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# Adsorption of lead and zinc from used lubricant oil using agricultural soil: equilibrium, kinetic and thermodynamic studies

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## Abstract

In this study we examined the adsorption, kinetics and thermodynamics of  heavy metals of used engine oil that come during engine operation and forsaw the possibility of polluting soil and ground water.  the effect of temperature on adsorption was investigated in the range (15 – 45$^o$C) and results showed that maximum removal occurred at 45$^o$C. Effect of pH indicated that maximum removal of both Zn and Pb was at pH =13. Increasing adsorbent (soil) dosage from 0.5 to 3g showed that maximum adsorption of both Zn and Pb onto soil occurred with 3 g of soil. Equilibrium concentration happened at 90 minutes. Lanqmuir and Freiundlich models were used to study adsorption process at equilibrium and the results showed that Frenundlich is better for Zn while Lanqmuir fits better with  Pb.  In order to investigate adsorption behavior of Zn and Pb on soil, three kinetic models applied; Pseudo-first order, Pseudo-second order and intra- particle diffusion models were applied to fit kinetics data. The rate constants and correlation coefficients were determined for the three models. Thermodynamic parameters such as Gibbs free energy, standard enthalpy and standard entropy change were calculated for both zinc and lead.

*Keywords:* used engine oil, adsorption, kinetics, lead, zinc, thermodynamics, pollution, equilibrium, contact time, soil.

## Introduction

Machinery is very important in our life and oil used in them plays an important role in its working life.  The oil 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 polychlorinated biphenyl, polycyclic aromatic hydrocarbons and heavy metals, which when released to environment particularly soil and water caused 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 has been 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 have entered the environment and contaminated the 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. 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 the air .There are no studies about the environmental impacts of used engine oil in Palestine while 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 an increase in metal concentrations in used oil samples compared to new samples [4].

In Port Harcourt, Nigeria 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 was 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 µg/g  (Ni) to 493 µg/g (Pb) in soil and 0.019 mg/l (Ni) to 0.147 mg/l (Pb) in water [5].

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 [6].

The 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 [7].

Finally, this study emphasis on the environmental pollution which comes from the disposal of used engine oil on ground without recycling. I think it's worth it to study the adsorption behaviour of those heavy metals in soil. To do so both metals Pb and Zn will be analyzed in both new and used engine oil and the adsorption models of both Freundlich and Langmuir will be applied in addition to the kinetics and thermodynamics study of the adsorption.

## 2. Materials and methods

### 2.1 Chemicals
The chemicals that have been used in this study are:
  1)   New engine oil (SAE 15 W- 40) Shell Oil Company, USA.
  2)   Used engine oil (SAE 15W -40) Shell. 3) Sulfuric acid, hydrogen chloride, sodium hydroxide, nitric acid, zinc nitrate, lead nitrate and hydrogen peroxide. All of the chemicals used were purchased from Sigma-Aldrich, Germany, with very high purity.

### 2. 2. Instrumentation
Flame Atomic Absorption Spectrophotometer model ZicE-3000SERIES, designed in UK FAA Spectrometer, pH and conductivity meter Jenway model 3540, Shaker model LSBO-15S, Centrifuge HermelZ200A, Balance 301S, hydrometer ASTM152-h, JLabTech  and oven modleLOD-060E.

### 2.3.  Soil characterization
#### 2.3.1. Soil collection and preparation.
In order to test soil for heavy metals a sample of soil was collected from area (500m$^2$) in Shufa located east of  Tulkarm which is very distant from any source of engine oil contamination. One kilogram was collected randomly from the sample, sieved by a 2 mm sieved and analyzed for organic matter, pH, conductivity, moisture, texture and specific gravity.

#### Soil digestion
 About 100 g of soil sample were dried at $105^0$C and then cooled for further use. A 1.0 g of dried and sieved soil was placed in the flask and 10 ml concentrated nitric acid was added to the flask. The mixture was heated on a hot plate near boiling and stirred by a magnetic stir bar. After cooling, a 5 ml of concentrated $HNO_3$ was added to the flask and refluxed for half hour, then  heated and stirred for an additional 10 minutes and cooled. After cooling, a  2 ml distilled water and 3 ml $H_2O_2$ were added to the mixture and then cooled again.  The solution appeared grey and then 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 [8].

#### 2.3.2. Physical characterization of Soil
The pH, moisture, specific gravity, soil texture and organic matter were analysed using approved analytical methods and are shown in Table 1.

**Table. 1** Soil characteristics

| SOIL PROPERTY | RESULT |
|---|---|
| Specific gravity | 2.34 |
| pH value | 7.5 |
| Conductivity | 182*us* |
| Organic matter | 6.4% |
| Moisture | 9.56% |

#### 2.3.3.  Engine oil digestion.

Small amount of used oil (0.5g) and new oil (15W-40) were placed in two digestion flasks separately and 4 ml of concentrated $H_2SO_4$ were added to each flask. A glass column was put at the top of each flask to remove acid vapor produced when refluxing for 5 minutes at 440C$^o$. A 10 ml of $H_2O_2$ were added by funnel and refluxed for two minutes. When the two solutions were cooled, deionized $H_2O$ water was added to make the volume of each solution 100 ml [9]. The two mixtures were filtrated and become ready for measuring concentrations of Pb, and Zn usin flame atomic absorption spectrophotometer.

*2.4. Heavy metals determination*
To determine metals (Zn, Pb) in used engine oil and comparing their concentrations with new engine oil. A spectrophotometric method was used for Zn and Pb Standard solutions were prepared for calibration. A 100 mg/L solution was prepared for Zn and Pb, then various concentrations were made by dilution in order to obtain the calibration curves for both Pb and Zn [10]. A calibration curves were obtained with $R^2 > 0.98$.

*2.5 Adsorption experiments*
Percentage removal of adsorbed solute was calculated from the following equation [11].

$$\% \text{ of removal} = [(C_0 - C_f)/C_0] \times 100\% \qquad (1)$$
$$q_e = [(C_0 - Ce)/M] \times V \qquad (2)$$
$$q_t = [(C_0 - C_t)/M] \times V \qquad (3)$$

where:
$C_e$: 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 (mg)
$q_t$: equilibrium adsorption capacity (mg/g)

*2.6 Adsorption isotherms*
Adsorption is widely used as a physical process to decrease concentration of dissolved pollutants. Adsorption isotherm means adsorate molecules distribute between liquid phase and solid phase when adsorption reaches equilibrium.
Many models have been used to describe adsorption isotherms, the most famous models are Langmuir and Freundlich isotherms.
In this study Lanqmuir and Frendlich isotherm models were used to describe the relationship between amounts of zinc and lead adsorbed and their equilibrium concentration in solution at 25$^o$C.
Fitting of adsorption data to Lanqmuir 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 (4 and 5) [12].
*Langmuir equation*

$$C_e/q_e = 1/q_{0b} + (1/q_0)C_e \qquad (4)$$

where Ce is the equilibrium concentration of the adsorbate (mg/L), qe is the amount of adsorbate per unit mass of adsorbent (mg/g), $q_o$ and b are Langmuir constants related to adsorption capacity and rate of adsorption ,respectively:
*Freundlich equation*        $\log (q_e) = \log (K_F) + (1/n) \log (C_e)$            (5)

where $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $q_e$ is the amount of adsorbate per unit mass of adsorbent (mg/g), $K_F$ and n are Freundlich constants with *n* giving an indication of how favorable the adsorption process is. $K_F$ ((mg/g) (L/mg)) is related with adsorption capacity of the adsorbent
The slope 1/n is a measure of heterogeneity and its value is between 0 and 1. When it closes to zero the surface becomes more heterogeneous [13] ,when n is greater than 1, this means efficient adsorption [14].

*2.7 Adsorption kinetics*
In order to study the mechanisms of zinc and lead adsorption on soil, pseudo -First- order- kinetic model; pseudo- second – order 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 [15], the integral form of this model is given by equation (6):

$$\text{Log} (q_e - q_t) = \log q_e - K_1 t/2.303 \qquad (6)$$

where qe (mg/g), qt (mg/g) are adsorption capacity at equilibrium and time  t respectively, $K_1$ the rate constant of pseudo first –order adsorption (1/min).

*Pseudo-second – order model:*  Adsorption also can be tested by pseudo-second order kinetic model.  This model is greatly affected by the amount of metals on the adsorbent's surface and amount of metals adsorbed at equilibrium using the equation (7):

$$t/q_t = 1/ K_2\, q_e^2 +  t/q_e \qquad\qquad (7)$$

$K_2$ is the pseudo-second order constant (g/mg/min).

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

The solute transfer is described well by intra-particle diffusion model. According to Weber and Morris theory [16].

$$q_t =  K_p\, t^{1/2} + A \qquad\qquad (8)$$

where $K_p$, is the  rate constant of intra-particles diffusion model (mg/g min$^{1/2}$) and A gives an idea about the thicknesses of the boundary layer.

### 2.8 Adsorption thermodynamics

Thermodynamic parameters $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ were considered in    order to determine the nature of the adsorption processes. When $\Delta G^0$ is negative, the process is spontaneous, when $\Delta H^0$ is negative the adsorption process is exothermic while positive values of $\Delta S^0$ indicate increasing randomness at the solid/liquid interface (Ho, 2006). These parameters were calculated from equations (9-11):

$$LnK_d =  (\Delta S^0/R) - (\Delta H^0/R)1/T \qquad\qquad (9)$$

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 (10):

$$K_d = (C_{Ae} / C_e) \qquad\qquad (10)$$

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

Also a plot of $\Delta G$ versus T was found to be linear and the values of $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept of the plot according to equation (11) [17]:

$$\Delta G^0 = \Delta H^0 – T\Delta S^0 \qquad\qquad (11)$$

### 2.9 Physical and chemical parameters of adsorption

#### 2.9.1  Effect of pH on soil adsorption of lead & Zinc

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

#### 2.9.2 Effect of temperature on soil adsorption of lead and Zinc

This experiment was performed by preparing four solutions. A 2g of sieved soil put in each beaker and 25ml of 50 mg/L solution were added to each beaker. At pH 7.5  the beakers were closed by Teflon and shacked for 30 minutes using a shaker model LSB-015S.

#### 2.9.3 Effect of concentration on soil adsorption of Zn and Pb

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

#### 2.9.4 Effect of dosage on soil adsorption of Zn and Pb

 Five different weights ( 0.5g, 1.0 g , 1.5g, 2g, 3g ) of sieved soil were taken and replaced in separate beakers. A 25 ml of 50 mg/L stock solution was added to each beaker at pH 7.5, temperature 25°C. The five beakers were closed by para film and shacked for 30 minutes using a shaker Model LSB-O15s.The five samples were filtrated and become ready for scanning by FAAS.

*2.9.5 Effect of contact time on soil adsorption of Zn and Pb*

A 2 g soil were placed in each beaker and 25 mL of 50 mg/L solution were added to each beaker. A shaker was kept at $25^oC$ and 150 rpm at pH 7.5. The first beaker was shacked 10 minutes, the second 30 minutes, the third 60 minutes and the fourth 90 minutes. The filtrates were analyzed using FAAS.

## 3. Results and discussion

Results of this work are represented in tabular and graphical forms. These results are devoted to understanding 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 adsorption of heavy metals into soil.

*3.1 Soil characteristics*

Sample of soil was analyzed in Poison Control & Chemical Biological Centre at Al- Najah National University and the results were shown in Table 1.

*3.2 Heavy metal concentration in engine oil*

As shown in Table. 2 there are obvious differences in the concentration of Zn, Pb 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.

**Table. 2** Zn, Pb, Mn, Cr and Cu 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 |

These differences can be explained by contamination 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 the increase in zinc concentration results from additives and galvanized piping wear. Lead in used oil may result from bearing cages alloyed with copper and Ti [18].

*3.3 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 [6].

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 [19].The relation is shown in Fig. 1. Zinc removal increases with increasing pH up to about 7.5. As Zn changes to $Zn(OH)_2$ and Pb removal increases with increasing pH. Below pH = 6, Pb takes the form of $Pb^{+2}$ and above that pH, Pb is hydrolyzed to $Pb(OH)_2$ and $Pb(OH)^+$.
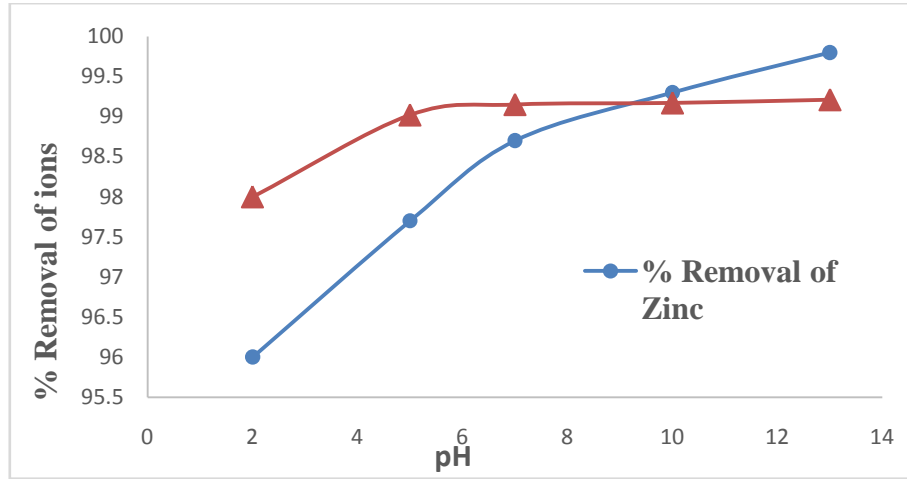
*3.4 Effect of temperature on Zn and Pb adsorption*

The effect of temperature on adsorption of Zn and Pb was studied in the range of $(15 – 45^oC)$. As we see in Fig. 2 adsorption of Zn is about 93% at $15^oC$ and more than 97% adsorbed at $45^oC$. Adsorption of Pb is more than 99% at $45^0C$ the entire range of temperature.
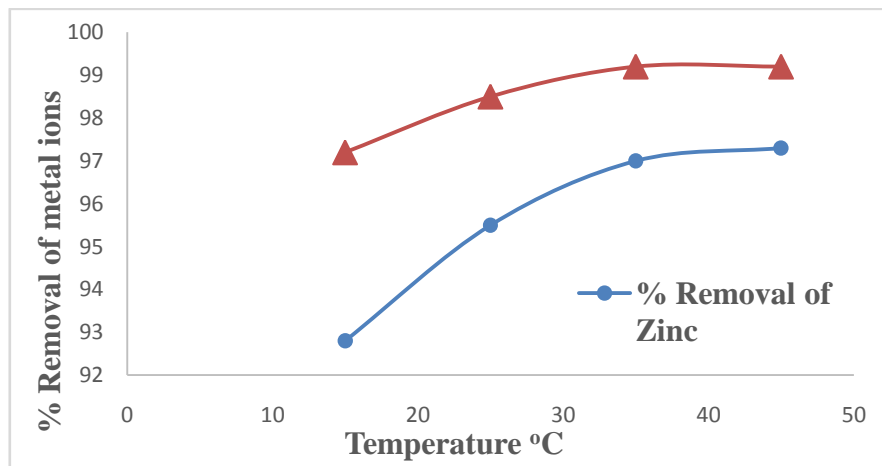
*3.5 Effect of concentration of Zn and Pb adsorption*

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 mg/L) the percent of removal of zinc changed from 99.9% at 10ppm to 94.3% at 50 mg/L as shown in Fig. 3, while for lead the percent removal changed from 99.25% at 10 mg/L to

88.15% at 50 mg/L as shown in Fig. 3. 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 of initial concentration [20].



**Figure 1:** Effect of pH on % removal of Zinc by soil (conc. 50ppm, temp.25°C and contact time 30 min).



**Figure 2:** Effect of temperature on % removal of Zn and Pb (initial conc. 50ppm, pH: 7.5 contact time 30min).
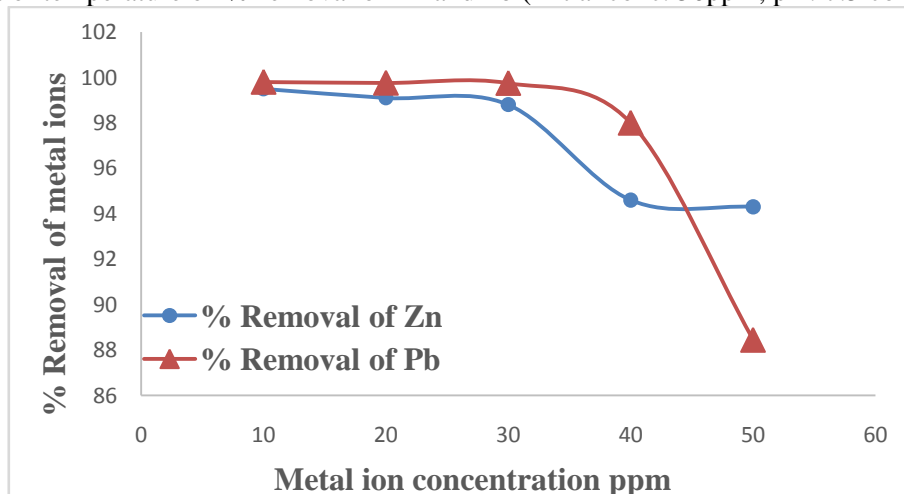


**Figure 3:** Effect of concentration on % removal of Zn and Pb (pH 7.5, temp.25°C, contact time 30min, 2g soil /25ml solution)

*3.6  Effect of adsorbent dosage on Zn and Pb adsorption*

 Increasing adsorbent dosage increases metal adsorption [7]. The study shows that adsorption of both metals Zn and 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 Fig . 4 more than 65% of zinc was adsorbed on 0.5 g soil and about 88% by 3 g soil; while 72% of lead adsorbed by 0.5 g soil and more than 95% of lead adsorbed by 3 g soil. Also results showed that %removal Pb > %Zn .
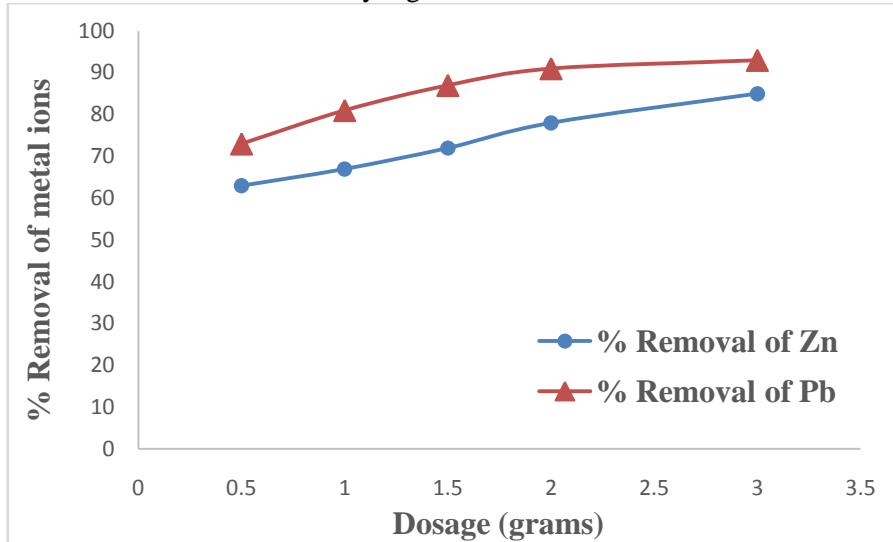


**Figure 4:** Effect of dosage on %removal of Zn and Pb (initial conc. 50ppm, pH 7.5, temp.25$^{o}$C, contact time 30min, 2g soil/25ml solution) .

*3.7 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. More than 70% of zinc was adsorbed during the first 10 minutes and the adsorption increases fast with time up to 30 minutes, then adsorption increases slowly up to equilibrium. Results for Pb adsorption showed that lead adsorption is very fast; more than 78% was adsorbed during the first 10 minutes. Results are in Fig. 5.
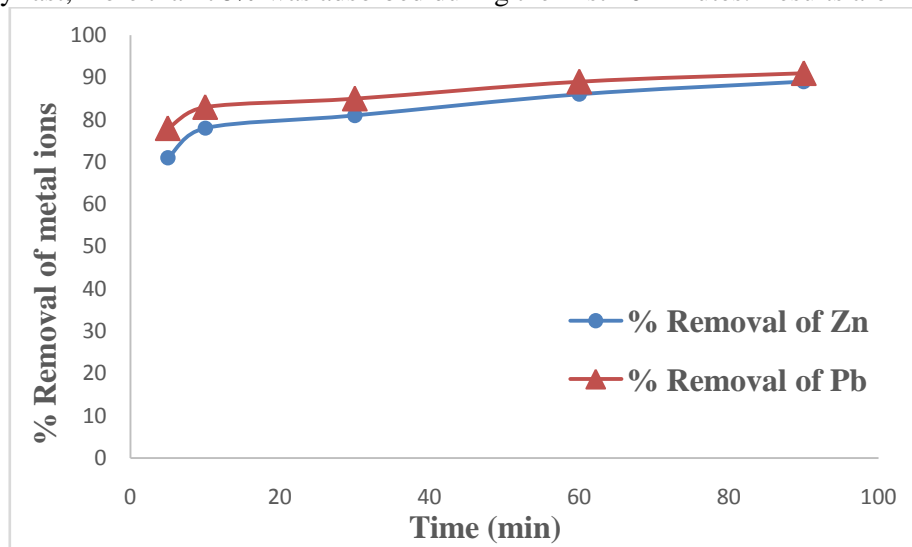


**Figure 5:** Effect of contact time on % removal of Zn and Pb (initial conc.50ppm, pH 7.5, temp.25$^{o}$C).

*3.8  Lanqmuir and Freuindlich isotherm*
In this study Lanqmuir and Frendlich 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$^{o}$C. The fitting of adsorption data to Lanqmuir and Freundlich isotherm models were used to describe the adsorption of zinc and lead onto soil.
Isotherm equations were investigated by plotting Ce/qe versus Ce for Lanqmuir isotherm (equation. 4) and log $q_e$ versus log $C_e$ for Freuindlich isotherm (equation. 5).  The results are shown in Figs 6 and 7. Their parameters

were calculated from slopes and intercepts and summarized in Table 3. From values of $R^2$ we conclude that both Lanqmuir and Frendlich equations describe experimental data here, noting that Frendlich is better for Zn while Lanqmuir is better for Pb. $R_L$ 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 $R_L=0$ [21]. In this study the value of $R_L$ was founded to be 0.006 for Zn and 0.0026 for lead 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.
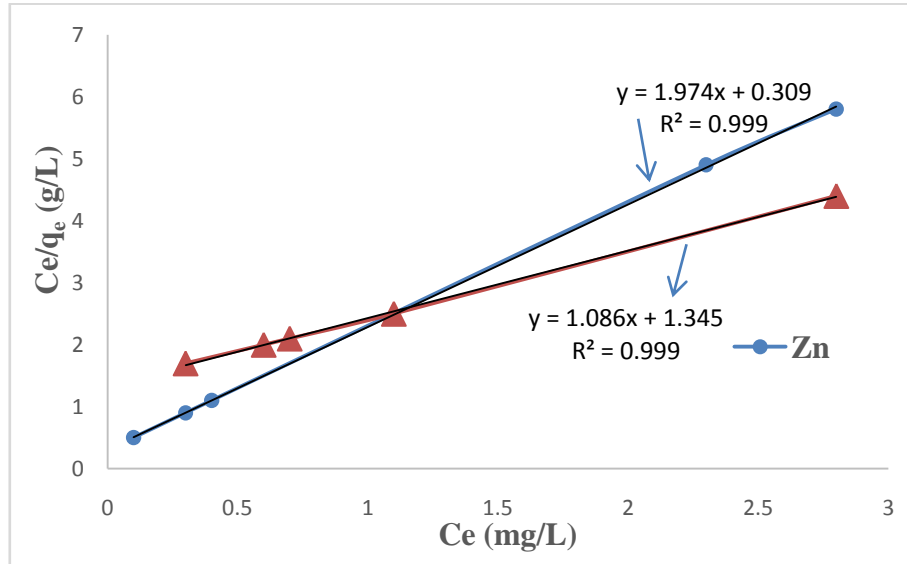


**Figure 6:** Langmuir isotherm of Zn and Pb adsorption on soil at (temp. $25^{\circ}$C, pH = 7.5, and 2g soil/25ml).

**Table. 3** Lanqmuirr and Freundlich isotherm parameters and correlation coefficients for zinc and lead adsorption onto soil (temperature $25^{0}$C, pH 4.7, contact time 30 minutes and 25 ml solution/2g soil).

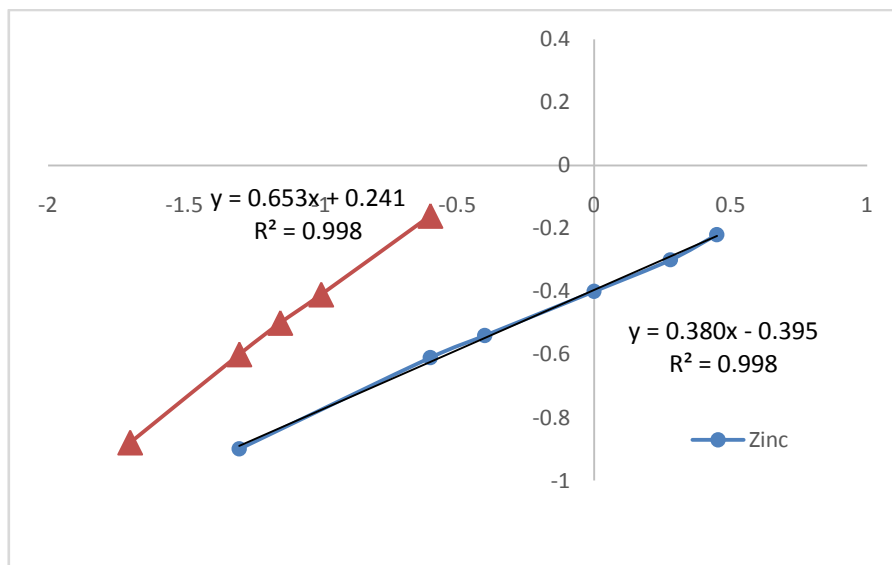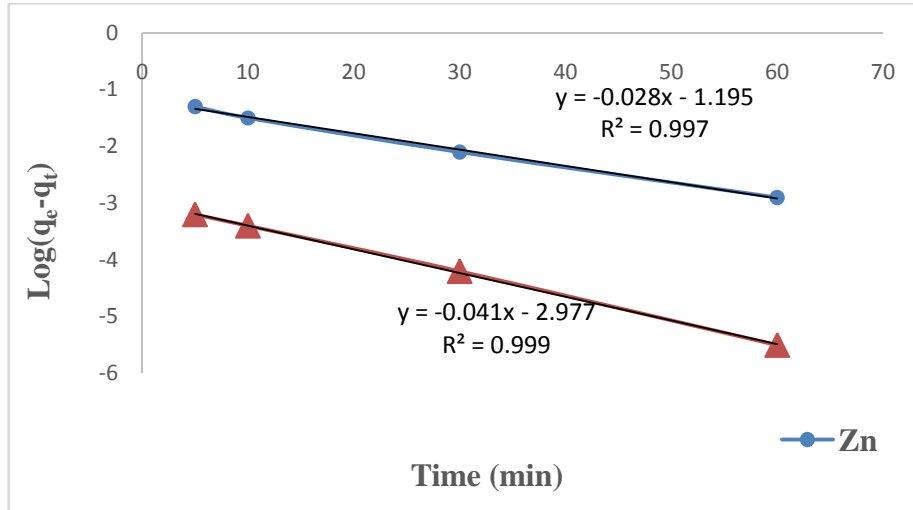| Isotherm | Lanqmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | Parameters | | | parameters | | |
| Adsorbate | $q_m$ | $K_a$ | $R^2$ | $k_F$ | n | $R^2$ |
| Zn | 0.599 | 3.316 | 0.999 | 0.4 | 2.62 | 0.998 |
| Pb | 0.943 | 7.63 | 0.999 | 1.735 | 1.53 | 0.998 |



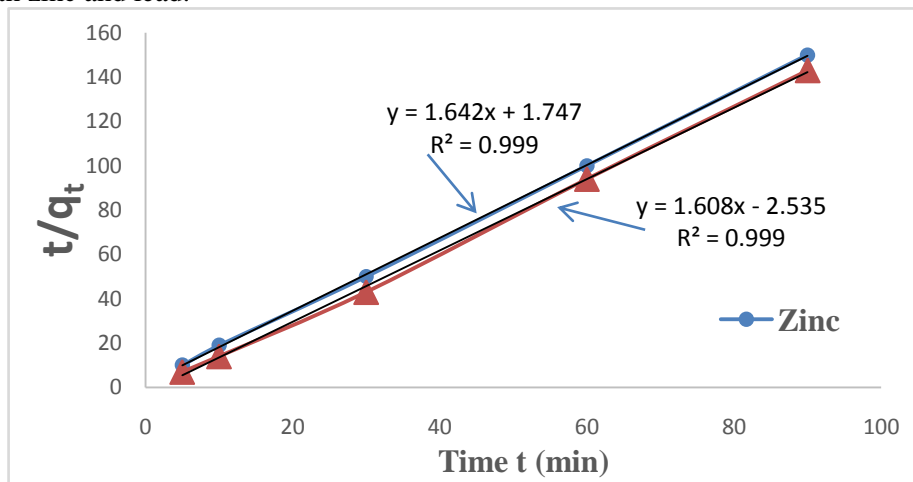**Figure 7:** Freundlich plot for Zn adsorption (at temperature $25^{\circ}$C, pH 7.5, and 2g soil/25ml).

**Figure 8:** Pseudo-first order model for adsorption of Zn and Pb onto soil at (initial concentration 50ppm, $25^0$C, pH 7.5.

**Table. 4** Pseudo-first order and Pseudo-second order kinetic models parameters for adsorption of Zn and Pb on soil at (pH 4.7, temperature $25^0$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 | | |
|---|---|---|---|---|---|---|---|
| | | K1(min)$^{-1}$ | $q_e$(cal) (mg/g) | $R^2$ | $K_2$ (g/mg.min) | $q_e$(cal) (mg/g) | $R^2$ |
| Zn | 0.6059 | 0.0645 | 0.0535 | 0.997 | 3.38 | 0.6093 | 1 |
| Pb | 0.6237 | 0.098 | 0.0013 | 0.999 | 209.64 | 0.623 | 1 |

Values of correlation coefficients show that Langmuir model is more suitable than Freundlich to describe adsorption of both zinc and lead.



**Figure 9:** Pseudo- second order model for adsorption of Zn and Pb onto soil at (initial concentration 50ppm, temperature $25^0$C, pH 7.5.

*3.9 Adsorption kinetics*
Linear plots of log $(q_e-q_t)$ versus t (equation 6) and $t/q_t$ versus t (equation 7) 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 8) 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(min) and $t/q_t$ versus t (min) which are obvious in Figs. 8 and 9. Values of $K_1$, $q_e$, $K_2$ and $R^2$ are summarized in Table 4. It is observed that correlation coefficients of pseudo – second order is greater than correlation coefficients for pseudo – first order. Values of $q_e$(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 [22].
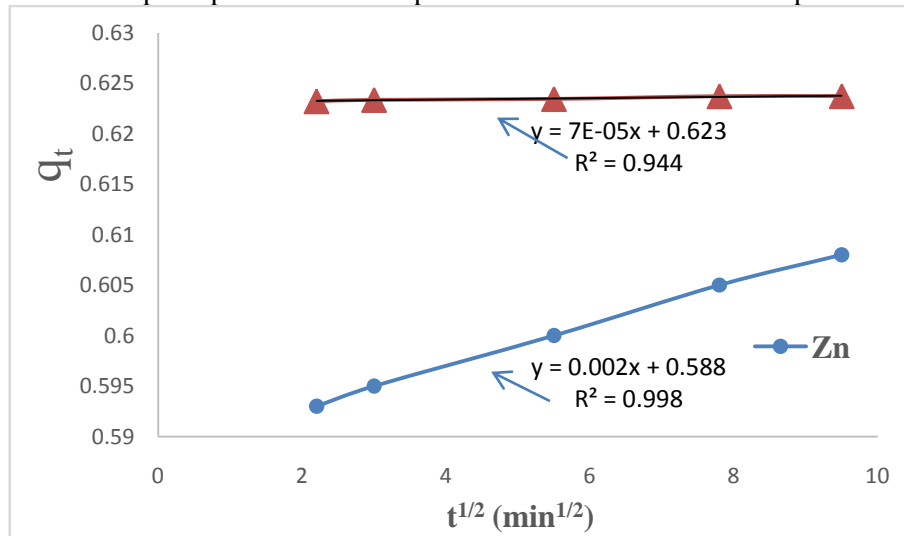


**Figure 10:** Intra-particle diffusion plot for adsorption of Zn onto soil at (25 $^o$C, pH 7.5, 50ppm solution, 25 ml /2g soil).

Values of intra-particle diffusion constants and the correlation coefficients obtained from linear plots of qt versus $t^{1/2}$ are obvious in Fig.10 and Table 5.  According to these values $R^2$ for lead is less than $R^2$ for zinc, the linear plots didn't pass through the origin, and this deviation from the 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 [23].

**Table. 5** Intra-particle diffusion parameters for adsorption of Zn and Pb onto soil

| Adsorbate | $K_p$ (mg/g min$^{1/2}$) | $R^2$ | A |
|-----------|--------------------------|-------|---|
| Zn | 0.007 | 0.998 | 0.58 |
| Pb | 0.005 | 0.944 | 0.62 |

*3.10 Adsorption thermodynamics*
Values of $\Delta H^0$ and $\Delta S^0$ are calculated from the slopes and intercepts of linear plots of $lnK_d$ versus reciprocal of absolute temperature (equation 9), the results are shown in Figs 11 and 12 and thermodynamic parameters are given in Table 6.
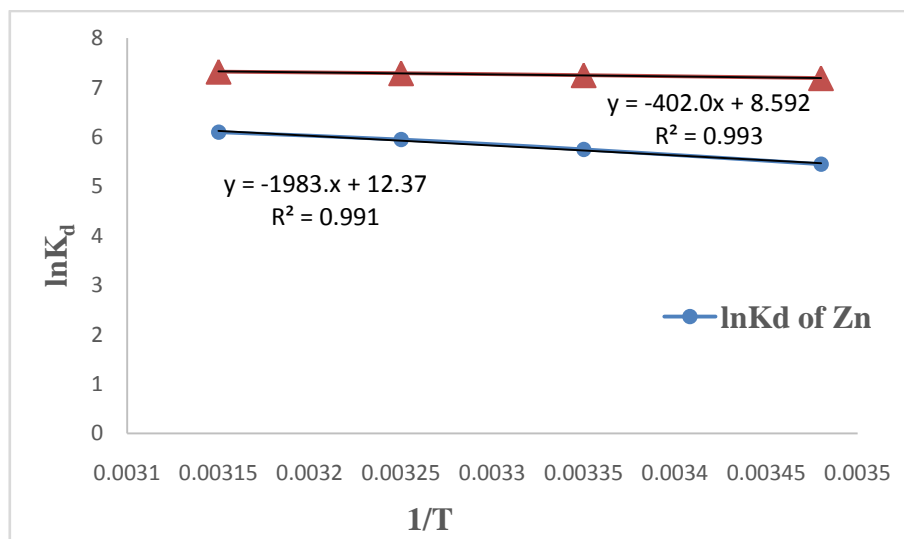


**Figure 11:** Plot of ln Kd versus reciprocal of absolute temperature of 50mg/L of Zn and Pb solution for adsorption on soil.

**Table. 6** Thermodynamic parameters of adsorption of zinc & lead onto soil.

| Adsorbate | $\Delta H^0$ (KJ/mol) | $\Delta S^0$ (J/molK) | $\Delta G^0$ (KJ/mol | | | |
|---|---|---|---|---|---|---|
| | | | 288k | 298k | 308k | 318k |
| Zn | 26.1775 | 133.914 | -12.1903 | -13.8992 | -15.3866 | -16.1147 |
| Pb | 2. 88387 | 69.954 | -17.225 | -17.9924 | -18.7378 | -19.2993 |

Negative values of $\Delta G^0$ at different temperatures indicate that adsorption process of zinc and lead on soil is spontaneous and preferable, while positive $\Delta H^0$ indicates that adsorption is endothermic and positive $\Delta S^0$ means increasing randomness at solid/liquid interface. Also the decrease in $\Delta G^0$ with increasing temperature indicates spontaneity at higher temperatures while positive indicates good affinity of zinc and lead toward soil to be adsorbed [24, 12].
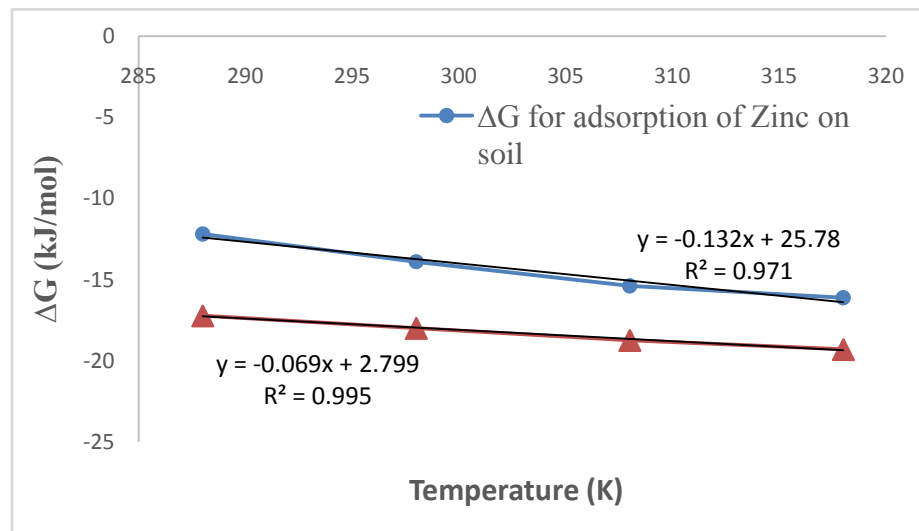


**Figure 12:** Plot of Gibbs free energy $\Delta G$ versus absolute temperature (K) of adsorption of Zn and Pb onto soil (pH: 4.7 contact time 30 min, initial concentration 50 mg/L).

**Conclusion**

Based on this study the following conclusions are obtained:

* Experimental data showed that concentration of several heavy metals Zn and Pb in used lubricating oil are higher than concentration of these metals in new oil.
* 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 but well fitting Freundlich.

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