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Faculty of Graduate Studies

**Study of Heavy Metals distribution in Used
Engine Oil Using Soil Column
Chromatography**

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This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science of Environmental Science, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.


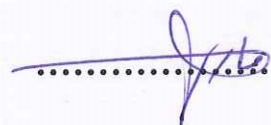


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This thesis was defended successfully on 2/12 / 2013 and approved by:

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Dedication

This work is dedicated to all Palestinian people, to the martyrs, wounded and prisoners.

To my mother, brothers, sisters and wife for tremendous help.

To my solemn father (mercy to him) who had sacrificed for our education.

To every one who helped me in my research with love and respect.

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Thanks to my friends and various people who direct and indirect help me to produce this thesis.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Study of Heavy Metals distribution in Used Engine Oil Using Soil Column Chromatography

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تم الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أي درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name:

اسم الطالب:

Signature

التوقيع:

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التاريخ:

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**Study of Heavy Metals distribution in Used Engine Oil Using Soil
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Abstract

Today interest of public regarding environmental pollution has raised concerns because of adverse impacts on various parts of environment such as soil, plants, drinking water, air pollution and aquatic life. This thesis focuses on studying environmental impacts of used engine oil; these impacts are on soil and water.

The main aim of this research is to study heavy metals of used engine oil that come during engine operation and the possibility of polluting soil and ground water.

In this study: five liters of used engine oil and similar amount of new engine oil (15W-40) was bought from SHELL station in Nablus. Amount of red soil was collected from area 500 m² in Shufa village 4 km to the east of Tulkarm, after performing soil tests (pH, texture, moisture, and organic matter) it was filled in three columns 140 cm long and 15.24 cm (six inches) diameter. Used and new engine oil samples were digested, centrifuged and filtrated, and concentration of Zn, Pb, Cr, Mn and Cu were measured by flame atomic absorption spectroscopy. Concentrations of Zn and Pb into the depths of soil columns (used, new and 50ppm stock solution) were measured. Results clarified that there is an obvious difference in the

concentration of metals studied in this research between used and new engine oil: zinc concentration is 23.23ppm, Pb is 0.6 ppm, Mn is 34 ppm Cr 0.097 ppm and Cu 0.072ppm in used oil while zinc concentration is 3.9 ppm, Pb 0.4 ppm, Mn 28.8, Cr 0.064 ppm and Cu is 0.01 ppm in new engine oil respectively. Effect of temperature on adsorption was investigated in the range (15 – 45°C) and results showed that maximum removal is at 45°C. Effect of pH indicated that maximum removal of both Zn and Pb was at pH13. Also maximum adsorption is reached at 10 ppm. Increasing adsorbent (soil) dosage from 0.5 to 3g showed that maximum adsorption of both Zn and Pb onto soil occurred at 3 g of soil. Equilibrium concentration happened at 90 minutes. Soil column experiment was performed by adding two litters of used engine oil to the first column, similar amount of new oil to the second and amount of 50 ppm solution to the third column, and adding distilled water to each column for five days gradually until water was leached, distribution of zinc and lead was studied in the three columns, results showed significant concentrations of Pb and Zn in the effluent. Equilibrium adsorption data were studied using Lanqmuir and Freiundlich models to study adsorption process at equilibrium and the results showed that both Lanqmuir and Frendlich fit data of Zn and Pb adsorption onto soil. In order to investigate adsorption behavior of Zn and Pb on soil, three kinetic models; Psedo-first order, Psedo-second order and intra- particle diffusion models were applied to fit kinetic data, rate constants and correlation coefficients were computed for the three models, results indicated that Pseudo-second –order model is

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more suitable to describe the adsorption process q_e (exp) is more close to q_e calculated meaning chemisorption process or ion exchange .

Thermodynamic parameters such as Gibbs free energy, standard enthalpy and standard entropy change were calculated for both zinc and lead; the results indicated that adsorption process is spontaneous and endothermic.

Chapter One

General Introduction

1.1 Overview:

Machinery is very important in our life and oil is said to play an important role in its working life, it can be said that oil is considered a blood for the machine like blood in our bodies, it doesn't only protect the machine but it provides it with working condition [1]. More than 35 million tons of used lubricating oil are produced annually in the world, these large quantities contain amounts of contaminants such as polychlorinatedbiphenyle, polycyclic aromatic hydrocarbons and heavy metals, which when released to environment particularly soil and water it will cause harmful impacts to ecosystem[2]. Locally used engine oil during changing operation is not recycled but spilled at station site, there by polluting soil and water. In recent time combustion of engine oil in Palestine is increasing at very high rate due to increase in number of vehicles and other machines that use engine oil, the total number of licensed vehicles in West Bank is 138644 at the end of 2011 with an increase of 1.7 percent as compared to 2010 according to Palestinian Central Bureau of Statistics [3]. These huge quantities of spent oil enter the environment and contaminate ecosystem. Initial compounds of synthetic oils were developed by Carbide and Carbon Chemicals Corp; additional developments of these chemicals were synthesized by many companies and institutes as labs of Linde Air products Co. Today large number of companies around the world competes to produce various types of engine oils. In many places around the world

they recycle used engine oil and store it for heating but in Palestine it is dumped in the soil and burned in air. There are no studies about the environmental impacts of used engine oil in Palestine while many were found in other places.

1.2 Previous Studies:

Many studies concerning pollution caused by used engine oil were carried out in different places around the world:

Concentrations of wear metals in new engine oil and their used oil counterparts were compared in four samples of new engine oil and similar samples of used oil. The samples were subjected to atomic absorption spectrometric analysis. It was found that there is increase in metal concentrations in used oil samples compared to new samples [4].

A study showed that 80% of used engine oil is spilled in the environment while 20% only is recycled. Samples of soil and water were gathered from sites in which used engine oil is spilled, these samples were analyzed to test concentrations of copper, lead, nickel and zinc using atomic absorption spectrophotometer. The results indicated that concentrations of the four metals studied in soil and water are higher than permissible concentrations, these concentrations ranged from 20 $\mu\text{g/g}$ (Ni) to 493 $\mu\text{g/g}$ (Pb) in soil and 0.019 mg/l (Ni) to 0.147 mg/l (Pb) in water [5].

Spent lubricating oil was sourced from heavy machines and mixed with soil plots. Samples of soil were digested and analyzed for heavy metals and results indicated accumulation of Cr, Ni, Pb and Zn, the study showed higher concentration of Cr followed by Zn relative to other metals [6].

Toxicity characteristic leaching procedure (TCLP) was used to measure heavy metals contained in oil and sludge samples from auto mechanic workshops. The result indicated that concentration of Pb in oil and sludge samples are considered toxic, also high concentrations of other heavy metals such as barium and chromium were measured in that test [7].

In order to study the effect of used engine oil on plants and soil characteristics the following studies were carried out:

A group of plants were treated by used engine oil, the plants were analyzed and it was observed a reduction in nitrate content which means that used oil possesses an inhibitory effect [8].

Two species of plants were irrigated with used engine oil at a rate of 5L/m². This study showed that soil pollution by used engine oil had reduced leaf and root volume, reduction in chlorophyll pigment and caused xylem damage (Young. Ney.T. (2007) [9].

In Benin City, Nigeria soil was treated by five concentrations (0.0, 0.2, 0.3, 0.4, 0.6 and 0.8l/kg oil to soil). Soil samples were analyzed and the results showed decrease in p and increase in heavy metals (Fe, Zn, Pb and Cu) concentration in soil with increasing oil concentration [10].

During growing seasons of 2007, 2008 in Delta State University, several concentrations of spent engine oil were applied on six cultivars, the experiment was made with four replications and the results had shown important effects on reducing growth in terms of leaf area, stem diameter and number of leaves when compared to control plants [11].

Direct toxicity and plant retardation were obvious in plants irrigated by used lubricating oil [12].

Five planting pots were filled with 3000 g sandy-loamy topsoil for each in the department of plant science of ADO -EKITI university Nigeria, 500 ml of used lubricating oil was added to each pot and allowed to drain through the soil, the control and the treated pots were watered at the same rate, after five replicates chemical and physical properties of the soil were determined. Results showed increase in bulk density, water porosity, organic carbon and organic matter and decrease in soil capillarity, aeration, nitrogen, phosphorous, sodium, manganese and potassium content [33].

There are different studies concerning adsorption of metal ions by soil: Heavy metals have affinity to different types of soil, in an experiment to determine Cd, Cu, Pb and Zn by sequential extraction method soil and its chemical properties (pH, CEC, organic carbon and buffer capacity) were analyzed and results showed that Cd was associated to carbonates, Zn was mainly bound to metallic hydroxides and carbonates while Pb and Cu were mostly bound to organic matter and metallic hydroxides [69].

Adsorption of zinc and lead ions by sediments collected from river Kali, Pradish in India was studied and results showed that uptake of these metals increases with increasing pH of the solution, increasing adsorbent dose and decreases with increasing metal particle size [73].

Adsorption of Pb (II) by calcareous soil was evaluated and it was observed that removal of Pb (II) from aqueous solutions is dependent on many factors such as pH, adsorbent dose, stirring rate initial metal concentration,

temperature and contact time. The results indicated that %removal of Pb (II) decreased with increase in lead concentration while it increased with increase in contact time and soil dosage up to a certain level, maximum removal was at pH 6.0. Equilibrium data fitted very well Langmuir isotherm equation confirming monolayer adsorption, adsorption kinetics followed pseudo- second-order model, activation energy was -34.64 KJ/mol meaning exothermic and thermodynamic analysis showed spontaneous process [71]. Removal of Pb(II) ions by natural clay was investigated and the results indicated that percentage removal increases with increasing adsorbent dosage and decreases with increasing initial ion concentration, maximum removal occurred at pH 4.46, before 15 minutes adsorption rate is very fast and 120 min adequately reached equilibrium. Thermodynamic investigation showed that adsorption was exothermic and spontaneous [67]. Kaolinite was studied to adsorb Pb(II), Zn(II) and Cu(II) from aqueous solutions and the effect of metal concentration and adsorption efficiency at pH 4.5, results showed pseudo- second-order model was more applicable than pseudo-first-order model. Values of correlation coefficients showed that Redlich-Peterson isotherm model was more suitable than Langmuir, Freundlich and Temkin isotherms, and % removal of $Pb > Zn > Cu$ [34]. sorption of zinc onto ten calcareous soils in Hamadan in west of Iran was evaluated using adsorption isotherms, results revealed increasing sorption with temperature and adsorption was described by linear, Freundlich, Temkin and D- R models. Evaluating thermodynamic parameters indicated that sorption of zinc was spontaneous and endothermic [35].

1.3: Objectives:

The objectives of this study are:

- * Determination of metals (lead, zinc, manganese, copper and chromium contained in used engine oil.
- * Study transport of heavy metals contained in used engine oil using soil columns.

1.4: justification:

Due to the increase source of environmental pollution in Palestine, this study was chosen for the following reasons:

- Large quantities of engine oil are used in the world for vehicles and other various machines as one of the petroleum hydrocarbon products.
- More than 13% of used engine oil is disposed improperly (**Motor Oil Facts**).
- No recycling agencies for used engine oil in Palestine, so most of used engine oil goes to soil and waste water manholes.
- A lot of contaminants and additives contained in engine oil like metals and hydrocarbons which may pollute water and ecosystem.
- For these reasons used engine oil is considered one of the environmental pollutants and it was chosen for this study.

Chapter Two

Background

2.1: Used engine oil:

According to environmental protection agency used oil is defined as any oil that has been refined from crude oil or any synthetic source and has been contaminated by physical and chemical impurities as a result of use.

Used engine oil refers to oil that has been collected from oil changed workshops, garages and industry sources as hydraulic and turbine oils [13].

Waste used engine oil is lubricating oil removed from the internal combustion engine. Unused oil composed from base oil which is a mixture of hydrocarbons, 80 to 90 % by volume with pH higher than 6.5 and a group of various additives 20 to 10% by volume .These oils are changed through engine operation because of breakdown of additives and by contamination with metals that result from tear and wear of engine, therefore composition of used oil cant be described by exact chemical terms. Main constituents of used engine oils are aliphatic and aromatic hydrocarbons such as phenol, naphthalene and flourathene [14].

When used engine oil escapes the motor, it can move long distance and reach waterways through runoff [15].

Once used engine oil in waterways it is toxic to plants and aquatic animals, and it can affect natural processes such as oxygen replenishment and photosynthesis through preventing sunlight by films of oil on surface water [16].

Also used engine oil is considered a contaminant to soil and drinking water, one gallon of used engine oil can contaminate million gallons of drinking water according to Environmental Protection Agency (EPA). Small amounts of used engine oil (50 to 100 ppm) can foul water treatment process when it reaches treatment plants. It decreases soil productivity [17]. Unused engine oil contains fresh and lighter hydrocarbons than used engine oil, so unused oils may cause acute toxicity to organisms while used engine oil contains heavy metals and heavy polycyclic aromatic hydrocarbons (PAHs) which may cause chronic toxicity and may be carcinogenic. Heavy metals in oil include lead, zinc, chromium, cadmium, arsenic [18].

Wear metals can come from different sources such as corrosion of engine components as pistons, bearings, etc, during operation. Many additives as detergents, anti-oxidants and anti-wear agents are added to reduce friction and protect from corrosion but these additives contain heavy metals [19].

Lubricant base oils are obtained from crude oil by distillation, which is a method by which components of crude oil are separated to useful components through thermal decomposition at atmospheric pressure [20].

2.2: Management of used engine oil:

Because used engine oil is harmful to environment, it is necessary to manage it in order to decrease its environmental impacts. There are different methods to do so and the most famous are:

2.2.1: Recycling of used engine oil:

Recycling of used engine oil is changing it to oil that can be used again in lubricating. Used engine oil is dark because of carbon coming from wear.

The cost of recycling is relatively lower than production of engine oil from crude petroleum [21], it was found that when 25 liters of used engine oil were recycled 10 liters of new engine oil were produced while 250 liters of crude petroleum must be refined to get 10 liters of new engine oil.

There are various methods of recycling used engine oil, some of these techniques are:

*** Recycling by hydrocarbon solvents:**

This method uses hydrocarbon solvents such as liquefied petroleum gas and stabilized condensate solvent which can make extraction to carbon residue, ash content, asphaltene and heavy metals [22].

*** Recycling used engine oil by acetic acid:**

Another method for recycling spent engine oil is by using acetic acid .In this method glacial acetic acid is added to the used engine oil by the ratio of 0.8% acetic acid to used engine oil, the process is executed at room temperature and pressure, after removing the contaminants it needs mixing acid and used oil settling , centrifugation and mixing with kaolinnate in order to remove the dark color that results from oxidation of oil components, then additives are added to the recycled base oil and it becomes suitable for reuse [23].

2.2.2: Re-refining used engine oil:

In this process used engine oil is treated physically and chemically in order to remove impurities from it, then additives are added to the oil and mixed with virgin oil. The process begins by filtering, heating and settling used oil in order to extract solid impurities and water, then it's subjected to

distillation, finally distilled oil is treated with hydrogen to bind with some pollutants. Its disadvantage is complexity of the way [24].

2.2.3: Direct burning: Used engine oil is burned directly to produce energy for boilers, industrial furnaces, producing electricity, and cooled air. Burners should be suitably equipped to reduce emissions [25].

2.3: Historical background of engine oil:

People had developed and used lubricants in the past mostly with birth of civilization around 1400 B.C, when they used animal fats to decrease friction of chariot wheel axle. Improvements and developments continued during middle Ages (450 – 1450 A.D), through the industrial revolution (1750 – 1850A.D). Improvements to lubricants increased in order to protect machines from wear and friction. After 1850 discovery of petroleum industry leaded to production of petroleum products and during 1920s mineral oils were produced as a result of crude oil refinery. In 1923 Society of American Engineers SAE classified engine oil according to viscosity: light, medium and heavy [26].

Various chemicals were developed in order to increase performance and efficiency of engine oils, these chemicals are called lubricant additives. World war II encouraged development of lubricant additives especially for military .Consumption of lubricant additives in U.S.A. was 127000 metric ton in 1950, it had increased to 710000 metric ton in 1978 A.D. [27]. Today common lubricants are mineral oils produced from petroleum refinery, and synthetic oils produced from poly alphaolefines.

2.4: Elemental composition of vehicular engine:

Many heavy metals that are found in used engine oil are the ones used in manufacturing different parts of the motor. In order to explain used engine oil analysis, it is important to know where metals come from. In addition to iron there are chromium, nickel, lead, zinc, manganese and copper. For example chromium is added to steel in order to increase its hardness and to enhance its resistance against corrosion, it enters in manufacturing rollers for bearings, and balls, and also nickel chromium steel is used in axles and crankshafts. Manganese is added to steel in small ratio 1.5% in addition to carbon with a ratio 0.4% in order to form very strong alloys that used in axles gears and shafts [28].

Copper whose concentration in used engine oil is found to be higher than new oil is used in various parts in vehicle engine like brakes, tire wear, fuel and oil leakage and wear of engine parts. Lead is used in tire wear, paints, and batteries [29].

Lead is also used in bearings, old clutch design, coatings, drums and it was an additive to petrol. Aluminum metal is used in manufacturing pistons and hydraulic pump, plain bearings and its an additive to some greases. Zinc is also used in cooling system, brass components and used as an additive. Aluminum, iron and chromium are used together in mining of liners, pistons.

2.5: Petroleum products:

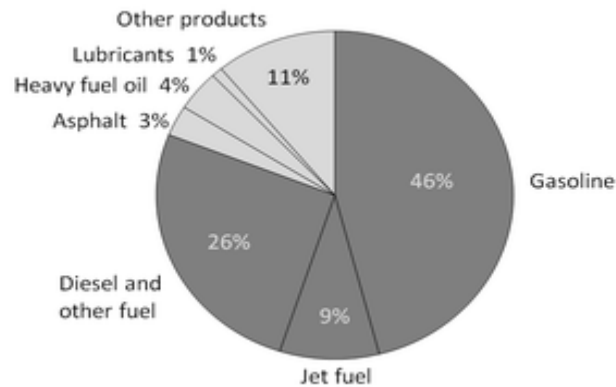


Figure 2.1: http://en.wikipedia.org/wiki/motor_oil

Petroleum is a mixture of hydrocarbons that can be classified into different groups such as:

- * Saturated hydrocarbons; which consist from carbon atoms whose all valences are combined to hydrogen atoms like alkanes or parafines.
- * Unsaturated hydrocarbons in which number of hydrogen atoms decreased because carbon atoms are combined with each other.
- * Ring hydrocarbons in which carbon atoms form rings as naphthaline and aromatics as benzene.

The main hydrocarbon groups present in diesel fuel are the normal alkanes which can be rapidly degraded, cycloalkanes which are very resistant, and aromatics which are more soluble than other hydrocarbons [30].

In crude oil the percentage of hydrocarbon kinds are shown in (table2.1).

Table 2.1: (Percentage range of hydrocarbons in crude oil)

Hydrocarbon	Percentage range
Paraffins	30%
Naphthalines	49%
Aromatics	13%
asphaltics	6%

Alkanes: named paraffins which are saturated hydrocarbons with molecular formula C_nH_{2n+2} , those containing more than 16 carbon atoms can be refined to fuel oil and lubricating oils. Cycloalkanes: named naphthenes are saturated hydrocarbons that contain one or more carbon rings and hydrogen atoms according to the formula C_nH_{2n} , their properties are similar to alkanes but their boiling points are higher. Aromatic hydrocarbons are unsaturated having one or more planar six-carbon rings called benzene rings. These molecules are separated by fractional distillation [31].

Total petroleum hydrocarbon (TPH): A mixture of chemicals composed from hydrogen and carbon named hydrocarbons. These chemicals include mineral oils, benzene, xylene, naphthalene, toluene, these may enter environment through accidents, industrial release and mine effects [32].

2.6: Composition of engine oil:

Engine oils are composed from base oils or base stocks made from minerals (petroleum) or crude oil at a refinery or man-made (synthetic) in addition to various kinds of chemicals called additives to improve its properties. These chemicals include:

- * Detergents: they are metallic compounds to control deposits and maintain the engine clean.

- * Dispersants: organic non metallic chemicals which can prevent deposits from foaming.
- * Friction modifiers to reduce engine friction.
- * Oxidation inhibitors: they prevent oxygen oil oxidation and reduce oil thickening.
- * Rust and corrosion inhibitors: to keep metal surfaces from acids.
- * Antiwear: antiwear agents: like zinc, phosphorus....
- * Pour point dispersants: to prevent crystallization.

2.7: Functions of engine oil:

In addition to protection against corrosion engine lubricating oils can perform various functions to motors among these are [36]:

- * They lubricate motor components over a wide range of temperatures so these components can move easily without friction.
- * They cool the motor by transferring heat which is produced from burning fuel and from friction, when lubricating oil passes on the surfaces of engine parts it carries heat and dissipates it to surrounding.
- * Oil cleans motor from contaminants by suspending them until trapping by oil filter.
- * Lubricating oils form seals between piston and liner.

2.8: Soil:

Soil is formed from parent materials(unconsolidated mass of mineral or rock from which topsoil is formed) which is changed into soil by physical and chemical processes, constituents of soil are living and nonliving materials that

have the forms: solid composed from minerals 45% and organic matter 5% ,liquid and gaseous states which are water and air 50%. [37].

2.8.1: Physical properties of soil:

Soil texture: texture refers to percentage of sand, silt and clay particles in the soil. These types are distinguished by diameter of the particles as tabulated below:

Table 2.2: Soil texture

Particle soil	Diameter (mm)
Gravel	>2.0
Sand	0.02 – 2.0
Silt	0.002 – 0.05
Clay	< 0.002

Soil structure: structure refers to binding of particles of soil and making greater masses called aggregates .This property is important because aggregates resists soil erosion and increases porosity facilitates movement of water [38].

Soil pH: It is an important physical property that refers to acidity or alkalinity and it's a measure of the concentration of hydrogen ions in the soil .pH is defined by the equation:

$$\text{pH} = - \text{LOG} [\text{H}^+] \quad (2.1)$$

Soils with large concentration of hydrogen ions is acidic , this acidity increases solubility of elements which increases their mobility and probability of leaching to ground water, while when concentration of hydrogen ions is low then pH is high (soil is basic) cations will be on the particle exchange sites so lower probability of leaching.

Soil colloids: refers to finest clay and organic matter in the soil, colloids are important because they are considered the site of physical and chemical processes. More soluble substances tend to move easier within water than which are less soluble because they tend to attach to organic matter near the surface of the soil.

2.8.2: Heavy Metals:

Heavy metals are considered natural constituents of soil when exist in normal levels, but they are considered pollutants when their levels exceed permissible concentration or when they are accumulated in soil.

There are various sources of heavy metals in soil as fertilizers, atmospheric deposition, agrochemicals, organic wastes, inorganic pollutants, crop removal, and volatilization [39]. Toxic heavy metals that enter ecosystem lead to bioaccumulation and geoaccumulation.

Discarding used engine oil by pouring it into soil releases different heavy metals that can be changed into aqueous phase by activity of bacteria, this change increases mobility of metals in soil. Used engine oil can change microbial communities, so adverse effects occur in biological cycles in soil which may inhibit development of plants [40].

Lead: When soil is contaminated by lead it becomes source of risk via direct ingestion of vegetables, fruits and drinking water. When lead enters body its fate depends on different factors such as age, health status and chemical form of lead [41].

Lead is known to be toxic to different organs of human and experimental animals, for instance nervous system of human changes in neurotransmitter

levels. Reproductive system suffers from irregular estrus and lowering in sexual hormones, biochemistry system suffers from vitamin D metabolism and immune system is affected through lowering in antibody formation. Also agency for toxic substances and disease registry **ATSDR** has not developed minimum level for lead because there is no threshold (any exposure has adverse effect) [42].

Zinc: Zinc is an element commonly present in earth from both natural and anthropogenic sources .Zinc in soluble form like zinc sulphate is moderately mobile in most soils, its mobility is limited to slow rate of dissolution so movement towards ground water is expected to increase when it is in soluble form such as agricultural applications or when accompanied by corrosive substances [43].

Several studies show that zinc has adverse effects on human health such as: oral exposure to high levels can result in systemic effects, the most sensitive of which is related to diminished copper status [44].

Although Zinc is considered important to animals and plants, it's considered toxic to organisms when it's in millimolar concentrations [45].

Manganese: Manganese is an important element for human and many other organisms, so it must be taken in suitable amounts, but it has adverse effects when taken in large quantities. Many epidemiological studies of workers exposed to manganese at levels lower than 5mg/m^3 showed neurobehavioral, reproductive and respiratory effects [46].

Persons who are exposed to high levels of manganese suffer from neurotoxicity especially in basal ganglia which lead to parkinsonian disorder [47].

Manganese can enter human body through various routes such as inhalation when person exposed to dust, fine particles may reach alveoli and then to blood. Also it can enter body through drinking water and food; highest concentrations are measured in food whose origins are plants such as rice and wheat [48].

Chromium: Chromium as a contaminant can be found in water either dissolved as Cr(VI) compounds or as insoluble Cr(III) oxides so Cr(VI) is more dangerous than Cr(III) because of its solubility [49].

Different health effects are caused from exposure to chromium, breathing air with high levels of Cr causes shortness of breathing and lung cancer. Ingestion of contaminated food or drinking polluted water can cause ulcers in stomach and anemia, while direct contact causes skin ulcers [50].

Copper: Human exposure to both copper deficiency and high levels can cause adverse health effects, so copper dose –response curve is similar to U-shaped. Chronic deficiency of copper causes anemia, bone marrow abnormalities and Neutropenia [51].

While excessive copper intake may cause adverse health effects to liver, bones, central nervous and immune systems [52].

2.8.3: Adsorption

Adsorption phenomenon in solution systems plays an important role in environmental area. Adsorption refers to an excess concentration at the

surface rather than in the bulk of the medium. It results from the attraction or Adhesion of solute molecules to the surface of soil particles at an interface between two faces such as liquid – solid, so adsorption is a surface phenomenon [53].

Some definitions related to adsorption phenomenon [54] .

Adsorbate: the adsorbed material.

Adsorbent: the solid material where adsorption process occurs.

Sorption: adsorption and desorption.

Chapter Three

Methodology

3.1: Chemicals

Some chemicals were purchased from the local market while others were from chemistry labs in the university. Chemicals used in this study are:

- * New engine oil (SAE 15 W- 40) SHELL station.
- * Used engine oil (SAE 15W -40) SHELL station.
- * Sulfuric Acid (H_2SO_4) (p100010522)
- * Hydrochloric acid (HCl) (hcl 201)
- * Sodium hydroxide (NaOH) (SDFCL, 37140110)
- * Nitric Acid (HNO_3) (Frutarom, 2355525100)
- * Zinc nitrate $\text{Zn}(\text{NO}_3)_2$ (Adrich-23006)
- * Lead Nitrate $\text{Pb}(\text{NO}_3)_2$ (Riedel, 11520)
- * H_2O_2 (Merck, 7210)

3. 2: Instrumentation:

Flame Atomic Absorption Spectrophotometer modelZicE-3000SERIES

Serial number c113500021deigned in UK AA Spectrometer, PH&

Conductivity meter Jenway model 3540, Shaker model LSBO-15S,

Centrifuge HermelZ200A, Balance 301S, hydrometer ASTM152-h,

JLabTech furnace modleLOD-060E .

3.3: Soil characterization:

3.3.1: Soil collection and preparation:

In order to test soil for heavy metals a sample of soil was collected from area (500m^2) located in the east of Tulkarm, this area is called Shufa far

from any source of engine oil contamination. One kilogram was collected randomly from the sample, sieved by 2mm sieve and analyzed for organic matter, pH and conductivity, moisture, texture and specific gravity.

Soil digestion:

The extraction procedure was followed by acid digestion of soil. About 100g was dried at 105⁰C and then cooled ,250ml Erlenmeyer flask was washed by a dilute HNO₃ solution ,one gram of homogeneous sieved soil was placed in the flask and 10 ml concentrated nitric acid was added to the flask ,the mixture was heated on a Fisher heat pad near boiling and stirred by a magnetic stir bar .After cooling ,5 ml of concentrated HNO₃ was added to the flask and refluxed for half hour ,then its heated and stirred for additional 10 minutes and cooled .After cooling 2 ml distilled water and 3 ml H₂O₂ were added to the mixture and cooled again the solution appeared grey, diluted by distilled water to 100ml.The flask was closed by Para film and inverted several times, finally it was filtered using filter paper number 4 [56].

3.3.2: Physical characteristics of soil:

*** Soil moisture:**

Soil moisture was measured on the base of oven dried weight. Crucible was placed in the oven at a temperature 105⁰c for three hours and cooled to room temperature in a desiccators, the weight of empty crucible was measured (w1). About 10 g of 2mm sieved soil was put in the crucible and weighed again (w2) ,the crucible with soil was heated approximately 14 hours in the oven at 105 –

110°C, then it was cooled to room temperature and its weight was measured again (w_3). Soil moisture was calculated from relation (3.1):

$$M \text{ (moisture content) \%} = (w_2 - w_3) / (w_3 - w_1) * 100\% \quad (3.1)$$

Where:

W_1 : weight of empty dried crucible

W_2 : weight of un dried soil + weight of dried crucible.

W_3 : weight of dried soil + weight of dried crucible.

* **Specific gravity of soil:**

Specific gravity of soil is defined as the ratio between mass of a sample of dry soil to the mass of the same volume of distilled water. In order to measure the specific gravity of soil " G_s " a volumetric flask (500ml) was filled with distilled water and its weight was measured (w_1) at a temperature T_1 , 10g of air dry soil was put in the flask and filled with distilled water to about its half, the flask was filled by distilled water to 500ml mark and weighed again (w_2).

The mass of dry soil was measured (w_s) and the specific gravity was calculated from relation (3.2).

$$G_s = W_s / W_w \quad (3.2)$$

Where W_s : weight of dry soil given in equation (3.3).

$$W_w = W_1 + W_s - W_2 \quad (3.3)$$

*** Organic matter:**

Soil was analyzed in the Poison Control & Chemical/Biological Center in An-Najah national university for organic matter.

3.4: Engine oil digestion:

Small amount of used oil (0.5g) and new oil (15W-40) was placed in two digestion flasks separately and 4 ml of concentrated H_2SO_4 added to each flask and column put at the top of each flask to remove acid vapor produced by refluxing about 5 minutes at 440°C , then 10 ml of H_2O_2 were added by funnel and refluxed for two minutes. When the tow solutions were cooled deionized H_2O water was added to make the volume of each solution 100 ml [57]. Then the two mixtures were filtrated and become ready for measuring concentrations of Pb, Zn, by flame atomic absorption spectrophotometer.

3.5: Preparation of stock solution:

In order to study the kinetics of metals contained in used engine oil especially lead and zinc a stock solution (1000ppm) was prepared and different concentrations (10ppm, 20ppm, 30ppm, 40ppm, 50ppm) were made from this stock solution by dilution with distilled water.

3.6: Heavy metals determination:

In order to determine metals (Zn, Pb) in used engine oil and comparing their concentrations with new engine oil, spectrophotometric method was used. Standard solutions were prepared for calibration and calibration curves were obtained with $R^2 > 0.98$. 100 ppm solution was prepared for

Zn and Pb then various concentrations were made by dilution to 5ppm, 10ppm and 20ppm, the same method was performed to other metals [58].

3.7: Adsorption experiments:

Percentage removal of adsorbed solute is calculated from the equation (2.2) [55].

$$\% = [(C_0 - C_f) / C_0] \times 100\% \quad (2.2)$$

$$q_e = [(C_0 - C_e) / M] \times V \quad (2.3)$$

$$q_t = [(C_0 - C_t) / M] \times V \quad (2.4)$$

Where:

%: percentage removal of the solute by adsorption process.

C_0, C_f : initial and final concentrations (mg/l).

C_e : equilibrium adsorbate concentration in the solution (mg/l).

C_t : Solution phase adsorbate concentration at time t (mg/l).

V : volume of the solution (L)

M : weight of soil (g)

q_t : equilibrium adsorption capacity at time t (mg/g).

3.7.1: Adsorption isotherms:

Adsorption is widely used as a physical process to decrease concentration of dissolved pollutants. Adsorption isotherm means adsorbate molecules distribute between liquid phase and solid phase when adsorption reaches equilibrium.

Many models used to describe adsorption isotherms, the most famous models are Langmuir and freundlich isotherms.

In this study Langmuir and Freundlich isotherm models were used to describe the relationship between amounts of zinc and lead adsorbed and their equilibrium concentration in solution at 25°C.

Fitting of adsorption data to Langmuir and Freundlich isotherm equations was investigated by plotting C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$ using equations (3.4, 3.5): [59]

Langmuir equation:

$$C_e/q_e = 1/(K_a q_m) + (1/q_m) C_e \quad (3.4)$$

Freundlich equation:

$$\log (q_e) = \log (K_F) + 1/n \log (C_e) \quad (3.5)$$

C_e : (mg/L) (Equilibrium concentration of the adsorbate, q_e : Amount of adsorbate per unit mass of adsorbent (mg/g) .

q_m : and K_a : Langmuir constants related to adsorption capacity and rate of adsorption respectively.

K_F & n : are Freundlich constants with such that n gives indication of the process of adsorption and K_F is related to adsorption capacity. The slope $1/n$ is a measure of heterogeneity, its value is between 0 and 1, as it closes to zero the surface becomes more heterogeneous [60], when n is greater than one this means efficient adsorption [61].

The main properties of Langmuir equation can be expressed by the relation (3.6):

$$R_L = 1/(1 + K_a C_0) \quad (3.6)$$

where: R_L is the separation parameter that gives indication on the

adsorption nature, C_0 is the initial concentration (mg/L) and K_a is Langmuir adsorption constant [62].

3.7.2: Adsorption kinetics:

In order to study the mechanism of zinc and lead adsorption on soil, pseudo -First- order- kinetic model, pseudo- second – order kinetic model and intra-Particle diffusion model were used to test the experimental data as follows.

- * **Pseudo- first – order model:** This model was used in order to study the specific rate constant of the adsorption process of zinc and lead onto soil.

Lagergren proposed the pseudo –first –order kinetic model [63], the integral form of this model is given by equation (3.7):

$$\text{Log } (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (3.7)$$

- * **Pseudo-second – order model:** Adsorption also can be tested by pseudo-Second order kinetic model because this model is greatly affected by the amount of metals on the adsorbent's surface and amount of metals adsorbed at equilibrium using equation (3.8):

$$t/q_t = 1/ K_2 q_e^2 + t/q_e \quad (3.8)$$

- * **Intra-particle diffusion model:** Predicting the rate limiting step is important in adsorption process, for a solid-liquid sorption process.

The solute transfer is described well by intra-particle diffusion model According to Weber and Morris theory, Weber and Morris equation [64]:

$$q_t = K_p t^{1/2} + A \quad (3.9)$$

Where:

q_e (mg/g), q_t (mg/g) are adsorption capacity at equilibrium and time t respectively, K_1 the rate constant of pseudo first –order adsorption (1/min)
 K_p : rate constant of intra-particles diffusion model (mg/g min^{1/2})
 A : gives an idea about the thicknesses of the boundary layer [65]
 K_2 : pseudo-second –order adsorption rate constant (g/mg/min) .

3.7.3 Adsorption thermodynamics:

Thermodynamic parameters ΔG^0 , ΔS^0 and ΔH^0 were considered in order to determine the nature of the adsorption processes, when ΔG^0 is negative the process is spontaneous, when ΔH^0 is negative the adsorption process is exothermic while positive values of ΔS^0 indicate increasing randomness at the solid/liquid interface [66]. These parameters were calculated from equations (3.10, 3.11, and 3.12).

$$\ln K_d = (\Delta S^0/R) - (\Delta H^0/R) 1/T \quad (3.10)$$

$R = 8.314$ J/mol k: universal gas constant, T : Absolute solution temperature, K_d : distribution coefficient (L/g) which can be calculated from the equation (3.11):

$$K_d = (C_{Ae} / C_e) \quad (3.11)$$

C_e : equilibrium concentration (mg/L), C_{Ae} : amount adsorbed on solid at equilibrium (mg/g), ΔG^0 (KJ/mol): Gibbs free energy change, ΔS^0 (J/mol k) standard entropy change, ΔH^0 (KJ/mol): standard enthalpy change. ΔS^0 & ΔH^0 were calculated from the slope and intercept of the linear plot of $\ln K_d$ versus reciprocal of absolute temperature.

Also a plot of ΔG^0 versus T was found to be linear and the values of ΔH^0 and ΔS were calculated from the slope and intercept of the plot according to equation (3.12) [67]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3.12)$$

3.8: Physical and chemical parameters of adsorption:

3.8.1: Effect of pH on soil adsorption of lead & Zinc:

Five beakers were cleaned by distilled water and dried. 2g of 2mm sieved soil were placed in each beaker, 25ml of 50ppm stock solution of were added to each beaker. pH was changed in each beaker by using 0.1M HCl and 0.1M NaOH, pH values were 2, 5, 7, 10 and 13, pH was measured by pH & conductivity meter. The beakers were shaken for 30 min at 25°C and concentration 50 ppm. The beakers were centrifuged at 150 rpm for 10 minutes and then filtrated, the samples become ready for scanning by flame atomic absorption spectrophotometer.

3.8.2: Effect of temperature on soil adsorption of lead and Zinc:

This experiment was performed by preparing four beakers, they were cleaned by distilled water and dried. 2g of 2mm sieved soil were put in each beaker and 25ml 50 ppm of stock solution were added to each beaker. At pH 7.5 the beakers were closed by Teflon and shaken for 30 minutes using a shaker model LSB-015s. The first beaker was shaken at temperature 15°C, the second at temperature 25°C, then the third at 35°C and finally the fourth at 45°C. The beakers were centrifuged for 10 minutes and filtered for scanning.

3.8.3: Effect of concentration on soil adsorption of Zn and Pb:

A 2g of 2mm sieved soil was placed in each flask .different concentrations (10ppm, 20ppm, 30ppm, 40ppm, and 50ppm) of lead and Zinc were prepared from the stock solution by successive dilutions. The five volumetric flasks were shaken for 30 minutes at pH 7.5 and temperature 25°C and then the flasks were centrifuged and filtrated so they were ready for scanning by FAAS.

3.8.4: Effect of dosage on soil adsorption of Zn and Pb:

Five different weights (0.5g, 1.0 g, 1.5g, 2g, 3g) of 2mm sieved soil was put in the beakers respectively. 25 ml of 50 ppm stock solution were added to each beaker, at pH 7.5, temperature 25°C and 150 ppm the five beakers were closed by parafilm and shaken for 30 minutes using a shaker Model LSB-O15s. The five samples were filtrated and become ready for scanning by FAAS.

3.8.5: Effect of contact time on soil adsorption of Zn and Pb:

Five beakers were cleaned by distilled water and dried, 2g soil was placed in each one, and then 25ml of 50ppm stock solution were added to each beaker. A shaker was kept at 25°C and 150 rpm, at pH 7.5 the first beaker was shaken 5minutes, the second 10 minutes, the third 30 minutes and the fourth 60 minutes and the fifth 90 minutes, after shaking all beakers they were filtrated and become ready for scanning.

3.9: Soil- column Experiment:

This experiment was performed to study the possibility of leaching metal contained in used engine oil. Three PVC plastic columns were prepared

with 1.5 meter long and 15.25 cm (six inch) diameter. The soil was filled in the three columns and compressed, the first column was for used engine oil, the second for new engine oil while the third for study of metals distribution (lead and zinc) contained in the stock solution (50ppm) prepared particularly for this experiment. 2 litres of both types of engine oil used and new were added to the first and second columns respectively, and then one litre of distilled water was added to each column for five days gradually while the 500ppm stock solution was added to the third column and distilled water also added to it at the same rate.

Distribution of metals in soil columns:

After adding distilled water to the three columns for five days, both used and new oils were leaked from columns.

Each column was cut into six parts (0-20, 20-40, 40-60, 60-80, 80-100, and 100-120) cm. Soil samples were prepared by taking five grams of soil at each depth from the three columns. Soil samples were digested by Nitric acid and H_2O_2 as mentioned in section 3.3.1, then samples were centrifuged and filtrated, so they were ready for scanning by flame atomic absorption spectrophotometer.

Chapter Four

Results and discussion

Results of this work are represented in tabular and graphical forms .These results are devoted to understand the effect of used engine oil on the environment and comparing it with effect of new engine oil, these results based on experimental study of releasing heavy metals into soil and adsorption of zinc and lead onto soil using soil columns and analysing of soil samples by flame atomic absorption experiment.

4.1: Soil characteristics:

Sample of soil was analyzed in Poison Control & Chemical /Biological Centre in Al- Najah National University and the results were shown in table 4.1

Table 4:1: soil characteristics

SOIL PROPERTY	RESULT
Specific gravity	2.34
pH value	7.5
Conductivity	182 μ S
Organic matter	6.4%
Moisture	9.56%

4.2: Heavy metal concentration in engine oil:

As shown in the table 4.2 there are an obvious differences in the concentration of five metals Zn , Pb ,Mn , Cr and Cu between used and unused engine oil (15W – 40) according to three replicates of acid oil digestion by method mentioned in methodology and measuring concentration by flame atomic absorption spectrophotometry.

These differences can be explained by contaminating of lubricating oil with dirt and metal parts worn out from engine surfaces during operation, and all metals measured are used in manufacturing various parts of the motor. Since engine components are composed from various alloys, increases in concentration of some metals may indicate a failure in specific component or resulting from wear of that component, for example increase in copper concentration in used oil indicates piston wear and increase in chromium concentration indicates bearing wear, increases in zinc concentration results from additives and galvanized piping wear. Lead in used oil may result from bearing cages alloyed with copper and Ti [68].

Table 4.2: Heavy metal concentrations in used and new engine oil (15W-40)

metal	Wavelength	Oil type	Concentration(ppm)
Zn	213.9nm	Unused	3.8996
		Used	23.2255
Pb	217nm	Unused	0.3954
		Used	0.5672
Mn	279.5nm	Unused	28.7523
		Used	33.9551
Cr	357.9nm	Unused	0.0643
		Used	0.0971
Cu	324.8nm	Unused	0.0101
		Used	0.0724

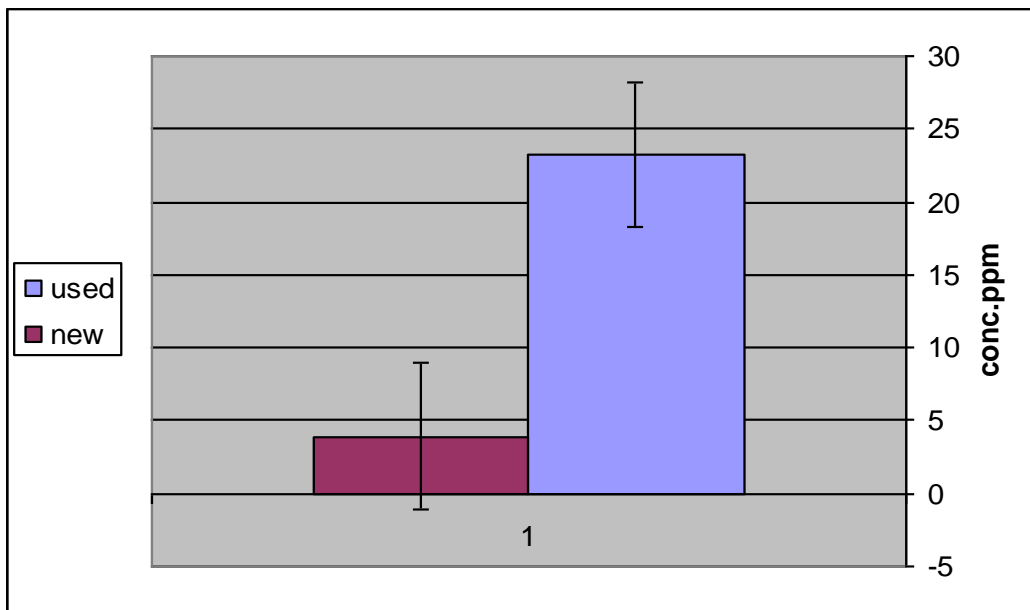


Figure 4.1: Zinc in used and new engine oil 15W-40

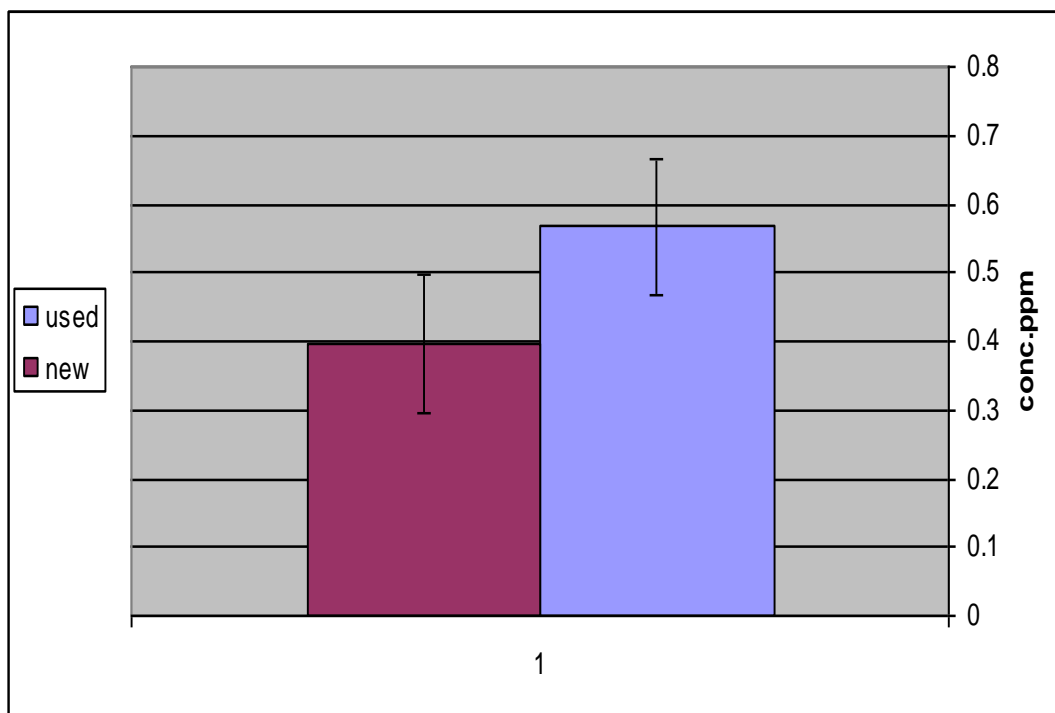


Figure 4.2: Lead in used and new engine oil 15W-40

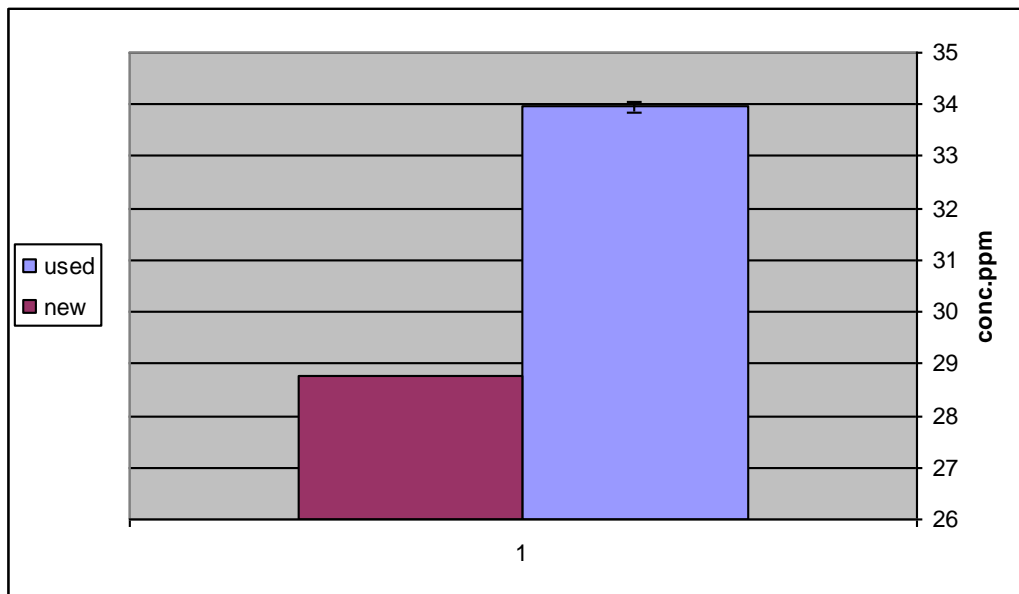


Figure 4.3: manganese in used and new engine oil 15W-40

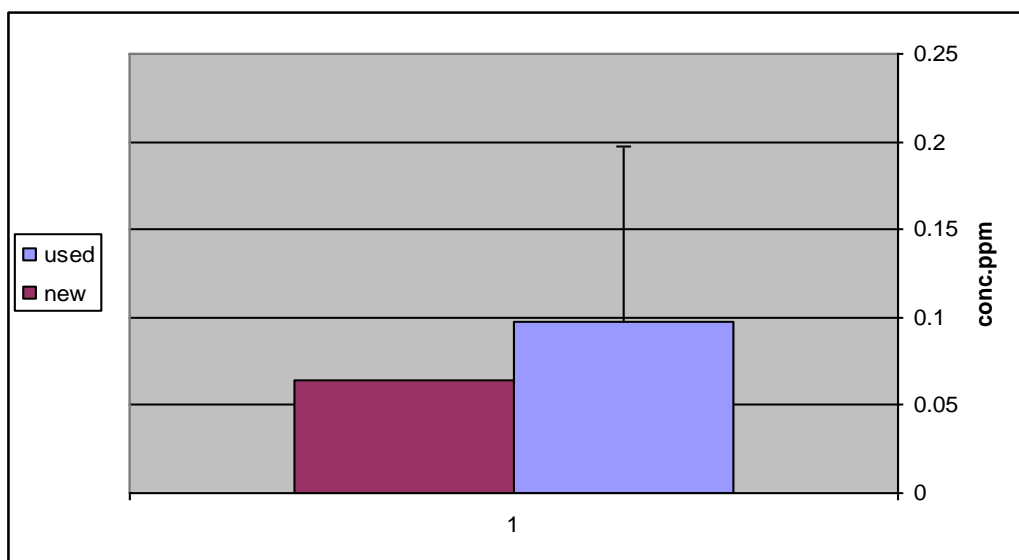


Figure 4.4: Chromium in used and new engine oil 15W-40

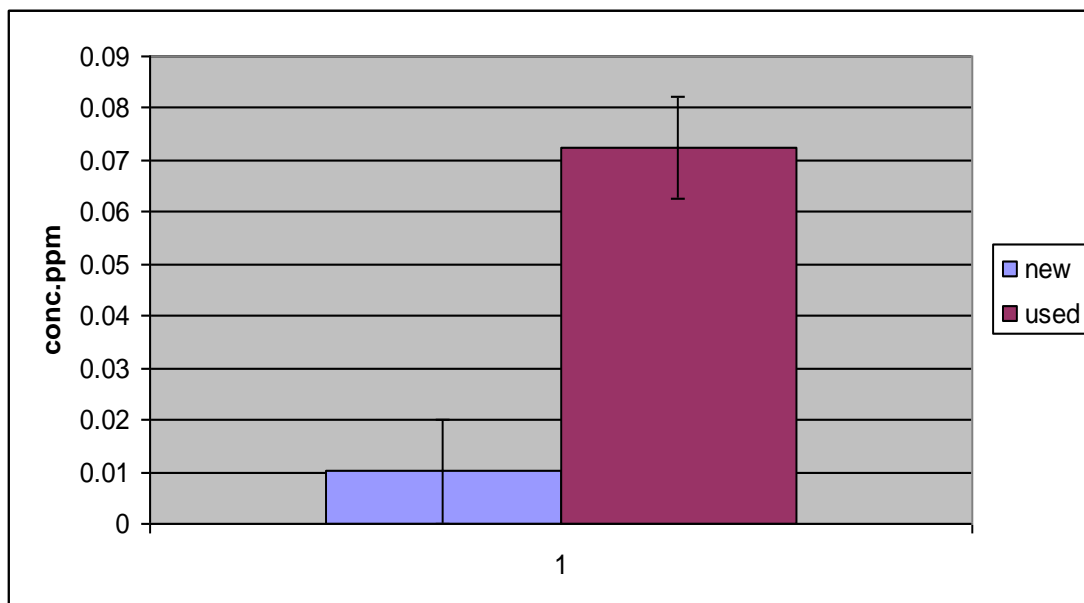


Figure 4.5: copper in used and new engine oil

4.3: Adsorption experiments:

Calibration curve for zinc:

Stock solution was used to prepare different concentrations 5, 10, 20, 30 and 40 ppm of both Zn and Pb, and then the samples were scanned by FAAS. Absorbance reading and calibration curve for zinc were recorded at 213.9nm at the previous concentrations. The calibration curve was constructed by plotting values of absorbance vs. concentration (figures 4.6, 4.7)

4.3: Calibration data for Zinc at 213.9 nm

Conc.(ppm)	5	10	20	30	40
abs	0.331	0.568	0.905	1.573	2.101

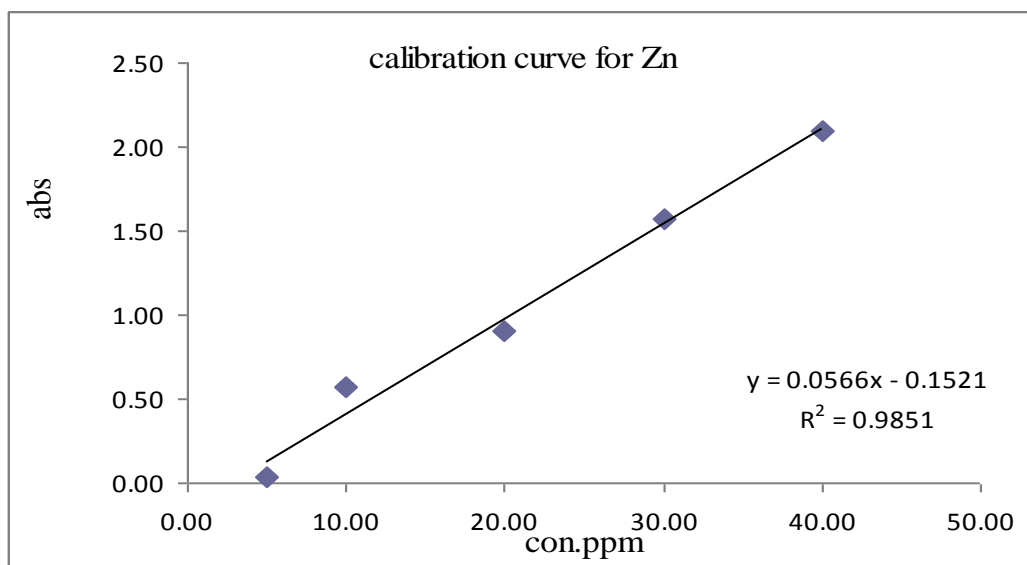


Figure 4.6: Calibration curve of Zinc

Absorbance reading and calibration curve for lead were recorded at 217 nm at different concentrations.

Table 4.4: Calibration data for lead at 217.0nm

Conc.(ppm)	5	10	20	30	40
abs	0.055	0.112	0.213	0.351	0.408

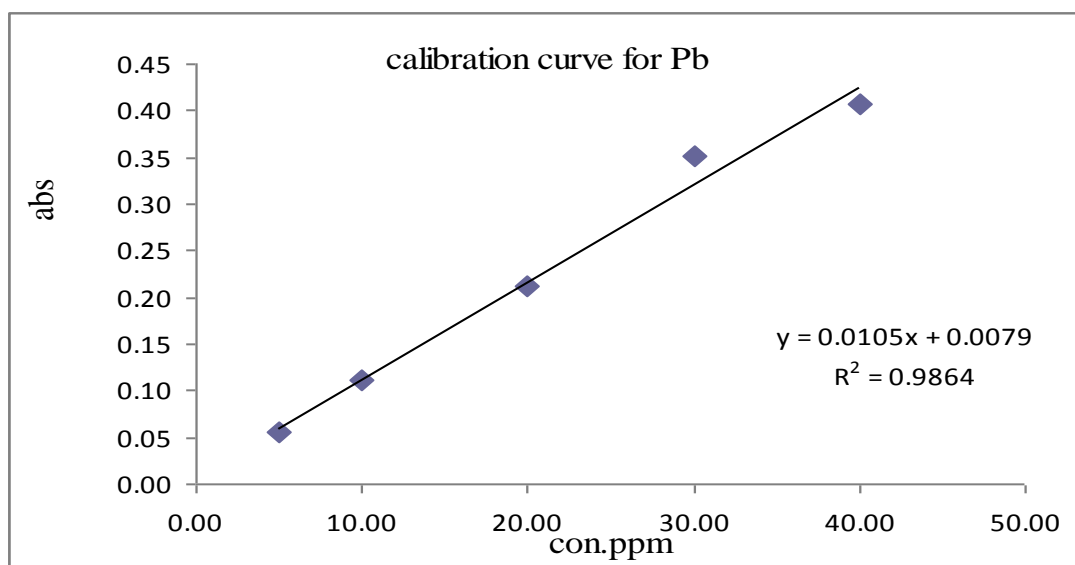


Figure 4.7: Calibration curve of Lead

4.3.1: Effect of pH on Zn and Pb adsorption:

The study shows that adsorption of zinc and lead by soil is very high and it is strongly affected by pH. So pH is a parameter that influences adsorption and movement of heavy metals in soil. The degradation of organic acids results in the increases of pH and this will increase the adsorption of metals [69].

Results show that adsorption increases with increases of pH. This can be explained by presence of hydroxyl groups on surfaces of soil which are deprotonated and leading to competition between metal ions and these protons. When pH is high, solubility of metals decreases, and this increases the cationic heavy metals on soil surfaces which increase adsorption [70]. The relation is obvious in figure 4.8. Zinc removal increases rapidly from 96% at pH 2 to about 99% at PH 7.5, then the increase is slower up to about 99.8% at PH 13 as Zn changes to $\text{Zn}(\text{OH})_2$, also Pb removal increases rapidly from 98% at pH 2 to about 99.4% at PH 5.7 then approximately constant with increasing PH, below pH= 6, Pb takes the form of Pb^{+2} and above that Pb is hydrolyzed to $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OH})^+$.

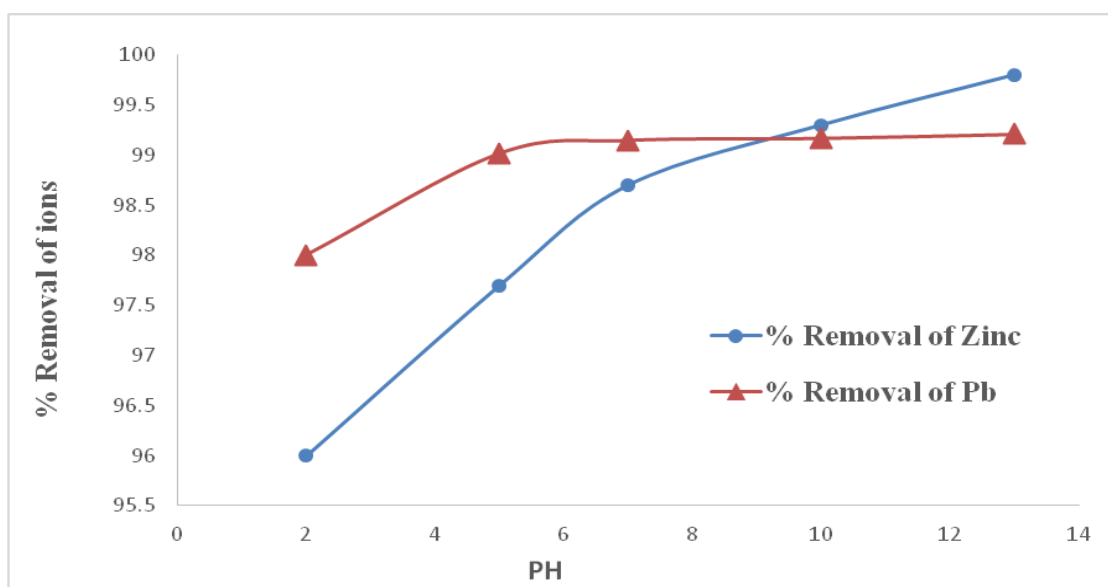


Figure 4.8: Effect of pH on % removal of Zn and Pb by soil (conc.50ppm, temp.25°C and contact time 30 min)

4.3.2: Effect of temperature on Zn and Pb adsorption:

Effect of temperature on adsorption of Zn and Pb is studied in the range of (15 – 45°C). As we see in figure 4.9 adsorption of Zn is about 93% at 15°C and about 97% 35°C then approximately equilibrium up to 45°C. Adsorption of Pb is more than 97% at 15°C up 99% at 35°C then equilibrium to 45°C. Increasing adsorption with temperature may be because of swelling effect in soil particles which facilitates penetration of metal ions.

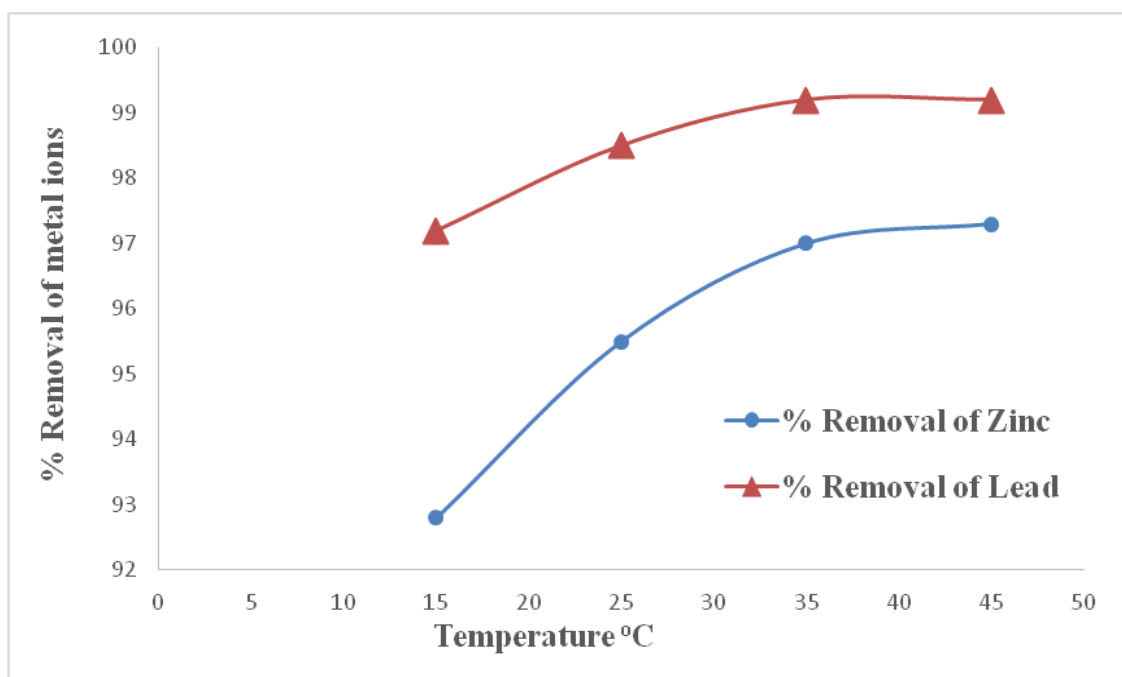


Figure 4.9: Effect of temperature on % removal of Zn and Pb (initial conc.50ppm, pH 7.5, contact time 30min)

4.3.3: Effect of concentration on Zn and Pb adsorption:

Results of experiment of metal adsorbate concentration indicated that adsorption of both zinc and lead is high when concentration of metal adsorbate is low and it decreases with increasing metal concentration. When metal concentration is changed from (10 to 50 ppm) the percent of removal of

zinc changed from 99.9% at 10ppm to 94.3% at 50ppm, for lead percent removal changed from 99% at 10ppm to 89% at 50ppm figure 4.10. This can be explained by presence of limited adsorption sites for each adsorbent system, at lower adsorbate concentration there is enough adsorption sites, and fractional adsorption decreases at higher concentrations since the sites become limited and at certain concentration the active sites become saturated, however adsorption capacity at equilibrium increases with increasing initial concentration [71, 72].

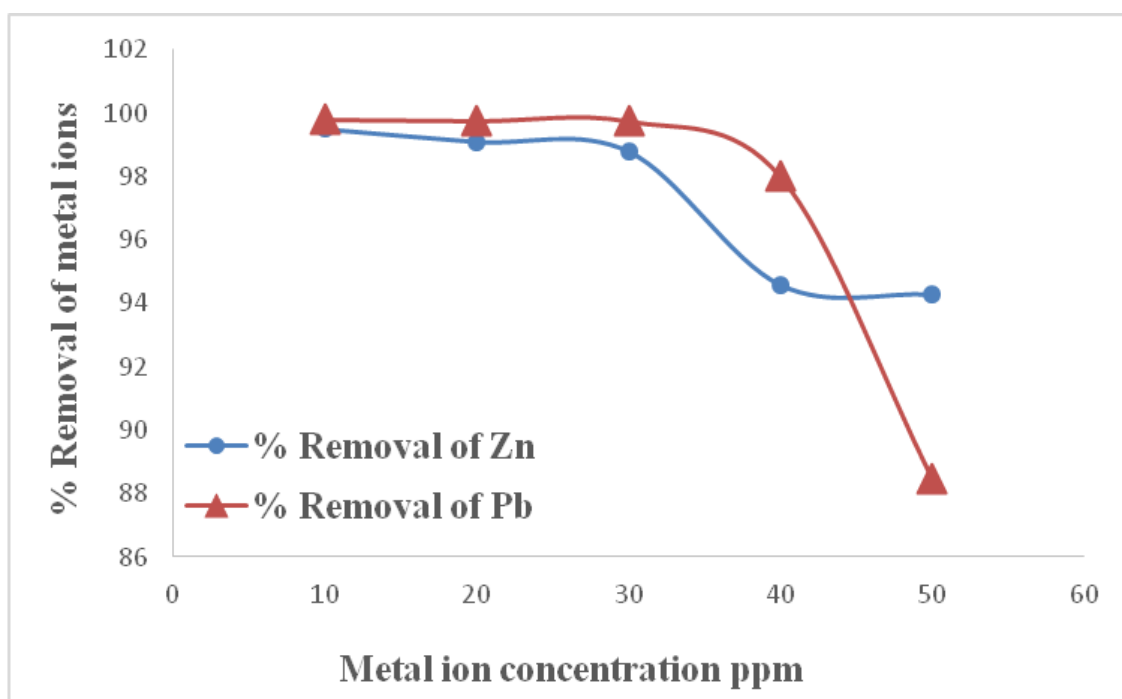


Figure 4.10: Effect of concentration on % removal of Zn and Pb (pH 7.5, temp. 25 °C, contact time 30min, 2 g soil/25 ml solutions)

4.3.4: Effect of adsorbent dosage on Zn and Pb adsorption:

Increasing adsorbent dosage increases metal adsorption [73]. The study shows that adsorption of both metals Zn & Pb increases with increasing soil dosage. This can be explained by: increasing adsorbent dosage of soil

at constant concentration and constant pH increases the available adsorption sites on the soil. As obvious from figure 4.11 more than 60% of zinc was adsorbed on 0.5 g soil and about 85% by 3 g soil; while more than 70% of lead adsorbed by 0.5 g soil and about 99% of lead adsorbed by 3 g soil. Also results showed that %removal Pb > %Zn .

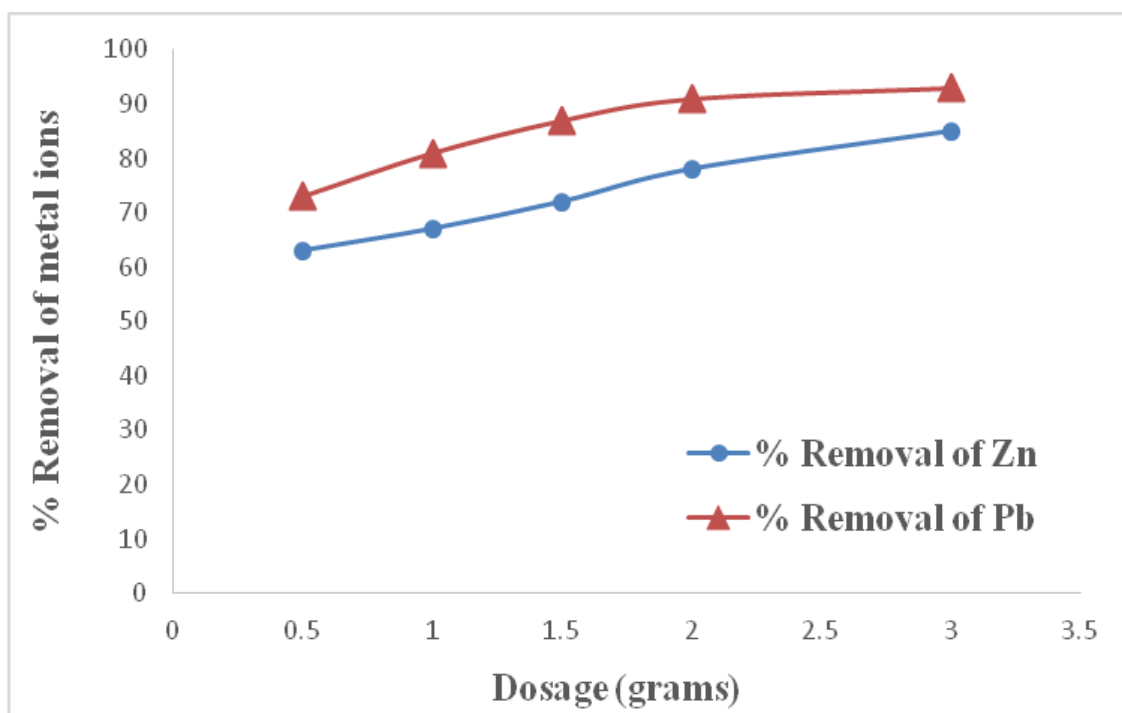


Figure 4.11: Effect of dosage on %removal Zn & Pb (initial con.50ppm, pH 7.5, temp.25⁰C, contact time 30min)

4.3.5: Effect of contact time on adsorption of Zn and Pb:

Results of the experiment of contact time showed that adsorption of both zinc and lead is spontaneous. About 70% of zinc was adsorbed during the first 5 minutes and the adsorption increases fast with time up to 10 minutes, then adsorption increases slowly up to equilibrium. Results for Pb adsorption showed that lead adsorption is very fast during the first 10

minutes, it increases from 75% to about 85% then adsorption increases slowly up to equilibrium figure 4.12.

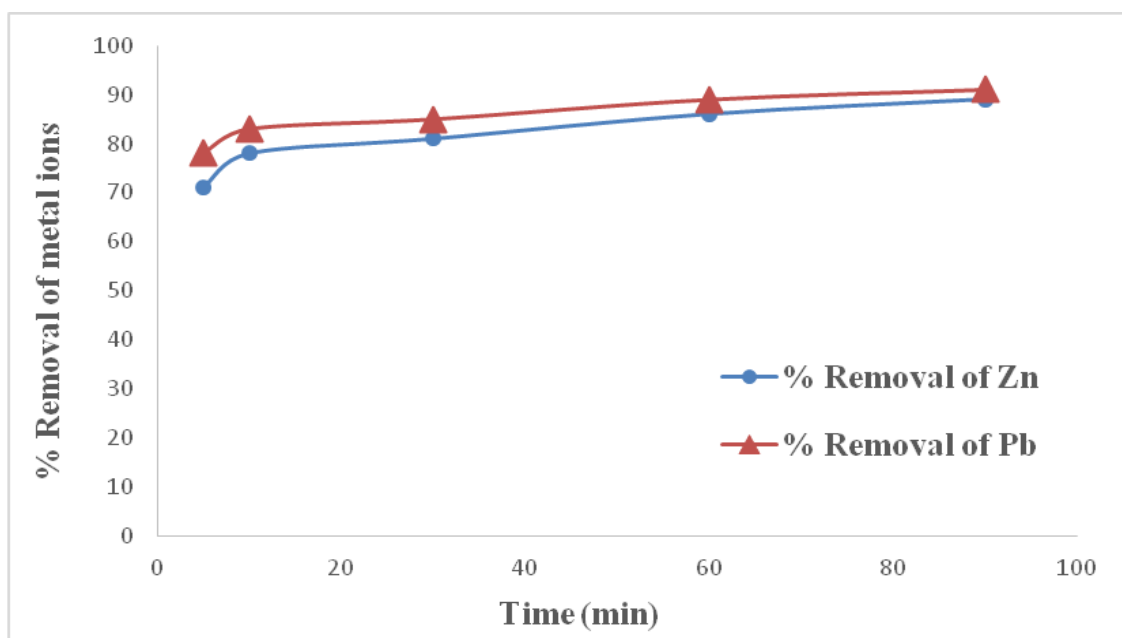


Figure 4.12: Effect of contact time on % removal of Zn and Pb (initial conc.50ppm, pH 7.5, temp.25°C)

4.4: Soil- column experiment:

Concentration of both Zinc and lead at different depths of the three columns of soil (used, new and 500ppm stock solution) were explained from graphs (4.13 and 4.14). Results indicated that there is a possibility of leaching these metals since measurable concentrations are noticed after more than 120 cm depth of the soil. Also it's obvious that lead is more adsorbable to the soil used in this experiment since its concentration is higher in the upper part of the column.

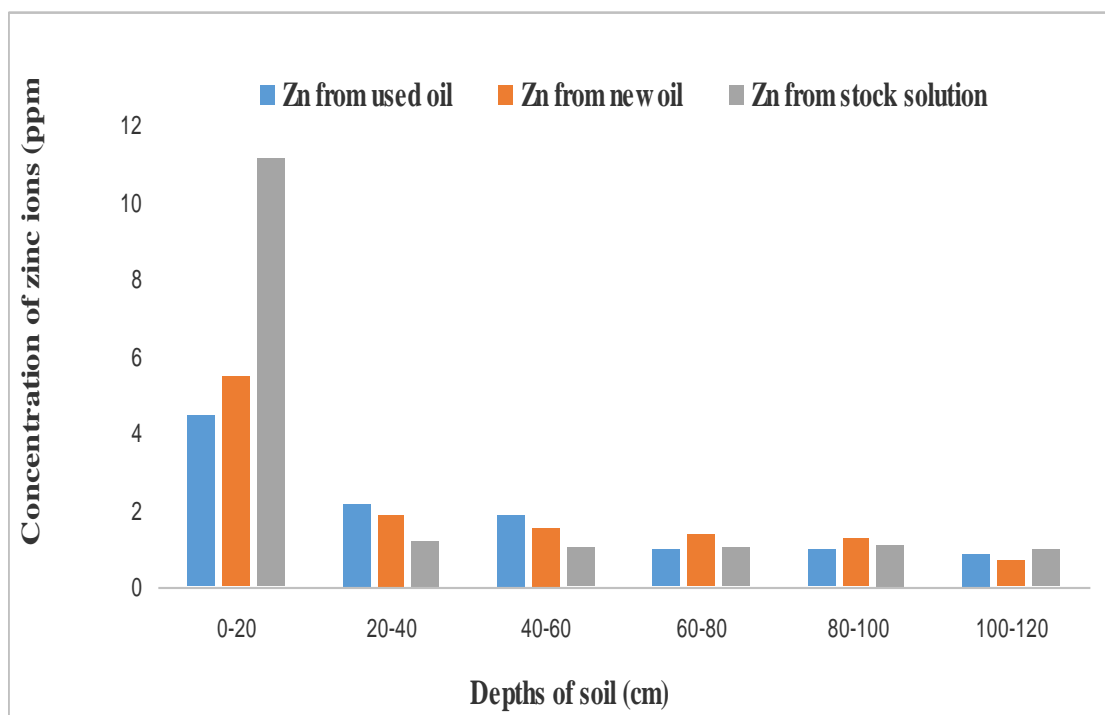


Figure 4.13: zinc concentration at various depths of used engine oil, new engine oil and 50ppm stock solution.

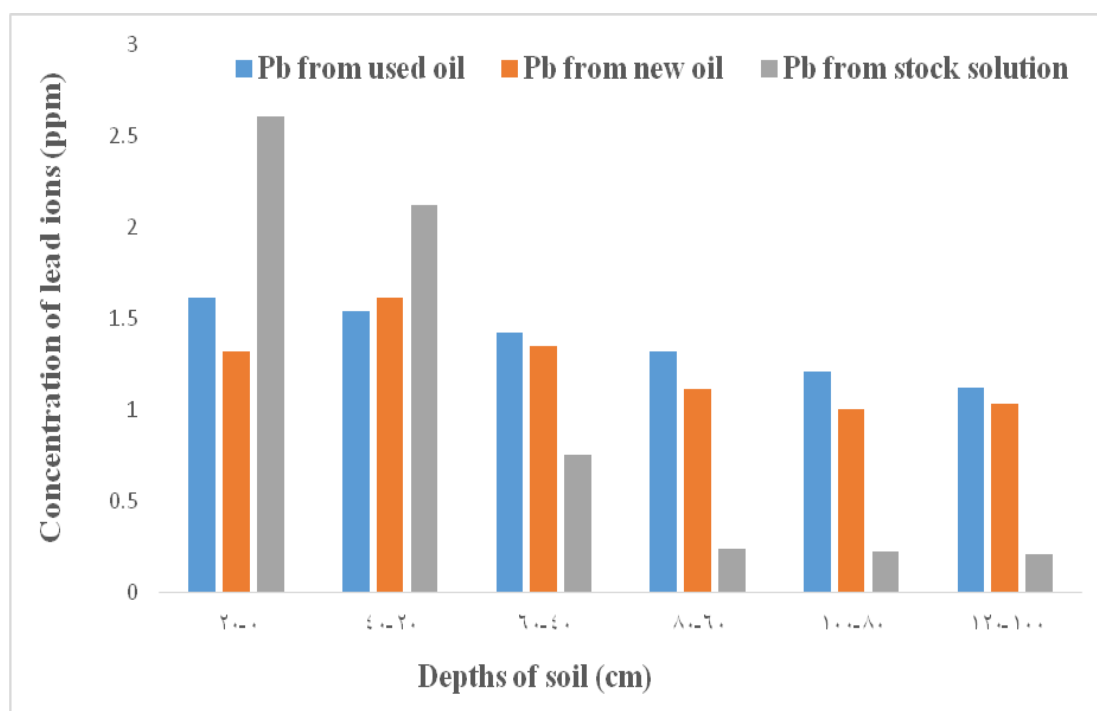


Figure 4.14: Lead concentrations at various depths of soil from used engine oil, new engine oil and stock solution.

4.5: Langmuir and Freundlich isotherm:

In this study Langmuir and Freundlich isotherm models were used to describe the relationship between amounts of zinc and lead adsorbed onto soil and their equilibrium concentration in the solution at 25°C. The fitting of adsorption data to Langmuir and Freundlich isotherm models were used to describe the adsorption of zinc and lead onto soil.

Isotherm equations were investigated by plotting C_e/q_e versus C_e for Langmuir isotherm (equation 3.4) and $\log q_e$ versus $\log C_e$ for Freundlich isotherm (equation 3.5) and results are shown in figures (4.15, 4.16). Their parameters were calculated from slopes and intercepts and summarized in table 4.5. From values of R^2 we conclude that both Langmuir and Freundlich equations describe experimental data here. R_L value shows the adsorption to be favorable when $0 < R_L < 1$, unfavorable when $R_L > 1$, linear if $R_L = 1$ and irreversible when $R_L = 0$ [74]. Values of R_L were founded from equation 3.6, ($K_a = 6.38$ at $C_0 = 50$ ppm for Zn and $K_a = 0.807$ at $C_0 = 50$ ppm for Pb) to be 0.003 for adsorption of Zn on soil and 0.024 for lead in this research which means favorable adsorption. Values of n are (2.62 for Zn and 1.53 for Pb) lies between 1 and 10 indicating favorable adsorption.

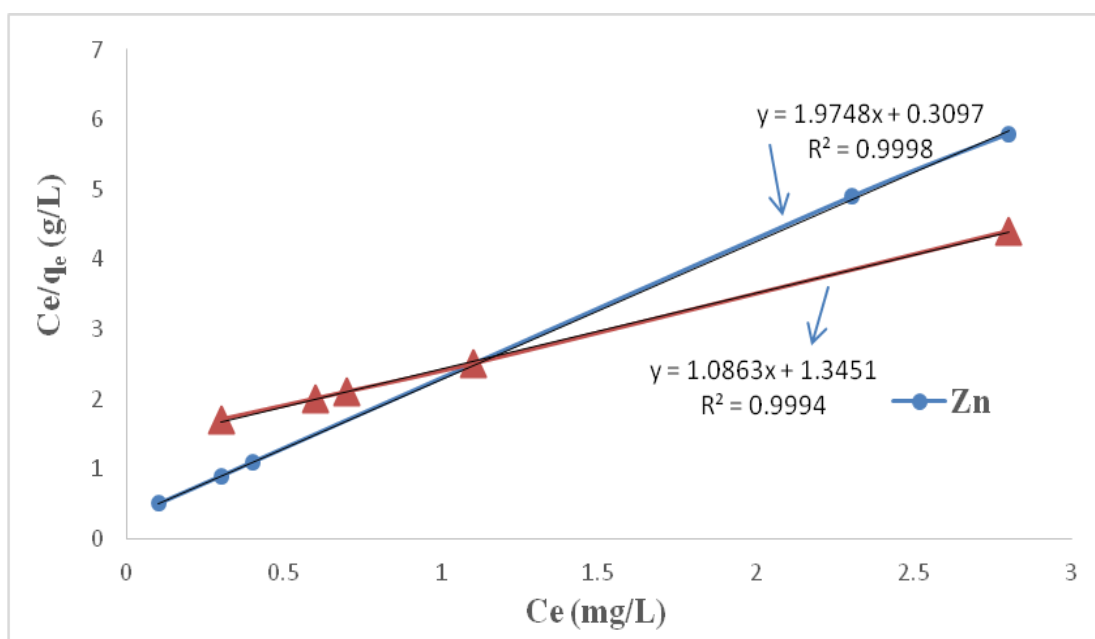


Figure: 4.15: Langmuir isotherm plot of Zn and Pb adsorption on soil at (temperature 25°C, pH 7.5, and 2g soil/25ml))

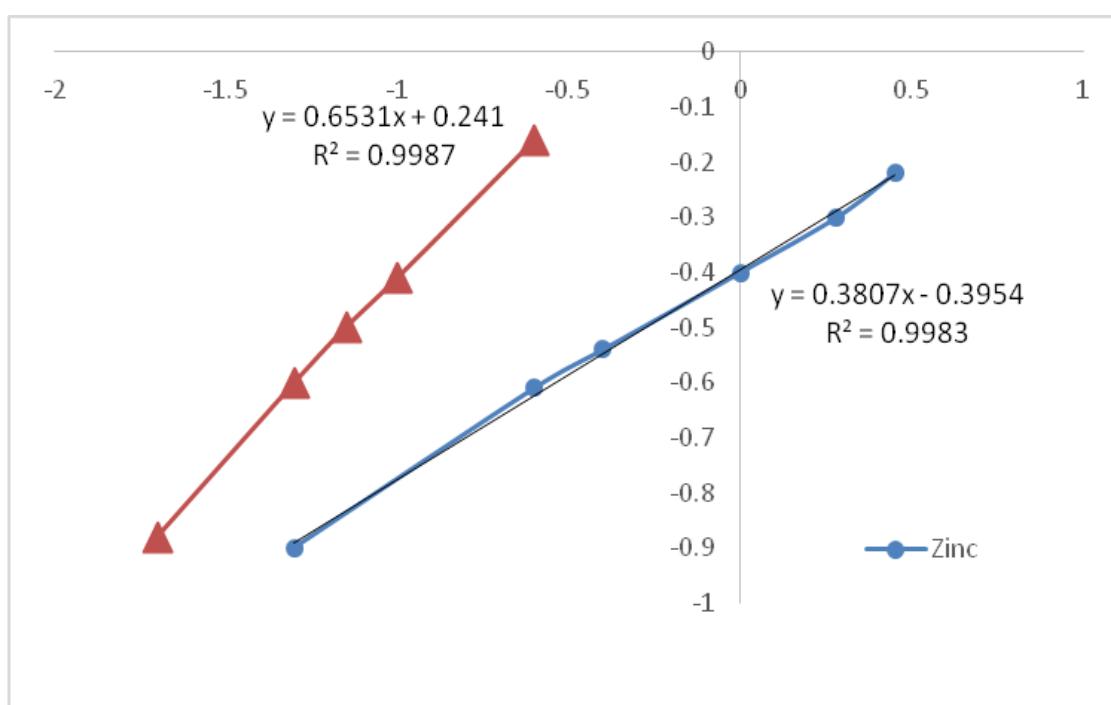


Figure 4.16: Freundlich plot $\log(q_e)$ versus $\log(c_e)$ for Zn and Pb adsorption on soil (at temperature 25°C, pH 7.5, and 2g soil/25ml)

Table 4.5: Langmuir and Freundlich isotherm parameters and correlation coefficients for zinc and lead adsorption onto soil (temperature 25°C, pH 7.5, contact time 30 minutes and 25 ml solution/2gsoil)

Isotherm	Langmuir			Freundlich		
	Parameters			parameters		
Adsorbate	q_m	K_a	R^2	k_F	n	R^2
Zn	0.506	6.38	0.999	0.4	2.62	0.998
Pb	0.920	0.807	0.999	1.735	1.53	0.998

4.6: Adsorption kinetics:

Linear plots of $\log (q_e - q_t)$ versus t (equation 3.7) and t/q_t versus t (equation 3.8) were used to check the fit of pseudo-first order and pseudo-second order respectively. To check intra-particle diffusion model q_t versus $t^{1/2}$ (equation 3.9) was plotted. Correlation coefficients and pseudo-first order and pseudo-second order parameters are calculated from plots of $\log (q_e - q_t)$ versus $t(\text{min})$ and t/q_t versus t (min). Values of K_1 , q_e , K_2 and R^2 are summarized in table 4.6, it is observed that values of $q_e(\text{exp})$ for pseudo-second-order model are more close to values of q_e calculated, so pseudo-second order kinetic model is more suitable to describe the adsorption process in this experiment which means chemisorption or ion exchange[75]. Results are shown in figures 4.17, 4.18.

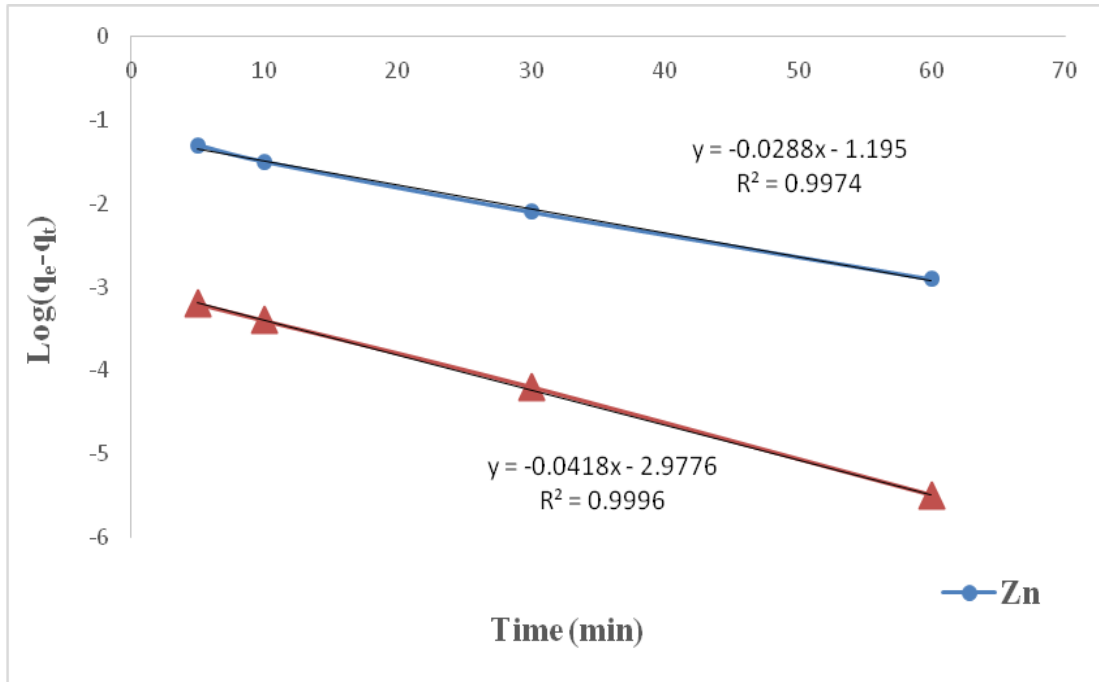


Figure: 4.17 Kinetics adsorption of Zn and Pb onto soil according to pseudo-first order model at (initial concentration 50ppm, 25 °C, pH= 7.5)

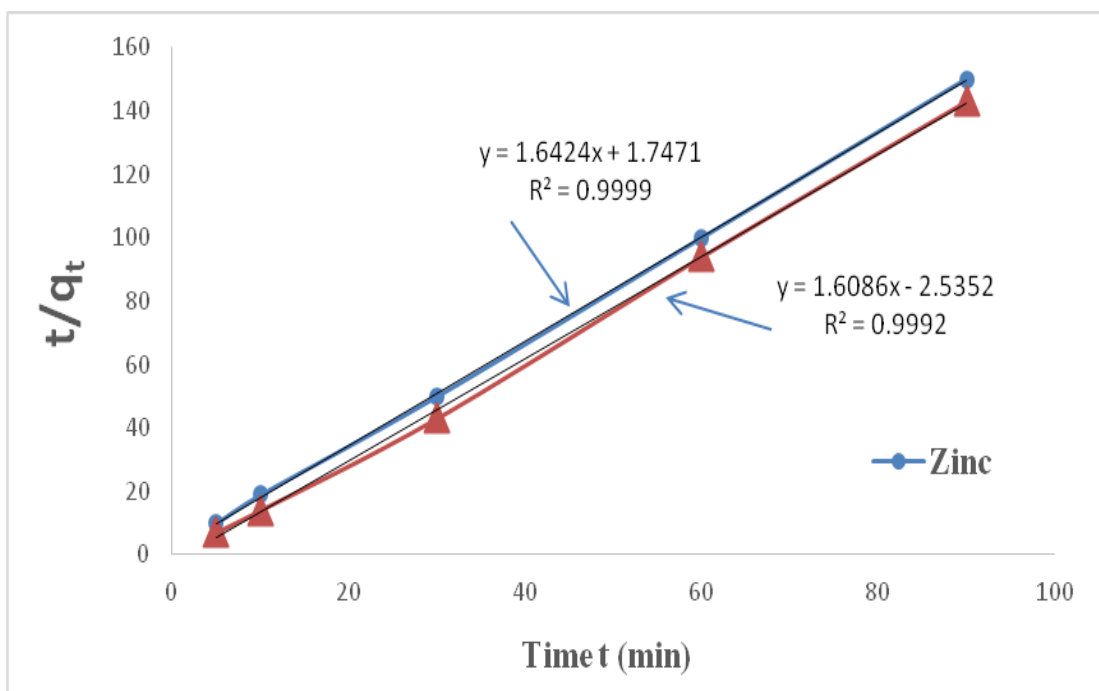


Figure: 4.18 kinetics of pseudo- second order model for adsorption of Zn and Pb onto soil at (initial concentration 50ppm, temperature 25°C, pH 7.5)

Table. 4.6 Pseudo-first order and Pseudo-second order kinetic models parameters for adsorption of Zn and Pb on soil at (pH 7.5, temperature 25°C, initial concentration =50ppm and 25ml solution/2g soil).

Adsorbate	q_e (exp) (mg/g)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		$K_1(\text{min})^{-1}$	$q_e(\text{cal})$ (mg/g)	R^2	K_2 (g/mg.min)	$q_e(\text{cal})$ (mg/g)	R^2
Zn	0.6059	0.066	0.0535	0.997	1.543	0.6093	0.999
Pb	0.6237	0.094	0.0013	0.999	1.016	0.623	0.999

Values of intra-particle diffusion constants and the correlation coefficients obtained from linear plots of q_t versus $t^{1/2}$ are obvious in figure (4.19, and table 4:7). According to these values R^2 for zinc is higher than R^2 for lead, the linear plots didn't pass through origin, and this deviation from origin is due to differences in the rate of mass transfer and also implies other phenomena affect adsorption. The value of A for lead ($A=0.62$) is higher than A for ($A=0.58$) zinc which means greater contribution of the surface sorption [76].

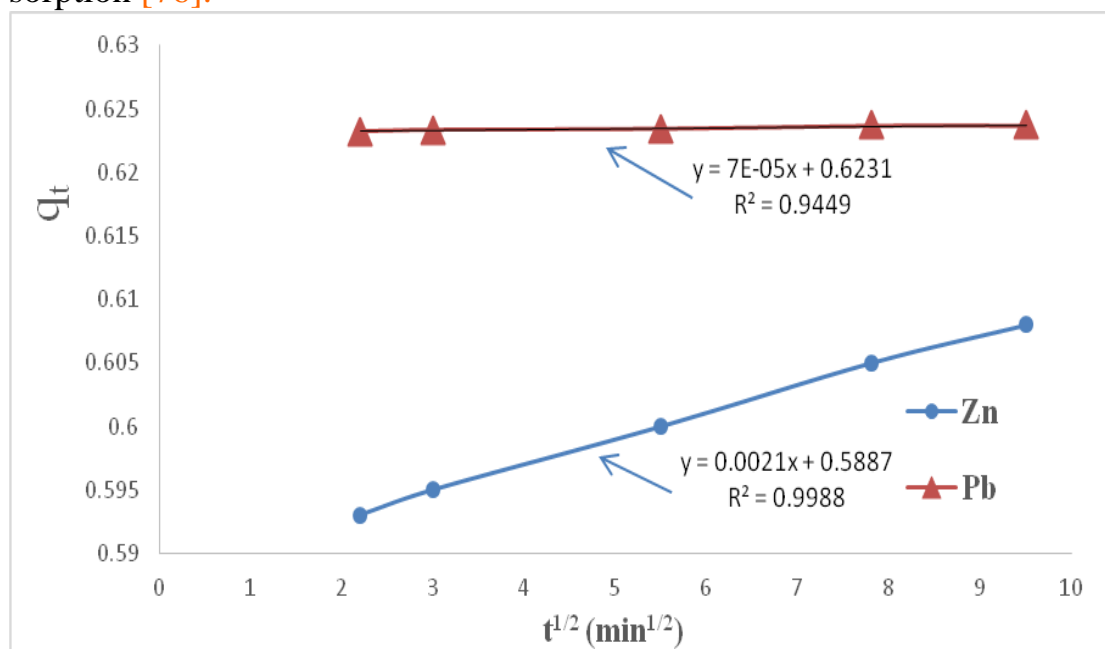


Figure: 4.19: Intra-particle diffusion plot for adsorption of Zn and Pb onto soil at (25°C, pH 7.5, 50ppm solution, 25 ml /2gsoil)

Table: 4.7: Intra-particle diffusion parameters for adsorption of Zn and Pb onto soil

Adsorbate	K _p (mg/g min ^{1/2})	R ²	A
Zn	0.002	0.998	0.58
Pb	0.00005	0.944	0.62

4.7: Adsorption thermodynamics:

Values of ΔH and ΔS are calculated from the slopes and intercepts of linear plots of $\ln K_d$ versus reciprocal of absolute temperature (equation: 3.10), figure 20 and plot of ΔG^0 versus absolute temperature figure 4.21 the results are given in table 4.8.

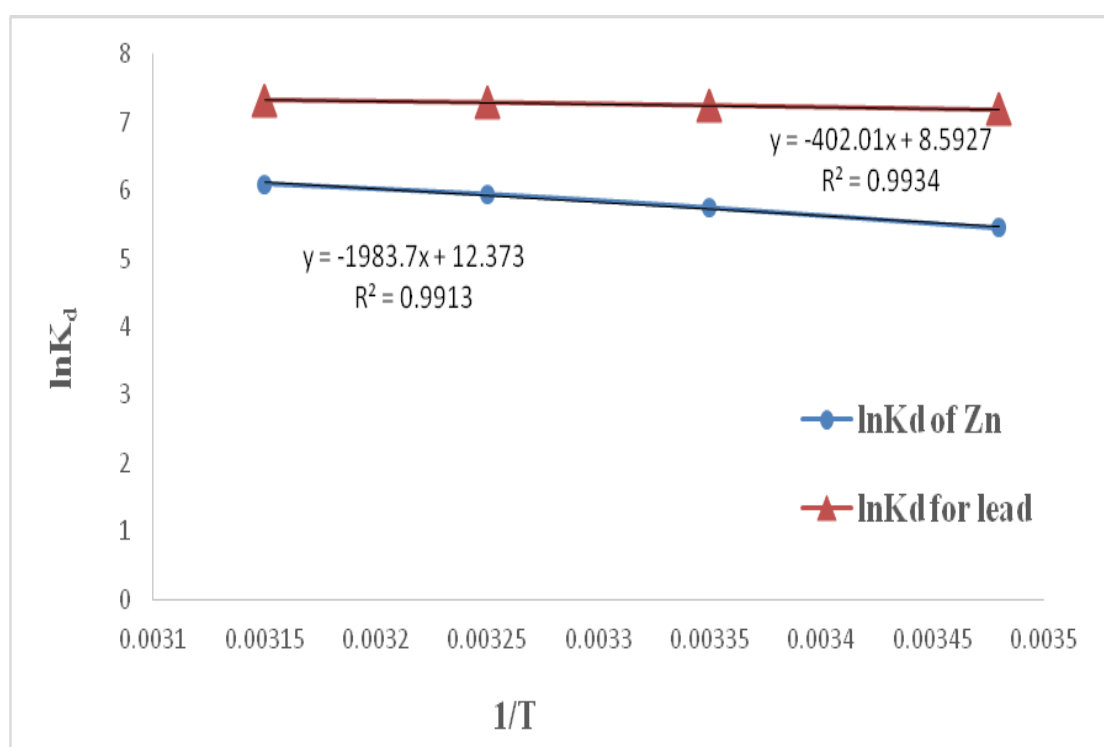


Figure: 4.20: Plot of $\ln K_d$ versus reciprocal of absolute temperature of 50ppm Pb and Zn solution for adsorption on soil.

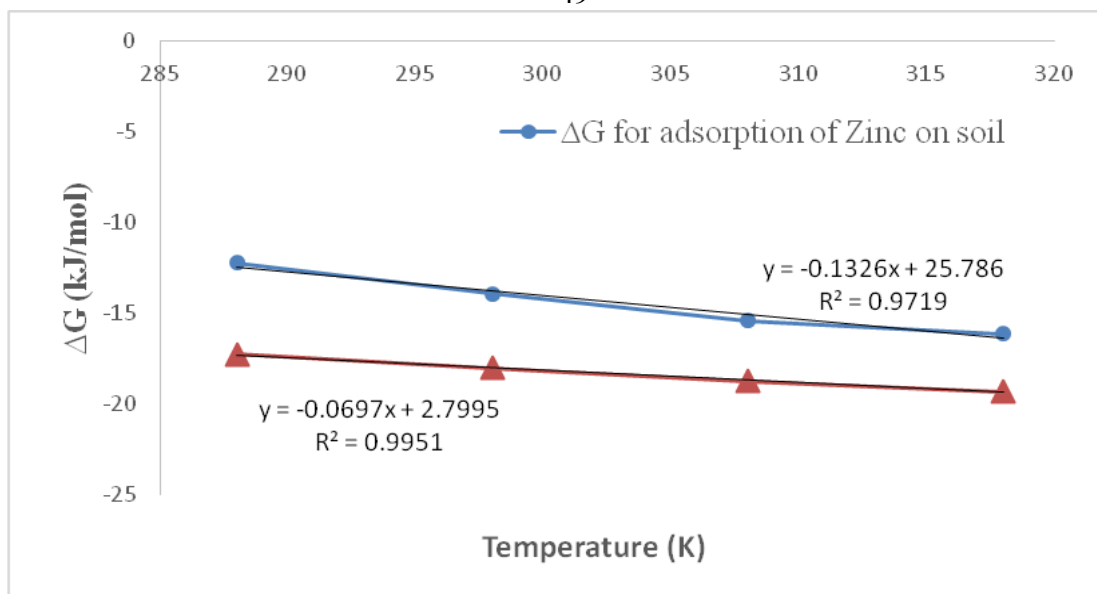


Figure: 4.21: Plot of Gibbs free energy ΔG versus absolute temperature of for adsorption of Zn and Pb onto soil (pH 7.5 contact time 30 min, initial concentration 50ppm).

Table: 4.8: Thermodynamic parameters of adsorption of zinc & lead onto soil

Adsorbate	ΔH^0 (KJ/mol)	ΔS^0 (J/molK)	ΔG^0 (KJ/mol)			
			288k	298k	308k	318k
Zn	16.492	102.87	-12.1903	-13.8992	-15.3866	-16.1147
Pb	3.342	71.44	-17.225	-17.9924	-18.7378	-19.2993

Negative values of ΔG^0 at different temperatures indicate that adsorption process of zinc and lead on soil is spontaneous and preferable, while positive ΔH^0 indicates that adsorption is endothermic and positive ΔS^0 means increasing randomness at solid/liquid interface. Also the decrease in ΔG^0 with increasing temperature indicates spontaneity at higher temperatures while positive indicates good affinity of zinc and lead toward soil to be adsorbed [77, 66].

Conclusion and Recommendation

Conclusion:

Based on this study the following conclusions are obtained:

- * Experimental data showed that concentration of several heavy metals (Zn, Pb, Cr, Mn, and Cu) in used lubricating oil is higher than concentration of these metals in new oil.
- * Used lubricating oil pollutes environment when poured improperly into soil.
- * Heavy metals (Zn, Pb) possess high affinity to be adsorbed by soil.
- * Adsorption of zinc and lead increases with increase adsorbent dosage (soil), temperature and time of contact.
- * Changing pH can change adsorption of zinc and lead: adsorption is increasing when pH is high (alkaline).
- * Both Zn and Pb adsorption decreases by increase in adsorbate (metal) concentration.
- * Results showed that Zn and pb follow Freundlich and Lanqmuir isotherm models.
- * Column soil experiment showed that there is possibility of leaching heavy metals contained in lubricating oils, so they can pollute ground water.

Recommendation:

In order to reduce environmental pollution caused by used engine oil:

1. Don't pour used engine oil on the ground, in the sewer or put it in trash.
2. Used lubricating oil must be disposed of properly, the best environmentally method is to return used oil to the service station for recycling. All stations Possess suitable tanks for storage used oil before recycling.
3. Storage tanks should be strong and safely covered.
4. Don't make oil change to your vehicle by your self but make it in service facility.
5. You have to use reusable sorbent material (pads).
6. Don't throw filters on ground but put them in the collection place of used oil.
7. A big source of pollution is leaky car, so cars must be tested continuously.
8. Drivers must follow machine's manual for oil change, so they are recommended to drive for long distances between oil changes without harming the engine.
9. Don't mix wastes (dirt, gasoline, paints) with used oil because these wastes make recycling process more difficult.
- 10.Grants to collection centers.
- 11.Strict regulations to service facilities.

12. Encourage public to change to synthetic lubricants that are less harmful to environment.

13. Finally according to American petroleum Institute (API): recycling 2 gallons of used engine oil can produce electrical energy enough to run average household for 24 hours.

Suggestions for future work:

Additional studies concerning environmental effects of used lubricating oil are suggested, these include:

1. Adsorption behavior of other heavy metals contained in used lubricating oil.
2. Effect of organic matter on metal adsorption.
3. Investigating of synthetic lubricants which are friendlier to environment.
4. Studying adsorption thermodynamics of used lubricants.
5. Studying economic efficiency of changing used lubricating oils to beneficial source of energy.

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جامعة النجاح الوطنية

كلية الدراسات العليا

دراسة توزيع المعادن الثقيلة في زيوت المحركات المستخدمة بواسطة تحليل عينات من اعمدة التربة

اعداد

رسمي حلمي مصطفى عوده

اشراف

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قدمت هذه الاطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم البيئية من
كلية الدراسات العليا في جامعة النجاح الوطنية، نابلس - فلسطين.

2013م

ب

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الملخص

في وقتنا الحاضر ازداد الانتباه الجمهور بمشكلة التلوث البيئي لما له من آثار سلبية على مختلف مكونات البيئة كالتربة والنبات ومياه الشرب والهواء والحياة المائية . هذه الاطروحة تركز على الآثار البيئية لزيوت المحركات المستخدمة لهذه وخاصة من نوع (15W-40) على التربة والمياه. الهدف الرئيسي لهذا البحث هو دراسة المعادن الثقيلة التي تتلوث بها زيوت المحركات المستخدمة خلال عمل المحرك واحتمالية تلويث تلك الزيوت للتربة والمياه الجوفية. في هذه الدراسة تم استخدام 5 لترات من زيت غير المستعملة ومثلها من الزيت المستعمل وكلاهما من نوع (15W-40) والتي تم شراؤها من محطة شيل لزيوت السيارات في مدينة نابلس.

تم جمع كمية من التربة الحمراء من مساحة نصف دونم في قرية شوفة التي تقع على بعد حوالي 4 كيلومتر الى الجنوب الشرقي من مدينة طولكرم مع مراعاة ان المنطقة التي تم جمع التربة منها بعيدة عن مصادر التلوث.

تم اجراء فحوصات لعينة من التربة في مركز البحوث البيولوجية والكيميائية وفي مختبر التربة التابع لكلية الهندسة في جامعة النجاح الوطنية حيث تم قياس درجة الحموضة والرطوبة ونسبة المواد العضوية وتحليل نسيج التربة ثم تم تعبئة تلك التربة في ثلاثة انابيب بلاستيكية بقطر 6انش وطول 140 سم لكل منها.

في هذا البحث تم قياس تراكيز كل من الزنك والرصاص والكروم والمنغنيز والنحاس في كمية من زيت المحركات المستخدم (15W-40) وفي كمية مماثلة من نفس النوع من الزيت غير المستخدم

ت

حيث كان هناك فرقا في التركيز فوجد ان تركيز المعادن الخمسة التي تم قياسها في الزيت المستخدم اعلى منه في الزيت غير المستخدم. فوجد ان تركيز الزنك 23,23 ، والرصاص 0,6 والمنغنيز 34 والكروم 0,097 والنحاس 0,072 جزء في المليون في عينة الزيت المستخدم بينما وجد ان تركيز الزنك 3,9 والرصاص 0,4 والمنغنيز 28,8 والكروم 0,064 والنحاس 0,01 جزء في المليون في عينة الزيت الجديد (غير المستخدم).

في هذا البحث تم دراسة خصائص ادمصاص التربة لكل من عنصري الزنك والرصاص من خلال دراسة اثر

درجة الحرارة في المدى (15-45⁰س) فوجد ان اكبر ادمصاص حصل عند 45⁰س ثم اثر درجة الحموضة في المدى (2-13) فكان الادمصاص الاكبر عند درجة الحموضة 13 لكل من الزنك والرصاص. كذلك اثر تركيز الملوثات الابتدائي في المدى (10- 50 جزء في المليون) فكان اكبر ادمصاص عند التركيز الاقل (10 جزء في المليون) اما عامل كمية التربة فقد تم دراسته في المدى (0,5 - 3 غم) فكانت اكبر ازالة لكلا المعدنين عند 3 غم ترب، وفي حالة زمن التعريض فقد تم تغيير الزمن من (10 - 90 دقيقة) وحصل الاتزان عند الزمن 90 دقيقة.

تم اضافة لترين من الزيت المستخدم للعمود الأول ولترين من الزيت الجديد للعمود الثاني بينما اضيفت الـ (50 جزء في المليون) للثالث وبعد ذلك تم اضافة ماء مقطر للاعمدة الثلاثة ولمدة خمسة أيام متتالية حتى رشح الماء من الانابيب الثلاثة ثم تم قياس تراكيز كل من الزنك والرصاص في عينات تربة اخذت من ارتفاعات مختلفة للاعمدة الثلاث وأشارت الفحوصات ان التركيز اكبر ما يمكن في المنطقة العلوية الا انه وجد تراكيز اقل في المناطق السفلية للاعمدة مما يدل على امكانية تسرب تلك الملوثات للمياه الجوفية.

تم تفسير نتائج الادمصاص عند الاتزان من خلال لانجمور وفريندليش فكان النموذجان مناسبين لتفسير عملية الادمصاص لكل من الزنك والرصاص. للتحقق من آليات الادمصاص تم تطبيق نماذج الحركة: نموذج الاعتماد من الدرجة الأولى ظاهريا ونموذج الاعتماد من الدرجة الثانية وكذلك نموذج تدفق الدقائق الى داخل الجسيمات وقد اتفقت تلك النماذج مع النتائج التي تم الحصول عليها الا ان نموذج الاعتماد من الدرجة الثانية كان هو الاكثر توافقا. كذلك تم حساب

ث

ثابت تيرموديناميكية مثل طاقة جيبس ΔG^0 والمحتوى الحراري ΔH^0 والتغير في الاعتلا ΔS^0 .
وقد اظهرت النتائج ان عملية الادمصاص كانت تحدث تلقائيا وكانت طاردة للحرارة.