

**Batch and Column Extraction of Lead from Al-Doura Oil Refinery
Soil**

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Abstract:

The aim of this research is to investigate the extraction of lead (Pb) from soil of Al-Doura oil refinery in Baghdad/Iraq. Ethylenediaminetetraacetic acid disodium salt (Na₂EDTA) and Hydrochloric acid (HCl) solution were used as extractants. Soil washing method was practiced in two ways, batch extraction and column extraction experiments. A set of batch experiments were carried out at different conditions of extractant (Na₂EDTA, HCl) concentration, contact time, pH and agitation speed. From the batch experiments, the maximum removal percentages of Pb that have been obtained were 70 % using Na₂EDTA (0.1M) at pH 4 , agitation speed 200 and at equilibrium time 4 hours and 65 % using HCl (1M) at pH 1.08 , agitation speed 200 at equilibrium time 5 hours.

Column experiments were conducted at different conditions of extractant (Na₂EDTA, HCl) concentration, contact time and flow rate. The maximum removal percentages of Pb were 78% using Na₂EDTA (0.1M) at pH 4 , flow rate 30 ml/hr and equilibrium time 8 hours and 75% using HCl (1M) at pH 1.08, flow rate 20 ml/hr and equilibrium time 10 hours.

The column extraction proved that the extractant volume required to achieve high removal efficiency is less than that of the batch extraction, but requires a longer contact time.

The experimental data of batch and column extraction were applied in four kinetic models; first order, parabolic diffusion, two constant and Elovich model to find best fit model for extraction system. For batch extraction, the parabolic diffusion and two-constant models gave the best correlation {coefficient of determination (R^2)} with experimental data using HCl

and Na₂EDTA respectively. While for column extraction, Elovich model gave good correlation with experimental data.

Keywords: contaminated soil, lead, extraction, soil washing, kinetics models.

1. Introduction

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. They are often problematic environmental pollutants, with well-known toxic effects on living systems [1]. They are introduced into the environment during mining, refining of ores, combustion of fossil fuels and industrial processes. They cannot be degraded or destroyed [2].

Among the physical and biological processes in the subsurface soils, geochemistry plays a major role in the distribution, speciation, as well as the remediation potential of heavy metals. Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) [3].

Heavy metals represent major risks regarding contamination of natural waters after release by metal-bearing soil constituents and migration via the soil solution downward to the water table [4]. The impact of contamination on the environment should be of scientific concern, in order to minimize the threat of soil and groundwater contamination [5].

The adequate protection and restoration of soil ecosystems contaminated with heavy metals require their characterization and remediation [6]. Technologies available for remediating metal contaminated soil can be divided mainly into two namely, immobilization methods and separation/concentration methods. In the first type of remediation, contaminants are immobilized thereby preventing the leaching of contaminants into the groundwater, the second type of remediation deals with separating the contaminants from the soils or reducing the volume of contaminated soil [7].

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Soil washing is represented one of the most suitable in-situ (on-site)/ex-situ physical/chemical treatment technologies. Soil washing has been successfully used for the treatment of soils contaminated with heavy metals, hydrocarbons and semi-volatile organic compounds (SVOCs) [8]. Soil washing usually employs different extractants such as acids, bases, chelating agents, electrolytes, oxidizing agents and surfactants [9-13].

The technique of soil washing is to separate the metal from soil by using chelating agents by organic acid, ethylenediaminetetraacetic acid disodium salt Na_2EDTA , a representative chelating agent, can extract heavy metals from contaminated soils with high efficiency. Strong inorganic acid can be used for useful washing solutions in terms of reasonable cost and simple handling of the effluent solution. It is an effective solvent due to high its removal efficiency on heavy metal extraction, especially hydrochloric acid (HCl) [14].

Soil washing is a variable treatment alternative for metal contaminated sites chemical extraction to enhance the efficiency of heavy metals extraction. Process parameters in soil washing include the mode of extraction (batch or column), extractant type and concentration, pH, liquid-to-solid ratio (L/S), retention time. The soil related parameters are pH, particle size distribution and mineral type of metal to be extracted and their concentration, distribution and physicochemical forms in the soils [15-17].

In the present study, soil washing method was used to extract lead from Al-Doura oil refinery soil. The samples of soil were taken, exactly, from department of receiving and pumping of TEL (Tetraethyl lead, $(\text{C}_2\text{H}_5)_4\text{Pb}$) in the refinery. TEL is an organic lead compound used as an anti-knock additive for petrol. It is highly toxic, causing nervous system and brain damage. It, when burned, forms inorganic lead oxides and carbonates of lower toxicity. However, the toxicity of these compounds requires a strict design for blending plant that holding these compounds to prevent the leakage of TEL.

2. Materials

2.1. Soil Characterization

Al-Doura oil refinery soil was used in the experiments conducted in the present study. After collecting samples from surface (0-20) cm, these were air dried at room temperature, sieved by using 2mm sieve to remove stones and large particles, and then mixed with hand to ensure uniformity. Table (1) summaries the composition and properties of soil. The required tests for specifying the characteristics of soil are carried out at State Company of Geological Survey and Mining/ Ministry of Industry and Minerals.

2.2 Chemical Analysis

Contaminant in different soil sections were extracted by performing acid digestion in accordance with the Haswell (1991) [18]. Total concentration of lead was determined using this extraction procedure. For this procedure, the soil sample was crushed and approximately of 1 g of a representative sample was weighed accurately in a beaker (capacity of 250 ml) and then mixed with (15) ml of concentrated hydrochloric acid (HCl) and (5) ml of concentrated nitric acid (HNO₃), the mixture was then heated in the heating sandy bath until the brown evaporation was disappeared and the sample arrived to dry state, this step takes about (45-60) minutes. Then cooling the beaker to laboratory temperature and then add 5 ml of concentrated hydrochloric acid (HCl) and then heated in the heating sandy bath, this step takes about (5-10) minutes. Then cooling the beaker and add 5 ml of concentrated hydrochloric acid and 50 ml of heated distilled water to wash the sides of beaker from remains dissolved sample. After that heating the mixture to the boiling points to (2-3) minutes. Then filtrate the sample with filtration paper No. 42, and then keep it in volumetric flask capacity of 100 ml, then, washing the precipitate with distilled water and add the previous washed water to filtration and complete the size to 100 ml. Finally, the metal concentration was determined by atomic absorption spectrophotometer (AAS).

Table (1): Composition and properties of Al-Doura oil refinery soil used in the present study.

Property	
Particle size distribution (ASTM D 422)	
Sand (%)	12
Silt (%)	61
Clay (%)	27
Cation Exchange Capacity (meq/100g)	17
Initial pH	7.8
concentration of lead (mg/kg)	6800
Organic matter (%)	0.24
Electrical conductivity EC ($\mu\text{S}/\text{cm}$)	3066
Surface area (m^2/g)	36.008
Bulk density (g/cm^3)	1.37
Porosity (n)	0.476
Specific weight	2.74
Soil classification	Silty loam

2.3. Extractants

Two types of the extractants (Na₂EDTA and HCl) were used for removing lead from contaminated soil.

3. Experimental Methodology

3.1. Batch Extraction Experiments

Batch equilibrium tests are carried out to specify the best conditions of contact time, pH, concentration of extractant and shaking velocity. This means that these tests are suited to identify the activity of the chemical extraction using Na₂EDTA and HCl . Series of 250 ml flasks are employed; each flask contained 2 g of soil and 20 ml of (Na₂EDTA or HCl) extractant with a solid to liquid ratio (S/L) 1/10. The Na₂EDTA concentrations were (0.001,0.005,0.01,0.05 and 0.1) M, and HCl concentrations were (0.01,0.05, 0.1,0.5 and 1) M. pH values of the five HCl solutions were (2 ,1.7,1.44,1.16 and 1.08) respectively. The shaking of solutions were achieved by an orbital shaker at a speed of 200 and 250 rpm at temperature (25±1 °C) at different contact times (1, 2, 3, 4, 5 and 6 hours).

Then, the solution is filtered using a whatman No.42 filter paper. The supernatant was analyzed for heavy metal using atomic absorption spectrometry (AAS). All tests were performed in triplicate and the results were presented as average of the duplicates extracts.

The removal of lead was calculated using the following equation [19, 11, 13]:

$$\text{Lead removal} = \frac{\text{contaminant mass in superntant } (C_L V_L)}{\text{initial contaminant mass in soil } (C_S M_S)} \times 100\% \quad (1)$$

Where C_L and C_s are the concentration of lead in supernatant (in mg/L) and soil (in mg/kg), respectively. V_L is the volume of supernatant (in L), and M_s is the dry mass of the soil (in kg).

3.2. Column Extraction Experiments

Figure (1) shows the schematic diagram of the chemical extraction used in the present study. This setup is constructed of the experimental apparatus consisted of plexiglas column with an internal diameter of 5 cm and a height of 15 cm. Sample include (100 gm) of the contaminated soil was placed in column above a layer of glass wool in order to obtain a uniform distribution of the soil , a plastic mesh ($D = 0.2$ mm) was placed at the bottom of the column to retain the soil. The column washing solutions were passed through the corresponding soil column by using a peristaltic pump. The supernatant volume was analyzed for heavy metal using atomic absorption spectrometry (AAS) after filtering using a whatman No.42 filter paper. The concentration of washing solutions of Na_2EDTA were (0.001, 0.005, 0.01, 0.05 and 0.1) M, and for HCl were (0.01, 0.05, 0.1, 0.5 and 1) M.

However, three values of washing solution flow rate (20, 30 and 50 ml/hr) and contact time 12 hours were investigated in order to evaluate the conditions that ensured the highest heavy metal extraction yield. The column washing were performed in duplicates to ensure reproducibility of the results. The washing solution of Na_2EDTA or HCl was prepared and poured into a plexiglas beaker.

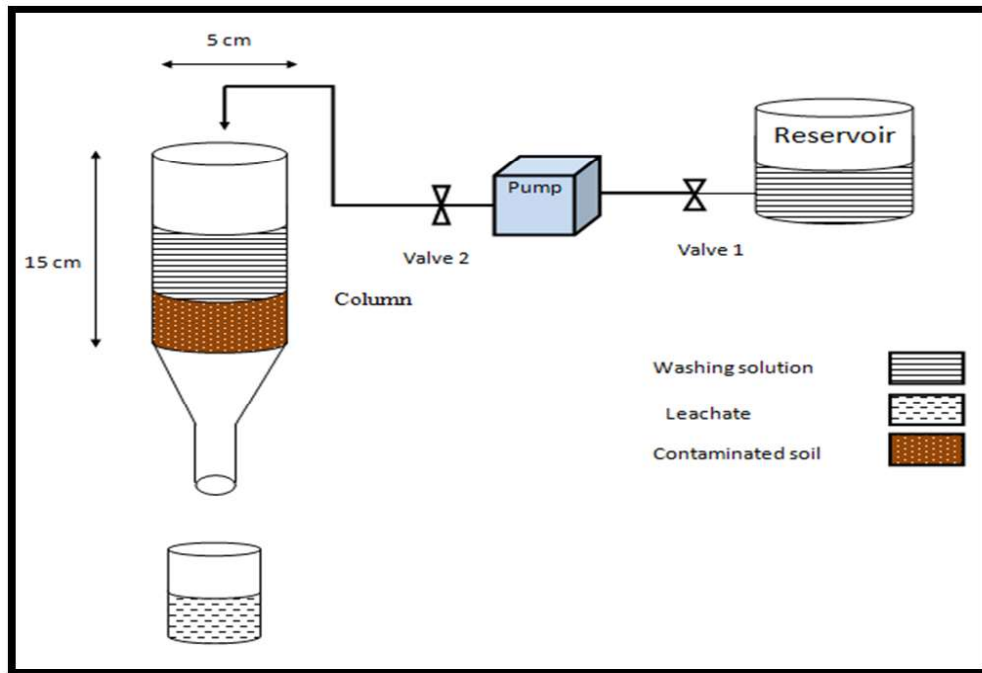


Fig.(1)Schematic representation of the column test.

The flow rate (Q) of extractant (Na_2EDTA , HCl) solution was calculated using the following equation:

$$Q = A \times V \quad (2)$$

Where:

A = Cross section area of the column (cm^2).

V = Darcy velocity (cm/hr).

Which is calculated from the following equation:

$$V = v / n \quad (3)$$

Where:

v = Real or seepage velocity (cm/hr).

n = porosity of the soil.

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The calculated seepage velocities of extractant solution, using equations (2) and (3), for the three flow rates are 0.476, 0.714, 1.19 cm/hr. These velocities were adopted in the column extraction experiments.

4. Results and Discussion

4.1. Batch Experiments

A number of batch experiments were carried out for the contaminated soil. The effects of contact time and extractant (Na₂EDTA, HCl) concentration were studied. The concentrations of lead in supernatant were obtained as shown in table (2), the value of lead concentration used in equation (1) to calculate the removal efficiency.

Table (2): Concentration of Pb in supernatant, batch extraction.

Time (hr)	Concentration of Pb in supernatant (C _L) (mg/L)									
	Na ₂ EDTA					HCl				
	0.1 M	0.05M	0.01M	0.005 M	0.001 M	1M	0.5M	0.1M	0.05 M	0.01 M
1	515	485.7	291.4	194.3	126.3	311	291.4	262.3	194.3	204
2	651	582.9	534.3	437.1	320.6	612	398.3	369.1	291.4	174. 9
3	622	582.9	495.4	485.7	446.9	534	485.7	485.7	427.4	291. 4
4	680	650.9	534.3	485.7	388.6	622	582.9	495.4	427.4	349. 7
5	680	650.9	544	514.9	388.6	631	582.9	514.9	437.1	388. 6
6	680	650.9	544	514.9	388.6	631	582.9	514.9	437.1	388. 6

4.1.1 Effect of Extractant Concentration

Effect of extractant concentration on the removal efficiency of lead, at pH 4 and agitation speed 200 rpm, is shown in figures (2) and (3). These figures illustrate that the removal percentage increase with increasing extractant (Na_2EDTA , HCl) concentration, this was expected due to the fact that the higher concentration of extractant in soil, the greater availability of extraction. The maximum removal percentage of lead in batch extraction at 0.1M Na_2EDTA and 1M HCl were 70% and 65 % respectively.

4.1.2. Effect of Contact Time

Figure (4) shows the effect of contact time on extraction of lead from soil. Removal efficiency of lead increase as the contact time increase and it remains constant after reaching the equilibrium. Because of a large amount of extractant became exhausted, the extraction rate is controlled by the rate at which the extract is transported from the soil exterior to the interior sites of the extractant, because buffering capacity for soil reaching equilibrium. The equilibrium time of lead extraction in batch mode was 4 hr and 5 hr using Na_2EDTA and HCl extractants respectively.

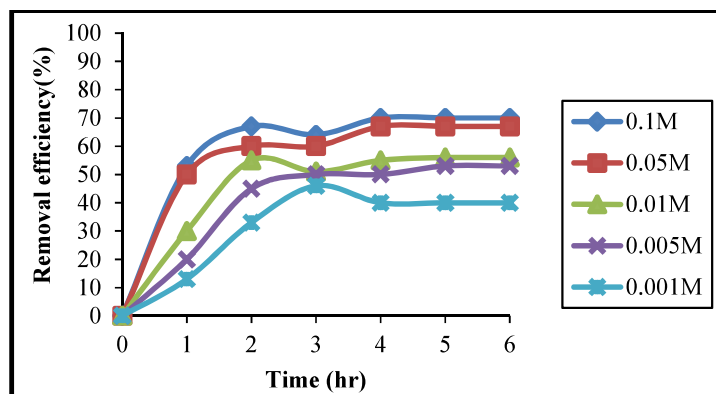


Fig.(2)Effect of Na_2EDTA concentration on removal efficiency of lead as a function of contact time in batch extraction (pH = 4; agitation speed =200 rpm).

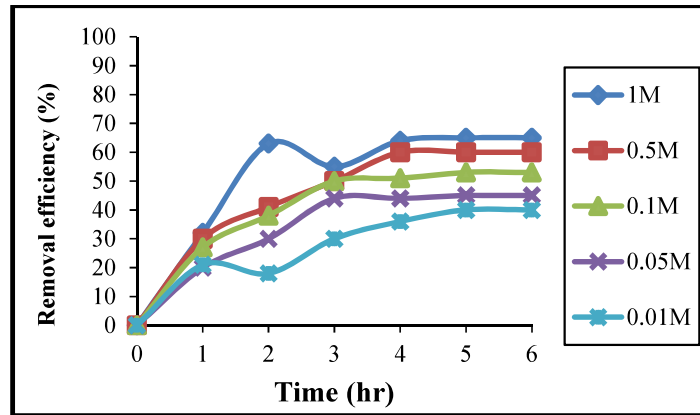


Fig.(3) Effect of HCl concentration on removal efficiency of lead as a function of contact time in batch extraction (agitation speed =200 rpm, pH=1.08).

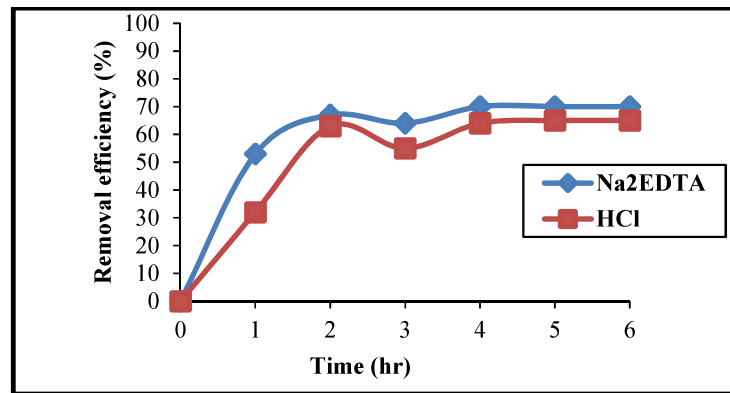


Fig.(4) Removal efficiency of lead as a function of contact time in batch extraction using Na₂EDTA (pH=4,concentration=0.1M) and HCl (pH=1.08 ,concentration=1M) ,speed=200 rpm.

4.2. Column Experiments

A number of the column experiments for contaminated soil were conducted . The effect of different contact times, extractant concentrations, and extractant solution flow rates were studied. Tables (3) and (4) shows the concentrations of lead in supernatant in column extraction system.

Table (3): Effect of flow rate on concentrations of Pb in supernatant; column extraction; using Na₂EDTA.

Time (hr)	Concentration of Pb in supernatant (C _L) (mg/L)														
	Q=20ml/hr					Q=30ml/hr					Q=50 ml/hr				
	0.1	0.05	0.01	0.005	0.001	0.1	0.05	0.01	0.005	0.001	0.1	0.05	0.01	0.005	0.001
	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
2	3060	3043	2781	2513	2016	3400	2890	2210	2040	1700	3060	2863	2717	2601	2363
4	5100	4923	4872	4414	4033	6290	5270	5100	4250	3060	5780	5677	5514	5334	5218
6	7480	6429	6943	7415	6704	7820	7480	7140	6290	5100	6800	6833	6841	5956	5643
8	12580	9973	8976	8676	8139	13260	10880	9350	7310	6800	11220	9810	9722	9446	8261
10	4080	2097	1929	1624	1710	5100	3060	2720	2210	1700	5100	4713	3985	2861	1918
12	3400	1144	1834	1517	1281	4080	2040	1700	1360	1360	3060	3021	2804	2644	1910

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Table (4): Effect of flow rate on concentrations of Pb in supernatant; column extraction; using HCl.

Time (hr)	Concentration of Pb in supernatant (C_L) (mg/L)														
	Q=20 ml/hr					Q=30 ml/hr					Q=50 ml/hr				
	1	0.5	0.1	0.05	0.01	1	0.5	0.1	0.05	0.01	1	0.5	0.1	0.05	0.01
	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
2	3400	3400	3060	2720	2210	3060	3233	2416	1141	1040	2380	2183	2014	1667	1601
4	4590	3570	2890	2550	1870	3400	3721	3326	2973	2755	3400	3623	3523	2824	2343
6	6800	5780	5100	4590	3910	5780	4392	4004	3825	3793	5100	4458	4114	4229	4240
8	8500	7480	6970	6970	5440	7480	6940	5243	4793	4053	6970	7211	6923	5353	5061
10	12750	11900	10540	9520	3570	12240	10113	9483	8944	6778	10540	9623	9643	8910	8493
12	3570	3570	2720	2380	1190	3400	2421	1232	1234	1022	2720	1714	1400	1304	1302

4.2.1. Effect of Extractant Concentration

Effect of extractant concentration on the removal efficiency is shown in figures (5, 6). These figures show that the removal percentage of lead increase with increasing extractant (Na_2EDTA , HCl) concentration, this was expected due to the fact that the higher concentration of extractant in soil, the greater availability of extraction. The maximum removal percentage of lead in column was 78% and 75% at 0.1 M Na_2EDTA and 1M HCl respectively. The values of removal percentage at different conditions are tabulated in tables (5) and (6).

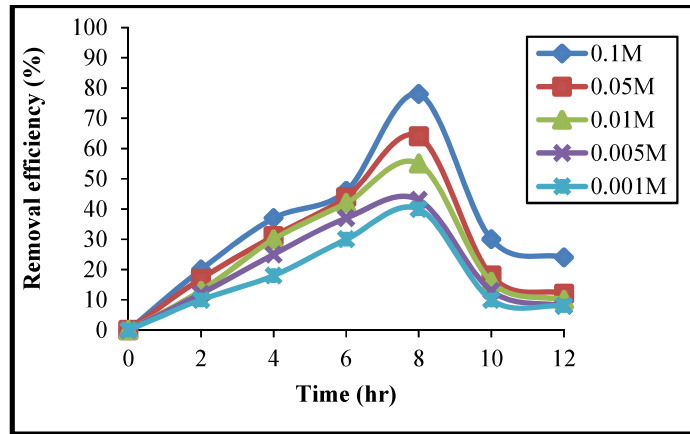


Fig.(5): Effect of Na₂EDTA concentration on removal efficiency of lead as a function of contact time in column extraction (pH = 4; flow rate = 30 ml/hr).

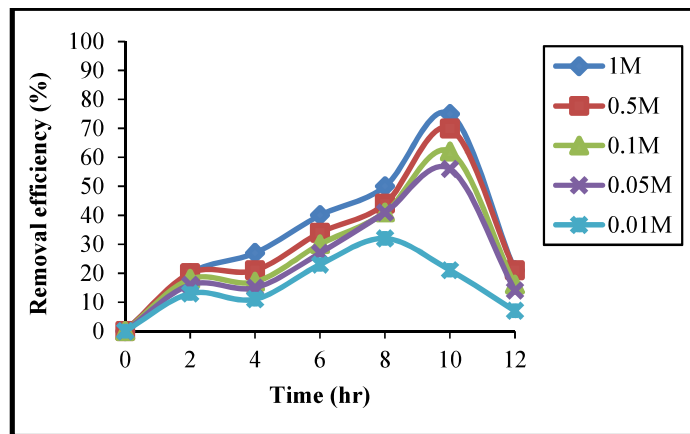


Fig.(6): Effect of HCl concentration on removal efficiency for lead as a function of contact time in column extraction (flow rate = 20 ml/hr, pH=1.08).

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Table (5): The values of removal percentage at different conditions, using Na₂EDTA; column extraction.

Time (hr)	Removal Efficiency (%)														
	Q = 20 ml/hr					Q = 30 ml/hr					Q = 50 ml/hr				
	0.1 M	0.0 5 M	0.0 1 M	0.0 05 M	0.00 1 M	0.1 M	0.0 5 M	0.0 1 M	0.00 5 M	0.00 1 M	0.1 M	0.0 5 M	0.0 1 M	0.00 5 M	0.00 1 M
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	18	18	16	15	12	20	17	13	12	10	18	17	16	15	14
4	30	29	29	26	24	37	31	30	25	18	34	33	32	31	31
6	44	38	41	44	39	46	44	42	37	30	40	40	40	35	33
8	74	59	53	51	48	78	64	55	43	40	66	58	57	56	49
10	24	12	11	10	18	30	18	16	13	10	30	28	23	17	11
12	20	7	11	9	10	24	12	10	8	8	18	18	16	16	11

Table (6): The values of removal percentage at different conditions, using HCl; column extraction.

Time (hr)	Removal Efficiency (%)														
	Q = 20 ml/hr					Q = 30 ml/hr					Q = 50 ml/hr				
	1	0.5	0.1	0.05	0.01	1	0.5	0.1	0.05	0.01	1	0.5	0.1	0.05	0.01
	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	20	20	18	16	13	18	19	14	7	6	14	13	12	10	9
4	27	21	17	15	11	20	22	20	17	16	20	21	21	17	14
6	40	34	30	27	23	34	26	24	23	22	30	26	24	25	25
8	50	44	41	41	32	44	41	31	28	24	41	42	41	31	30
10	75	70	62	56	21	72	59	56	53	40	62	57	57	52	50
12	21	21	16	14	7	20	14	7	7	6	16	10	8	8	8

4.2.2. Effect of Contact Time

Figure (7) shows the effect of contact time on extraction of lead from soil. Removal efficiency increase with contact time increase until reach a maximum metal extraction then the removal efficiency decrease, because of the subsequent decrease of the metal available in soil drop in extraction efficiency, the extractant rapidly exhausted the available heavy metals and the prolonged percolation became useless [20]. Also an increase in the time after the arrival of the high removal efficiency means access to the state of saturation between the contaminated soil and extractant which prevents the extraction process. The equilibrium time of lead extraction in column using Na₂EDTA and HCl was 8 hr and 10 hr respectively.

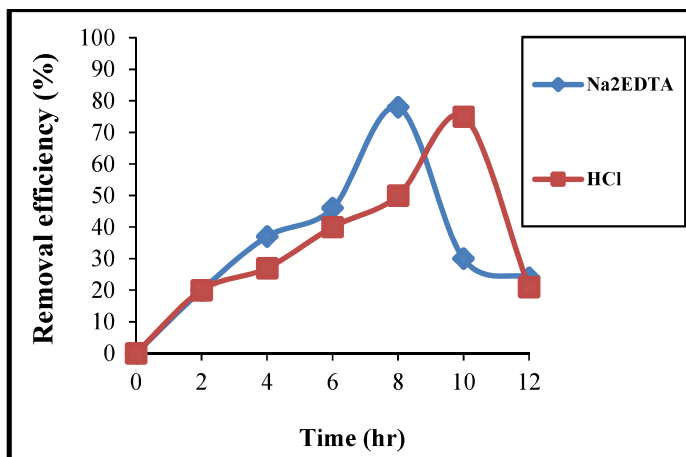


Fig.(7)Removal efficiency of lead as a function of contact time using Na₂EDTA (pH =4 ,concentration =0.1M, flow rate =30 ml/hr) and HCl (pH =1.08 , concentration =1M, flow rate =20ml/hr),in column extraction.

4.2.3. Effect of Flow Rate

Effect of different flow rates on the removal efficiency of lead is shown in figure (8). This figure illustrates that the removal percentage increase with decreasing flow rate. The lower flow rate allows a large surface area of contaminated soil contact with the solvent; this could indicate that very low percolation rate favours the dissolution of metal with extractant.

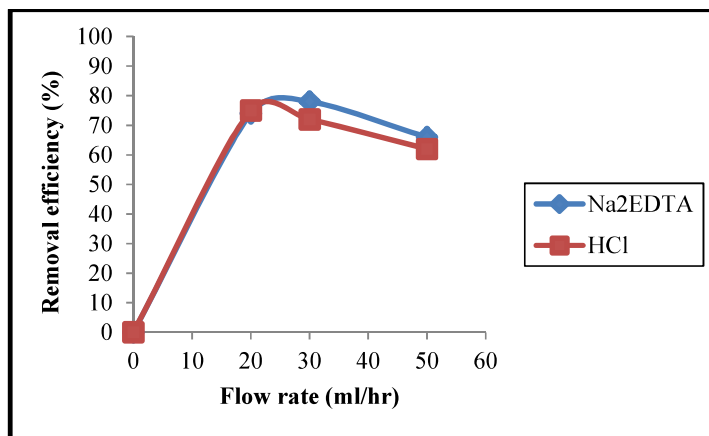


Fig. (8) Effect of different flow rates on removal efficiency of lead using Na₂EDTA (pH= 4, concentration =0.1M) and HCl (pH= 1.08, concentration =1M).

4.3. Kinetic Models

In order to examine the heavy metals extraction mechanism, kinetic data were fitted with four mathematical models: first order, parabolic diffusion, two constant and Elovich model. Min et al. (2008) [21] presented the linear forms of these mathematical models as shown in table (7), which were applied for experimental data in the present study.

Table (7): The mathematical models applying to fit experimental data.

Model	Linear form	Reference
First –order	$\ln(S_0 - S) = A - Bt$	[22]
Parabolic diffusion	$S = A + Bt^{1/2}$	[23]
Two-constant	$\ln S = A + B \ln t$	[24]
Elovich	$S = A + B \ln t$	[25]

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Where:

t: contact time (hour).

S₀: initial pollutant content in soil (concentration of contaminant in soil) (mg/kg).

S: pollutant removal content at time (concentration of removal from soil with time) (mg/kg).

A: the intercept.

B: the slope.

$$S = \frac{C_L \times V_L}{M_S} \quad (4)$$

Where

C_L: Concentration of contaminant in supernatant (mg/L)

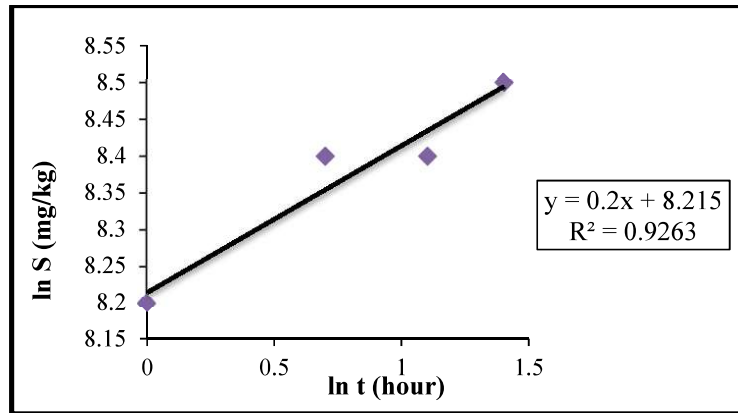
V_L: Volume of supernatant (L)

M_S: Dry mass of soil (kg)

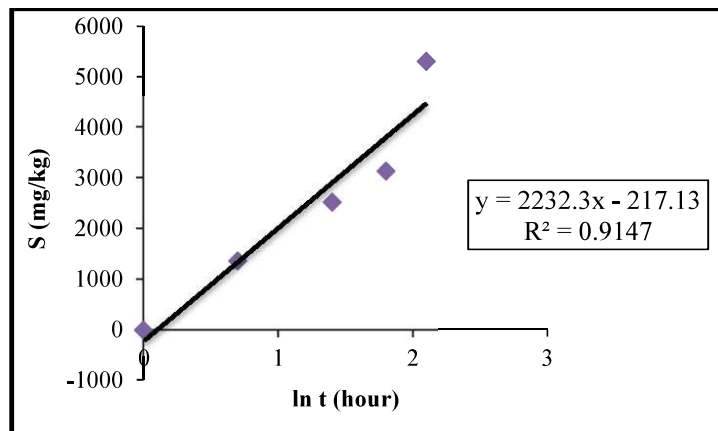
The experimental data of batch and column extraction were applied in the four kinetic models; where the relation of $\ln(S_0-S)$ and time for first –order model, the relation between S and $t^{1/2}$ for parabolic diffusion model, the relation between S and $\ln t$ for two-constant model, and the relation between S and $\ln t$ for elovich model. The kinetic constants of each model were obtained using Microsoft excel software.

The best fitting of experimental data with kinetic model obtained for batch and column experiments are shown in figures (9) and (10). These figures illustrate that parabolic diffusion, two-constant and elovich kinetic models gave the best fit with experimental data. This fitting can be intercept by the higher coefficients of determination (R^2) as shown in table (8).

From the application of various kinetic experiments, Elovich model get good correlation (coefficient of determination(R^2)) in column mode; and in batch extraction, the parabolic diffusion and two-constant models obtained the best correlation (coefficient of determination(R^2)).

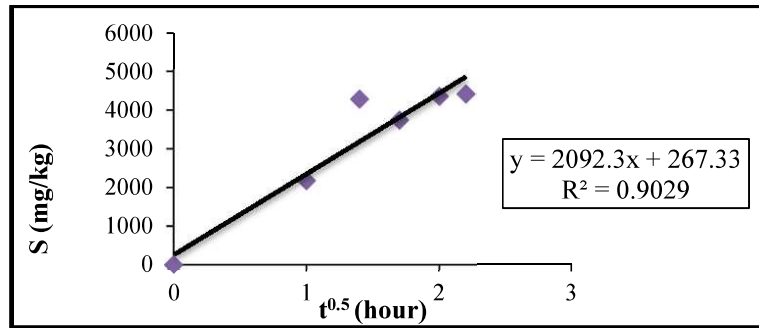


(a) Two-constant model in batch extraction.

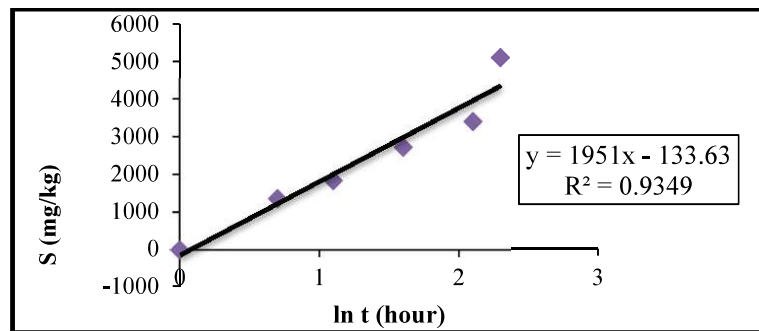


(b) Elovich model in column extraction.

Fig.(9)The best kinetic models for soil washing of Pb using Na₂EDTA.



(a) Parabolic diffusion model in batch extraction.



(b) Elovich model in column extraction.

Fig. (10) The best kinetic models for soil washing of Pb using HCl.

Table (8): The coefficient of determination (R^2) of kinetic models for batch and column extraction.

Models	Coefficient of determination (R^2)			
	Batch		Column	
	Na ₂ EDTA	HCl	Na ₂ EDTA	HCl
First –order	0.7	0.529	0.851	0.863
Parabolic diffusion	0.8999	0.9029	0.8646	0.8905
Two-constant	0.9263	0.6991	0.7525	0.7165
Elovich	0.8069	0.7411	0.9147	0.9349

5. Conclusions

5.1. Batch Extraction

1- The batch result indicated that several factors such as extraction or equilibrium time, pH of solution, extractant concentration and agitation speed effect on the extraction process .The best values of these factors will achieve the maximum removal efficiency of heavy metals.

2- Contact time was four hours and extractant concentration 0.1 M were the best condition for removing lead using Na₂EDTA. While five hours contact time and 1M extractant concentration when using HCl as extractant.

3- The removal efficiency of extraction increases with:

- a- Increasing time until reach equilibrium time.
- b- Decreasing pH solution.
- c- Increase extractant concentration.
- d- Decrease agitation speed.

4- The parabolic diffusion and two-constant models gave the best correlation {coefficient of determination (R^2)} with experimental data using HCl and Na₂EDTA respectively.

5.2. Column Extraction

1-The column results indicated that several factors such as extraction or equilibrium time, solvent of extraction dosage and flow rate effect on the extraction process. However, the best values of these factors will achieve the maximum removal efficiency of heavy metals.

2- Contact time eight hours, extractant concentration (0.1M) and flow rate (30 ml/hr) were the best conditions for removing lead using Na₂EDTA. While ten hours contact time, (1M) extractant concentration and flow rate (20 ml/hr) were the best conditions when using HCl as extractant.

3- The removal efficiency of extraction increases with:

- a- Increasing time until reach maximum metal extraction then the removal efficiency decrease.
- b- Increase extractant concentration
- c- Decrease flow rate.

4- Elovich model gave good correlation with experimental data {coefficient of determination (R^2)}.

References

1. Evanko, C.R., and, Dzombak, A.D., 1997. "Remediation of metals-contaminated soils and groundwater". Technology Evaluation Report, TE-97-01.
2. Davydova, S., 2005."Heavy metals as toxicants in big cities". Microchemical Journal, 79, 133–136.
3. GWRTAC, 1997. "Remediation of metals –contaminated soils and ground water". Technology Evaluation Report ,TE-97-01.
4. Van Ort, F., Jongmans, A.G., Citeau, L., Lamy, I., Chevallier, P., 2006. "Microscale Zn and Pb distribution patterns in subsurface soil horizons: an indication for metal transport dynamics ". European Journal of Soil Science, 57,154-166.
5. Matos, A.T., Fontes, M.P.F., Costa, L.M., Martinez, M.A., 2001. "Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils". Environ. Pollution, 111, 429-435.
6. Wuana, R.A., Okieimen, F.E., and, Imborvungu, J.A., 2010. "Removal of heavy metals from a contaminated soil using organic chelating acids ".International Journal of Environmental Science and Technology.7 (3),485-496.
7. Khodados, A., Reddy ,R., and, Maturi, K., 2005."Effect of different extraction agent on metal and organic contaminated removal from field soil ".J. of Hazardous Material, 117, 15-24.
8. Peters,R.W.,1999."Chelant extraction of heavy metals from contaminated soils". Journal of Hazardous materials, 66,151-210 .
9. Hong, J.J., Yang, S.M., Choi, Y.K., Lee, C.H., 1995. "Precipitation of tricarboxylic acid biosurfactant derived from spiculisporic acid with metal ions in aqueous solution". Journal of Colloid and Interface Science .173 (1), 92–103.
10. Schramel, O., Michalke, B., Kettrop, A., 2000."Study of copper distribution in contaminated soils of hop field by single and sequential extraction procedures ". Science of the Total Environmental, 263, 11-22.

No.13 Journal of Petroleum Research & Studies (JPR&S)

11. Reddy, K.R., and ,Chinthamreddy, S., 2000."Comparison of extractants for removing heavy metals from contaminated clayey soils". *Soil and Sediment Contamination*.449-462.
12. Sun, B., Zhao, F.J., Lombi, E., Mc Grath, S.P.,2001."Leaching of heavy metals from contaminated soils using EDTA ".*Environmental Pollution*, 113,111-120.
13. Gzar, H.A., Abdul-Hameed, A.S. and Yahya, A.Y. ,2014. "Extraction of Lead, Cadmium and Nickel from Contaminated Soil Using Acetic Acid". *Open Journal of Soil Science*, 4, 207-214. <http://dx.doi.org/10.4236/ojss.2014.46023>.
14. Isoyama, M., and, Wada, S.I.,2007." Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil ". *J. Hazard. Mater.*, 143 , 636–642.
15. Tandy , S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R., and ,Nok,B.,2004."Extraction of heavy metals from soils using biodegradable chelating agent" . *Environ. Sci. Technol.*, 38,937-944.
16. Lim, T.T., Tay, J.H., Wang, J.Y.,2004 ." Chelating-agent-enhanced heavy metal extraction from a contaminated acidic soil" . *J. Environ. Eng.*, 130 ,59-66.
17. Reed, B.E., Carries, P.C ., and, Moor,R.,1990."Flushing a Pb contaminated soil using HCl, EDTA and CaCl₂ ". *J. of Environmental Engineering* . 48-50.
- 18 Haswell, S. J., 1991. " Atomic absorption spectrometer; theory, design and applications". Elsevier, Amsterdam.
19. Lim, T.T., Chui, P.C., Goh, K.H.,2005. "Process evaluation for optimization of EDTA use and recovery for heavy metal removal from a contaminated soil". *Chemosphere* , 58, 1031-1040.
20. Di Palma, L., Ferrantelli, P., Merli, C., Petrucci,E. , and , Pitzolu, I.,2007." Influence of soil organic matter on copper extraction from contaminated soil". *Soil & Sediment Contamination*, 16,323–335.
21. Min, Z., Bohan, L., Ming, L., Young, Z., Qingru, Z.,Bin, O., 2008. "Arsenic removal from contaminated soil using phosphoric acid and phosphate". *Journal of Environmental Sciences*, 20, 75-79.

No.13 Journal of Petroleum Research & Studies (JPR&S)

22. Kue, S., and, Lotes , E.G .,1973. "Kinetics of phosphate adsorption and desorption by hematite and gibbsite". *Soil Science*, 116, 400-406.
23. Khater, A.H., and, Zaghloul, A.M., 2002." Copper and zinc desorption kinetics from soil: Effect of pH". In ' the 17thWorld Conference on Soil Science, 47, 1-9.
24. Dang, Y.P., Dalal, D.G., Edwards ,D.G., Tiller, K.G .,1994. " Kinetics of zinc desorption from vertisols". *Soil Sci. Soc. Am. J.*, 58, 1392-1399.
25. Polyzopoulos, N.A., Keramidas, V.Z., Pavlatou, A., 1986."On the limitation of the simplified Elovich equation in describing the kinetics of phosphate sorption and release from soils". *Journal of Soil Science*, 37, 81-87.