME as a powerful technique keeps us recommends tracking more enhancement manipulations.

Recommendation 2

We also recommend the continuous monitoring of both water and sea food for a deliberate detection of any threats of contamination.

Recommendation 3

One of the goals of developing these methods was to inspire developing countries in monitoring and surveillance of their local contamination levels. Cost, time and environment were taken into consideration when the goals achieved. For these significant reasons we recommend using the developed methods.

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