Chelating-Agent-Enhanced Copper, Lead and Zinc Extraction From Iraqi Contaminated Sandy Soil.

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Abstract

This research aims to investigate extraction of copper, lead, and zinc from Iraqi sandy contaminated soil. Two systems were tested single and ternary component systems. Chelating agent ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) was utilized as extractant. Amount of 500 mg of metal per kg soil was prepared to form artificially contaminated soil. Extraction of metals was achieved using column extraction mode. Experimental tests were conducted at different conditions of Na_2EDTA concentration, flow rate, and contact time. The results illustrated that the maximum removal percentages for single component system were 92% ,76% and 68% at equilibrium time 6, 8, and 8 hours for Pb , Cu and Zn, respectively. While for ternary system were 82%, 72% and 65%, respectively, at equilibrium time 6 hours for Cu and 8 hours for Pb and Zn. In addition to the best equilibrium time, the other optimum conditions for both systems were 0.1 mol/L extractant concentration, pH 4 and flow rate 20 ml/hr. The sequence of heavy metals removal was Pb > Cu >Zn. The experimental data were tested by applying it in four kinetic models; first order, two constant, parabolic diffusion, and Elovich model. Elovich and parabolic diffusion were the most fitted models to the experimental data.

Keywords: *Column extraction; heavy metal; kinetics models; remediation; sandy soil.*

1. Introduction

Pollution of soil by overwhelming metals is an essential ecological issue on the planet [1,2]. Substantial metals collection and its lethality for organic frameworks; human, plants, creatures, and microorganism has been accounted for [3,4]. Overwhelming metals are substance risks, nonbiodegradable and remaining inconclusively in the dirt [5].

In the subsurface soils physical and natural procedures are occurred, geochemistry among these procedures is a noteworthy job in the speciation and dispersion. Gathering of perilous inorganic synthetic substances is shaped from ordinarily discovered substantial metals, for example, zinc (Zn), copper (Cu), lead (Pb), chromium (Cr), cadmium (Compact disc), mercury (Hg), nickel (Ni) and arsenic (As) [6]. Overwhelming metals consider a noteworthy hazard for groundwater when moved from soil by soil arrangement and transported descending to the water table [7]. With the end goal to diminish the risk of soil and groundwater contamination, the ecological effect of tainting ought to be of logical concern [8].

The portrayal and remediation are required for adequate security and rebuilding of soil from the pollution of substantial metals [5]. Advances for the remediation of metal sullied soil can be isolated fundamentally into two sections, the first is immobilization techniques and the second is division/focus strategies. First sort of remediation incorporates immobilization of contaminants to obstruct the contaminants from filtering into the groundwater. The second kind is partition of contaminants from soil or limit the volume of debased soil [9].

In-situ and ex-situ soil washing are fitting physical/concoction treatment innovations. Soil washing is fruitful method for soils remediation by expelling metals, semi-unstable natural mixes, and hydrocarbons [10]. Diverse extractants, for example, acids, bases, oxidizing operators, chelating specialists, electrolytes and surfactants can be utilized in soil washing [11-16]. Na2EDTA is a successful chelating specialist utilized in soil washing procedure due to its high expulsion proficiency on metals extraction from contaminated soil [17].

In-situ soil washing process (soil flushing) the washing arrangement is constrained through the set up soil framework. Metals can be activated by draining contaminants from soils. These poisons can be extricated without exhuming the tainted soils. The extractant arrangement is showered on the polluted region to evacuate the contaminants by solubilization. This arrangement can be connected by surface flooding, drain fields, vertical or level infusion wells, sprinklers, bowl or trench invasion frameworks [18].

In Ex-situ soil washing process there are two modes: (1) Bunch extraction of soil slurry in a reactor: The unearthed soil is at first screened to expel the surface garbage. The debased soil is firmly blended with the extractant arrangement, and after that isolated by filtration or second screening venture, after that the dirt came back to the ground [19]. (2) Pile/segment filtering of soil: the extractant arrangement is gravitationally penetrated through a dirt pile or segment [14,16,20]. The debased soil with substantial metals is exhumed, screened and put in a hill on a cushion. Washing arrangement goes through the dirt utilizing any sort of fluid dispersion framework to expel metals from sullied soil. The emanating is gathered in a pit and afterward prepared to evacuate metals. Ex-situ process parameters incorporate convergence of extractant, extractant type, extractant fluid to strong proportion (L:S), pH , and contact time. The fundamental parameters that identified with soil are molecule measure conveyance, sort of metals, grouping of metals, pH, physicochemical shapes and dispersion in the dirt [21-

23]. Soil washing is straightforward process and can be viewed as a sparing treatment strategy for a lot of soil. Higher filtering effectiveness is gotten for soils with higher porousness [24].

In this examination soil washing system was drilled tentatively utilizing section mode to separate copper, lead and zinc from Iraqi sandy sullied soil. Single and ternary segment frameworks were embraced to think about the extraction of Cu, Pb and Zn from the defiled soil utilizing Na2EDTA as extractant arrangement. The test information were connected in four motor models; first request, two consistent, allegorical dispersion, and Elovich model to decide the best fit model.

2. Materials

2.1. Soil characterization

Iraqi sandy soil was used in the experimental tests of the present study. Soil brought from public quarry in Karbala governorate south of Iraq. The soil was contaminated artificially with contaminant/contaminants termed in single component (soil contaminated with one metal) and in ternary components (soil contaminated with three metals) contaminated soil. Table 1 shows the composition and properties of the used soil.

Table 1: Properties and composition of the studied sandy soil.

Property	Value
Particle size distribution: Sand (%) Silt (%) Clay (%)	93 5 2
pH	7.4
Cation Exchange Capacity (meq/100g)	3.8
Electrical conductivity EC (μS/cm)	1836
Organic carbon (%)	0.26
Bulk density (g/cm^3)	1.62
Porosity (n)	0.36
Specific Gravity (g/cm^3)	2.58

2.2. Preparation of contaminated soil

In every single exploratory test, the dirt was misleadingly tainted. The coveted convergences of Cu, Pb and Zn were set up by weighting the required measures of Cu(NO3)2.3H2O, Pb(NO3)2.6H2O and Zn (NO3)2.6H2O and broke up exclusively in refined water. For single part framework, each subsequent contaminant arrangement was added to 1 Kg of dry soil. 500 mg metal for each kg dry soil was readied. For ternary segment framework, the three arranged arrangements were gathered together and blended with 1 kg dry soil. Blending of arrangement with soil was accomplished by utilizing treated steel spatula to ensure the consistency. The readied sullied soils were put in plastic compartments and refrigerated. Tainted examples were equilibrated and dried by introduction to air at room temperature for somewhere around about fourteen days.

Overwhelming metal in soil test was extricated by directing corrosive assimilation as per the [25]. This extraction method was utilized to decide add up to grouping of toxin. In this system, the dirt example was squashed physically. A delegate test of 1.0 g was weighed precisely by touchy equalization (demonstrate: OHAUS GT 8000) and putted in a measuring utencil of 250 ml. Two concentrated acids HCl and HNO3 with volumes of 15 and 5 ml separately were included and blended in the carafe.

Warmed sandy shower (it comprises of a vessel of sand and electrical radiator) was utilized for warming the blend until the point when the darker shading dissipation was vanished and the example came to dry express, this progression charms around 45-60 min. After that the container with test was cooled to research cen-

ter temperature and 5 ml of concentrated HCl was included, after that warming sandy shower utilized for warming the example with measuring utencil for 5 - 10 min. At that point the measuring utencil was cooled and 5 ml of concentrated HCL was included. 50 ml of warm refined water used to wash and clean the sides of measuring glass from stays broke up test. After that the blend warmed to the breaking point for 2-3 min. The example filtrated with channel paper No. 42. Keep the example in volumetric jar of 100 ml, at that point, the accelerate washed with refined water, and add the past washing water to the filtrate and finish to 100 ml volume. Nuclear assimilation spectrophotometer AAS (novAA 300; Germany) was utilized to decide metal focus.

2.3. Extractant

Removing of Cu, Pb and Zn from contaminated soil was carried out by using chelating agent Na2EDTA as extractant.

3. Experimental methodology

The schematic diagram of extraction process using column mode is shown in figure 1. In the experimental setup a plexiglas column of 5 cm internal diameter and 20 cm height have been used. Contaminated soil 100 gm amount was placed inside the column. Glass wool strata kept at the bottom of column below the soil to obtain a uniform distribution of the contaminated soil. A plastic mesh with diameter of 0.2 mm placed under the soil to retain it. Peristaltic pump (Elados EMP wesumat, type 1.481.08, Germany) was used for pumping the extractant solution to the column. A whatman No. 42 filter paper has been adopted for filtration of supernatant. AAS was used for analyzing of heavy metals in supernatant.

Concentrations of 0.001, 0.005, 0.01, 0.05 and 0.1 mol/L of Na2EDTA solution were used to conduct the extraction of heavy metals from contaminated soil. Flow rates of 20, 30 and 50 ml/hr at different contact time 2, 4, 6, 8, 10 and 12 hr were examined in order to determine the best conditions that give higher metal extraction efficiency.

Each experiment was conducted at 2, 4, 6, 8, 10 , and 12 hours and the supernatant volume was taken at the end of contact time. This means that the soil in column was replaced with a new contaminated soil sample (100 gm) after finishing each experiment. The experimental tests were performed in duplicates to guarantee reproducibility of the obtained results.

The removal efficiency of metal was determined using the following equation [13,15,26, 27]:

$$\text{Re}\,moval\ percentage = \frac{conta\min ant\ mass\ in\ superna\tan t\ (C_S V_s)}{initial\ conta\min ant\ mass\ in\ soil(C_0 M_d)} \times 100\% \quad (1)$$

where C_s is the concentration of metal in supernatant (mg/L), C_o is the concentration of metal in soil (mg/kg). V_s is the supernatant volume (L), and M_d is the mass of dry soil (kg).

The following equation used to determine the flow rate Q of extractant solution:

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

where A is cross sectional area of the column (cm^2), and V is Darcy's velocity (cm/hr) can be calculated from the following equation:

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

where υ is the seepage or real velocity (cm/hr) , and n is porosity of the soil.

Equations 2 and 3 were used to estimate the seepage/real velocities of Na2EDTA solution. The three velocities which adopted in the experiments were 0.48 , 0.71 , 1.19 cm/hr.
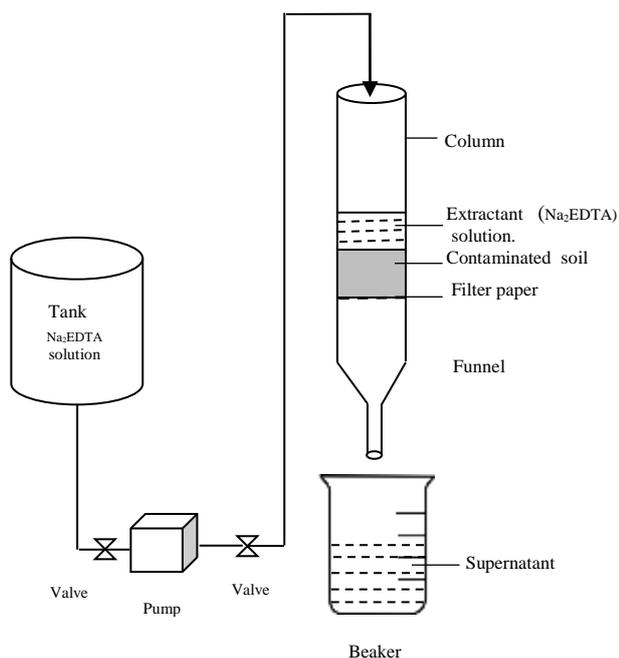

Fig. 1: Schematic diagram of the experimental column mode used in the present study.

4. Results and discussion

The investigation of capability of applying soil extraction technique using column mode to remove single and multiple Cu, Pb, and Zn from contaminated Iraqi sandy soil was carried out in this study. The effect of extraction time, extractant concentration, and extractant flow rate on the extraction efficiency was examined to determine the best conditions for removing metals from contaminated soil. All figures were drawing using Microsoft Excel Software.

4.1. Effect of contact time

Figure 2 shows the removal efficiency of Pb, Cu and Zn as a function of contact time under the conditions of pH 4, Na2EDTA concentration 0.1mol/L, Na2EDTA solution flow rate 20 ml/hr in single component system (Figure 2a) and multiple component system (Figure 2b).
The efficiency of metal separation increases when time increases until reaching maximum value then the efficiency decreases. Di Palama et al. [28] mentioned that the reason for decreasing efficiency after a certain time may be attributed to the subsequent decrease in the availability of metal in soils which cause reduction in efficiency. The continuation in process becomes useless when Na2EDTA exhausted rapidly all the available metal.
During mixing time a dynamic reaction between solution and soil occurred, this will lead to increase of pH of the solution constantly with extraction in column [29], in this case the reaction will cause precipitation of metals and inhibit the removal of heavy metals from soil, and added an increase in the time after arriving high extraction efficiency, this means that the case between the extractant and soil reached to saturation, which prohibit the extraction. From figure 2 the best contact time to remove Pb, Cu and Zn are 6, 8 and 8 hr in single component system, the maximum removals are 92%, 76% and 68%, respectively. While in multiple component system 8, 6 and 8 hr and maximum removal are 82%, 72% and 65%, respectively.
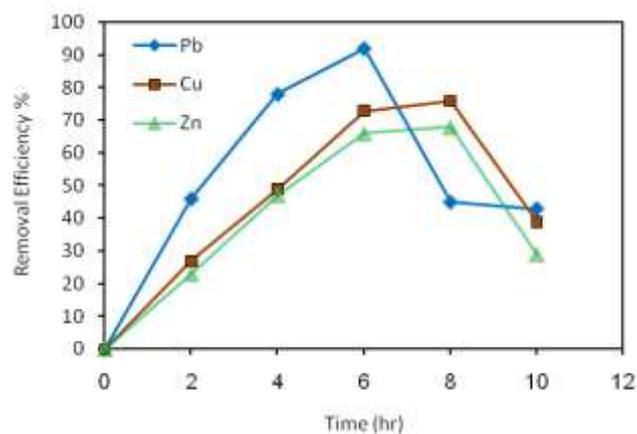

(a) Single component system
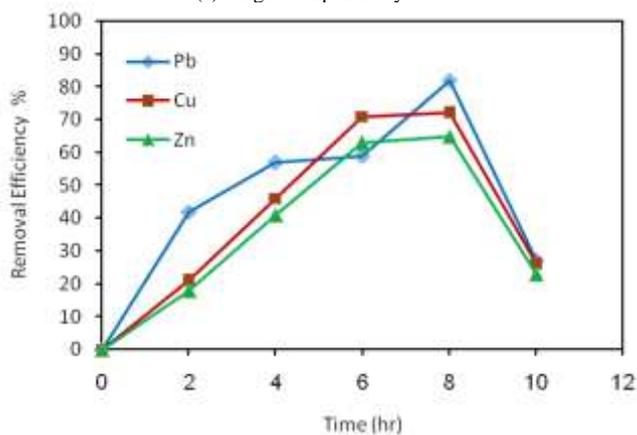
(b) Multiple component system

Fig. 2: Removal efficiency of Pb, Cu and Zn as a function of contact time; (a) single component system, and (b) Multiple component system.

Greatest rate expulsion is gotten with Pb instead of Cu and Zn, this might be expected to the physical and synthetic properties of Pb to be more positive to be desorbed than copper and zinc. This could be clarified based on ionic radii. Ionic radii of Pb, Cu and Zn are 1.54, 1.45 and 1.42°A, separately. Lead having higher ionic radii, in this way, the Pb will be evacuated more productive. Besides, the sub-atomic weight of Pb, Cu, and Zn are 331.2, 249.70 and 136.28, individually. As the particle trade identified with the atomic weight of metals and as the sub-atomic weight builds the conversion standard increments and Pb having higher sub-atomic weight, in this way Pb was the more noteworthy expulsion proficiency.

4.2. Effect of extractant concentration

Five extractant (Na2EDTA) concentrations 0.001, 0.005, 0.01, 0.05 and 0.1 mol/L were adopted in the experiments at pH 4. Three values of flow rate 20, 30 and 50 ml/hr of Na2EDTA solution were tested. Metal removal from contaminated soil increased with increasing extractant concentration. The reason for that is the higher concentrations of Na2EDTA in soil is the greater availability of extractant. Increasing concentration led to increase the removal percentage of metals from soil.
Maximum removal percentages were 92%, 76% and 68% for Pb, Cu and Zn respectively in single component system, and 82%, 72% and 65% in multiple component system. These results were at the highest concentration of extractant, Na2EDTA 0.1 mol/L, and at flow rate 20 ml/hr. The effect of different dosages of extractant solution in column experimental tests for single and multiple component system is shown in Figures 3 and 4, respectively.
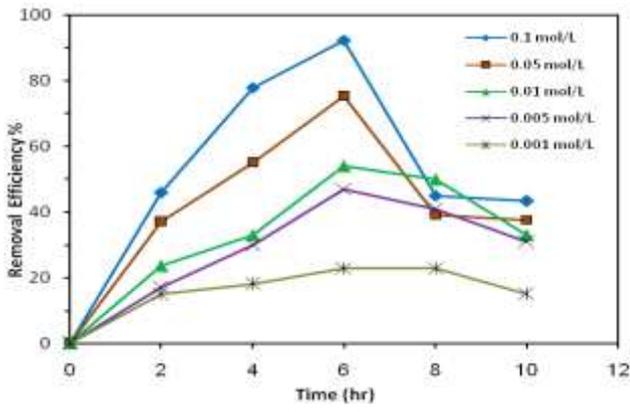
(a) Lead
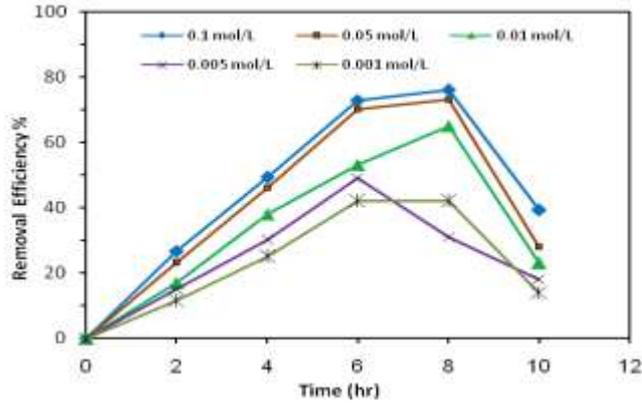
(b) Copper
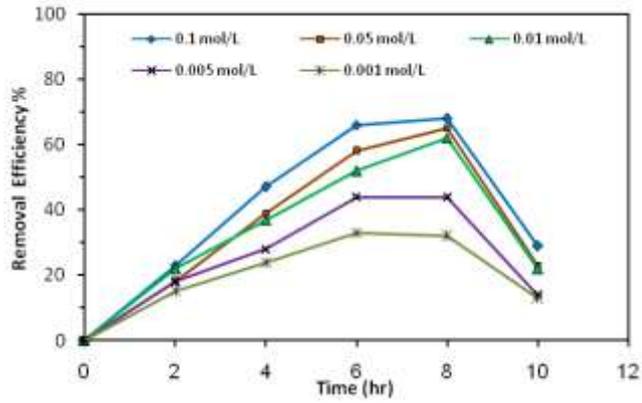
(b) Copper

(c) Zinc

Fig. 3: Metal removal efficiency as a function to contact time, (a) lead, (b) copper and (c) zinc; pH = 4, flow rate =20 ml/hr; **single** component system.
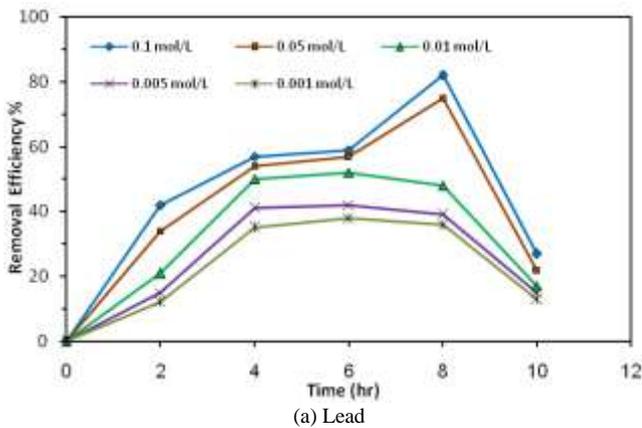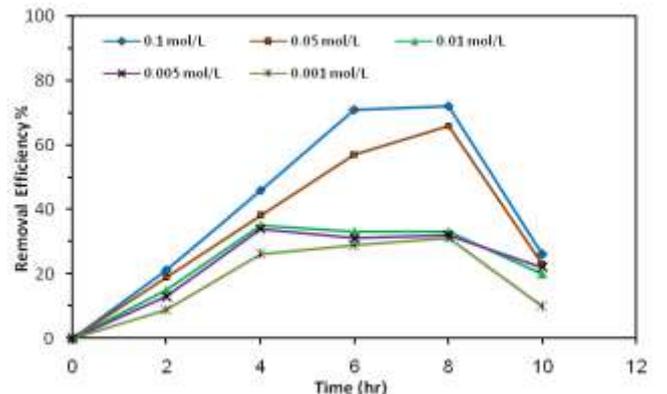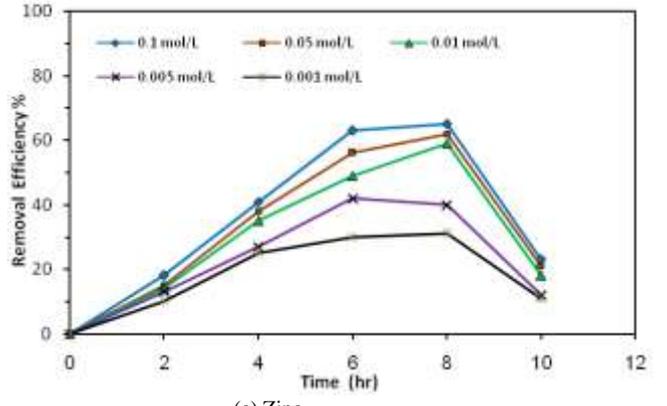

(c) Zinc

Fig. 4: Metal removal efficiency as a function to contact time, (a) lead, (b) copper and (c) zinc; pH = 4, flow rate =20 ml/hr; **multiple** component system.

4.2. Effect of extractant flow rate

The effect of extractant (Na₂EDTA) solution flow rate on removal percentages of heavy metals in column for the single and multiple component system are shown in Figure 5. This figure illustrates that the maximum removal of metals was achieved at flow rate 20 ml/hr. The remaining of contaminated soil in survival with extractant solution after reaching saturation necessary allows extracting the largest amount of contaminants.

When the flow rate is decreased a large surface area of soil will contact with Na₂EDTA solution. The very low percolation rate of extractant indicates to favour dissolution of metal with extractant. In addition, the volume of extractant is increased when the flow rate increase, In this case saturation of the contaminated soil with Na₂EDTA solution occurs before extracting the metal.


(a) Lead
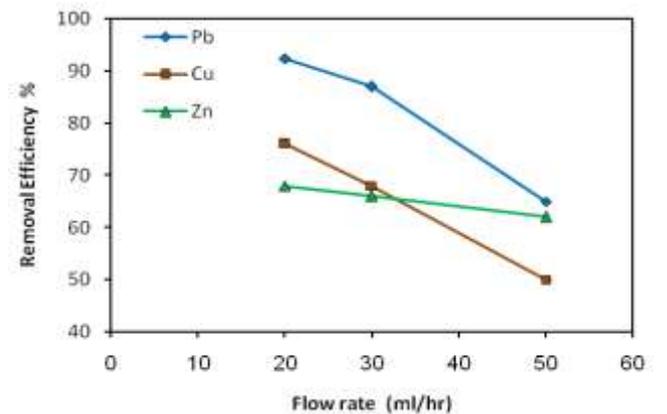
(a) Single component system
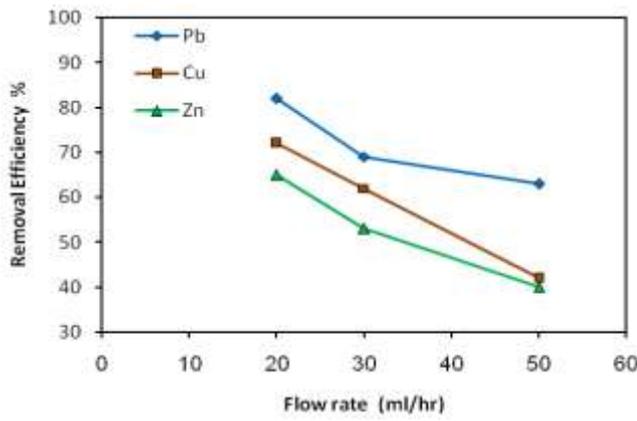
(b) Multiple component system

Fig. 5: Removal efficiency of metals as a function of Na$_2$EDTA solution flow rate (a) single component system, and (b) Multiple component system. Extractant concentration 0.1 mol/L , pH= 4.

4.4. Kinetics models

Kinetic data of this study were fitted to four mathematical models in order to examine the metals extraction mechanism. These models are first order, two constant, parabolic diffusion and Elovich model. Min et al. [30] reported linear forms for these models as shown in Table 2.

Table 2: The mathematical models used in the present study for fitting experimental data.

Model	Linear form	Reference
First -order	$\ln(C_0 - C_R) = A - Bt$	[31]
Two-constant	$\ln C_R = A + B \ln t$	[32]
Parabolic diffusion	$C_R = A + Bt^{1/2}$	[33]
Elovich	$C_R = A + B \ln t$	[34]

where t is contact time (hr), C_0 is the initial concentration of contaminant in soil (mg/kg), C_R is the concentration of contaminant removed at time t (mg/kg), A and B are intercept and slope respectively.

$$C_R = \frac{C_S \times V_S}{M_d} \qquad (4)$$

where C_s is the contaminant concentration in supernatant (mg/L), V_s is the volume of supernatant (L), M_d is dry mass of soil (kg).

The four kinetic models were utilized for applying the experimental data. The first order model was represented by the relation of $\ln(C_0 - C_R)$ with time t. In the two-constant model, the relation is between C_R and $t^{1/2}$. The relation between C_R and $t^{1/2}$ is for parabolic diffusion model, and for Elovich model the relation is between C_R and $\ln t$.

Microsoft Excel Software was used to find the constants of kinetic models. The best fit model was found from estimating the determination coefficient (R^2) for each model. Figures 6 and 7 show the best fitting of column obtained experimental data with kinetic models for both systems single and multiple components, respectively. From these figures the Elovich model result best fit with experimental data of copper and zinc in single component system (Figures 6b and 6c) and multiple component system (Figures 7b and 7c). Parabolic diffusion model gave the best fitting with lead obtained experimental data in both systems (Figures 6a and 7a).
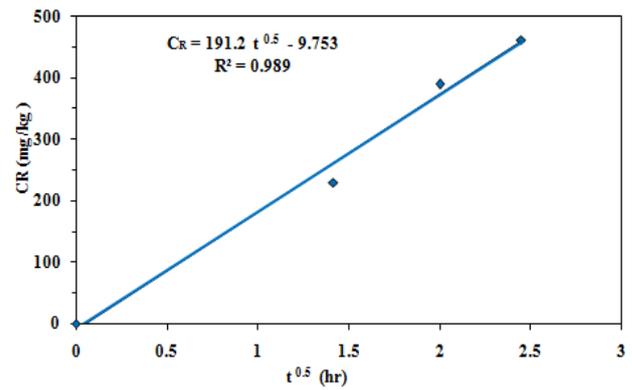
(a)   Parabolic diffusion model for Lead.
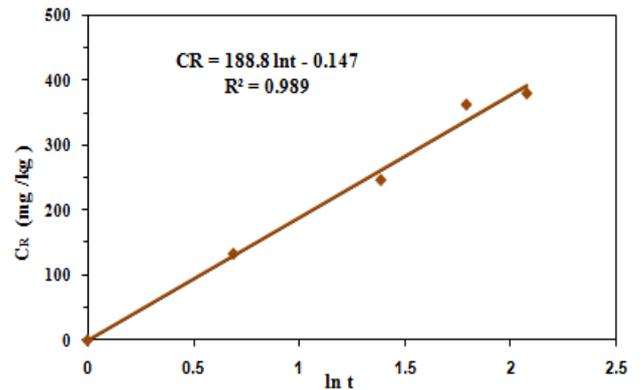
(b)   Elovich model for Copper.
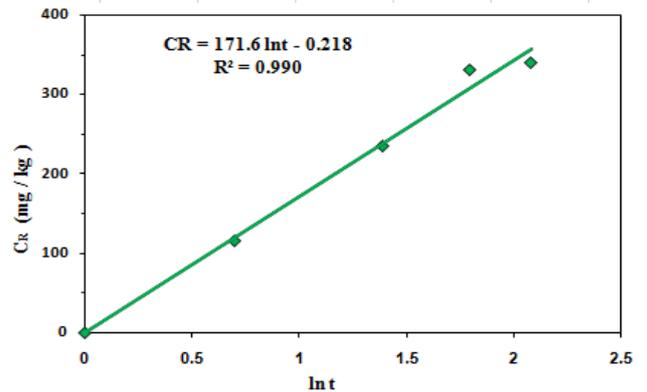
(c) Elovich model for Zinc.

Fig. 6: Best kinetic models for soil extraction ;(a) parabolic diffusion model for Lead, (b) Elovich model for Copper, and (c) Elovich model for zinc; single component system.

(a) Parabolic diffusion model for Lead.
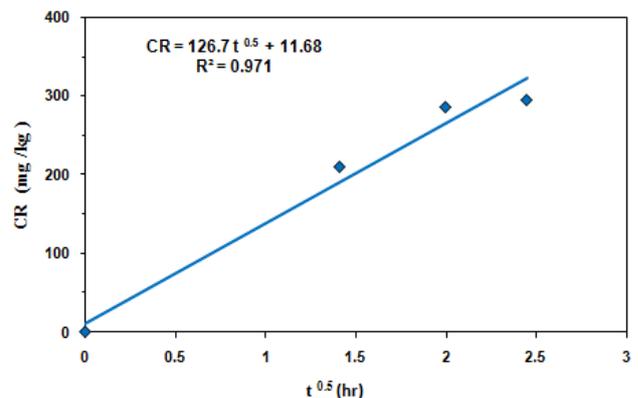
(b) Elovich model for Copper.


(c) Elovich model for Zinc.
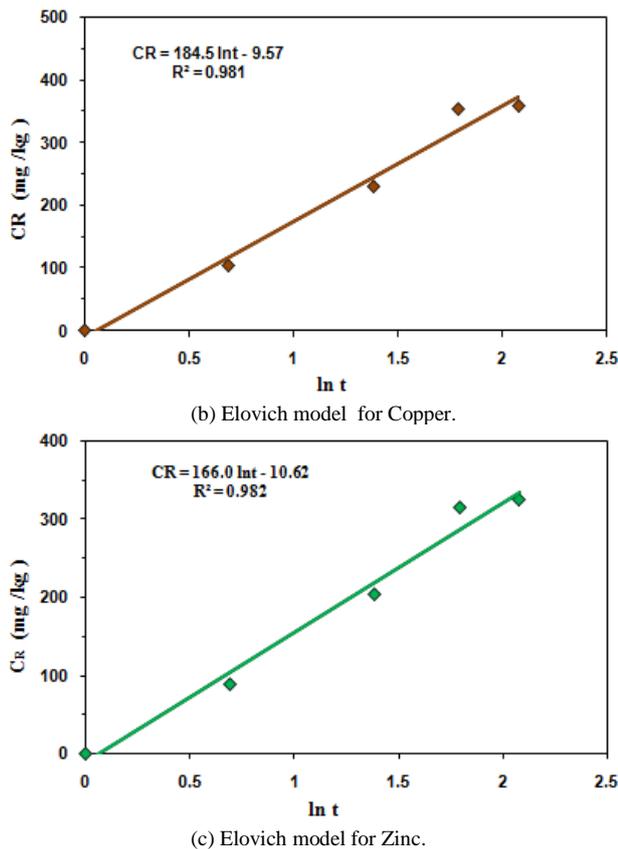
Fig. 7: Best kinetic models for soil extraction; (a) parabolic diffusion model for Lead, (b) Elovich model for Copper, and (c) Elovich model for zinc; multiple component system.

The best fitting of experimental data with the mathematical models can be interpreted by the higher value of determination coefficient (R^2). Table 3 shows the values of R^2 for the two adopted systems.

The sequence of kinetic models fitting with the experimental data was Elovich > parabolic diffusion > two- constant > first- order. The Elovich model was the higher fitting while first order was the lowest fitting. On the other hand, Elovich model gave closest results for copper and zinc in both systems.

The values of A and B which obtained from fitting the experimental data with the kinetics models are shown in Table 4 for Elovich and parabolic diffusion models.

Table 3: The determination coefficient (R^2) of different kinetic experiments for single and multiple component systems.

Kinetics Model	Determination coefficient (R^2)					
	Single component system			Multiple component system		
	Pb	Cu	Zn	Pb	Cu	Zn
First - order	0.277	0.377	0.360	0.332	0.330	0.365
Two-constant	0.759	0.770	0.776	0.703	0.796	0.805
Parabolic diffusion	0.989	0.958	0.954	0.971	0.929	0.927
Elovich	0.984	0.989	0.990	0.923	0.981	0.982

Table 4: Values of A and B for Elovich and parabolic diffusion kinetic models which resulted from fitting these models with experimental data.

Metal	System	Kinetic Model	A	B	R^2
Pb	Single Comp. System	Parabolic diffusion	191.2	- 9.753	0.989
Cu		Elovich	188.8	- 0.147	0.989
Zn		Elovich	171.6	- 0.218	0.990
Pb	Multiple	Parabolic	126.7	11.68	0.971

	Comp. System	diffusion			
Cu		Elovich	184.5	- 9.57	0.981
Zn		Elovich	166.0	- 10.62	0.982

5.   Conclusion

The aftereffects of segment trial tests pointed that the extraction procedure relies upon a few parameters, for example, extraction dose, stream rate, extraction or harmony time. The greatest effectiveness of overwhelming metals extraction can be gotten at the best estimations of these parameters. Utilizing Na2EDTA as extractant, and for single segment framework, the best contact time was six hours for expelling lead, and eight hours for evacuating copper and zinc. While in ternary (different) part framework the best contact time was six hours for copper, and eight hours for lead and zinc. Most extreme evacuation level of lead, copper and zinc in segment extraction tests was accomplished at extractant grouping of 0.1mol/L for single and ternary segment frameworks. The best Na2EDTA arrangement stream rate was 20 ml/hr for evacuating the three components (Pb, Cu and Zn) for the two frameworks. The effectiveness of metal detachment increments when time increments until achieving most extreme esteem then the productivity diminishes. Likewise, the proficiency increment with expanding extractant focus and diminishing Na2EDTA arrangement stream rate. The grouping of substantial metals expulsion from soil was Pb > Cu >Zn. Elovich and illustrative dissemination models furnished the best connection with exploratory information.

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