REMOVAL OF LEAD FROM SOLUTION BY USING LOW COST ADSORBENTS FROM APIACEAE FAMILY

BY

WEETARA BOONTHAM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF
ENGINEERING (ENGINEERING TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
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A Thesis Presented

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Submitted to
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Abstract

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Access to clean and safe drinking water is basic right of human. Water contamination by heavy metals such as lead, arsenic, mercury, aluminum, zinc, chromium and iron is a major environmental problem due to their acute toxicity and their accumulation in food chains. One of such toxic heavy metals is lead, which can occur naturally or manufacture from industries such as storage batteries, radiators and solder for joints. World Health Organization (WHO) suggests that the tolerance limit of lead concentration in drinking water is 0.01 mg/l and not over than 0.05 mg/l by Thailand Pollution Control Department (PCD) and the limit of discharge wastewater for lead in Thailand is 0.2 mg/l. Therefore, this research work has been carried out on the feasibility of three low cost adsorbents for the removal of lead from contaminated water. This thesis organized results of the laboratory based studies on lead removal in synthetic water. Plants from Apiaceae family namely parsley, coriander and culantro were selected as low cost adsorbents for the lead adsorptions experiments, and their efficiency was compared with the other studies.

Physical and chemical characterization of selected adsorbents were carried out by Brunauer–Emmett–Teller (BET) in order to define the BET surface area, pore volume and average pore size, scanning electron microscope (SEM) for exploring the surface morphological and shape of external cell wall, Fourier Transform Infrared (FTIR) for surface functional groups analysis and Cation Exchange Capacity (CEC) for determine the number of exchangeable cations that adsorbents are capable of holding.

The influence of various parameters like adsorbent dose, pH, agitation speed, contact time and initial lead concentration was investigated by a series of batch experiments at 25 ± 3 °C. The percentage removal of lead was found to increase with the increasing dose of adsorbents, agitation speed and time for 10 mg/l initial Pb (II) concentration, whereas the percentage removal of lead was found to decrease with the increase in pH value greater than 4 and lead concentration. Although, it seems that all of parameters affected to the adsorption process, the noticeable parameters are dosage, pH and initial lead concentration. Contact time and agitation speed did not influence much. The maximum lead uptake was found to be 96.61%, 95.95% and 96.55% by parsley, coriander and culantro, respectively.

The equilibrium adsorption data after the experiments were designed with appropriate isotherms and kinetic models. The equilibrium data were well described for parsley and coriander by the Langmuir isotherm model, suggesting that the adsorption of Pb(II) onto these adsorbents is a mono-layer process and the adsorption behavior is homogeneous rather than heterogeneous for culantro data fitted well to Freundlich isotherm model indicating heterogeneous in the system. Kinetics data were best fitted by the pseudo second-order model for all of selected adsorbents, indicating that the adsorption process is chemisorption.

Moreover, the tea bags were used in the final stage of the experiment. It was found that at neutral of pH and without centrifuge under various contact time with 1 mg/l lead initial concentrations, the lead removal efficiency was found greater than 85% for 12 hrs. contact time and at this suitable time, it found that concentration of lead remaining in synthetic wastewater reached Thailand’s wastewater quality standard. Therefore, three selected adsorbents from Apiaceae family can be used as low cost adsorbents with high efficiency for removing lead at low concentration from wastewater because it can prepare without chemical and physical treatments.

Keywords: Lead, Adsorption, Low-cost adsorbents, Isotherms, Kinetics

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I gratefully acknowledge the support of Thailand Advanced Institute of Science and Technology and Tokyo Institute of Technology (TAIST-Tokyo Tech) and Sirindhorn International Institute of Technology, Thammasat University, Thailand for funding this study.

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Table of Contents

List of Tables

List of Figures

Chapter 1
Introduction

1.1 Problem Statement

Accessibility to safe and clean available water is considerable for public health. General Assembly of United Nations (UN) in 2010 clearly acknowledged that everyone has the right to adequate, continuous, safe, acceptable, physically accessible and affordable water both for personal and domestic use. Contaminated water risks both the physical and social health of all people. It is not only demolished to environment, but it also can pose a severe effect on the human health.

Lead is in a group IV element on the periodic table which is notably highly resistant to corrosion in most acid and naturally occur as element buried in the earth crust in insoluble and biologically inoffensive forms. Lead is also naturally present in soils and atmosphere. The important cause of soil lead contamination in inhabited areas where is the weathering, chipping, scraping, sanding, and sand-blasting of structures bearing lead-based paint whereas major sources of lead in the air are ore, metals processing and piston-engine aircraft operating on leaded aviation fuel. Other sources are waste incinerators, utilities, and lead-acid battery manufacturers. The highest air concentrations of lead are usually found close to lead smelters. Lead hazards can be found in homes such as household furniture, painted toys, lead pipes or pipes connected with lead solder which water supply can contaminated.

Lead exposure is recognized as a major risk factor for several human diseases such as anemia, kidney malfunction and brain tissue damage once it goes above the World Health Organization (WHO) maximum admissible limit 0.01 mg/l in drinking water and the limit of discharge wastewater for lead in Thailand is 0.2 mg/l by Thailand Pollution Control Department (PCD). Hence, it must be eliminated as much as possible from effluents to protect environmental hazard from its discharge. According to the severe environmental protection legislation and public environmental concerns of lead and other toxic heavy metals like zinc, cadmium, nickel, chromium, silver, copper and arsenic, these heavy metals can be removed from wastewater by conventional techniques such as chemical precipitation, membrane filtration, reverse osmosis, electro-coagulation, chelation and ion exchange. However, these methods are often inefficient and/or very expensive for low concentrations of metals. Therefore, cheaper metal removal from aqueous technology solutions has recently been sought out. One of these technologies is adsorption.

Adsorption process is preferred due to its efficiency of removal from dilute solutions. The most popular adsorbents for heavy metal removal from aqueous solutions are zeolites, activated carbon, silica gel and chitosan. Although the use of commercially available adsorbents are still very widespread, but these materials are very expensive. Recently, biosorption of contaminants by sorbents of natural origin has gained important reliability because of its good capability and low cost of these complexing materials. Due to high uptake capacity and very cost effective source of raw materials, biosorption is a progression towards a perspective method. The potential advantages of use of low cost adsorbents are: 1. Abundant availability, 2. Low cost, 3. Good adsorption capacity. 4 Easy for chemical modification 5. Easy renewal and 6. Less disposal problem after adsorption.

In the present study, parsley (*Petroselinum crispum*), coriander (*Coriandrum sativum*), and culantro (*Eryngium foetidum*) plants from Apiaceae family were employed to investigate the biosorption of lead(II) from aqueous solution. Effect of different parameters such as dosage, pH, contact time, agitation speed and initial concentration on the lead removal process are studied. The experimental data obtained have been evaluated and fitted using adsorption isotherms and kinetic models.

1.2 Research Objectives

The main objective of the present study is to evaluate of adsorption capacities of three different adsorbents, namely, parsley, coriander and culantro in the removal of lead ions in batch systems. In order to accomplish this objective, the following investigations are carried out:

1.2.1 To explore adsorbents of biogenic origin for the removal of lead from contaminated water and to investigate their adsorption capacities.

1.2.2 To compare the efficiency of selected adsorbents with other low cost adsorbents.

1.2.3 To investigate the effect of different experimental parameters on the lead adsorption process.

1.2.4 To fit the experimental result with suitable isotherm models and investigate the adsorption mechanisms using appropriate kinetic models.

1.3 Scope of Research

The adsorption characteristics of Apiaceae family are studied with respect to lead removal from the prepared synthetic water. The scope of this study is briefly summarized under the following points.

1.3.1 Plants from Apiaceae family (parsley, coriander and culantro) were bought from the local vegetable market Talad Thai, Pathum Thani, Thailand.

1.3.2 Adsorbents were characterized in detail using the techniques like BET for surface analysis, Fourier transform Infrared Spectroscopy (FTIR) analysis for functional groups identification, Scanning Electron Microscope (SEM) to find textural properties of the selected adsorbents and Cation Exchange Capacity (CEC) to define the total amount of exchangeable cation.

1.3.3 The optimum condition required to achieve maximum removal efficiency were determined by investigating the effect of dosage, pH, contact time, agitation speed and initial concentration using synthetic wastewater in batch studies.

1.3.4 Both Langmuir and Freundlich adsorption isotherms studies were used to understand the adsorption process, and to calculate adsorption capacities of the respective adsorbents.

1.3.5 Evaluate the adsorption kinetic process of adsorbents by using pseudo-first order and pseudo-second order reaction models.

Chapter 2
Literature Review

2.1 Lead

Lead is a metal that pertain to the group IV elements and period 6 of the periodic table. Its atomic number is 82, atomic mass 207.2, density 11.4 g/cm^3, melting point 327.4 °C and boiling point 1725 °C. It is a physically occurring; bluish-gray metal usually found as a mineral contaminated with other elements such as oxygen or sulphur [1]. Lead is used in industries such as printing, storage-battery manufacture, pigment manufacturing, fuel combustion, petrochemicals and photographic materials. The present annual worldwide production of Pb(II) is about 5.4 million tons and continues to manufacturing of batteries (automobile batteries, in particular), while the remainder is used in the production of solder, pigments, gasoline additive, glazes, plastics, ammunition, cable sheathing, weights and a variety of other products [2].

It is a highly toxic metal and has the potentiality to accumulate in living things organisms. Similarity in the human body, it can damage almost all tissues, especially the immune system and kidneys. Lead exposure in high levels from 100 - 200 g/day causes encephalopathy with the following symptoms: vertigo, insomnia, migraine, irritability, and even convulsions, seizures, and coma [1].

2.1.1 Sources and Environmental Levels

Lead is one of the most plenty heavy metals and its toxic effects create environmental problems because of its durability in contaminated site and complexity of mechanism in biological toxicity. The following article focuses on the effect of lead on different components of the environment like atmosphere, soil and water.

Lead in atmosphere

Lead is one of the most abundant dangerous heavy metals in the atmosphere. It remains in particulate matter in the atmosphere and is shipped to a great extent by air flow [3]. Lead is one of the most abundant dangerous. Around 98% of lead in the atmosphere comes from human activities. Lead can be present in outdoor and indoor air. Lead in outdoor air comes generally from industrial sources such as lead-acid battery manufacturers, waste incinerators, smelters and utilities). Wind-blown soil and road dust can compose naturally occurring lead same as lead from industrial sources like deteriorated paint, the combustion of leaded gasoline and aviation fuel. Sources of lead can occur both indoor air and outdoor air for example making stained glass objects by using lead solder and shooting using lead bullets at indoor firing ranges. Lead in dust and soil stay around for several years because it do not decay or decompose [4].

Lead in soil

Lead contaminant in soil is commonly on the surfaces of very fine clay and organic matter particles. Hence, when lead is combined to the soil surface, it tends to gather in the upper 1 - 2 inches of soil. Lead also will become most intensified in very fine soil particles, which tend to attach to human skin and garment and form airborne soil dust.

The availability of lead in soil depends on how solidly it is carried by soil particles and on its solubility. At low soil pH (acidic conditions), it is carried less tightly and it is more soluble. At high soil pH (neutral to basic conditions), it is carried more strongly, and its solubility is very low. Lead is carried very tightly by soil organic matter. Therefore, as lead availability decreases, organic matter increases.

Some lead added to soil may combine with other soil elements to form lead-containing minerals. One such mineral that has exceedingly low solubility is lead phosphate ($Pb_5(PO_4)_3Cl$) or pyromorphite. Formation of this mineral is favored by high pH soil, high levels of lead and phosphate. These conditions would occur with the appliance of ground agricultural limestone and large amounts of phosphate fertilizer to a lead-contaminated soil [5].

Lead in water

Lead has long been used in the solder and plumbing materials that can link with drinking water as it is transported from its origin into homes [6]. Lead is present in tap water from its dissolution from original sources. Lead can be found in Polyvinyl chloride (PVC) pipes and it can be leached and produce high lead concentrations present in drinking water. The amount of lead dissolved depends on various factors and including the presence of dissolved oxygen (DO) and chloride, temperature, pH, water softness and standing time of the water. Even though lead can be leached from lead piping exceedingly, it shows that the leaching of lead from soldered joints and brass taps decreases with time. The level of lead in drinking water may be decreased by measures of corrosion control such as the accretion of lime and pH adjustment in the distribution system from less than 7 – 8 or 9. Flaking lead carbonate deposits on lead pipe and iron sediment from old galvanized plumbing can also release and accumulated lead from lead sources such as plumbing and service connections, even when the water is no longer plumbosolvent [7].

Contamination of lead in ground and surface waters can occur naturally by storm water (normally slightly acidic) comes in touch with lead contaminated soil then the lead can be dissolved into the water and transported to close groundwater or surface water. If adequate lead is mobilized, environmental receptors can be affected and harmful to human health can occur if these sources are used for drinking water. Furthermore, contamination of lead in groundwater may also result from the dissolution of lead from earth crust, where it is usually present in a form of carbonate and hydroxide complex, with varying degree of solubility Contamination of lead in ground and surface waters can occur naturally by storm water (normally slightly acidic) comes in touch with lead contaminated soil then the lead can be dissolved into the water and transported to close groundwater or surface water. If adequate lead is mobilized, environmental receptors can be affected and harmful to human health can occur if these sources are used for drinking water. Furthermore, contamination of lead in groundwater may also result from the dissolution of lead from earth crust, where it is usually present in a form of carbonate and hydroxide complex, with varying degree of solubility [8].

Lead in food

There are several ways that lead can contaminate in foods. The most common way has been during the growth and development of plants grown in soil containing an extraordinarily high amount of lead. The plant surfaces become contaminated with soil or dust, or the plants may take up the lead from the soil as they mature. Container which contains lead can also release lead in foods – including any paint decorations or poorly burned ceramic coat.

Likewise, lead may be present in meat, as cattle may take in lead as they graze, feeding on grasses and plants which have grown in soils with unusually high in lead due to sump oil, paint chips, discarded paint tins, lead batteries, scrap lead, and a number of other items containing lead that are used for running a farm but not dispose safely.

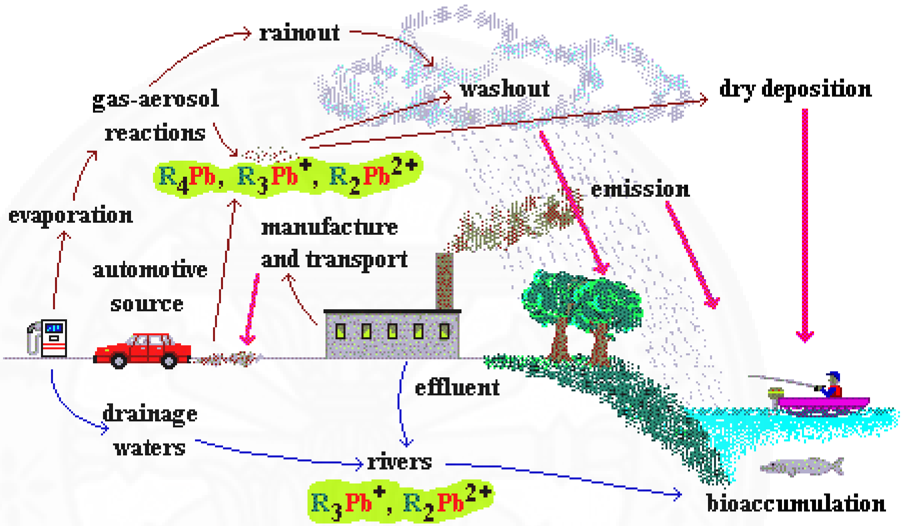


Figure 2.1 Environmental cycling of lead species [9]

2.1.2 Health Impacts of Lead

Lead can get into human body by two ways, first through inhaling it in or by consuming it. For example, lead can approach the body through eating or inhaling paint dust. Soil around house can carry lead from outside painting. Lead can also enter into drinking water through plumbing. Both adults and children are sensible to the effects of lead. Young children under five years old are specifically vulnerable, because their body, brain, and metabolism are still developing. Two years old are more likely to have the highest blood level concentration, because they can put many things into their mouth, including toys or other products that may contain lead.

Effects of lead in children

Lead exposure can have an extensive range of effects on a development and behavior of children. Blood lead levels lower than 10 μg/dL are connected with increased behavioral effects, delayed puberty, and decreases in hearing, cognitive performance, and postnatal growth or height. Some of these health effects are found even at low blood lead levels lower than 5 μg/dL, including lower IQ scores, decreased academic achievement, and increases in both behavioral problems and attention related behaviors. There is a wide range of lead associated behavioral effects in the area of attention. Attention deficit hyperactivity disorder (ADHD) is one example on the more severe end of the spectrum.

The impact of lead in children more dangerous into the children who are from poor families. This is because they are more likely to live in improper locations such as nonstandard housing and near industries or heavy traffics (Tong, et al., 2000). According to the Centers for Disease Control and Prevention, on average, between 1999 and 2004, African children were 1.6 times more likely to test positive for lead in their blood than American children. And among children who tested positive for extremely high lead levels (≥10 μg/dL), the contradiction was even more stark. Black children were nearly three times more likely than white children to have highly elevated blood-lead levels, the type of lead poisoning where the most damaging health consequences occur.

Effects of lead in adults

Lead exposure has been connected to a number of health effects in adults. Generally, the more lead in body, the more to get health problems. High blood lead levels over than 15 μg/dL are associated with decreased kidney function, cardiovascular effects, nerve disorders and fertility problems, including delayed conception and adverse effects on sperm and semen, such as lower sperm counts and motility. Blood lead levels lower than 10 μg/dL are associated with decreased kidney function and increases in blood pressure, hypertension, and incidence of essential tremor, a degenerative disorder of the central nervous system whose most recognizable feature is a tremor of the arms or hands during voluntary movements, such as writing and eating. There is also evidence indicating that adults who have low levels of exposure to lead lower than 5 μg/dL may have decreased kidney function.

Particularly, in pregnant women need to be cautious around lead. Pregnant women lead levels lower than 5 μg/dL are associated with deducted fetal growth. The study showed that lifetime lead exposure may raise the risk of developing cataracts, a clouding of the eye lens resulting in partial loss of vision, which can be common in older people. Most adults with high blood lead levels are exposed to lead at work. Those in careers related to ironwork, welding, mining, construction, firing ranges, smelters, the manufacture and disposal of car batteries, metal shop work, automobile radiator repair and the manufacture of pottery or stained glass are especially at risk for lead exposure [11]. Table 2.1 shows the health effects associated with blood lead levels in adults and children.

Table 2.1 Health effects from lead

Blood Lead Level	**Health Effects**	
	Children	**Adults**
Blood lead levels lower than 5 μg/dL	- Reduced academic achievement, IQ, and extra cognitive measures - Increased incidence of problem and attention-related behaviors	-Reduced kidney function -Reduced fetal growth
Blood lead levels lower than 10 μg/dL	-Delayed puberty -Reduced postnatal growth - Decreased IQ and hearing ability	-Reduced blood pressure -Risk of hypertension -Incidence of essential tremor

Source: Retrieved from National Institute of Environmental Health Sciences [11]

2.1.3 Worldwide distribution of Lead

Lead infrequently occurs as a native metal. Therefore, it is sourced from different of ores. The most major commercially important lead ore is Galena (PbS) and other minerals which are either associated with or originated from galena deposits. The lead resources in the world are mainly distributed in: Europe (Siberia and Russia), Asia (central and western regions of China), Australia (Queensland, Broken Hill, Elura and Woodlawn, Tasmania, and North Bay, MacArthur River), US (the southeastern area of Missouri and Mississippi River valley), Mexico (Zacatecas and San Luis Potos) and Peru (Cerrode Pasco and Morococha). The greatest lead reserves are in Australia (40%), China (15%), Russia (10%), the United States (5.6%), Peru (8.4%) and Mexico (6%), respectively. The lead reserves of these six countries overspread 85% of whole reserves in the world. Table 2.2 shows reserves data of lead in mainly distributed countries.

Presently, around 240 mines in more than 40 countries produce lead. World mine production was estimated to be 4.1 million metric tons in 2010, and the leading manufacturers were China, Australia, the United States, and Peru, in descending order of output. Additionally, secondary or recycled lead is an important part of the global lead supply. World expenses of refined lead was 9.35 million metric tons in 2010. The leading refined lead consuming countries were China, the United States, and Germany. Demand for lead worldwide is estimated to grow largely because of enlarged consumption in China, which is being driven by growth in the electric bicycle and automobile markets [12].

Table 2.2 Reserves data of lead in mainly distributed countries

Countries	**Thousand metric tons**
United States	5,000
Australia	36,000
Bolivia	1,600
China	14,000
India	2,600
Mexico	5,600
Peru	7,500
Poland	1,700
Russia	9,200
Sweden	1,100
Other countries	3,000
World total (rounded)	89,000

Source: Retrieved from Lead- U.S. Geological Survey, Mineral Commodity Summaries, February 2014 [13].

Occurrence of Lead in Thailand

In Thailand lead deposits scatter sporadically in the western part of the country and in Loei province, northeastern Thailand. There are three types of deposits have been identified, namely, quartz-sulphide vein, stratabound, carbonates. Only a few deposits have been found in the Jurassic carbonates. Common mineral associations are zinc, copper, silver and small amounts of barite [14]. Table 2.3 shows occurrence of lead in Thailand.

Lead poisoning near lead mines has had a long record in Thailand. Urbanization and industrialization have increased these risks, with an increase in demand for lead, leaded gasoline, and factories (especially electronics) using lead for soldering. In 1989, streams and ponds in the western part of Thailand were found to have more than 10,000 times the World Health Organization's suggested healthy limit of 10 - 15 mg/dl of blood. High intensity of lead in blood may bring to inhibited development in children, a range of chronic illnesses. Acute levels of lead may lead to death.

In Lamphun province where is an importantly agricultural town. At least eight persons died in factories involved with making electro-ceramic circuit boards, circuitry or lenses using soldering or solvents, and at least one worker also burnt chemical waste in the factory grounds from well-known Japanese electronics companies. The fatalities also included with two children, who may have had lead poisoning passed via breast-feeding, or physical contact with people covered with dust. This day, there have been no further major health scandals at Lamphun. However, national attention was once again directed to lead poisoning in 1999 when cases of water-borne lead pollution were found in the forest district of Klity in the Thung Yai Naresuan wildlife sanctuary in the western province of Kanchanaburi [15].

Lead contaminated in water at Klity Creek was reported and villagers suffered with dangerously high blood lead levels as high as 110 times the lead levels found in an average person. Since 1994, children in this area have been diagnosed with Down's syndrome and have had physical deformities, whereas the adults have endured from an unidentified illness which caused the body to swell and ache. The causes of lead are both natural and a result of lead mining. Lead has been mined more than 30 years in this area, and the untreated wastewater from the ore-dressing was released into Klity Creek [16]. The highest lead concentrations in sediment were found to be as high as 65,771–143,097 mg/kg which is 20–100 times higher than the surrounding area without mining. Lead levels in fish were ten times higher than the allowable maximum level in food (1 mg/kg) [17].

Table 2.3 Occurrence of lead in Thailand

Region	Deposition Name	Area	Geological Characteristics
Northern	Mae Ho	Mae Sariang district, Mae Hong Son province	Galena is found in quartz veins in N-S direction across the country rocks which consist of Cambrain quartzite, argillaceous limestone and calc-silicate.
	Ban Muang Gid	Mae Taeng district, Chiang Mai province	The dominant galena is found in skarn along the contact zone of the Triassic granite and Permian limestone.
	Bo Sam Kleaw	Long district, Phrea province	Galena is the dominant mineral in quartz vein with sphalerite, chalcopyrite and barite associate.
Southern	Tham Talu	Bannage Sata district, Yala province	The ore mineralogy is rather complicated with tin and galena occurring as the main minerals in skarn rocks formed along the contact between granites and the Permian limestones.
Western	-	Thong Pha Phum district, Kanchanaburi province	Lead subordinate zinc of stratabound type occurs in a well-defined zone no less than 100 kilometers long in the Middle Ordovician limestone extending in NNW-SSE direction.

Retrieved from Atlas of mineral resources of the ESCAP region 16 Mineral resources of Thailand [14]

2.2 Treatment Technologies for Lead Contaminated in Water

Innovative processes for treating lead contaminated water often related to technologies for decrease of toxicity to achieve with treatment standards. This article reviews the modern developments and technical applicability of different treatments for lead removal. A specific focus is given to innovative physicochemical removal processes are chemical precipitation methods, electrodialysis, filtration and ion exchange method.

2.2.1 Chemical Precipitation Methods

Chemical precipitation is the most commonly used process for lead removal from solution. The most widely used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant, and case of automatic pH control. Hydroxide precipitates tend to solubilize when solution changes pH, however the removal of mixed metal wastes may not be proficient because the minimum solubilities for various metals occur at different pH condition.

The 1,3-benzenediamidoethanethiol dianion ($BDET^{2-}$) has been developed to selectively bind soft lead from aqueous stock solutions as highly stable metal-ligand compounds. $BDET^{2-}$ is aimed to decrease lead concentrations to lower than 0.5 mg/l and operate stable Pb-BDET precipitates. The potassium salt of this ligand was also used to field samples gathered from an operating lead battery recycling site (LBRS) which creates wastewaters containing concentrations of lead from 2 - 300 mg/l at an average pH of 1.5. The result showed that more than 99.4% of lead was remove from a mean initial concentration of 3.61 mg/l at a pH of 5.0 could be achieved within 15 min by using an equimolar dose of the $BDETK_2$ (potassium salt) ligand. Moreover, the concentrations of other heavy metals like iron, copper, manganese, zinc, stibnite, and nickel can also be remarkably reduced in this time frame and the precipitates left stable during 30 days leaching experiments [18].

Sodium di-(*n*-octyl) phosphinate and sodium di(dodecyl) phosphinate also can remove lead from aqueous solutions. These organophosphorus reagents are known in solvent extraction and considered to be the most appropriate extractants for the recovery and separation of cobalt and nickel from acidic leach solutions. The study showed that lead was removed from nitrate and chloride solutions by precipitation with sodium di-(*n*-octyl) phosphinate to form PbL_2. Reducing the pH of the feed decreased the percentage removal, due to some acid precipitated. The residence of chloride or calcium had no impact on the lead removal. While adding the chain length reduced the residual concentrations of lead and of the precipitating agent in the aqueous phase [19].

The single component and multi-component hydroxide precipitation was studied for lead(II) from aqueous solutions by using the jar tester Magnesia (MgO) as a precipitator at various doses. The process involves the addition of either magnesia or lime-water suspensions (associated with cationic polyelectrolyte, CPE) in different doses, 1.0 – 5.0 g/l for lead samples to study the effect of various dosages on the treatment efficiency. The results showed that the lead percent removal increased in the range of 95% - 99% with increasing the MgO dose to some limits (1.0 - 2.0 g/l). The pH value between 9.5 - 10 with MgO precipitant whereas the use of cationic polyelectrolyte, alone as a precipitating agent at concentrations of 1.25 - 1.5 mg/l. causes low pollutants removal efficiencies, and causes rapid clogging of sand filter due to its physical nature [20].

Although precipitation is proven relatively simple and effective technique. Precipitation can be used to obtain good results with a number of substances that are hard to remove with other techniques. And very specific components can be removed by this technique, while it is not removing other substance. However, this method demands a large amount of chemicals to deduct metals to a passable level for discharge. Other disadvantages are its overwhelming sludge production that requires more treatment [21].

2.2.2 Electrodialysis

Electrodialysis (ED) is a membrane separation which ionized species in the solution are moved pass through an ion exchange membrane by using an electric potential. The membranes are thin sheets of plastic materials with anionic or cationic characteristics. When a solution comprising ionic species moves through the cell compartments, the anions transfer to the anode and the cations to the cathode, crossing the anion exchange and cation-exchange membranes [21].

In a research carried by Mansoorian et al, concluded that electrocoagulation can practically decrease the high amounts of lead ions by using hydroxide iron ($Fe(OH)_2$) and steel flocs as adsorbents. Lead was removed by chemical sedimentation by hydroxide ions (OH^-) formed at the cathode by water electrolysis and by co sedimentation by iron and steel hydroxides. The removal efficiency depends on in current density. The results of this study showed that optimum lead removal in current density of 6 mA/cm^3 and 8 mA/cm^3 was achieved which was respectively 96.7% and 95.2%. In direct current the maximum removal of lead by iron rod electrodes was 97.2% with 30 min and with stainless steel rod electrodes was 93.2% in current density of 8 and 6 mA/cm^3 with 30 and 40 min optimum electrolysis time, respectively. According to the investigations this process can be used as a proper method for a wide use of electrolyte reactors in the industrial scale and for removing lead from aqueous environments [22].

The other study from electrochemical removal of lead ions by using paper electrode of polyaniline/attapulgite composites (PANI/ATP) carried by Li S., et al, [23] the result showed that Negatively polarized PANI/ATP is profitable to the electrosorption of lead due to the electrostatic interplay between lead and the negatively charged PANI/ATP. Moreover, an increased content of the aromatic amino groups on the PANI/ATP polarized at –0.3 V is justified by the FT-IR spectra, which makes the chelation between lead and PANI more simply. Physisorption took from ATP also supports to lead removal, even though this support is not as great as that from chelation and electrostatic interplay. Hence, the attractive benefit of the PANI/ATP paper electrode is that it can undergo ten successive electrosorption/electrodesorption cycles without a major decline in lead removal, making it an assuring electrode material for the electrochemical removal of lead and other toxic metal ions.

It was found that potential of an ED cell is almost free on the kind of ions and only relies on the operating circumstances and the structure of cell. Despite its limitation, ED provides advantages for the treatment of wastewater laden with heavy metals such as the capable to generate a highly concentrated stream for recovery and the denying of unpleasing dirt from water [21]. However, this process the disposal of hazardous wastes, and must locate company that will redeem and salvage metals from the sludge.

2.2.3 Filtration

Membrane filtration has considerable attention for lead treatment. It can remove suspended solid, organic compounds and inorganic contaminants such as heavy metals. Depending on the scale of the particle that can be maintained, different types of membrane filtration such as Reverse Osmosis (RO), nanofiltration (NF) and microfiltration (MF) can be employed for lead removal from wastewater by using hydrostatic constraint to press lead in contaminated water pass through semi permeable membrane [24].

In a study of RO carried by Mixon conducted laboratory tests to determine the effectiveness of RO in removing lead. Result showed that the removals greater than 99.5 and 97 percent for initial lead concentrations of 0.95 and 9.3 mg/l respectively. In addition, the result of studies on lead removal by RO conduted by Fox support the findings of Mixon's study. The rejection rates for lead removal from drinking water were greater than 97% when used both hollow fiber and spiral wound in the membrane systems. For raw water concentrations varying from 0.15 to 0.61 mg/l, both membrane systems produced product water with less than the minimum detectable resolution (0.005 mg/l) until raw water lead concentrations reached 0.23 mg/l. From 0.23 to 0.61 mg/l, the lead concentrations in the product water increases, but did not go over the maximum contaminant level (MCL) of 0.05 mg/l. A range of pH values from 5.0 to 7.0, and operating pressure ranges from 1.2 to 1.4 MPa for the spiral wound system did not affect percent removal, which remained above 97 percents. Therefore, Fox stated that RO can be an effective treatment technique for removing lead, and assuming a 97 percent removal rate and a single stage RO unit could achieve the MCL treating water with lead concentrations ≤ 1.6 mg/l [25].

Nanofiltration (NF) has resemble working principle as RO unless that the operation is performed at low pressure with the same permeate flux. The results on the removal of toxic lead ions from aqueous wastewaters by using two commercial thin-film composite polyamide NF concentration in feed. The solution pH is a limiting factor influencing into a greater extent the separation by the AFC 40 membrane. The optimum rejection of Pb^{2+} is above 80 % for AFC 40 and 98 % for AFC 80, respectively, demonstrating that these NF membranes have a real potential some promise for efficient removal of highly toxic Pb^{2+} and polluting from wastewaters [26].

Likewise, complexation microfiltration, it can be used for lead ions removal by using Diethylaminoethyl cellulose (DEAE 23) as a complexing agent. The lead removal capacity of this process strongly depends on pH values, whether in the presence of complexing agent or not. In alkaline conditions, retention coefficients above 99% were attained. The retention coefficient also depends on concentration of ions in the solution. The retention coefficient smoothly increases with increasing concentration of complexing agent, due to higher amount of metal ions bound to DEAE 23 [27].

Although membrane filters have exact advantages and disadvantages. Except for those with the smallest pore sizes, membrane filters are relatively inexpensive, do not clog easily, and can filter huge volumes of fluid reasonably rapidly. Whereas, this method consumes more electricity, may need pretreatment, demands membranes replacement and the major disadvantage of this process is sludge generation [28].

2.2.4 Ion Exchange Method

In this process, ions of same charge are exchanged between the solution and an insoluble resin. Ion exchange and adsorption process are explained by using same models as the exchange of ions replace between solution and internal surface of the solid in both processes. Nevertheless, the materials should be interchanged within the ion exchange membranes which are different from adsorption processes.

In the research carried by Arar, lead was removed from the commercially available chelating resin with the di (2-ethylhexyl) phosphate functional group. The studies investigated the removal of lead ions in different resin doses and pH removal efficiency performance of resin. The obtained results showed that the removal performance of resin strongly depends on solution pH and more than 99% removal of lead ions was accomplished at pH greater than or equal to 3 [29].

732 cation-exchange resin in sodium type (732-CR) has also been studied in batch experiments to investigate the removal of lead ions from aqueous solution at various parameters. The experimental data showed that the ion-exchange process was dependent on pH and temperature, the optimal exchange capacity was found at pH 4.0, and at higher temperature it was beneficial to lead sorption. The equilibrium exchange capacity could be reached at around 4 hrs. and the maximum sorption capacity of lead ions at pH 4.0 was 396.8 mg/g resin. As well as in the column tests were conducted by using both synthetic solution and effluents from lead battery industry. The regeneration of resin was performed effectively for two sorption-regeneration cycles by 1 M NaOH [30].

In the same way, the enhance study of using 732 cation-exchange resin in hydrogen type (732-CR) in order to investigate the kinetics and thermodynamics for the removal of Pb^{2+} from an aqueous solution under the temperature range of 298 – 328 K and lead concentration range of 5 – 50 mol/m^3. The results found that the ion exchange process was favored under the particle diffusion control mechanism. The maximum monolayer exchange capacity for $Pb^{2+}$was found to be 484.0 mg/g at 308 K and thermodynamic studies show that Pb^{2+} onto 732-CR is spontaneous and exothermic in nature [31].

Ion-exchange resins have recently found interesting in the market of water and wastewater treatment. It is efficient in removal of dissolved solids from normally dilute spent rinse waters, and it is well suited for use in water purification and recycles. It may be able to treat in high purity heavy metal solution and sequential operation. In contrast, it requires pretreatment process to reduce suspended solid concentration in solution to protect channeling or fouling.

Though these conventional treatment technologies for removing lead as mentioned above have high effective for lead removal but there are some disadvantages especially in term of operation cost. Table 2.4 shows the comparison between advantages and disadvantages of each conventional metal removal technology. Moreover, these methods are often ineffective and not suitable for low concentrations of metals. Therefore, recently have been sought a cheaper heavy metals treatment technology. One of these attractive technologies is adsorption. The studies on adsorption by using commercially available materials such as activated carbon, alumina and zeolite have often been investigated for many several years. Recently, studying low cost adsorbent is also become a new trend and widely investigated in the research area to challenge the commercially available materials.

Table 2.4 Conventional metal removal technologies

Method	Disadvantage	Advantage
Chemical Additive Methods	- pH dependence - Difficult separation - Adverse effect by complexing agent - Resulting sludges - Chemical required	- Simple and chip
Electrodialysis	- Takes time - Large electrode surface area required - Fouling - Expensive	- Metal Selective
Filtration	- High capital and operating cost - The necessity of pretreatment	- Pure effluent
Ion exchange	- Sensitive to particles - High operational cost - No selective to alkaline metals - Metallic fouling	-No sludge generation - Pure effluent metal recovery possible

Retrieved from Environmental Bioengineering Vol. 11 by Wang, et al., 2010 [32]

2.2.5 Adsorption

Adsorption is one of the most efficient wastewater treatment technologies because of its low cost, compared to the other technologies highlighted in the above section, its simple operation and it does not produce a large amount of sludge. Adsorption is defined as ―a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The materials used as adsorbents must have high content of carbon or oxygen for efficient adsorption.

The main factors that impact the efficiency of adsorption are surface area of the adsorbent material, nature and concentration of adsorbate, pH of the solution, temperature, properties and dose of the sorbent and contact time. Adsorbents can be classified into two main groups, which are conventional adsorbents/ sorbents, and these are commercial adsorbents and some of them are commonly used, and unconventional adsorbents/ sorbents, which are mainly composed of cheap agricultural, and industrial wastes, naturally existing materials and other organic materials

Alumina and Aluminium based adsorbents

Activated alumina is a porous granular form of aluminum oxide (Al_2O_3) occupying a large surface area. It can adsorb lead from aqueous solutions by concentrating lead at the particle surface. Adsorption of lead by activated alumina is incidence by different parameters like pH, alumina surface area (particle size), and possession of background matrices. Particle size and pH play important roles in lead adsorption.

The application of using hydroxy-apatite microparticles as absorbers of heavy metals showed that the absorption percentage average of lead (84.72%) by this adsorbent is greater than that of cadmium (49.89%), zinc (72.90%), iron (74.50%) and nickel (79.25%). Lead removal capacity is in the highest percentage because its cation has a harder Louise acid than other cations and its removal capacity was depend on the pH solution. This means that the less in solution pH, the less absorption percentage of lead by hydroxyapatite. This event also occur with cadmium and copper elements [33].

The retention of Pb(II) onto activated alumina has also been studied. Batch adsorption experiments were used for analyzing the different effects. It is found that the percentage of adsorption increases on changing the pH of the medium from acidic towards neutral. More than 95% of lead removal was found under pH 7 condition. The time taken for lead attainment of equilibrium has been optimized as 40 min and the removal yield increases with increasing the adsorbent dosage and decreases with increase initial lead concentration. Hence, the study concluded that the effective removal of the lead is mainly dependent on the ratio of adsorbent dosage to the concentration of lead ions, which is of course a compromise between cost effectiveness of the process and the desired retention percentage [34].

For an effective utilization of modification alumina, newly modified alumina–physically loaded-dithizone adsorbent was investigated and developed as a function of the solution pH and contact time. The results showed the strong relevance toward Pb^{2+}, Cr^{3+} and Cu^{2+}. However, this modified alumina adsorbent are highly selective for Pb^{2+} by testing from real wastewater samples, it was achieved with 94 – 99 ± 1–2% lead percentage recovery, wheseas the results collected from the selective pre concentration of Pb^{2+} from drinking tap water demonstrated outstanding percentage recovery values of 96 – 99 ± 2–3 % and 94 – 99 ± 2 – 4% for 1.212 ng/ml and 4.800ng/ml concentration, respectively [35].

Table 2.5 Lead adsorption capacity of Alumina/Aluminum based adsorbents

Adsorbents	**Concentration Range (mg/l)**	**pH**	**Adsorption capacity/ Removal (%)**	**Ref.**
Hydroxy-apatite microparticles	0.08 - 0.76	-	84.72%	[33]
Activated alumina	0.02 - 0.08	7	~ 95%	[34]
Modified alumina by loaded-dithizone	0.001	-	94-99 %	[35]

Calcium based adsorbents

Many researchers have applied natural lime stone for the removal of toxic metal ions from wastewater and reported that limestone or calcium carbonate ($CaCO_{3)}$ is an effective material for the treatment of wastewater contained with heavy metals and provide highest removal efficiency for heavy metals [36]. Therefore, it can be effective adsorbents for removal of lead.

Limestone which is produced in wide quantities in many countries is a low cost reactive medium that can be applicable for heavy metals treatment and the subsequent cleaned up of industrial effluents, leachates, and contaminated ground water. The powdered limestone has been examined as a low cost and effective inorganic adsorbent for the removal of Pb^{2+} from aqueous solutions. Using 0.1 g of powdered limestone was used as an adsorbent to remove lead with concentrations range 2 to 80 mg/l. The time required to reach adsorption equilibrium was found to be 10 min for 2 mg/l Pb^{2+}, 20 min for 5.6 mg/l Pb^{2+}, 30 min for 10 and 40 mg /l Pb^{2+}, and 60 min for those 80 mg /l Pb^{2+}. At pH lower than 2, the removal of Pb^{2+} reached zero which may be attributed to the complete solubility of limestone, therefore hindering the sorption of lead ions occur. Above pH 2, the removal efficiency increased dramatically, reaching a maximum value 100% Pb^{2+} removal and lead removal efficiency dropped again at pH range 6 – 9. Although the temperature changed, the removal efficiency was still in the range of 98 – 99%.

The adsorption of lead ions emerged largely at the surface of the solid limestone and insignificantly by the internal pores and it could emerge through ion-exchange, adsorption of hydrolytic species, $Pb(OH)^{+}$, and the precipitation of lead carbonate onto fine powered limestone adsorbent depending on the pH value [37].

Other adsorbents like calcite, marble wastes and waste calcite sludge also indicate good sorption potential for Pb^{2+} removal as shown in Table 2.7 Marble wastes were found to be very efficient in removing lead for many experimental situations. Especially, for initial pH values higher than 3.6, a lead removal efficiency approximately 100 % was achieved even for high concentrations 200 mg/l, essential feeding flow rates was 60 ml/min with 2 g/1 marble waste dosage. Similarity, waste calcite sludge has maximum lead removal nearly 100 % when pH greater than or equal to 3 within 120 min of operation [38].

Table 2.6 Lead adsorption capacity of Calcium based adsorbents

Adsorbents	Concentration Range (mg/l)	pH	Adsorption capacity/ Removal (%)	Ref.
Powdered limestone	2-80	7	100%	[37]
Calcite	10	7-8	19.92 mg/g	[39]
Marble wastes	200	5	175.7 mg/g	[40]
Waste calcite sludge	1000	≥ 3	99.9%	[38]

Iron based adsorbents

Many iron-based sorbents such as iron oxide and magnetic graphene oxide have been studied. Super paramagnetic polyethylene glycol coated iron oxide nanoparticles (Fe_3O_4) with cubic spinel structure with particle size of 24 nm were successfully synthesized by the co-precipitation method and could be used as an alternate to the conventional adsorbents for the removal of metal ions from contaminated water with high removal efficiency within a very short period. The removal of Pb^{2+} by adsorption onto Fe_3O_4 magnetic nanoparticles was successfully accomplished. Adsorption was very rapid and equilibrium was reached within 10 min. It indicated that adsorption was highly depend on the Pb^{2+} concentration and pH value. At pH 6 under room temperature condition, the maximum removal efficiency was achieved. Therefore, the method is accurate, and economical and Fe_3O_4 magnetic nanoparticles were suggested as fast, effective, and inexpensive nanoadsorbents for rapid removal and recovery of high lead concentration from such wastewaters [41].

Magnetic graphene oxide also shows strong likelihood for lead adsorption. Graphene oxide (Fe_3O_4 GO) was used as an adsorbent for the removal for Pb(II) from environmental water samples. The adsorption procedure was optimized as follows: 60 min adsorption time, 50 mL sample volume, solution pH 4.5, and 25 mg adsorbent dosage. Under the optimum conditions, the adsorption efficiency obtained was greater than 75% (C = 50 mg/l). The maximum adsorption capacity (q_m) obtained was 86.2 mg/l. The results signified that the prepared Fe_3O_4/GO nanocomposite has a great adsorptive ability towards the Pb(II) from environmental water samples [42].

Likewise, iron-based adsorbents in nanoscale, the efficiency of nano zero-valent Iron shows good potential for lead removal from aqueous solution because it has special physicochemical properties. The removal percentage of lead in this adsorbent was increased from 83% up to 100% when pH values were increased from 5 to 9. Besides the effect of pH, adsorbent dosage also plays a significant factor. This is because it presents the adsorption capacity for obtaining the initial amount of the adsorbate. The study showed that when the adsorbent dosage increased from 0.1 to 5 g/L, the removal efficiency of lead ion decreased. Hence, it is a belief that at a low adsorbent dosage, the dispersion of adsorbent particles in aqueous solution is good because all active sites on the adsorbent surface are completely uncovered and they cannot accelerate the accessibility of lead molecules to a large number of adsorbent active sites [43].

Table 2.7 Lead adsorption capacity of Iron based adsorbents

Adsorbents	**Concentration Range (mg/l)**	**pH**	**Adsorption capacity/ Removal (%)**	**Ref.**
Superparamagnetic Monodispersed Iron Oxide (Fe_3O_4) Nanoparticles	100	6	100%	[41]
Magnetic grapheme oxide	10 - 150	4.5	> 75%	[42]
Nano Zero-Valent Iron	10	9	80% - 100%	[43]
Activated carbon/iron oxide magnetic composite	100	3.5-6.5	92.35%	[44]

Carbon based sorbents

Carbon based adsorbents especially in nano scale have been used widely for heavy metals removal in recent decades, due to their nontoxicity and high sorption capacities [74]. Carbon nanotubes (CNTs) are an innovative material that displays good adsorption behavior toward different toxic pollutants in aqueous solution. These adsorbents have a rapid adsorption rate and high adsorption efficiency, efficient to remove different pollutants and they are easy to recover and reuse. Hence, these attractive features emphasize the practicability of CNTs for the treatment of polluted water contain heavy metal ions and dyes [45].

The ability of carbon nanotubes (CNTs) to adsorb lead in aqueous solution was investigated to determine the effects of pH, agitation speed, CNTs dosage and contact time. The removal of Pb^{2+} reached maximum value 85% or 83% at pH 5 or 40 mg/L of CNTs, respectively. The result from Langmuir isotherm model with higher correlation coefficients indicated the strong adsorptions of Pb^{2+} on the surface of CNTs (adsorption capacity X_m = 102.04 mg/g). The highest percentage removal of Pb^{2+} equaled to 96.03% can be achieved at pH 5, 40 mg/L of CNTs, contact time 80 min, and agitation speed 50 r/min [46].

Furthermore, animals' bone can be applied and used as adsorbents. For example, bone powder, bone char and activated bone char from Swine bone. They were prepared and used to investigate the Pb^{2+} sorption capacity. The experiment shown that bone char is the best adsorbent and bone powder is the worst adsorbent for lead removal. The adsorption capacity were 417, 1828 and 690 mg/g for bone powder, bone char and activated bone char with higher than 99% of the removal for 10 mg/l of the initial concentration of lead with an agitation speed 175 rpm and bone char appears to have the suitable physical characterization with high overall surface areas and average appropriate pore size in the range of mesopores which provided the maximum adsorption capacity [47].

Besides that, fish bone and charcoal includes coffee, tea and caffeine solid substrates have also been used to remove lead from contaminated aqueous solutions through adsorption process. These adsorbents substrates were added 50 ml of 1300 mg/l and agitated for 48 hrs. at room temperature. The results showed that they could remove from 70% - 100% of lead from contaminated wastewater. Charcoal and fish bone can remove lead 100% and 76%, respectively. These results obviously demonstrated that not all solid biomaterials are able to adsorb lead and caffeine which is a component of coffee and tea does not collaborate in the removal of lead from contaminated aqueous solutions because its efficiency was found to remove lead only 1.3% [48].

Table 2.8 Lead removal efficiency of Carbon based adsorbents

Adsorbents	**Concentration Range (mg/l)**	**pH**	**Adsorption capacity/ Removal (%)**	**Ref.**
Mn oxide coated carbon nanotubes	40	5	96.03%	[46]
Bone powder	10	5 ± 0.1	417 mg/g	[47]
Bone char	10	5 ± 0.1	1828 mg/g	
Activated bone char	10	5 ± 0.1	690 mg/g	
Fish Bone	1300	neutral pH	100%	[48]
Charcoal	1300	neutral pH	76%	

Natural materials

Naturally occurring adsorbents have been used for removing lead for decades due to their ease of availability. Therefore, the adsorption capacity of some natural materials for lead such as fly ash, red mud, peat and crosslinked chitosan-clay beads were studied at different initial lead concentration parameters. The removal efficiencies of fly ash and red mud were 90.37% and 85.20%, respectively with 100 mg/l initial lead concentration. Whereas, peat adsorption efficiency reached 100% just after 3 min (15 and 30 mg/L), 5 min (50 mg/L) or 15 min (100 mg/L) of the process [49-51]. And crosslinked chitosan-clay beads maximum adsorption capacity was determined as 7.93 mg/g with 50mg/l initial lead concentration [52].

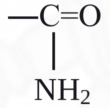
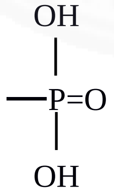
Table 2.9 Lead removal efficiency of natural materials based adsorbents

Adsorbents	**Concentration Range (mg/l)**	**pH**	**Adsorption capacity/ Removal (%)**	**Ref.**
Fly ash	100 mg/l	6	90.37%	[49]
Red mud	100 mg/l	2, 4, 6.5 and 8	85.20%	[50]
Peat	15-100 mg/l	1, 3, 5, 7 and 9	100%	[51]
Crosslinked chitosan-clay beads	50 mg/l	4.5	7.93 mg/g	[52]

Biopolymers and Agricultural wastes based adsorbents

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. Biosorption is caused by various metabolism-independent process which depends on type of biomass. Biosorbents contain chemical active groups within their structures as shown in Table 2.10 Biosorbents and agricultural wastes based adsorbents have attracted the attention in recent years as an alternative to conventional methods for heavy metal removal from water and wastewater [54].

Table 2.10 Major binding groups responsible for the biosorption process

Binding group	**Structural Formula**	**pKa**	**Ligand atom**	**Occurrence in selected biomolecules**
Hydroxyl	—OH	9.5 – 13.0	O	PS, UA, SPS, AA
Carbonyl (ketone)	C=O	-	O	Peptide bond
Carboxyl	—COOH	1.7 - 4.7	O	UA, AA
Sulfonate	$—SO_3$	1.3	O	SPS
Amine	$—NH_2$	8.0 - 11.0	N	Cto, AA
Amide	 $\begin{array}{l}—C{=}O \\ \;\;\vert \\ \;\;NH_2\end{array}$	-	N	AA
Imine	=NH	11.6 – 2.6	N	AA
Imidazole		6.0	N	AA
Phosphonate	 $\begin{array}{c}OH \\ \vert \\ —P{=}O \\ \vert \\ OH\end{array}$	0.9 – 2.1 6.1 – 6.8	O	PL
Phospodiester	 $\begin{array}{c}P{=}O \\ \vert \\ OH\end{array}$	1.5	O	TA, LPS

PS: polysaccharides, UA: uronic acids, SPS: sulfated PS, AA: amino acids, Cto: chitosan, Cti: chitin, PG: peptidoglycan, PL: phospholipids, TA: teichoic acid, LPS: lipo, PS.

Retrieved from Abbas, et al., 2014 [55]

Many kinds of biomass such as wood, leaves, agricultural residues, industrial byproducts, waste crustacean biomass, microbes, polysaccharide materials have already been examined for lead removal. Table 2.11 shows that the removal of lead (II) by using different adsorbents and its optimal parameters. Some low cost adsorbent used in this table which indicates that adsorbents were outstanding removal capabilities for lead in aqueous solution. Therefore, it is clear that maximum uptake capacity takes place by low cost adsorbents used in adsorption process and it gives better removal efficiency of lead ions.

Table 2.11 Adsorption capacities of different plants and agricultural residue wastes as adsorbents for lead.

Name of adsorbents	pH	Dosages	Contact time	Pb^{2+} Removal %	Ref.
Rice husk and Maize cobs	2.5 - 6.5	1.5g	120 min	98.5	[56]
Sour sop seeds	5	1.0 g	120 min	40.6	[57]
Spent tea leaf	Neutral	2.0 g	8 hrs.	55.2	[58]
Papaya seeds	5	10 - 1000 mg/l	90 min	90	[59]
Palm Kernel Shell Charcoal (PKSC)	-	80.0 g/l	50 min	89	[60]
Coconut Leaf powder	7	2.0 g	30-180 min	90	[61]
Tea waste	5 - 6	1.25 – 7.5g /l	15-20 min	96	[62]
Raw Banana Stalk	4 - 8	0.1 -1.0 mg/l	180 min	63.97	[63]
Coffee grounds	Neutral	0.5 mg/l	1 hr.	87.2	[64]
Banana Stalk	8	0.90 g	152 min	96.41	[63]
Agro-Waste	6	15.0 g/l	60 min	89.60	[65]

2.3 Adsorption Isotherm

Adsorption isotherms are mathematical models that explain the distribution of the adsorbate species between liquid and adsorbent, based on a set of hypothesis that are mostly related to the heterogeneity or homogeneity of the adsorbent, the type of coverage and possibility of interplay between the adsorbate species. Adsorption data are commonly explained by adsorption isotherms such as the Langmuir and Freundlich isotherms. These isotherms relate to metal uptake per unit weight of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase C_e [66]. The results of the adsorption in this study were fitted with two well-known adsorption models namely Langmuir and Freundlich adsorption models.

2.3.1 Langmuir Adsorption Isotherm

Langmuir isotherm model provides a clear concept of monomolecular adsorption where all energetically active sites have same relevance for adsorbate. The area of each site liable for adsorption is defined exclusively by geometry of adsorbate. Basically, this model is based on the following three hypotheses:

(a) Adsorption occurs only at limited number of same localized sites and optimum adsorption corresponds to saturated monolayer of adsorpbate molecules with uniform thickness on the adsorbent surface;

(b) This isotherm model implies that the adsorption is uniform or homogeneous, where each molecule occupies steady enthalpies and adsorption activation energy;

(c) There is no transmigration of adsorbate in surface plane and binding to adsorbent occurs mainly by physical forces

Langmuir model has good agreement with the experimental results and it is expressed in non-linear form as;

$$q_e = \frac{Q_0\, bC_e}{1+bC_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where, C_e is equilibrium concentration of adsorbate (mg/l), q_e is quantity of adsorbate adsorbed per unit mass unit mass of the adsorbent (mg/g), Q_o and b are Langmuir constants demonstrating measures of monolayer adsorption capacity (mg/g) and adsorption rate (L/mg). Explicitly, it is characterized by plateau in which an equilibrium saturation point is obtained where there is no more adsorption once the site has been occupied. This show q_e enters Q_o asymptotically as C_e approaches infinity. Although non-linear method offers better result, the linear least-square method is desirable due to its uncomplicatedness and expediency. Hence, Equation (I) can be converted into different linear forms as shown in Table 2.12 to compute the adsorption capacities for the given lead concentrations. For fitting nonlinear isotherm models to linear models, the dependent and independent variants are converted accordingly [67].

Table 2.12 The four linear forms of Langmuir isotherm model

Name	Linear form	Plot	Slope	Intercept
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}$	$\frac{C_e}{q_e}$ vs. C_e	$\frac{1}{Q_0}$	$\frac{1}{bQ_0}$
Langmuir-2	$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_oC_e}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	$\frac{1}{bQ_0}$	$\frac{1}{Q_0}$
Langmuir-3	$q_e = Q_0 - \frac{q_e}{bC_e}$	q_e vs. $\frac{q_e}{bC_e}$	$\frac{1}{b}$	Q_0
Langmuir-4	$\frac{q_e}{C_e} = bQ_0 - bq_e$	$\frac{q_e}{C_e}$ vs. q_e	B	bQ_0

2.3.2 Freundlich Adsorption Isotherm

The Freundlich isotherm model is an empirical relation explaining the adsorption of solutes from a liquid to a solid surface and supposes that various sites with several adsorption energies are involved. The Freundlich adsorption isotherm is the relationship between the amounts of lead adsorbed per unit mass of adsorbent (q_e) and the concentration of the lead at equilibrium (C_e). The non-linear form of this model is expresses as:

$$q_e = K_F C_e^{1/n} \quad \text{……………………………………… (i)}$$

The logarithmic form of this equation can be represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{……………………………………… (ii)}$$

where, K_F and n are the Freundlich constants characteristic of the system. K_F and n are the capacity of the adsorbent; the slope of 1/n demonstrates the result of concentration on the adsorption capacity and indicates adsorption intensity [66]. If n equals to 1 indicates the partition between the two phases are free of the concentration. If value of 1/n is lower than one, it presents an ordinary adsorption. On the contrary, if value of 1/n being over than one presents the cooperative adsorption [68]. Table 2.13 presents values of the Langmuir and Freundlich isotherm models constants for lead adsorption by using different adsorbents reported in literature.

Table 2.13 Isotherm constants and correlation coefficients for the adsorption of lead using different adsorbents at 298 K

Adsorbents	**Langmuir**			**Freundlich**			**Ref.**
	b	Q_0	R^2	K_F	N	R^2	
Prosopis juliflora seed powder	0.256	45.454	0.9719	14.3251	3.459	0.9282	[69]
Tea waste	0.0494	65	0.9579	9.6532	2.574	0.9614	[70]
Peat	0.449	82.31	0.992	18.72	1.86	0.525	[51]
Nano-TiO_2	39.46	23.25	0.881	388.1	2.5	0.922	[71]
Waste calcite sludge	0.02	566.4	0.90	99.0	4.20	0.88	[38]
Calcite	3.461	19.92	0.9963	1.482	1.015	0.9161	[39]
Biosurfactant	0.06	30	0.96	10	4.545	0.87	[72]
Hydroxyapatite nano-material	42.76	769.23	0.9998	508	14.75	0.969	[73]
Green algae *Spirogyra* sp.	0.021	140.84	0.990	8.010	1.870	0.916	[74]

2.4 Adsorption Kinetics

Kinetic models can support to understand the mechanism of lead adsorption and evaluate potential of the adsorbents for lead removal. It is based on the rate law, so a good knowledge of molecular details, interatomic distance and individual molecular steps involved in chemical reaction is essential. The easiest means of perception the experimental data from batch kinetic study is to get an idea about remain lead concentration in liquid phase at equilibrium time.

Even though there are several models such as heterogeneous diffusion model (also known as pore and diffusion model), pore diffusion model and homogeneous surface diffusion model are extensively used in batch adsorption, however their the mathematical complexity have limited usage for practical purposes.

At present, the applicability of pseudo-first-order model, pseudo-second-order model, Weber and Morris intraparticle diffusion model, and Elovich's equation are most commonly investigated in order to describe adsorption kinetics data. The adsorption of the lead from wastewater in this study was employed by using pseudo-first-order and pseudo-second-order kinetic models.

2.4.1 Pseudo-First Order Kinetic Model

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity [75]. Pseudo-first order is intuitively associated with the model of single site occupancy adsorption kinetics governed by the rate of surface reaction. The reaction rate is restricted by single mechanism and all sites are dependent on time. The kinetic data is very well presented by this model at insignificant sorbent interactions. The general rate expression of pseudo-first order equation is expressed as follows:

$$\frac{1}{t} = k_1(q_e\text{-}q_t) \text{ ……………………………….(i)}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). After integration and applying boundary conditions, qt = 0 – qt at t = 0 – t; the integrated form becomes as follows:

$$\log(q_e\text{-}q_t) = \log q_e - \frac{k_1 t}{2.303} \text{……………………………….(ii)}$$

The equation applicable to experimental results generally varies from a true first-order equation in two ways:

1. The parameter $k_1(q-q_t)$ does not indicate the number of available sites;
2. The parameter log(q) is an alterable parameter which is often not found equal to the intercept of a plot of log(q−qt) against t, whereas in a true first-order sorption reaction

log(q) should be equal to the intercept of a plot of log(q − qt) against t [76]. Table 2.14 shows the pseudo-first order kinetic model parameters of several adsorbent with several of lead initial concentration.

Table 2.14 Pseudo-first-order kinetic model parameters of various adsorbents for Pb^{2+} removal

Adsorbents	**Initial concentration (mg/l)**	**q_e (exp), mg/g**	**K_1, min^{-1}**	**q_e (cal), mg/g**	**R^2**	**Ref.**
Custard apple (*Annona squamosa*) bark powder	10	1.5275	0.000782	1.3726	0.95209	[77]
Multiwalled Carbon Nanotubes with Isatin	50	3.64	0.0532	7.28	0.9868	[78]
Multiwalled Carbon Nanotubes-COOH	50	16.63	0.0223	0.231	0.9766	
Myrtaceae Sawdust	10	0.9689	0.0728	0.0112	0.9971	[79]
Citrus limettioides peel	10	9.400	0.056	8.734	0.910	[80]
Carbon *Citrus limettioides* peel	10	9.980	0.053	8.515	0.892	
Citrus limettioides seed	10	3.480	0.018	2.806	0.910	
Carbon *Citrus limettioides* seed	10	9.900	0.045	9.190	0.742	

2.4.2 Pseudo-Second Order Kinetic Model

When the usage of pseudo-first order kinetic equation seems to be inappropriate, generalization for two-sites-occupancy adsorption system is suggested, namely pseudo-second order kinetic equation. In this model, the rate-limiting step is the surface adsorption that associates chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases occurring at the same time [81]. The first one is rapid and achieves equilibrium quickly and the second is a slower reaction that can continue for long time periods. The reactions can occur either in series or in parallel. The pseudo-second-order model is expressed as follows:

$$\frac{dqt}{dt} = k_2\,(q_e\text{-}q_t)^2 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

where q_e and qt are the biosorption capacity (mg/g) at equilibrium and at any time t = t (min), and k_2 is the rate constant of pseudo-second-order biosorption model (g/mg/min). The driving force (q_e - q_t) is directly proportional to the available fraction of active binding sites. The rearrangement of Eq. (i) gives the following equation:

$$\frac{dqt}{(q_e - q_t)^2} = k_2 d_t \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

After integration the above equation and applying boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$,

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$

This equation is known as integrated rate law for pseudo-second order reaction and the linear forms of this kinetic model is given in Table 2.15.

Linear 1 type of pseudo-second-order model is the most commonly employed in adsorption process. The values of k_2 and q_e can obtained from intercept and slop from plot of (t/q_t) and t. Table 2.16 shows the pseudo-second-order kinetic model parameters of various adsorbents and lead initial concentration.

Table 2.15 Pseudo-second-order kinetics and their linear forms

Type	**Linearized form**	**Plot**	**Parameters (S: Slope & I: Intercept)**
Linear 1	$\frac{1}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e}$	$\frac{1}{q_t}$ vs. t	$q_e = \frac{1}{S}$ $k_2 = \frac{S^2}{I}$
Linear 2	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{(k_2 q_e^2)}(\frac{1}{t})$	$\frac{1}{q_t}$ vs. $\frac{1}{t}$	$q_e = \frac{1}{I}$ $k_2 = \frac{I^2}{S}$
Linear 3	$q_t = q_e - \frac{1}{k_2 q_e}(\frac{q_t}{t})$	q_t vs. $\frac{q_t}{t}$	$q_e = Ik_2 = \frac{-1}{IS}$
Linear 4	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	$\frac{q_t}{t}$ vs. q_t	$q_e = \frac{-I}{S}$ $k_2 = \frac{S^2}{I}$

Retrieved from Rout, et al., 2015 [83]

2.5 Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) is a characteristic of soil which presents the capacity of soil to attract, retain and hold exchangeable cations like Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, etc. Many soil characteristics attraction the soil exchangeable capacity especially pH, texture, and organic matter content up to a certain extent. pH plays a significant role which is positively related with CEC, therefore, high pH values increase numbers of negative charges on the colloids and CEC [87].

In recent years, the search for low-cost adsorbents that have metal binding abilities has heightened. Materials available in large quantities such as natural materials can be utilized as low cost adsorbents such as natural bentonite, natural clay and natural zeolite can be tested with cation exchange capacity due to their physical and chemical properties. Especially in crystalline zeolites, there are some of effective cation exchangers and they have two to three times the cation exchange capacity than other clay minerals like smectites and vermiculite [88].

Table 2.16 Pseudo-second-order kinetic model parameters of various adsorbents for Pb^{2+} removal

Adsorbents	**Initial concentration (mg/l)**	**q_e (exp), mg/g**	**K_2, g mg^{-1} min^{-1}**	**q_e (cal), mg/g**	**R^2**	**Ref.**
Custard apple (*Annona squamosa*) bark powder	10	1.5275	0.0011358	2.5999	0.999	[77]
Multiwalled Carbon Nanotubes with Isatin	50	3.64	0.0124	13.91	0.998	[78]
Multiwalled Carbon Nanotubes-COOH	50	16.63	0.3954	16.67	1.000	
Anethum graveolens	330	122.76	0.0023	125	0.999	[84]
Glutamic Acid/Sepiolite	50	50.50	0.0347	50.00	0.979	[85]
	100	77.51	0.00289	74.89	0.805	
Dobera leaves	30	29.76	0.015	30.30	0.999	[86]
Myrtaceae Sawdust	10	0.9689	14.5327	0.9702	1	[79]
Citrus limettioides peel	10	9.400	9.461	0.012	0.997	[80]
Carbon *Citrus limettioides* peel	10	9.980	10.10	0.010	0.999	
Citrus limettioides seed	10	3.480	3.573	0.005	0.994	
Carbon *Citrus limettioides* seed	10	9.900	10.21	0.010	0.998	

Besides soil and clay are measured with CEC method, some materials can also be measured the cation exchange capacity in order to investigate the capability of exchangeable cations in adsorbents. Table 2.17 shows the different material cation exchange capacity values which is expressed as milliequivalent of hydrogen per 100 g of dry material (meq/100g) under the pH and specific surface area circumstances.

Table 2.17 Values of cation exchange capacity from different materials

Materials	**pH**	**Specific surface area (m^2/g)**	**CEC (Meq/100g)**	**Ref.**
Teak tree bark	7	17.45	2.824	[89]
Coconut husk	7	20.31	20.31	
Bentonite	-	72.2	89	[90]
Jimma (Ethiopia) clay soils	3.0 ± 12	39	29.9	[91]
Synthesized zeolite from cyclone ash	9.04	39	137.6	[92]
Moroccan bentonite	7.4	68	84.7	[93]
Saprist Newfoundland Sphagnum peat soils	7	-	70	[94]
Fibrist Newfoundland Sphagnum peat soils	7	-	45	
Ikpoba Clay	-	8.6932	4.8	[95]
Ukpor bentonite	-	28.6	58	[96]

Chapter 3
Methodology

The schematic outline (Figure 3.1) shows the experimental processes during the study.

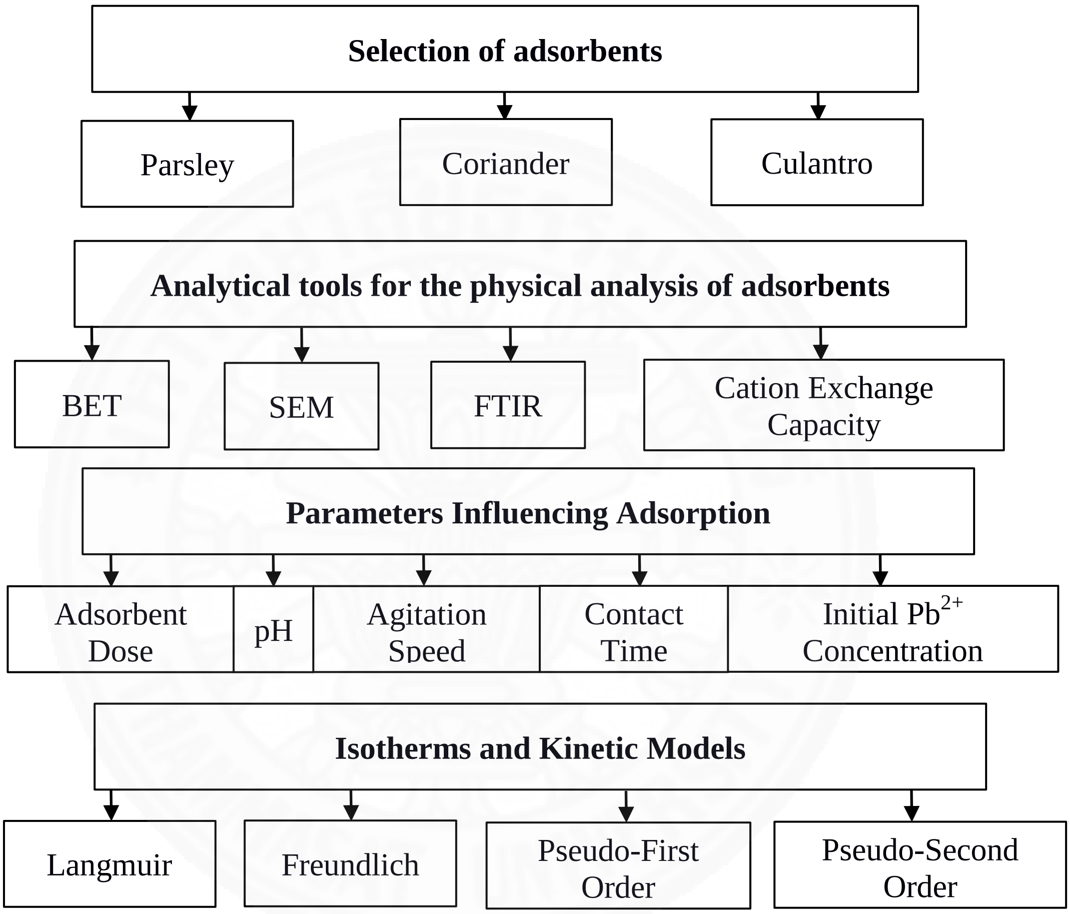


Figure 3.1 Research Framework

3.1 Materials and Chemicals

3.1.1 Preparation of Adsorbents

Parsley, coriander and parsley were bought from the local market in Talad Thai Pathum Thani, Thailand. The plants were washed with the tap water to remove any pulpy residues and then were cut down into small pieces, crushed and washed thoroughly with deionized water to remove any adhering dirt. Next, they were dried in an oven at 90 °C overnight. The dried plants were grounded and sieved through 250 mesh sieve size. The powder plants were stored in an air tight container for further application.

Figure 3.2 Preparation of adsorbents powder

3.1.2 Preparation of Synthetic Lead Water

Lead (II) nitrate ($Pb(NO_3)_2$) was used for the preparation of stock standard solutions of Pb(II). Stock solution of Lead containing 1 mg lead cm^3 was prepared by dissolving 79.95 mg of $Pb(NO_3)_2$ in deionized water. Then 5 ml of HNO_3 was added in order to ensure the long periods of time of the analysis remain in solution and diluted into 500 ml with deionized water. By using this stock solution other dilute standard solutions are prepared of different lead (II) concentrations.

For pH adjustment, 1 N hydrochloric acid (HCl) and/or 1 N sodium hydroxide (NaOH) were used as necessary.

3.2 Characterization of Adsorbents

In order to understand the prepared adsorbents physical and chemical properties, means of various techniques were used to investigate their natural properties such as surface area, functional groups and textural.

3.2.1 Scanning Electron Microscopy (SEM)

In this study, the characteristics of sample surface were examined and analysed by SEM (JEOL Model JSM-5410LV). The adsorbent morphology such as surface texture, pore organization and pore structure of prepared adsorbents before and after lead adsorption were viewed.

3.2.2 Brunauer–Emmett–Teller (BET)

Prepared adsorbents were first sieved in to 250 mesh sieve and then they were used for BET analyses to determine the total specific surface area. Surface area characterization was performed using Micromeritic physical adsorption apparatus, 3Flex USA, using nitrogen adsorption based BET theory. Degas conditions were done under vacuum from an initial heating rate of 10 °C per min up to a temperature of 110 °C kept for a minimum of 9 hours.

3.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The functional group of prepared adsorbents on surface was analzyed by Thermo Scientific Nicolet iS50 FT-IR spectrometer. The analysis was done automatically by OMNIC version 9.2 software which is attached to the system.

3.3 Experiment Procedure

All the experiments were carried out in 125 mL Erlenmeyer flasks with 50 ml test solution at room temperature (25 ± 2 °C). The adsorption tests for lead were performed in batch experiment. The freshly prepared solution was placed in the flask covered tightly with aluminum foil. The amount of adsorbents were weighed in balance and placed in to the flasks. The flasks were then shaken in the orbital shaker at 170 rpm.

This study consisted of the influence of various parameters such as adsorbent dose, pH, agitation speed, contact time and initial lead concentration on the lead uptake. As these factors play role in the adsorption process, the optimization of each parameter is essential to estimate the maximum removal, equilibrium time and kinetics and selection of an isotherm. The average pH values of the solutions at the initial of the experiments were determined by using the METTLER TOLEDO digital pH meter.

Figure 3.3 Adsorbent samples with lead solution were shaken in the rotary shaker

3.3.1 Data Analysis

The adsorption at equilibrium, q_e (mg/g), was calculated from the mass balance equation as in equation (i);

$$q_e = \frac{C_0 - C_e}{m} \; x \, V \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where, C_o and C_e are the initial and the final (equilibrium) lead concentration (mg/l) respectively; V is the adsorbate volume (L); and m is the mass of adsorbent used (g).

The percentage of lead ion removal was calculated as in equation (ii);

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \; x \, 100 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

where, C_0 and C_t are the initial and the final lead concentration (mg/l) at time t, respectively.

3.3.2 Optimization of Influencing Parameters

The standard test solution of 10 mg/l Pb^{2+} was considered as base concentration for experiments and all other various parameters. For optimizing certain parameter, all other variants were kept at constant values and only one specific parameter is changed.

3.3.2.1 Effect of Adsorbent Dose

A dosage study is a significant parameter in adsorption studies because it defines the capacity of adsorbent for a given initial lead concentration in aqueous solution. 0.1 to 4 g/l (0.1, 0.5, 1, 2, and 4) of adsorbent were mixed with 50 ml of 10 mg/l of lead solution in a 125 mL Erlenmeyer flask prior to shaking in the rotary shaker. After that the flasks were constantly agitated at 170 rpm in the rotary shaker for 2 hours. Then the minimum dose applied for maximum removal was considered as optimum dose.

3.3.2.2 Effect of pH Value

The adsorption of lead ion depends on the solution pH which influences the electrostatic binding of ions to correspondent metal groups. Change in pH influences the adsorption process through isolation of functional groups as the active sites on the surface of the adsorbent, which will subsequently create a transfer in reaction kinetics and equilibrium characteristics of the adsorption process.

The optimization of pH is necessary, so the effect of pH was studied in the range of 2- 10. For this purpose, 50 ml of the working lead solution (10 mg/l) was poured in different flasks and pH was adjusted from 2 - 10 (2, 3, 4, 5, 6, 7, 8, 9, 10) by adding 0.1N HCl and 0.1N NaOH drop wise. Then the selected optimum dose of each adsorbent was added in those flasks and was agitated at 170 rpm for 2 hours. Finally, the remaining lead concentration was analyzed in the filtrate and one optimum pH value was selected for each adsorbent at which the maximum removal occurs.

3.3.2.3 Effect of Agitation Speed

The effect of agitation of the sorbent/sorbate system in lead adsorption was controlled at speed range: 100 – 300 rpm agitation speeds (100, 150, 200, 250, 300 rpm). The chosen dose of each adsorbent was added in the 50 ml of 10 mg/l lead concentration maintained at appropriate pH value. Next, the conical flasks were agitated at 100-300 rpm for 2 hours and optimum speed was then determined.

3.3.2.4 Effect of Contact Time

It is important to examine the effect of contact time required to achieve equilibrium for designing the batch adsorption experiments. In order to determine the contact time required for equilibration, the kinetics of lead ion adsorption on the adsorbents were examined as a function of shaking time (10, 20, 30, 40, 50, 60, 120, 180, 360 min) at 25 ± 2 °C. 50 ml of sorbate was maintained at constant pH value and the optimum adsorbents were then added into the respective flask. After this, the flasks were shaken at the 170 rpm speed for the required time and the optimum residence time was determined for the maximum removal.

3.3.2.5 Effect of Initial Lead Concentration

Finally, once all the optimum parameters were identified for adsorption, finding the effect of increasing initial lead concentration becomes important. So, different adsorbate concentrations of 10 to 50 ppm were prepared by the serial dilution of 500 ppm stock solution. 50 ml of each of these sorbate concentrations were placed in the particular flasks and the optimum pH was maintained in each solution. With the addition of the required dosage of the respective three adsorbents, the rotary shakers were agitated at 170 rpm for 2 hours.

3.3.2.6 Tea Bags Application

Tea bags with initial [Pb^{2+}] = 1 mg/l, 1 g/l dosage under neutral pH and without centrifuge were used in this study in order to investigate if this can be used to adsorb lead from water in small scale. The samples settled in different of contact time started from 120 -720 min.

3.3.3 Cation Exchange Capacity (CEC)

The cation exchange capacities (CEC) of the adsorbent samples were determined by the US-EPA Method 9081 (Chapman, 1965) [97]. The experimental procedure is shown in figure 3.4 below.

4 grams of the adsorbent samples were exchanged with functional groups in an aqueous solution of sodium acetate solution for 5 minutes at room temperature (25 ± 2 °C). After that, the samples were centrifuged (High Speed Refrigerated

Centrifuge Himac, CR20G series, Hitachi) and adsorbent samples saturated with sodium. Finally, 1M ammonium acetate solution was then added which replace the adsorbed sodium with ammonium. The concentration of displaced sodium was then measured by the ICP-AES (SPS7800 Series, Seiko Instruments Inc.).

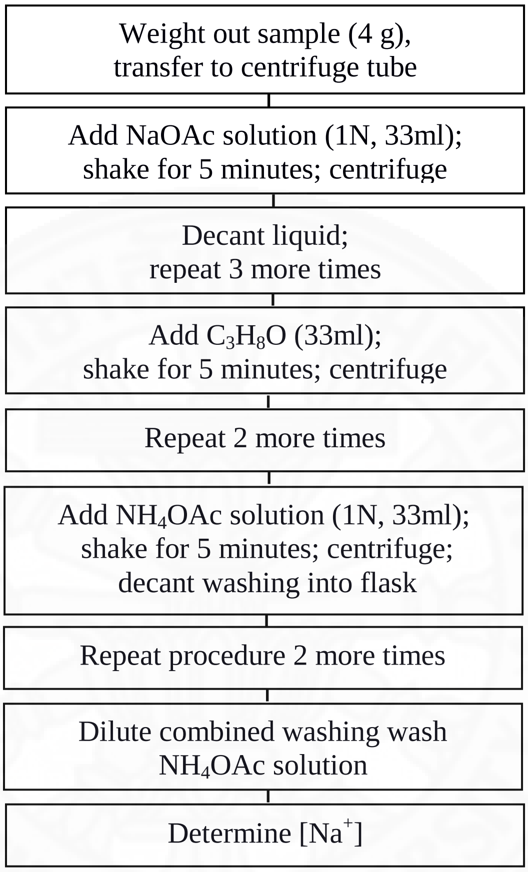


Figure 3.4 Experimental procedure of CEC

3.4 Application of Adsorption Isotherms

Adsorption isotherm plays a significant role in predictive modeling for analysis and design of adsorption systems. Langmuir and Freundlich were employed in this study. These two models are commonly chosen in adsorption because of their simplicity and they can be easily linearized. The study was carried out using different lead concentrations of 10 mg/l to 50 mg/l (10, 20, 30, 40 and 50) with the optimum adsorbent doses. The equilibrium value of lead adsorption by selected adsorbents was plotted against equilibrium lead concentration to estimate the suitability of these two models.

3.4.1 Langmuir Isotherm

Langmuir isotherm is based on the monolayer sorption of Pb^{2+} on the surface of carbon sites and is presented linearly by the following;

$$(C_e/q_e) = (1/Q_ob) + (C_e/Q_o) \quad \text{……………………………..…… (i)}$$

where, C_e equilibrium lead concentration (mg/l), q_e is amount of lead adsorbed per unit mass of adsorbent (mg/g), Q_o and b are Langmuir constants related to measures of monolayer adsorption capacity (mg/g) and adsorption rate (L/mg). Values of Q_0 and b are calculated from a plot of C_e/q_e against C_e which gave a straight line graph with a slope $1/Q_0$ and intercept of $1/bQ_0$.

The important features of the Langmuir isotherm can be explained in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1+bC_i} \quad \text{……………………………..…… (ii)}$$

where, C_i is initial lead concentration (mg/l) and b is reciprocal of concentration at which half saturation of adsorbent is achieved. R_L value represents the adsorption nature to be either unfavorable if R_L greater than 1, linear if R_L equals to1, favorable if R_L is in range 0 - 1 and irreversible if R_L equals to 0 [68].

If the adsorption process is non-ideal and reversible in nature, it will not be limited to the establishing of monolayer. So, for the multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface, Langmuir model does not work and then Freundlich isotherm need to be applied.

3.4.2 Freundlich Isotherm

Freundlich isotherm explains the heterogeneous surface energies by multilayer sorption and is presented by the following;

$$\log q_e = \log K_F + (1/n) \log C_e \quad \text{……………………………..…… (i)}$$

where, K_F and n are the Freundlich constants consolidating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium, respectively.

The values of n and K_F were obtained from slope and intercept of plots of linear graphs plot between log q_e against log C_e. If value of 1/n is lower than one it presents a normal adsorption [68].

The appropriateness of these two equations to describe experimental data was decided by comparing the correlation coefficient, R^2 values. A higher of the R^2 value means it is closer to unity, hence it is suggested model for describing isotherm parameters.

3.5 Application of Adsorption Kinetics

The adsorption kinetics explains the rate of adsorbate uptake on adsorbent, which determines the adsorption equilibrium time. Understanding of adsorption kinetics is helpful for modeling the adsorption process. In order to analyze the performance rate-controlling steps involved in the process of adsorption. In present study, kinetic parameters were estimated from the batch adsorption of 10 mg/l lead concentration. The time was various from 10 min to 360 min depending on adsorbents and lead removal percentage were computed. The experimental data from plotting between times against percent removal were fitted to the pseudo-first-order and pseudo-second-order models.

3.5.1 Pseudo-First Order Kinetic Model

The pseudo-first-order the rate of adsorption based on adsorption capacity;

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where q_e and qt are the amounts of Pb^{2+} adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the adsorption rate constant, which can be determined from the slope of linear plot of $\log(q_e - q_t)$ against t.

3.5.2 Pseudo-Second Order Kinetic Model

The pseudo-second-order expression is utilized to explain chemisorption involving valence forces and ion exchange. The pseudo-second-order adsorption kinetic model is expressed as;

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where q_t is the amount of solute adsorbed on the adsorbent at time t (mg/g), and q_e is the amount at equilibrium (mg/g), and k_2 is the rate constant of the model, which can be determined by plotting t/q_t against t.

To determine the best fitted kinetic model, it depends on correlation coefficient (R^2) value, the closest to 1 indicate the suitable kinetic model. If kinetic model best fits with pseudo-first-order reaction, it shows that the reaction is tender towards physisorption. Likewise, if the reaction fits well with the pseudo-second-order model it shows a tendency towards chemisorption.

3.6 Analysis of Samples

At the end of desired contact time, the conical flasks were removed from rotary shaker and stood for 2 min for settling the adsorbent. Finally, the samples were filtered by using Nylon Syringe Filters, 0.22 Micron, 13 mm and filtrates were analyzed for residual lead concentration by using an Inductively Coupled Plasma (ICP) Spectrometer (Optima 8000, PerkinElmer).

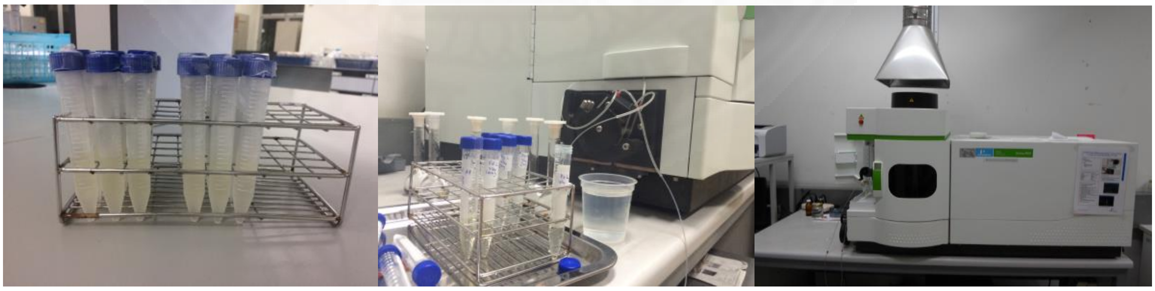


Figure 3.5 Steps for analyzing residual lead concentration in the sample using an Inductively Coupled Plasma (ICP) Spectrometer

Chapter 4
Results and Discussion

4.1 Characterization of Adsorbents

4.1.1 BET Surface Area and Pore Volume

Surface area and porosity are two significant physical properties that impact the quality of adsorbents. Surface area measurement may be the most commonly used means to characterize porous materials. Since the surface area coincides to the roughness of the particle external and its porous internal. Differences in the surface area and porosity of particles in each material, may have the same physical dimensions and these can influence material performance characteristics. According to International Union of Pure and Applied Chemistry (IUPAC), there are three classification of pore on the basic of pore diameter as shown in Table 4.1. The pore characteristics and surface area of adsorbents calculated by Micromeritic, 3Flex USA software Version 3.02 is presented in Table 4.2.

Table 4.1 Pore classification on the basic of pore diameter

Class	Diameter
micropores	$d_p < 20$ Å
mesopores	20 Å $\leq d_p < 500$ Å
macropores	$dp \geq 500$ Å

Retrieved International Union of Pure and Applied Chemistry (IUPAC)

According to the IUPAC classification, parsley, coriander and culantro are classified as mesopores size. The nitrogen isotherm adsorption of parsley, coriander and culantro are presented in Appendix A. Coriander has highest surface area followed by culantro and parsley. The surface areas of the selected adsorbents are high when comparing with other biogenic adsorbents such as litchi peel (3.02 m^2/g), banana peel (1.87 m^2/g) and orange peel (4.518 m^2/g) [98]. Therefore, the BET analysis of the selected adsorbents may assist lead adsorption capacity in the further batch adsorption studies.

Table 4.2 The BET surface areas and pore characteristics of prepared adsorbents

Adsorbents	**Correlation coefficient (R^2)**	**Sample mass (g)**	**BET Surface Area (m^2/g)**	**Total Pore Volume (cc/g)**	**Mean Pore Diameter (Å)**
Parsley	0.999	0.4105	75.4245 ± 0.6246	0.1560 at P/P_0 = 0.996	46.1120
Coriander	0.999	0.3626	88.7603 ± 0.7261	0.1556 at P/P_0 = 0.994	47.2345
Culantro	0.999	0.3863	75.9303 ± 0.6591	0.1560 at P/P_0 = 0.996	46.4445

4.1.2 Surface Morphology

Scanning Electron Microscope was employed to determine the surface characteristics of prepared samples and metal loaded samples in order to perceive the impact of Pb^{2+} sorption on the surface of prepared adsorbents. The surface of adsorbents can be described both exterior and interior depending on their depth and width ratio. As seen in the SEM micrographs, the change in surface texture and pore development of adsorbents are obviously distinct. The SEM images of prepared adsorbents before and after adsorption of lead are shown in Figure 4.1 – 4.3

All of three adsorbents before adsorption process exhibited irregular and rough surface morphology. After the adsorption of Pb^{2+} a rough surface with the possession of heterogeneous and disarrangement grooves was remarked, this presented that a change in the morphology of the material surface (less irregular) can be attributed to the lead adsorption process.

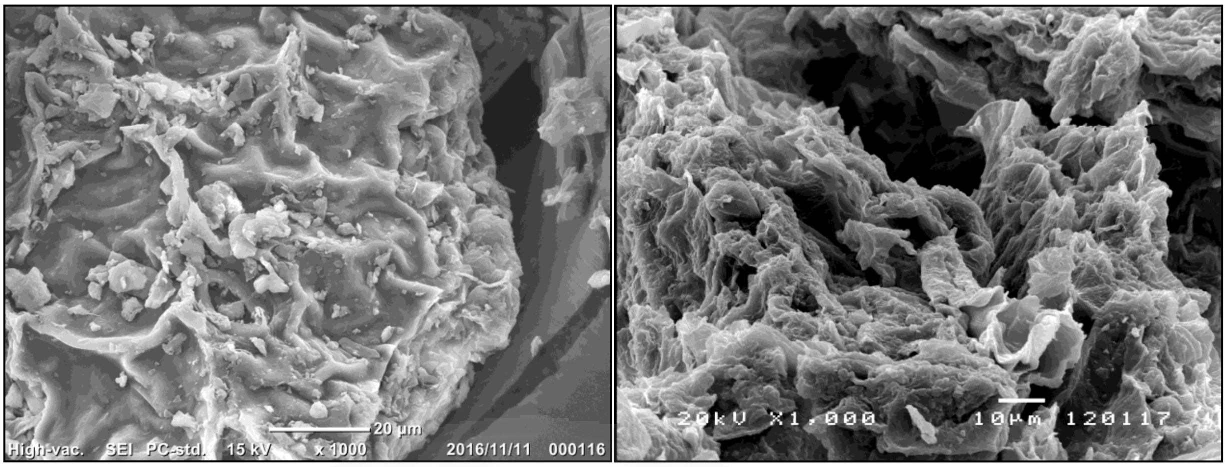


Figure 4.1 SEM images of parsley before (left) and after (right) sorption of Pb^{2+} (1000x)

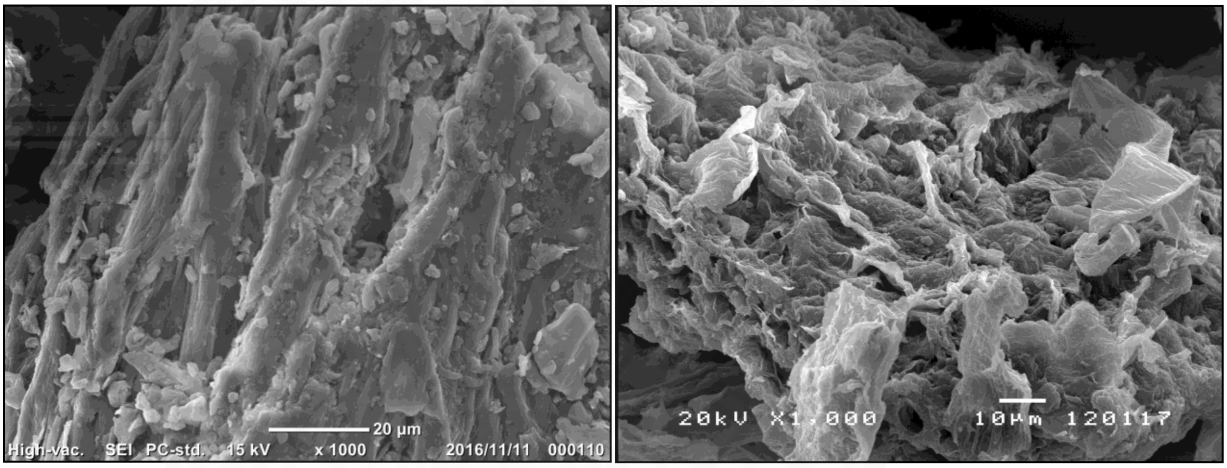


Figure 4.2 SEM images of coriander before (left) and after (right) sorption of Pb^{2+} (1000x)

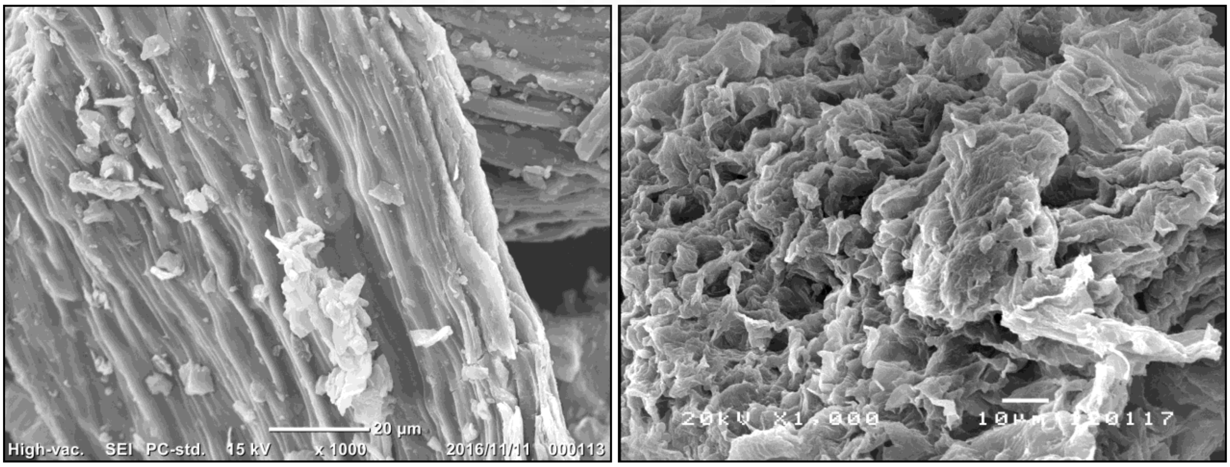


Figure 4.3 SEM images of coriander before (left) and after (right) sorption of Pb^{2+} (1000x)

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out for prepared adsorbents in order to determine the influence of the surface functional groups. The spectra of three adsorbents obtained from FTIR spectroscopy are presented in Appendix B and the functional groups favourable for lead adsorption are listed in Table 4.3. The spectrum reveals eight explicit bands in the wave number range of 3,300–1,000 cm^{-1} for the entire range of observation. From these results, it can be concluded that these adsorbents, mainly contain presence of amines, hydroxyl and aldehydes groups. According to the basic of acidic and basic character of adsorbent surface, the acidic behavior is associated with oxygen-containing functional groups like hydroxyl and phenols [99]. Oxygen surface groups are generally considered to be responsible for the adsorption of heavy metal ions. Therefore, some bands that corresponding to phenols includes proteins and the inhibition of the bands associated to the amino and hydroxyl groups expected to assist the efficiency of Pb^{2+} adsorption.

Table 4.3 FTIR spectroscopic band assignment of surface functional groups on adsorbents

Wave number (cm^{-1})			**Functional Group**	**Ref.**
Parsley	**Coriander**	**Culantro**		
3278.19 (Broad band)	3273.95 (Broad band)	3279.50 (Broad band)	Amine (–NH) and (–OH) hydroxyl stretching vibrations of plant proteins and phenols	[99]
2918.25	2920.29	2918.36	Aldehydic, C–H stretching	
2850.09	2851.19	2850.42	Symmetrical CH_2 stretching	[100]
1731.48	1733.51	1734.40	C=O stretching	
1604.08	1616.51	1600.99	C=O stretching vibrations (from amide I of proteins)	[99]
1369.95	1370.71	1315.66	C–N stretching of aromatic amino group	
1237.36	1235.75	1238.14	C–H vibration of methyl group and/or C–O stretching band.	
1014.18	1029.39	1010.34	C–N stretching vibrations of the amine	[101]

4.1.4 Cation Exchange Capacity (CEC)

The results of cation exchange capacity of selected adsorbents are shown in Table 4.4.

Table 4.4 Cation exchange capacity of selected adsorbents

Adsorbents	**Parsley**	**Coriander**	**Culantro**
CEC x 10^{-4} (mol/g)	10.0887	8.8804	9.5560

The CEC value of parsley provided the highest value of CEC followed by culantro and coriander, respectively. Differential of CEC values of these adsorbents may depend on two reasons. Firstly, some of these exchangeable cations are placed at unapproachable sites of adsorbents structure. Secondly, the exchangeable cations might consist of impurities. Therefore, not all exchangeable cations within adsorbents are available for ion exchange.

Exchangeable cations may become available to plants especially in roots. Hydrogen ions from the root hairs may replace nutrient cations from the exchange complex on soil colloids. The nutrient cations are then released into the soil solution where they can be taken up by the adsorptive surfaces of roots. The order of strength of adsorption also relies on valency associated with the abundance of different ion type and ion size; trivalent cations such as Al^{3+} and Fe^{3+} are held more tightly than divalent cations like Mg^{2+}, $Ca^{2+}$and Pb^{2+} and univalent like cations Na^{+}, K^{+} and Cs^{+} ions [102]. Therefore, in this present study, it is possible that large Pb^{2+} ions may tends to replace selected adsorbents with good efficiency.

4.2 Batch Adsorption Studies

The idea of the optimum operating conditions would assist and indicate better design and modelling adsorption processes. Therefore, the results from batch studies to find optimum adsorbent dose, pH, agitation speed, contact time and initial lead concentration are described concisely under the following sections.

4.2.1 Effect of Adsorbent Dose

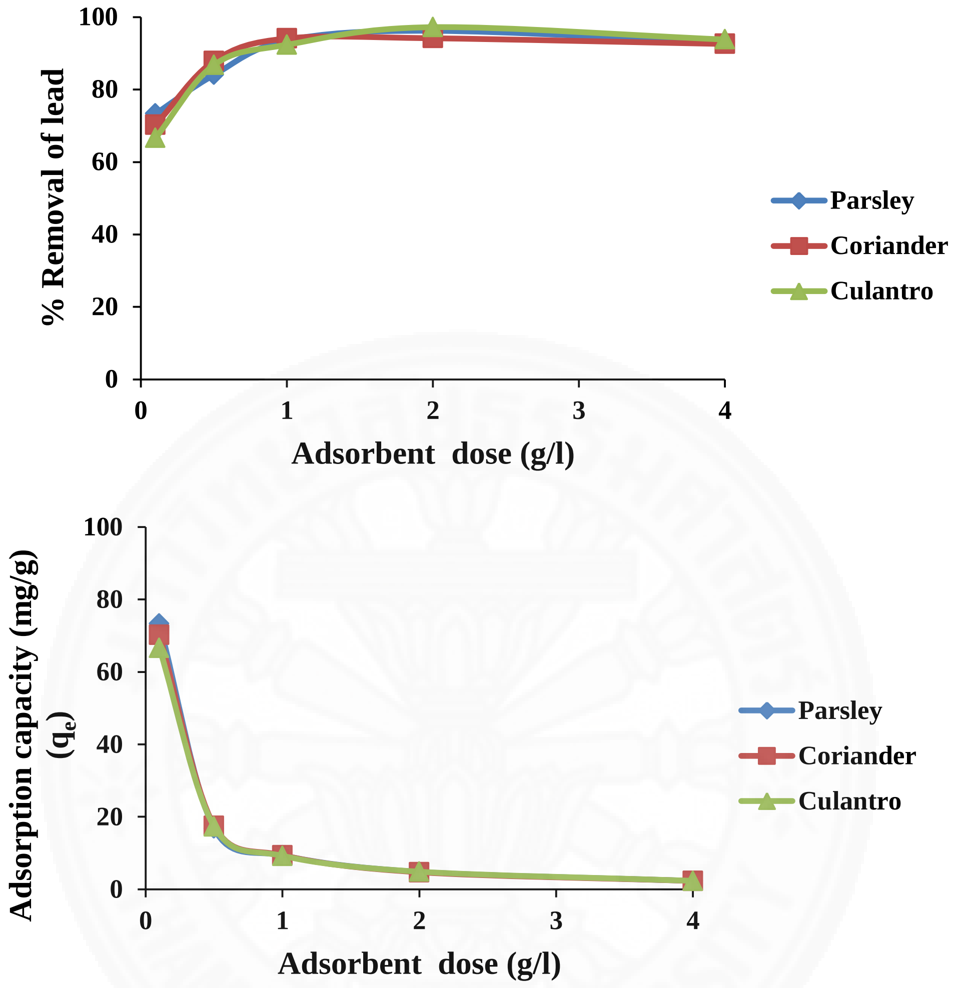


Figure 4.4 Effect of adsorbent dose on the removal of lead by parsley, coriander and culantro (Initial Pb^{2+} 10 mg/l, pH = 5, contact time = 2 hrs. with 170 rpm)

As seen from Figure 4.4, lead removal efficiency increased from 73.31 to 96.20 %, 70.24 to 94.15 % and 66.63 to 97.21 % for 0.1 to 2 g/l dose of parsley, coriander and culantro, respectively. The lead removal efficiency of adsorbents must be directly corresponding with surface area of adsorbents. This is because when the number of adsorption sites or surface area increases due to the weight of adsorbent and hence results in a higher percentage of lead removal at a high dose. However, the percent removal of three absorbents slightly decreased from 96.20 to 93.06 %, 94.15 to 92.57 % and 97.21 to 93.80 % for 4.0 g/l dose of parsley, coriander and culantro, respectively. This is because of the reduction in net surface area from the overlapping of binding sites at the higher adsorbent doses [70].

Whereas, with increasing of adsorbent dosage, the adsorption capacity of adsorbents was decreased. For parsley, coriander and culantro, the adsorption capacity shifted from 73.32 to 2.33 mg/g, 70.24 to 2.31 mg/g and 66.63 to 2.35 mg/g, when the dose was increased from 0.1 to 4 g/l for the respective adsorbents. This occurs because the adsorptive capacity of adsorbent available is not fully utilized at a higher adsorbent dosage in comparison to lower adsorbent dosage.

To achieve the maximum uptake and high removal efficiency, the surface loading or the mass ratio of lead to adsorbent dose must be less than optimum value. Therefore, in order to assure effective adsorption at lower adsorbent dose 1 g/l was chosen as the applied dosage for three adsorbents. At this dose, the lead removalefficiency of these adsorbents was 93.55 %, 94.10 % and 92.35 % for parsley, coriander and culantro, respectively.

4.2.2 Effect of pH

The pH of a solution has a crucial influence on lead uptake as it determines the surface charge of the sorbent, the degree of ionization and specification of the lead ions. When the solution is mixed with adsorbent, a colloidal suspension is accumulated with electrical charges. Hence, it is important to understand whether the adsorbent surface is positively or negatively charged, depending on different pH values.

As seen from Figure 4.5, the adsorption of lead increased at low pH of 2 – 3 and at pH of 4 afterward, the adsorption percent decreased, showing the maximum adsorption at pH 3 for three adsorbents. For parsley, coriander and culantro, the maximum lead removal efficiency of 96.30 %, 97.62% and 97.58% was recorded at pH 3. The low adsorption of Pb^{2+} ions at pH 2 was due to high concentration and high mobility of H^+ ions, which competed with Pb^{2+} ions for the adsorption sites, this interrupt the adsorption of Pb^{2+} ions. Protonated adsorption sites were incapable of binding Pb^{2+} ions due to electrostatic elimination between positively charged Pb^{2+} ions and positive charged sites. Therefore, only low percentages of Pb^{2+} ions were adsorbed. As the pH increased, there were fewer H^+ ions present in the solution and thus more negatively charged sites were made available and this accommodated greater Pb^{2+} ions uptake by electrostatic attraction.

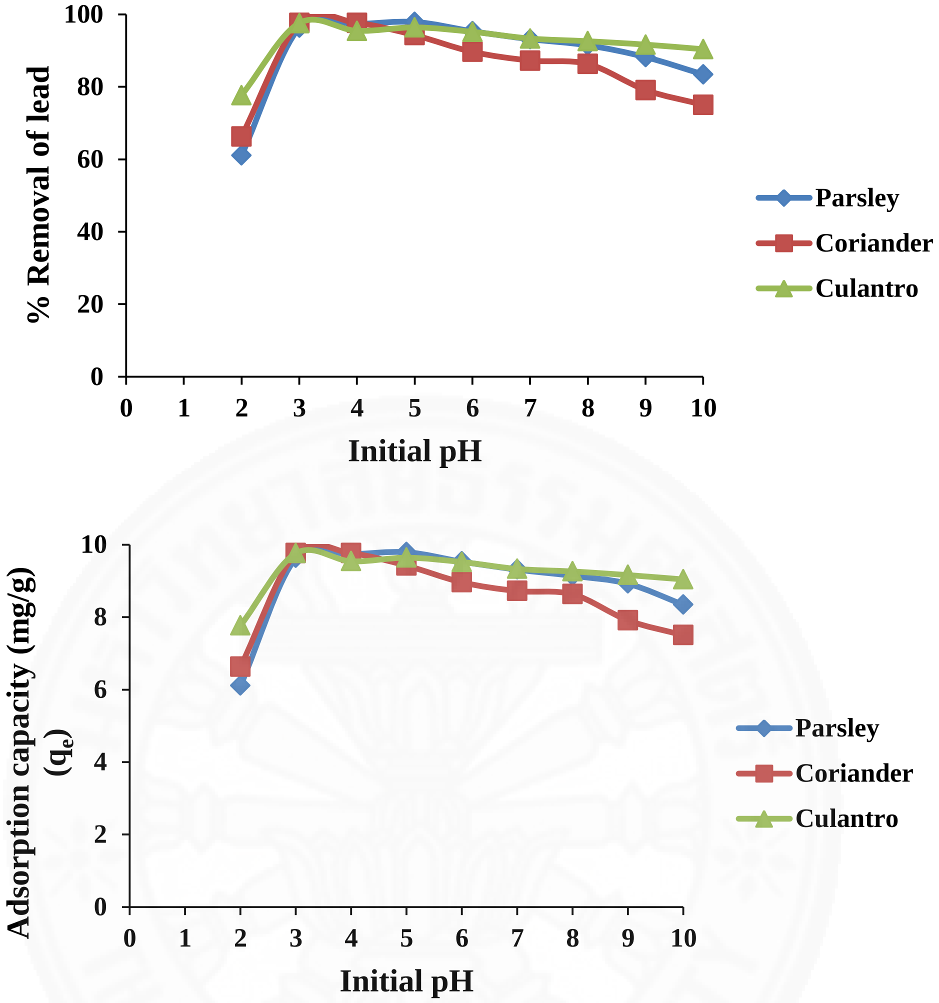


Figure 4.5 Effect of pH on the removal of lead by parsley, coriander and culantro (Initial Pb^{2+} 10 mg/l, 1 g/l dosage, contact time = 2 hrs. with 170 rpm)

Moreover, the effect of pH can be also explained by considering the FTIR analysis. In biomass materials, the functional groups basically hydroxyl (-OH) and carboxyl (-COOH) at low pH get protonated by H^+ ions leading to a net positive charge on the surface of the biosorbent as described by following equation:

$$ROH + H^+ \rightarrow ROH_2^+$$

$$RCOOH + H^+ \rightarrow RCOOH_2^+$$

Consequently, this establishes a repulsive force between cationic species of the Pb^{2+} ions and the positively charged surface of the sorbent, which hinders the biosorption process. Hence the small amount of removal achieved at low pH is due to protons H^+ exchange with Pb^{2+}. Whereas, at higher pH values, the removal efficiency was greatly facilitated resulting from the weakened protonation of -OH and -COOH groups while the predominant lead ions are positive; therefore, adsorption increases [103].

Hence, it can be concluded that the adsorption of lead onto the selected adsorbents is depend on pH values. It is always preferable to treat wastewater at neutral pH. This is because the extreme pH values for the utility of maximum lead removal will produce higher costs for post treatment. It was found 93.13%, 87.25% and 93.32% at neutral pH lead was removed by parsley, coriander and culantro from 10 mg/l Pb^{2+}, respectively. High removal efficiency at neutral pH indicates that it could be applied in the real environment.

4.2.3 Effect of Agitation Speed

Agitation speed plays an important factor because it affects outer boundary layer and it can help to estimate the lead removal on various velocities. The effect of agitation speed on lead removal by the selected adsorbents is presented in Figure 4.6.

It shows that stirring rate has same effect on the amount of lead adsorbed. As the stirring rate increased from 100 to 300 rpm, the percent removal of lead increased from 89.37 to 96.64 %, 91.32 to 94.64 % and 91.68 to 95.07 % for parsley, coriander and culantro, respectively. The increase in the lead percent removal at a higher stirring rate could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles. Consequently, near the adsorbent surface, the concentrations of Pb^{2+} ions would be increased. A higher stirring rate also contributes a better mass movement of Pb^{2+} ions from bulk solution to the surface of the adsorbent and shortened the adsorption equilibrium time. However beyond 250 rpm, removal efficiency almost became constant. This can be considered as an optimum speed.

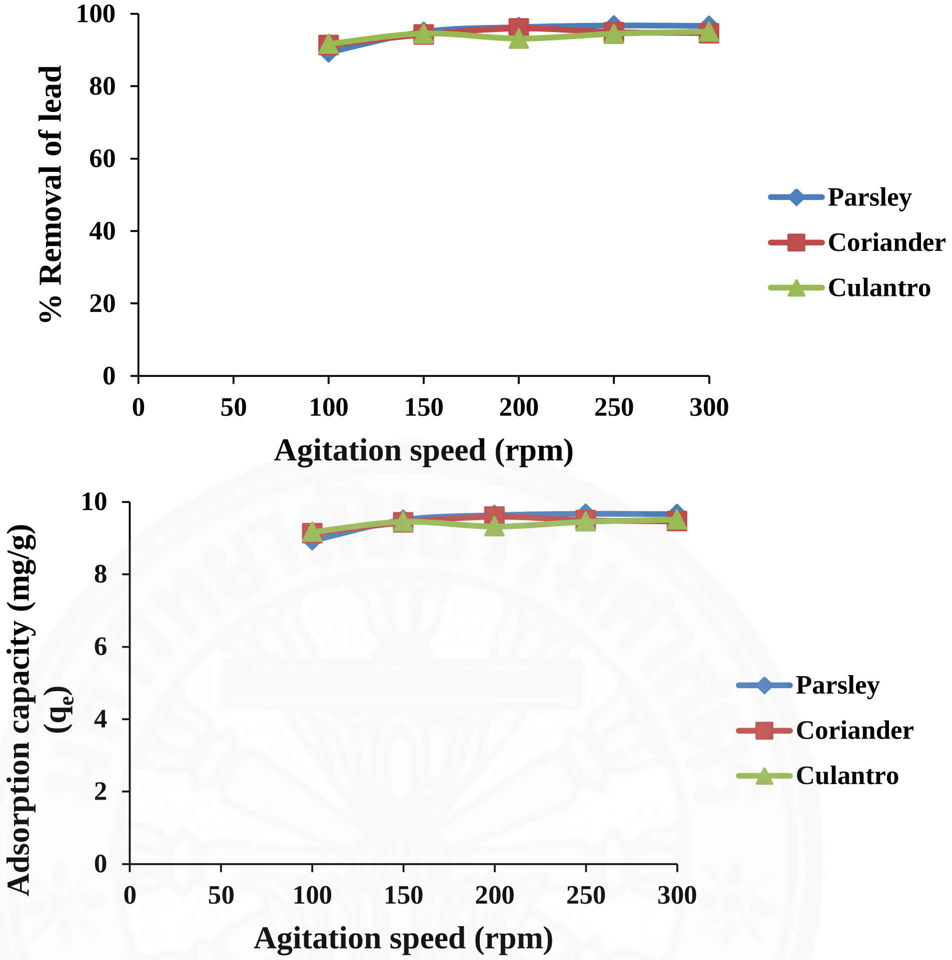


Figure 4.6 Effect of agitation speed on the removal of lead by parsley, coriander and culantro (Initial Pb^{2+} 10 mg/l, 1 g/l dosage, pH = 5 and contact time = 2 hrs.)

Similarly, in Figure 4.6 shows that the adsorption rate increased with the increase in agitation speed. When the agitation speed increased from 100 rpm to 300 rpm, the maximum adsorption capacity increased from 8.93 to 9.66 mg/g, 9.12 to 9.46 mg/g and 9.17 to 9.51 mg/g for parsley, coriander and culantro, respectively. Therefore, it can be concluded that the percent removal of lead correspond with the adsorption capacity for this parameter.

Although, at higher speed resulted in higher lead removal efficiency, it requires more energy input and it may also damage the physical structure of adsorbents [67]. Furthermore, in Figure 4.6 it is obvious seen that the effective removal of Pb^{2+} ions at 150 rpm were not much different from at 250 rpm. Therefore, a 150 rpm agitation speed is sufficient to ensure that all the surface binding sites are made readily available for lead uptake.

4.2.4 Effect of Contact Time

This experiment was carried out in order to detect the time needed for the biosorption process between selected adsorbents and lead to reach equilibrium. The uptake of Pb^{2+} ion as a function of contact time is shown in Figure 4.7.

The sorption of lead for three selected adsorbents was high even at the beginning. Thereafter 60 min of contact time, the adsorption rate became practically constant. The variation in the extent of adsorption may be due to the fact that initially all sites on the adsorbent surface were vacant and the solute concentration gradient was relatively high. Whereas, in the later stage, the binding sites became restricted and remaining sites were not occupied. This cause the sorption system reached equilibrium [104].

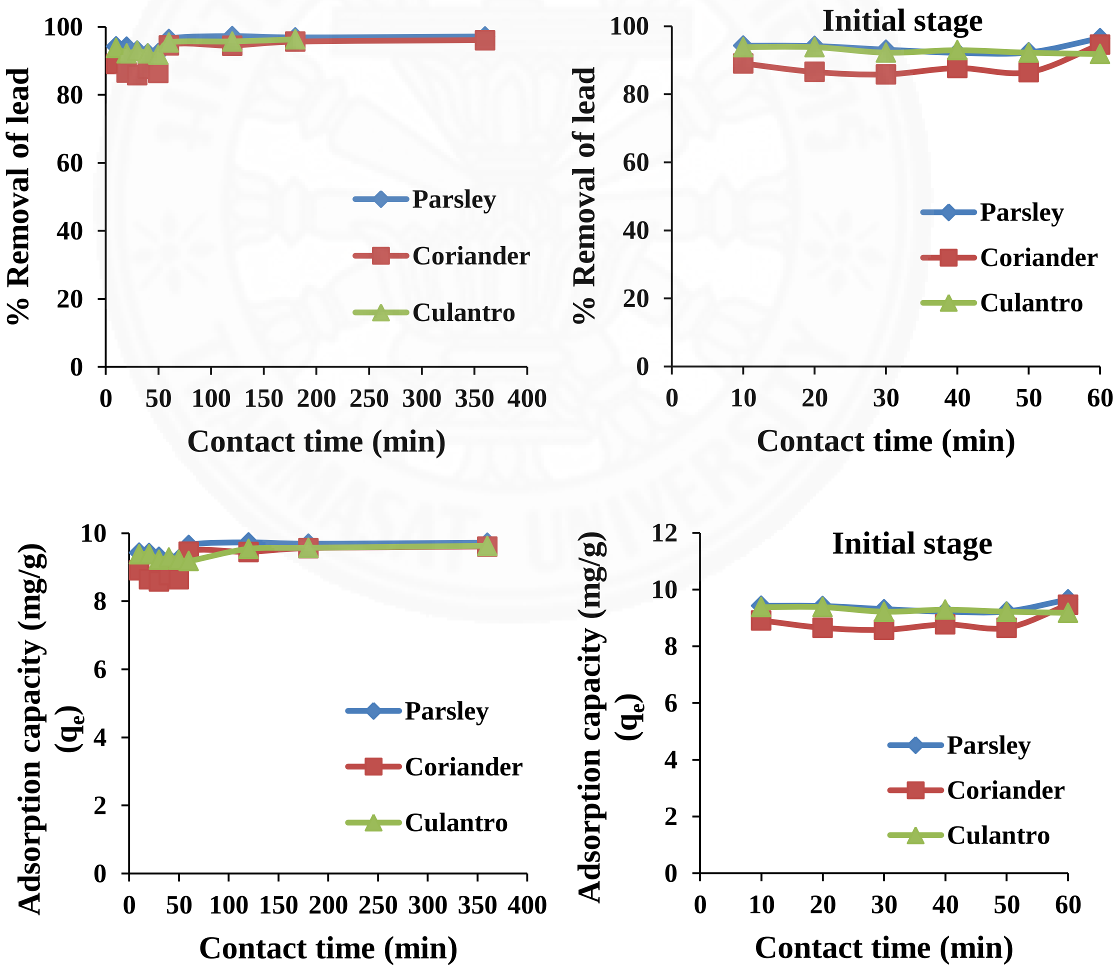


Figure 4.7 Effect of contact time on the removal of lead by parsley, coriander and culantro (Initial Pb^{2+} 10 mg/l, 1 g/l dosage and pH = 5 with 170 rpm)

The removal efficiency of three adsorbents is not much ddifferent. With the lapse of time, the removal gradually reached the constant values of 97.27 %, 94.49 % and 95.42 % for parsley, coriander and culantro for 10 mg/l Pb^{2+}, respectively. This signifies the attainment of equilibrium at the corresponding time of 120 min. When it was compared between percent removal of lead with adsorption capacity under specific time condition.

4.2.5 Effect of Initial Lead Concentration

The speed of adsorption is an operation of the initial concentration of the adsorbate, which makes it a significant factor to be considered for effective adsorption. The effect of various initial lead (II) ion concentration on adsorption of lead (II) ion onto three adsorbents is presented in Figure 4.8.

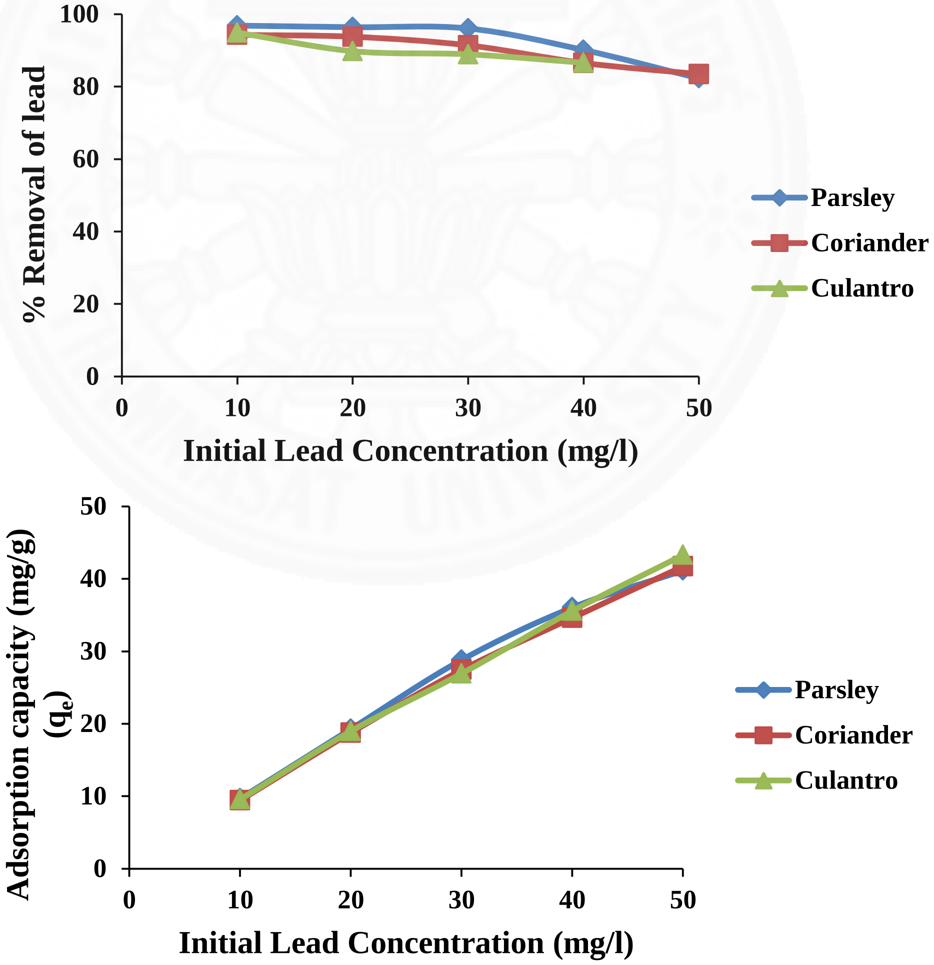


Figure 4.8 Effect of initial lead concentration on the removal of lead by parsley, coriander and culantro (1 g/l dosage, pH = 5 and contact time = 2 hrs. with 170 rpm)

Figure 4.8, it can be seen that 96.83 %, 94.26 % and 95.42 % lead was removed by parsley, coriander and culantro at 10 mg/l lead solution, respectively. This indicates that at lower initial concentrations, sufficient adsorption sites are available for adsorption of lead ions [104]. However, the removal efficiency value decreases with increasing initial concentrations of Pb^{2+} ions in its aqueous solutions. This phenomenon indicates that energetically less favourable sites become involved with increasing lead concentration in the aqueous solution. This occurrence also depends on many controlling factors such as internal structures, ion–exchange process and speed of lead movement through the adsorption process [105].

Additionally, with the increase of lead concentration the major driving force for evacuation of lead from bulk to adsorbent surface increases. This results in more adsorption of lead per unit mass of the adsorbent. In this study, adsorption equilibrium, q_e increased from 9.68 to 41.14 mg/g for parsley, 9.43 to 41.72 mg/g for coriander and 9.54 to 43.28 mg/g for culantro with the rise in initial lead concentration from 10 to 50 mg/l. The curve line shows that adsorption become easier with the enhance in concentration. Hence, it can be concluded that removal percentage and equilibrium adsorption capacity is greatly dependent on initial lead concentration.

4.3 Batch Adsorption Isotherms

The batch equilibrium experimental data of selected adsorbetns were fitted and analyzed via the most two commonly used models in the literature in the following sub-sections. The batch equilibrium data analyzed by Langmuir and Freundlich isotherms was obtained using the optimum dose; 1 g/l, over a wide range of initial lead concentrations; 10-50 mg/l.

4.3.1 Langmuir Isotherm Model

Langmuir isotherm model assumes monolayer sorption via physical forces. The data from adsorption experiments was examined by linear regression of Langmuir isotherm equation and the graphs are plotted as shown in Figure 4.9.

According to Figure 4.9, the graph of C_e/q_e against C_e create a linear line, which approved applicability of Langmuir isotherm. The Langmuir constants, Q_0 and b are computed from intercept and slope of obtained plots, and is listed in Table 4.5

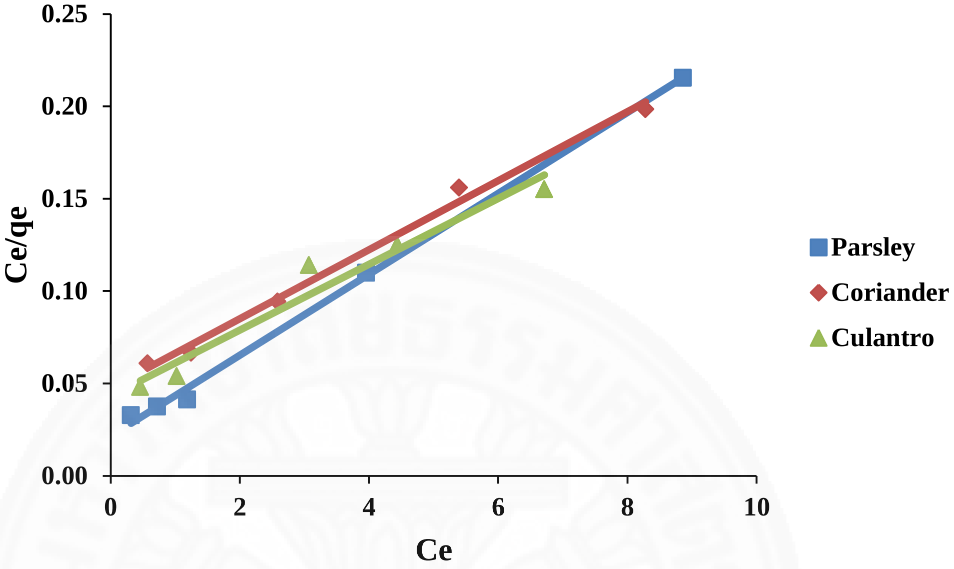


Figure 4.9 Langmuir adsorption isotherm for parsley, coriander and culantro at pH = 5 under a temperature of 298 K

Table 4.5 Results of Langmuir isotherm model for the adsorption of Pb(II) ions onto selected adsorbents at a temperature of 298 K and pH = 5

Adsorbents	**Equations**	**Correlation coefficient (R^2)**	**Surface energy (b)**	**Monolayer adsorption capacity (Q_0)**
Parsley	y = 0.022x + 0.021	0.998	1.022	45.66
Coriander	y = 0.019x + 0.048	0.993	0.392	53.55
Culantro	y = 0.018x + 0.043	0.955	0.411	56.20

As shown in Figure 4.9, the batch equilibrium data of parsley and coriander has perfectly fitted in the Langmuir model, with a correlation coefficient (R^2) greater than 0.99. This phenomenon demonstrates that there is a monolayer adsorption occurs on specific homogeneous sites. Culantro showed highest fit followed by coriander and parsley. Moreover, a higher value of surface energy implied the existence of stronger bonds between lead and adsorbents. To confirm the favorability of the adsorption process, the separation factor (R_L) was calculated and presented in Table 4.6.

Table 4.6 Separation factor (R_L) for selected adsorbents

Initial lead concentration (mg/l)	**R_L**		
	Parsley	**Coriander**	**Culantro**
10	0.089	0.203	0.196
20	0.047	0.113	0.108
30	0.032	0.078	0.075
40	0.024	0.060	0.057
50	0.019	0.049	0.046

As seen from Table 4.6, the R_L value for each adsorbent was found in the range 0 – 1 for 10 - 50 mg/l initial lead concentrations. This confirms that the lead adsorption by three selected adsorbents was favorable for uptake of lead by adsorption process [105]. Figure 4.10 shows a graph was plotted between the separation factor (R_L) values and initial lead concentration (C_i) for each adsorbent in order to interpret the critical features of Langmuir isotherm.

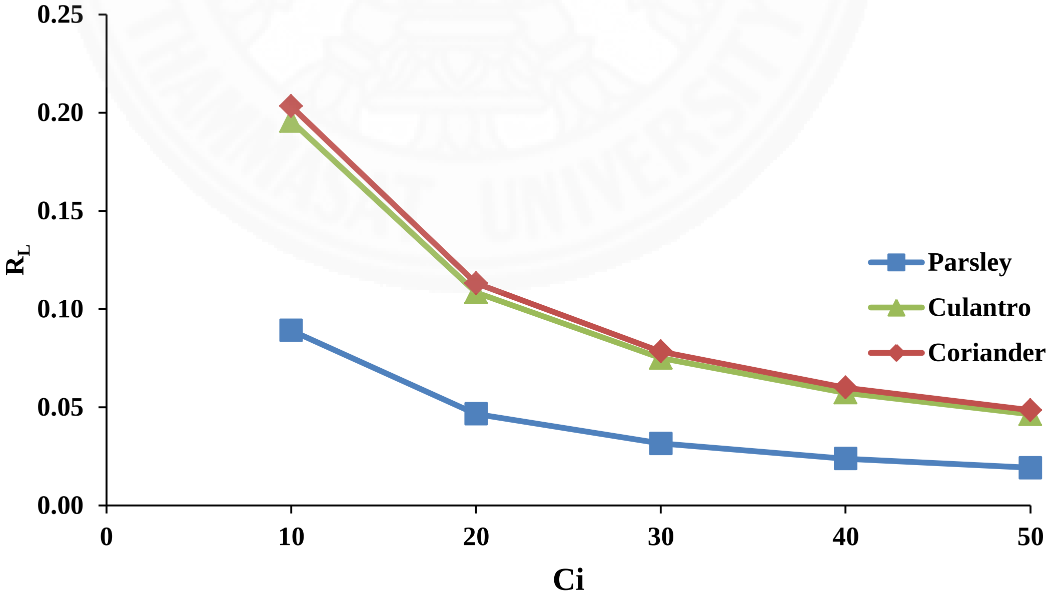


Figure 4.10 Separation factor R_L values initial lead concentration (C_i)

It can be seen that R_L values decrease with increase in the initial lead concentration. This indicated that adsorption was more favorable at higher concentration. The degree of favorability is generally related to the irreversibility of the system, giving a qualitative estimation of the adsorbent lead interactions [105].

4.3.2 Freundlich Isotherm Model

The basic assumption of Freundlich model is the heterogeneous surface energy of adsorption. The relationship the amount of lead adsorbed per unit mass of the adsorbents (q_e) and equilibrium lead concentration (C_e) was obtained from the Freundlich isotherm models as represented in Figure 4.11.

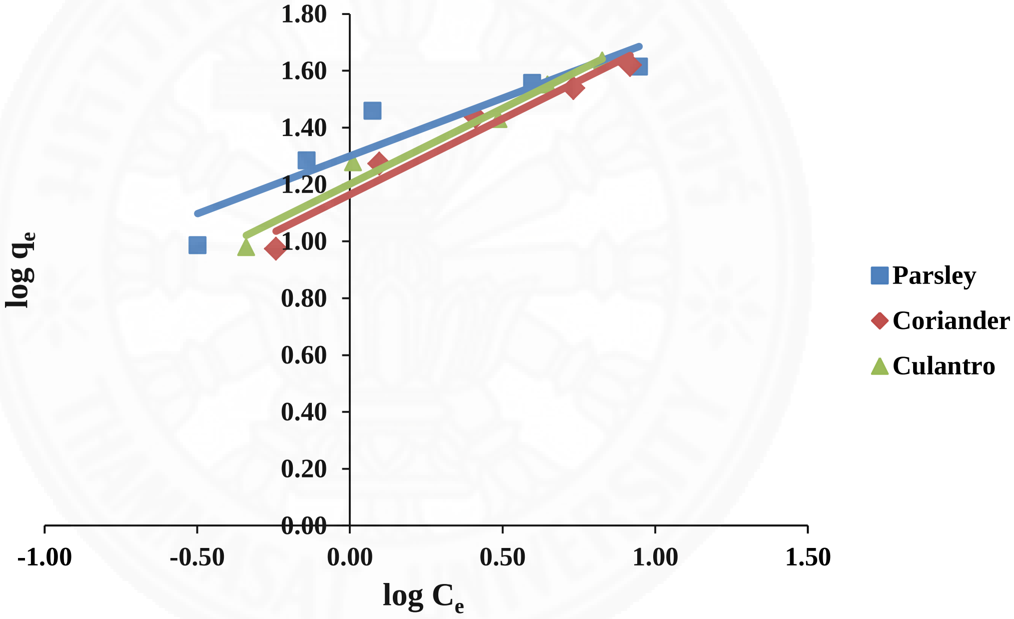


Figure 4.11 Freundlich adsorption isotherm for parsley, coriander and culantro at pH = 5 under a temperature of 298 K

As seen from Figure 4.11, the relationship from graph of log q_e vs. log C_e gave straight line with R^2. The constants in Freundlich isotherm can be calculated from the plot of log q_e versus log C_e and listed in Table 4.7

The R^2 value obtained from Freundlich model of parsley and coriander are not well fitted in this isotherm as compared to Langmuir isotherm. Whereras, culantro is better fitted in this isotherm more than Langmuir isotherm. The K_F values suggest that parsley has the highest capacity to adsorb Pb^{2+} followed by culantro and coriander under identical operating conditions. The value of slope (1/n) values lied between 0 – 1 for all three adsorbents and this confirms the increase in bond energies with the increase in planar density. The 1/n value less than one suggests favourable and chemisorption of the adsorption process.

Table 4.7 Results of Freundlich isotherm model for the adsorption of Pb(II) ions onto selected adsorbents at a temperature of 298 K and pH = 5

Adsorbents	**Equations**	**Correlation coefficient (R^2)**	**K_F**	**1/n**	**n**
Parsley	y = 0.406x + 1.301	0.860	19.984	0.406	2.462
Coriander	y = 0.533x + 1.164	0.957	14.601	0.533	1.875
Culantro	y = 0.531x + 1.202	0.971	15.906	0.531	1.882

When comparing R^2 values from these two isotherms, it can be concluded that the adsorption of parsley and coriander fitted well with the Langmuir model suggesting that the adsorption of Pb(II) onto these adsorbents is a mono-layer process and the adsorption behaviour is homogeneous rather than heterogeneous whereas culantro fitted well with Freundlich model since R^2 from Langmuir model was not close to unity, it could be conceivable that there might be some heterogeneity in the system.

4.4 Batch Kinetic Studies

Adsorption kinetics explains the lead removal rate as a function of equilibrium contact time. The batch kinetic data analyzed by pseudo first and second order kinetic models. These kinetic models were acquired using the optimum dose; 1 g/l, over a wide range of time; 10 - 360 min with 10 mg/l initial Pb(II) concentration.

4.4.1 Pseudo-First Order Kinetic Modeling

The adsorption rate of three adsorbents were estimated on the basis of their adsorption capacity by using pseudo first-order kinetic model. The charts obtained for three selected adsorbents are shown in Figure 4.12.

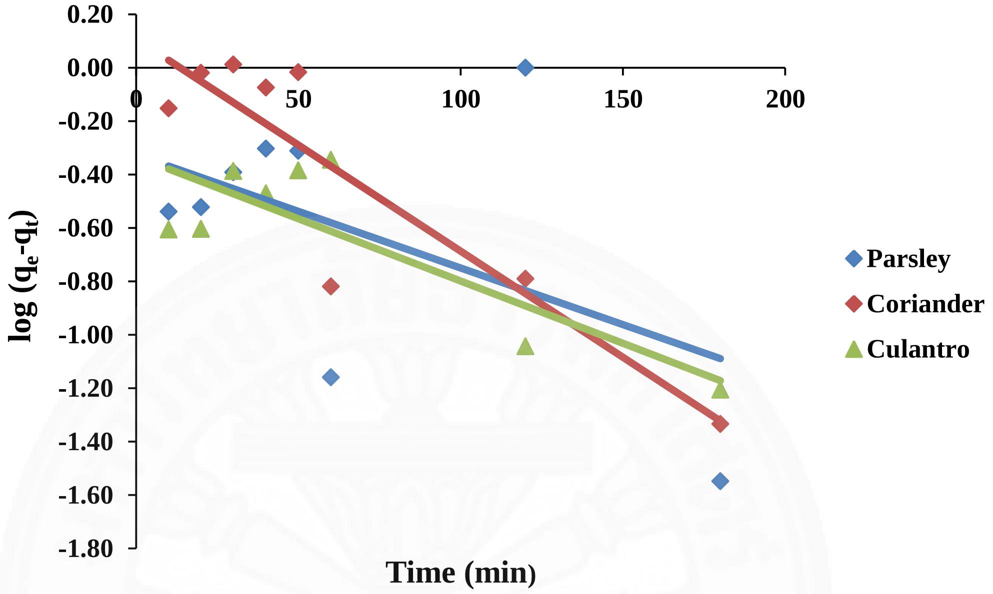


Figure 4.12 Pseudo-first-order kinetic model for parsley, coriander and culantro at pH = 5 under a temperature of 298 K

As seen from Figure 4.12, the correlation coefficient was not high and the equilibrium data were disrupted. Hence, trial and error method is employed to discover the equilibrium adsorption capacity, q_e to identify these kinetic models. The values of pseudo first-order rate constant (k_1) and adsorption capacities from adsorbents are listed in Table 4.8.

Table 4.8 Results of pseudo first-order model for the adsorption of Pb(II) ions onto selected adsorbents at a temperature of 298 K and pH = 5

Adsorbents	**Equations**	**Correlation coefficient (R^2)**	**First order rate constant (k_1)**	**q_e (cal)**	**q_e (exp)**
Parsley	y = -0.007x – 0.294	0.688	0.016	0.011	9.716
Coriander	y = -0.008x + 0.106	0.807	0.018	1.281	9.611
Culantro	y = -0.005x – 0.333	0.697	0.011	0.464	9.632

According to the low correlation coefficient and comparing between the q_e (calculated) and q_e (experimental) values, these finding do not agree with the pseudo first-order kinetic theory. Therefore, it can be concluded that the pseudo first-order equation did not fit well with complete range of contact time and adsorption of Pb(II) onto selected adsorbents is not occurring exclusively onto one site per ion. The first order rate constant indicates the speed of adsorption rate of the lead. Consequently, coriander can produce the highest adsorption rate followed by parsley and culantro, respectively.

4.4.2 Pseudo-Second Order Kinetic Modeling

The adsorption behavior of lead on to parsley, coriander and culantro is presented in Figure 4.13 by using pseudo second-order kinetic model.

This kinetic model provides better description of lead adsorption on the given adsorbents. For these type of reaction, the rate of adsorption is directly proportional to number of active sites on the adsorbent surface. With the assist of above graph the rate constant (k_2) and amount of lead uptake at equilibrium (q_e) were computed for all adsorbents and present in Table 4.9

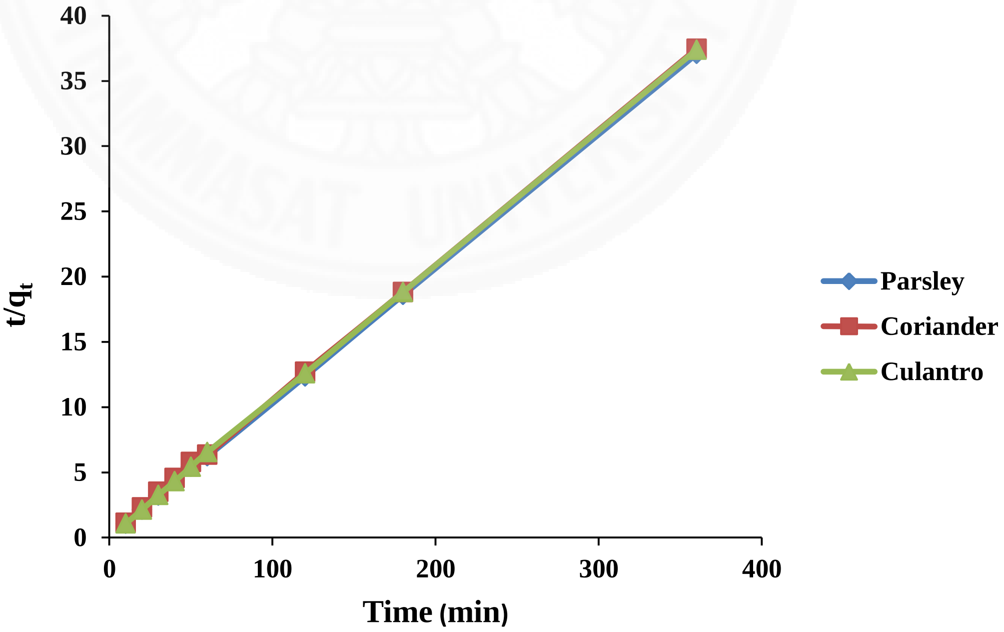


Figure 4.13 Pseudo-second-order kinetic model for parsley, coriander and culantro at pH = 5 under a temperature of 298 K

The correlation coefficients obtained were greater than 0.99 for all contact time studied and there were good agreement between $q_e$cal and $q_e$exp. The good agreement indicates that the pseudo second-order kinetic model is suitable to explain the adsorption behavior of selected adsorbents so that the rate limiting factor could be a chemisorption process, where interactions (chemical bonding) involved sharing or exchange of electrons between the adsorbate and the adsorbent. This indicates that there are strong interactions between Pb^{2+} and adsorbents [107].

Table 4.9 Results of pseudo second-order model for the adsorption of Pb(II) ions onto selected adsorbents at a temperature of 298 K and pH = 5

Adsorbents	Equations	Correlation coefficient (R^2)	Second order rate constant (k_2)	q_e (cal)	q_e (exp)
Parsley	y = 0.102x + 0.136	0.999	0.082	9.753	9.716
Coriander	y = 0.103x + 0.320	0.999	0.034	9.694	9.611
Culantro	y = 0.104x + 0.132	0.999	0.067	9.663	9.632

4.5 Lead Removal Efficiencies of Various Low Cost Adsorbents

The efficiency of three selected adsorbents for the removal of 10 mg/l lead solution at optimum reaction condition (Table 4.10) is presented in Figure 4.14.

Table 4.10 Optimum reaction conditions for selected adsorbents to treat 10 mg/l lead water

Adsorbents	pH	Dose (g/l)	Agitation Speed (rpm)	Contact Time (min)
Parsley	3	2	300	120
Coriander			200	360
Culantro			300	360

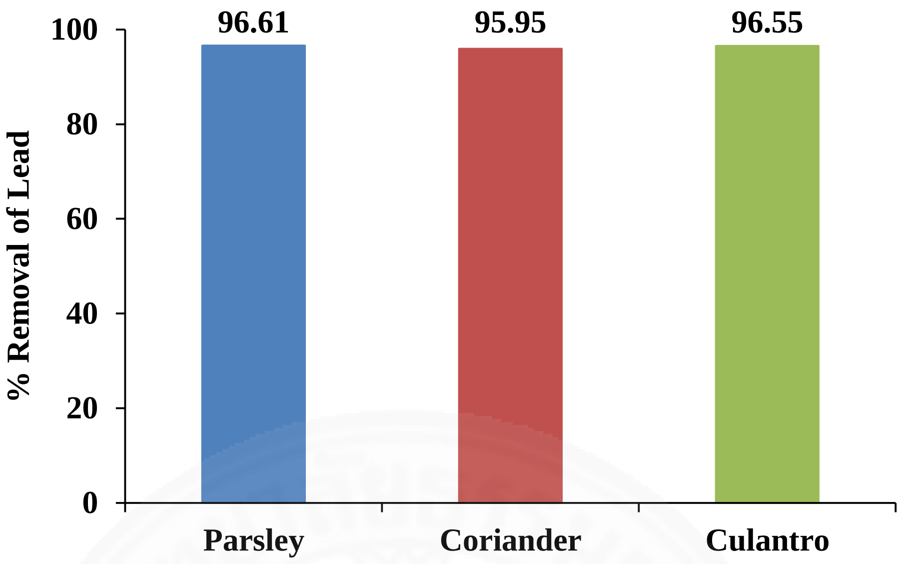


Figure 4.14 Order of effectiveness of adsorbents at their optimum conditions and initial lead concentration of 10 mg/l

As seen from Figure 4.14, lead removal efficiency from each adsorbent is less distinct. It was found that parsley (96.61%) has highest lead removal performance followed by culantro (96.55%) and coriander (95.95%) from 10 mg/l lead solution. Lead removal efficiency depends on adsorbents physical properties and various parameters. The adsorption capacity was greater for higher surface area materials (larger pore size) due to increasing pore volumes. The rich organic functional groups of hydroxyl (-OH) and carboxyl (-COOH) present in adsorbents played important role in lead removal when adjust the pH values. Moreover, cation exchange capacity of adsorbents may support adsorption capacity during adsorption process when the pH value increase.

In the batch studies, the remarkable parameters that effect to the adsorption efficiency are dosage, pH and initial lead concentration. Whereas the results from effect of contact time and agitation speed were similarities. Hence, 1 hr. and 150 rpm are required to practice in order to achieve high lead removal with low cost operation.

4.6 Application of Tea Bags

Tea bags with adsorbents were utilized in this study in order to investigate if this can be used to adsorb lead from water in small scale. The removal of lead of different contact time using tea bags is conducted at 1 mg/l initial Pb(II) concentration.

As seen in Figure 4.15, without centrifuge and at neutral pH under various contact time, lead removal efficiency increased from 11.00 to 84.90 %, 4.50 to 88.10 % and 19.70 to 87.47 % for parsley, coriander and culantro, respectively, when the contact time increased from 120 – 480 min.

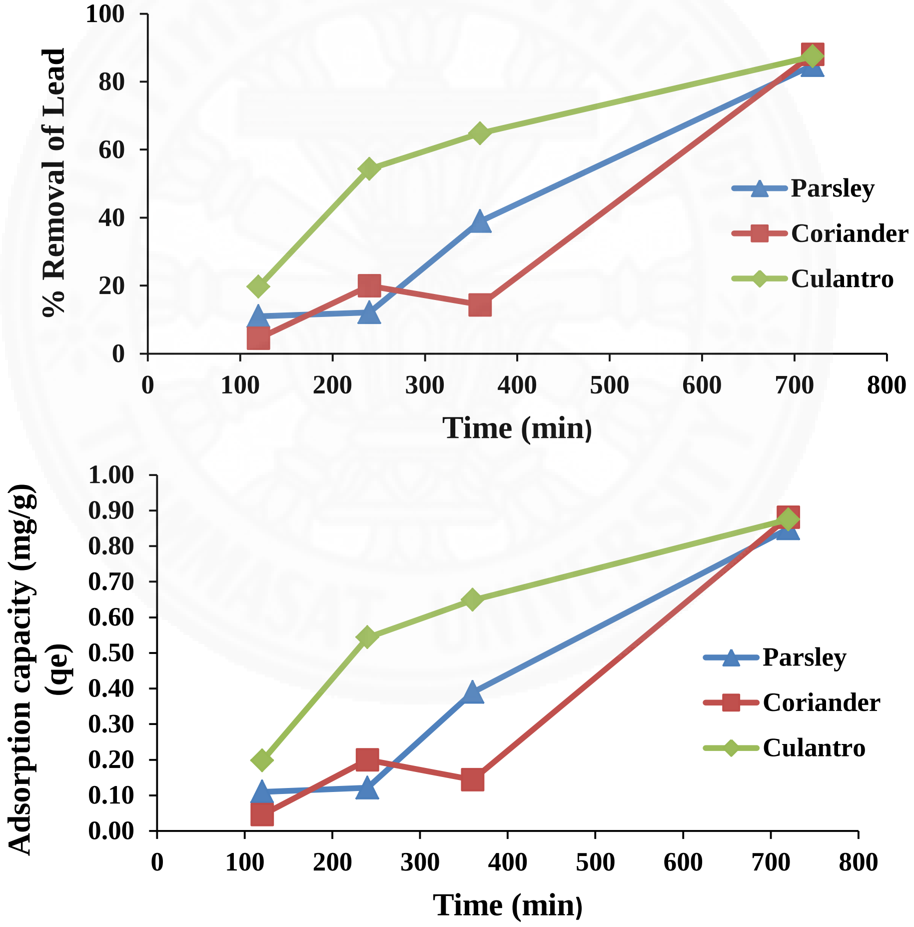


Figure 4.15 Effect of contact time on the removal of lead by parsley, coriander and culantro using tea bags (Initial Pb^{2+} 1 mg/l, 1 g/l dosage, neutral pH)

Table 4.11 shows the concentration of lead remaining using tea bags. According to Thailand’s water quality standard, maximum permitted value lead in drinking water is 0.05 mg/l and 0.01 mg/l for World Health Organization (WHO) standard. On the contrary, when consider Thailand’s wastewater quality standard, the maximum of lead level in wastewater is 0.2 mg/l. Therefore, the three selected adsorbents can remove lead in wastewater and reach Thailand’s wastewater quality standard by using 720 min or 12 hrs. of contact time and the batch studies from tea bags experiments is successful and can be utilized for removing lead at low concentration in the contaminated water areas.

Table 4.11 Concentration of lead remaining by using tea bags

Time (min)	**Concentration of Lead Remaining**		
	Parsley	**Coriander**	**Culantro**
120	0.890	0.955	0.803
240	0.879	0.801	0.457
360	0.611	0.857	0.352
720	**0.151**	**0.119**	**0.125**

Coriander and culantro are worth in the practical applications for treating lead contaminated water. This is because they are widely cultivated in all regions of Thailand. However, parsley requires special cultivation. It should grow best in moist and well-drained soil conditions which are not appropriate with tropical country like Thailand. It can be used in warm to cold regions such as European, Middle Eastern, and American. Taking the above advantages into consideration, it can be concluded that parsley, coriander and culantro in the present investigation can be employed as a potentially low cost adsorbents for the removal of Pb^{2+} ions from contaminated water because it can be prepared without chemical treatments.

Table 4.12 presents comparison of the adsorption percentage of selected adsorbents used in this study with other studies aimed at removal of Pb^{2+}. The percent removal of Pb^{2+} ions shows greater than 95% and it appears that selected adsorbents adsorb lead quite well when compared with other adsorbents. For example, spent tea leaf under neutral pH required 480 min or 8 hours to reach the equilibrium but it adsorbed lead 55.2% whereas the selected adsorbents under neutral pH can adsorbed greater than 85%. Because of the high sorption potential of selected adsorbents was achieved without any activation or additional treatment of the biomass. Therefore, selected adsorbents can be considered as a cost-effective and sustainable adsorbent compared to other adsorbents for remediation of water in small scale.

Table 4.12 The comparison of selected adsorbents with other adsorbents reported in the literature

Name of adsorbents	**pH**	**Dosages**	**Contact time**	**Pb^{2+} Removal %**	**Ref**
Rice husk and Maize cobs	2.5 - 6.5	1.5 g	120 min	98.5	[56]
Sour sop seeds	5	1.0 g	120 min	40.6	[57]
Spent tea leaf	Neutral	2.0 g	480 min	55.2	[58]
Papaya seeds	5	10 - 1000 mg/l	90 min	90	[59]
Palm Kernel Shell Charcoal (PKSC)	-	80.0 g/l	50 min	89	[60]
Coconut Leaf powder	7	2.0 g	30-180 min	90	[61]
Tea waste	5 - 6	1.25 – 7.5g /l	15-20 min	96	[62]
Raw Banana Stalk	4 - 8	0.1 -1.0 mg/l	180 min	63.97	[63]
Coffee grounds	Neutral	0.5 mg/l	60 min	87.2	[64]
Banana Stalk	8	0.90 g	152 min	96.41	[63]
Agro-Waste	6	15.0 g/l	60 min	89.60	[65]
Parsley	**3**	**2.0 g/l**	**120 min**	**96.61**	**This study**
Coriander	**3**	**2.0 g/l**	**360 min**	**95.95**	
Culantro	**3**	**2.0 g/l**	**360 min**	**96.55**	

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

- Lab scale examinations were carried out using three plants from Apiaceae family namely parsley, coriander and culantro for the lead removal. Results show that these plants which are readily available can be used effectively for removal of Pb^{2+} ions from aqueous systems for environmental protection purpose.
- The factors like surface area, pore volume and mechanical properties of adsorbents played a significant role in lead removal process. Adsorbents with higher surface area and smaller particle size.
- FTIR analysis of adsorbents exposed that carbon bonded with hydrogen and oxygen atom is essential for lead adsorption by three selected adsorbents which are lignocellulosic biomass. The hydrogen bonding and ligand exchange facilitated the binding of lead onto specific adsorption sites.
- The SEM images after adsorption process showed clearly change on adsorbents surface.
- The highest lead removal efficiency was observed at the pH values 3 for all adsorbents. It was found 96.30%, 97.62% and 97.58% for parsley, coriander and culantro, respectively. At the neutral pH, parsley, coriander and culantro rendered more than 87% removal efficiency from 10 mg/l Pb^{2+} solution. The high percentage of lead removal at neutral pH indicates the practical possibility of these adsorbents.
- At the optimum reaction condition, parsley showed the highest lead removal efficiency of 96.61% followed by culantro (96.55%) and coriander (95.95%) at 10 mg/l lead solution. The lead removal efficiency of the adsorbents increased with the increment of dosage, contact time and speed of rotation, whereas the removal rate decreased with the increase of pH value greater than 4 and initial lead concentration. The equilibrium was observed after 120 min for parsley and 360 min for coriander and cilantro.

- Langmuir isotherm fitted well to the parsley and coriander. This suggested that feasibility of mono and heterogeneous layer formation onto adsorbents surface. The values of R^2 for parsley and coriander in this isotherm were above 0.99. Whereas, for culantro correlation coefficient was found approximately 0.96. Freundlich isotherm was better fitted for culantro. The value of R^2 for culantro was 0.97 followed by parsley (0.86) and coriander (0.95). The R_L value in the present study was less than one, indicating that the lead adsorption is favorable. Similarly, value of slope (1/n) in Freundlich isotherm lied between 0 and 1 for three adsorbents and this showed the increase in the bond energies with the increase of surface density.
- The results from adsorption kinetics data analysis, pseudo second order kinetic model is more likely to be agreeable with obtained data from experiments, with less fluctuation in calculated and experimental uptake capacities (q_e).

Results shows that parsley, coriander and culantro plants biomass are attractive alternate low-cost adsorbent for removal of lead ion from aqueous solution. This new green material obtained from these plants are found to be effective, economical and environmentally friendly adsorbents for the removal of lead ions from aqueous solution and may potentially be used for removal of other heavy metal ions too.

5.2 Recommendations for Future Work

Recommendations for future research are listed below:

1. Studying the removal efficiency of selected adsorbents for other heavy metals, such as cadmium, chromium and mercury due to their adverse health impacts.
2. Further modification of selected adsorbents such as carbonization and chemical treatments can be done to extend the application of adsorbents.
3. Investigating the applicability of the research outcomes on real industrial wastewater.
4. Investigating the feasibility of regenerating metal loaded adsorbents.
5. Carrying out an economic feasibility study for the utilization of selected adsorbents in wastewater treatment.

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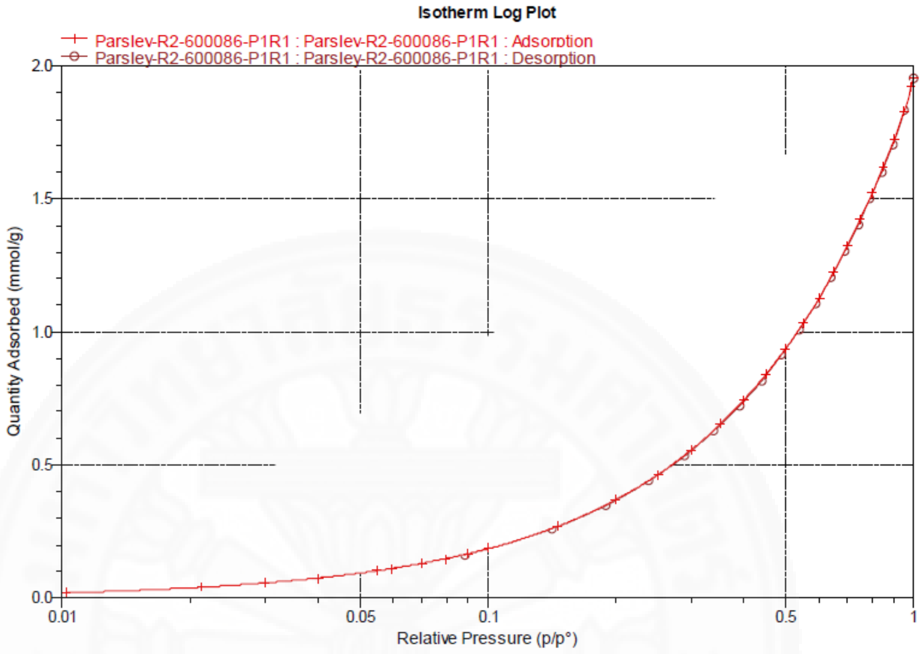
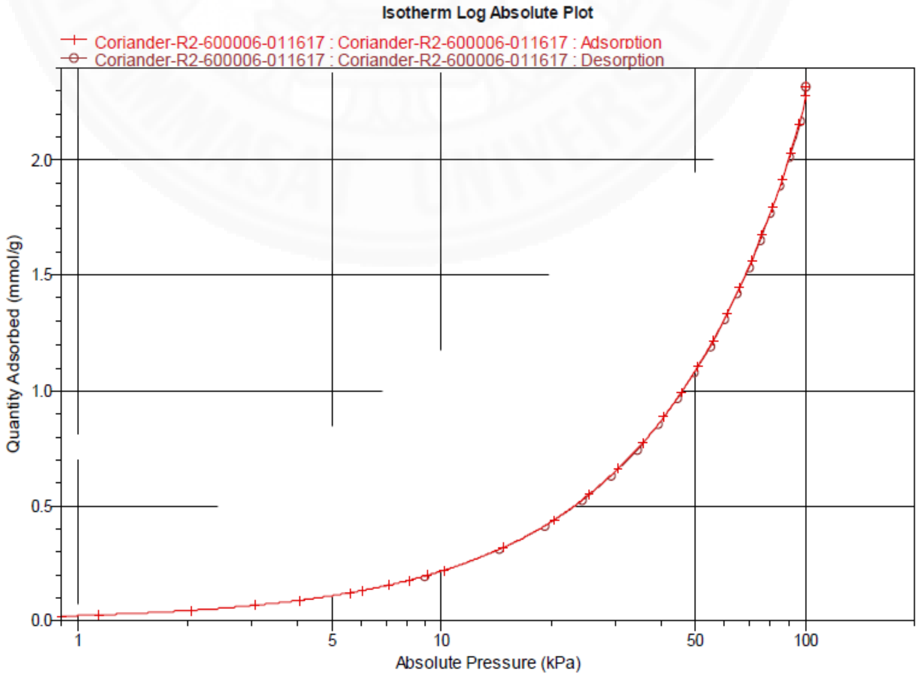
Appendices

Appendix A

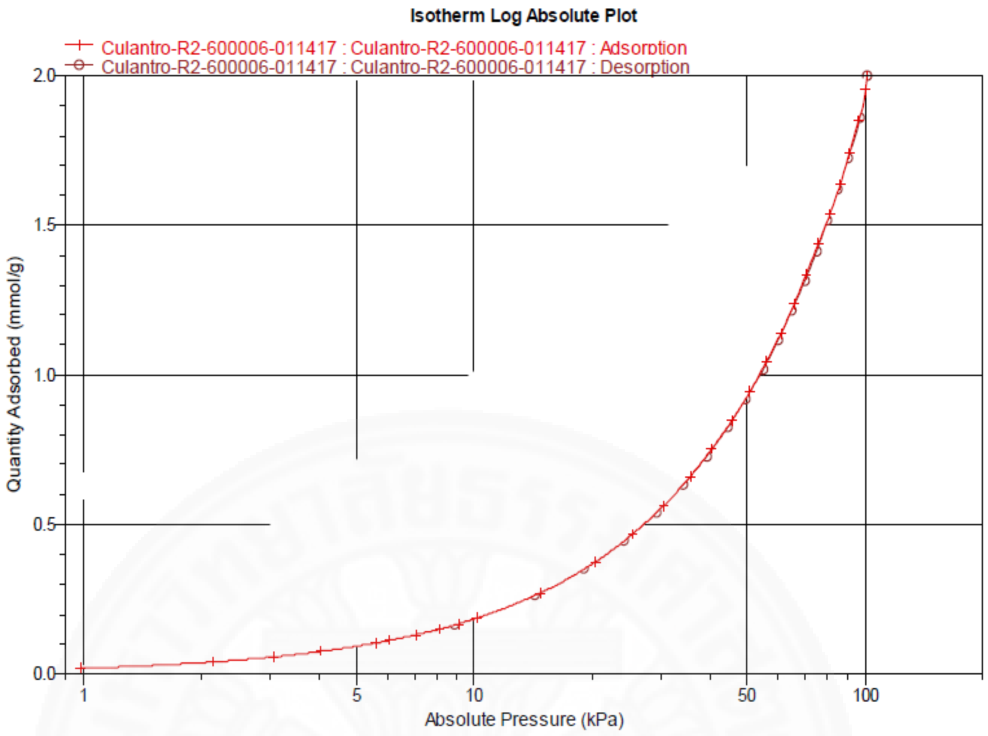
The nitrogen isotherm adsorption of selected adsorbents



Volume of N_2 adsorption isotherm versus relative pressure for parsley



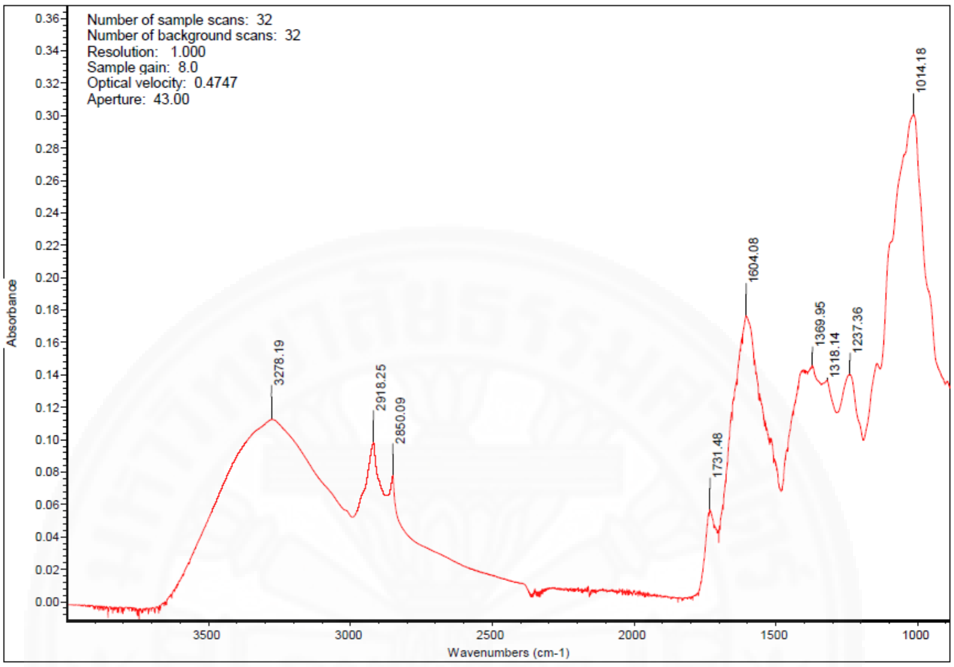
Volume of N_2 adsorption isotherm versus relative pressure for coriander



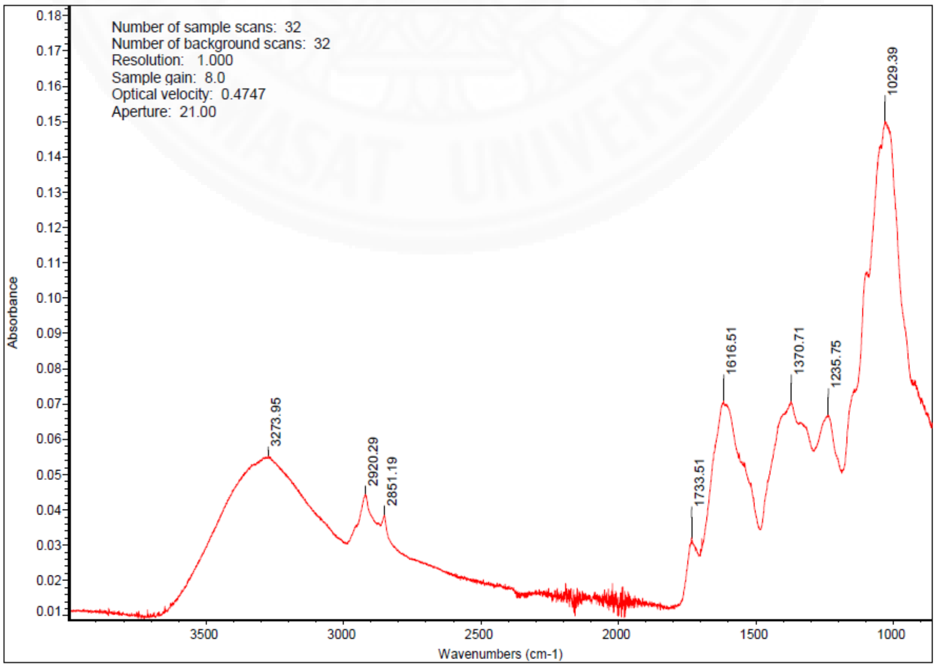
Volume of N_2 adsorption isotherm versus relative pressure for culantro

Appendix B

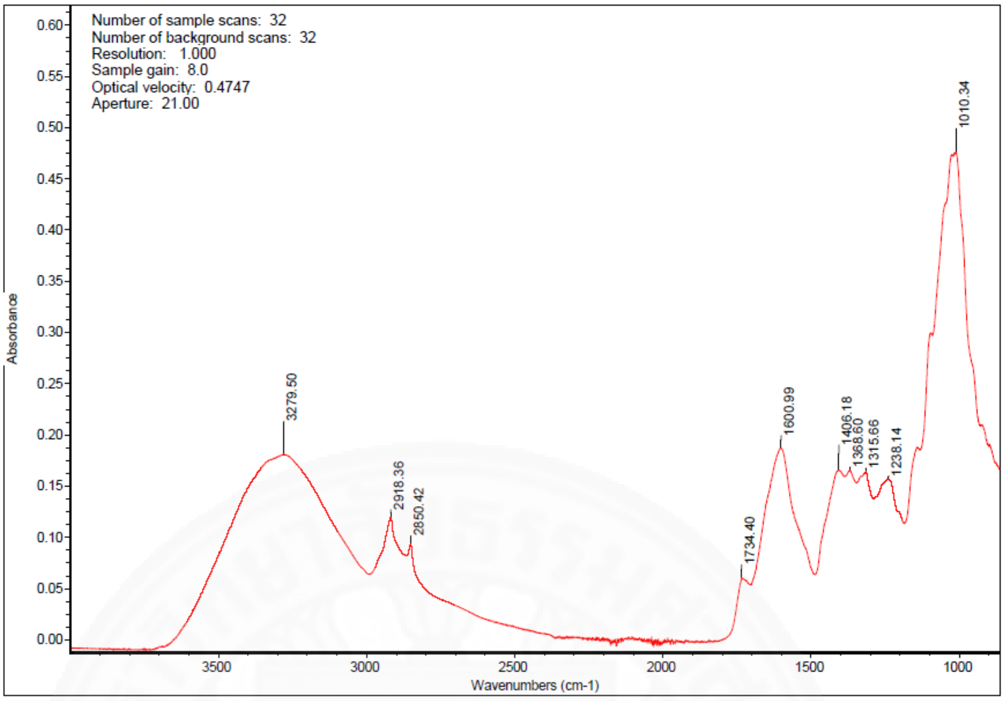
FTIR spectra of the selected adsorbents



FTIR spectra of parsley



FTIR spectra of coriander



FTIR spectra of culantro