



## Desorption Kinetics of Heavy Metals (Lead, Zinc, and Nickel) Coexisted with Phenanthrene from a Natural High Buffering Soil

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### ABSTRACT

This work aims to investigate the competitive time-dependent desorption rate of heavy metals (lead, zinc, nickel) coexisting with phenanthrene from natural high buffering soil. Two non-ionic surfactants (Tween 80 and Brij 35) combined with disodium ethylene diamine tetraacetate salt (Na<sub>2</sub>-EDTA) were utilized as the reagents. The contaminants' time-dependent desorption data was fitted with five kinetic models including parabolic diffusion, Elovich, fractional power function, pseudo-first and -second-order equations. The best removal of contaminants obtained by the mixture of Tween 80/EDTA; desorbing 93% of lead (Pb). The competitive desorption of nickel (Ni) and zinc (Zn) is affected by the stability of Metal-EDTA complexes. Moreover, phenanthrene removal in the soil studied was slow and laborious. The desorption kinetics are well described by parabolic diffusion (for phenanthrene) and pseudo-second-order (for heavy metals of interest). In the soil-surfactant-water system, soil structure changes were negligible; however, Tween 80 influenced the development of crystal faces of CaCO<sub>3</sub> during the process.

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## 1. INTRODUCTION

Anthropogenic activities left behind the contaminated sites with different quantities of hazardous materials. In most circumstances, heavy metals coexist with organic pollutants like polycyclic aromatic hydrocarbons (PAHs) [1]. These chemicals cause great concern because of their propensity to persist in soil and creating hazards to the environment [2]. Due to their toxicity, remediation strategies should be considered and implemented to reclaim soil and water [3].

Some factors including the adsorption of surfactants onto the soil, the solubilizing ability of surfactants and their toxicity should be considered to choose the appropriate surfactant for selective soils and contaminants [4]. Several researchers have investigated that the mineralogy of clay fraction affects the sorption

of surfactants [5, 6] following low decontamination rates. For instance, Shen[7] reported that soils with higher Si: (Al+Fe) ratio shows higher sorption capacity for the polyethylene surfactant, A<sub>9</sub>PE<sub>10</sub>. Organic matter and clay minerals with high cation exchange capacity and high specific surface area are the main sinks for heavy metals and PAHs [8, 9]. Hwang et al. [10] studied the sorption-desorption behavior of pyrene and concluded that the clay fractions play a leading role compared to organic matter.

The competitive desorption of pollutants from soil minerals and organic matter plays an important role in understanding their fate and behavior. Kinetics, as the study of time-dependent process, has been used to simulate the fate of organic and inorganic contaminants. A number of kinetic models, including pseudo first and pseudo second order models, had been developed for the sorption and desorption of heavy metals and PAHs. Previous works proposed that Pb and phenanthrene desorption from natural soils follow the pseudo-second-

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order kinetic [11, 12]. However, some other models – such as parabolic diffusion and Elovich have been less used for estimating effective parameters on contaminant desorption .

In practical, supplementary solvents like acids, surfactants and chelates are mostly added to enhance the remediation of mixed contaminants (heavy metals and PAHs) from soil [3]. Yan and Lo [13] assessed the effectiveness of iron-chelate-activated persulfate for the removal of naphthalene and heavy metals from an artificial soil. They achieved the 89% removal of naphthalene in 7 h and over 35, 36 and 45% removal of copper (Cu), lead (Pb) and zinc (Zn), respectively . The inimitable structure of surfactants enhances the mobilization of PAHs by reducing the surface and interfacial tension [14]. A surfactant molecule consists of a hydrophobic head group and one or more hydrophilic chain [15]. Above the critical micelle concentration (CMC), the solubilization of PAHs would increase by their incorporation to the hydrophobic core of surfactant micelles [12, 14]. Nonionic surfactants are the most relevant group used for remediation of petroleum hydrocarbons in the soil-water system [8, 15].

Many studies have been performed on artificial soils, while the behavior of natural soils could be different. Fonseca et al. [12] studied the desorption of Pb and phenanthrene from natural soil by using single and composed solutions and obtained the extraction of 48% Pb and 55% phenanthrene with EDTA/Brij 35 solution. In a study carried out by Jalali and Majeri [16], the sorption and desorption capacity of cobalt (Co) from various calcareous soils by the batch experiment were assessed and the desorption of Co obtained in the range of 3.6-11.4%. The findings also declared that calcareous soils strongly retain Co and prohibit its mobility. Buffering capacity of the soils define as the soil resistance over acidity in various conditions [17], and high buffer soils are challenging one in desorption of heavy metals.

The behavior of high buffering soils when the pollutants are simultaneously present yet to be fully studied. The objective of the present study is to assess desorption kinetics of both heavy metals (Pb, Zn, Ni) and phenanthrene from a natural high buffering soil sample. Also, the performance of the composed solutions of Na<sub>2</sub>-EDTA with nonionic surfactants (Brij 35 and Tween 80) in desorption batch experiments was

investigated. To the best of authors knowledge, reports focusing on the soil mineralogy under the effect of combined enhancing solutions in batch experiments for multiple contaminants removal are scarce [12]. Therefore, the structural changes in natural soil minerals during desorption, were considered to elucidate the role of combined solutions before and after batch experiments. For this reason, scanning electron microscopy analyses and X-ray diffraction analysis of contaminated and decontaminated soils were also performed.

## 2. MATERIALS AND METHODS

**2. 1. Materials** Disodium ethylene diamine tetraacetate salt (Na<sub>2</sub>-EDTA) (Sigma-Aldrich) was used as a complexing agent to improve metal removal. Two nonionic surfactants, Tween 80 (Sigma-Aldrich) and Brij 35 (Merck) with properties mentioned in Table 1, were utilized to ameliorate phenanthrene extraction in the assays. Phenanthrene as a representative PAH was purchased from Sigma-Aldrich Co. Zinc-Nitrate, Lead-Nitrate and Nickel-Nitrate (> 97% purity) obtained from Merck (Germany). All chemicals and solvents used in the experiments and analysis were of analytical purity.

**2. 2. Soil Preparation** Soil sample (0-10 cm depth) was collected from a pine forest near Shiraz oil refinery Co. located in 15km North-Eastern of Shiraz (Iran). The soil was air-dried and passed through a 2mm sieve in order to have a homogenous soil without foliage or any other rubbish. Soil properties and background values of lead, zinc, nickel, and phenanthrene are shown in Table 2. Quartz (SiO<sub>2</sub>), Calcium oxide (CaO) and Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>) are the main minerals in this soil. Laser scattering particle size distribution analyzer (HORIBA, LA-950, China) were used for particle size distribution (Table 2). According to the Unified Soil Classification System (USCS), the soil is categorized as the “lean clay”. The buffering capacity of the soil with a concentration of 7.4% was 7 equivalent per 1 kg of dry soil. The instruction of the titration analysis used in this study is well described by Reddy et al [18]. The titration analysis and high cation exchange capacity (CEC) of the soil point to the high buffering capacity.

**TABLE 1.** Properties of chemicals used in this study

Name	Formula	Molar mass (g mol <sup>-1</sup> )	Solubility (mg l <sup>-1</sup> )	HLB <sup>a</sup>	CMC <sup>b</sup> (g.l <sup>-1</sup> )
Na <sub>2</sub> -EDTA (Titrplex <sup>®</sup> III)	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> · 2H <sub>2</sub> O	372	186	-	-
Brij <sup>®</sup> 35	(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> C <sub>12</sub> H <sub>26</sub> O	1198	40000	16.9	0.1
Tween <sup>®</sup> 80	C <sub>64</sub> H <sub>124</sub> O <sub>26</sub>	1310	-	15.0	0.016

<sup>a</sup> HLB refers to hydrophilic-lipophilic balance of a surfactant [15].

<sup>b</sup> CMC refers to critical micelle concentration of a surfactant.

**TABLE 2.** Physicochemical properties of the real soil studied

Characteristics	Value	
Compounds (%)	SiO <sub>2</sub>	41.42
	CaO	14.67
	Al <sub>2</sub> O <sub>3</sub>	10.23
	Fe <sub>2</sub> O <sub>3</sub>	5.84
	MgO	3.98
	K <sub>2</sub> O	1.98
	Na <sub>2</sub> O	0.32
	MnO	0.08
	Sand	0
	Silt	60.08
Particle size distribution (%)	Clay	39.81
	Colloids	0.12
pH (ASTM-D4972)	7.5	
LOI at 550 °C (%)	5.7	
CEC (meq/100g dry soil) (ASTM-D9081)	35.7	
Phenanthrene (mg kg <sup>-1</sup> )	0	
Lead (Pb) (mg kg <sup>-1</sup> )	9.89	
Zinc (Zn) (mg kg <sup>-1</sup> )	42.45	
Nickel (Ni) (mg kg <sup>-1</sup> )	29.53	

The soil (500 g) was spiked by adding the acetone-phenanthrene mixture in the adequate ratio. The mixture was stirred with Plexiglas spoon and kept in a ventilation hood until the contaminated soil was dried. Luo et al. [19] proposed that the appropriate aging process of PAHs in natural soil is between 15-30 days. During 15 days, we kept the spiked soil sample in a dark place at 10 °C with occasional mixing. Then the required amounts of Ni (NO<sub>3</sub>)<sub>2</sub>, Pb (NO<sub>3</sub>)<sub>2</sub> and Zn (NO<sub>3</sub>)<sub>2</sub> were dissolved in deionized water and then added to the soil. The mixture was blended homogeneously and was kept under the hood until dried. The desired final concentrations after the 30 day-spiking procedure were 440 mg phenanthrene, 955 mg Pb, 955 mg Zn and 500 mg Ni in 1 kg dry soil. These concentrations are typically found near industrial sites [12].

### 2. 3. Batch Experiments

To evaluate desorption kinetics of heavy metals (Pb, Ni, and Zn) and phenanthrene, series of batch experiments were conducted using two different combined solutions; 1% Brij 35 + 0.1 M Na<sub>2</sub>-EDTA, and 1% Tween 80 + 0.1 M Na<sub>2</sub>-EDTA. One set of batch experiments were carried out only with 0.1 M Na<sub>2</sub>-EDTA. In addition, all solutions include 200 mg l<sup>-1</sup> Sodium Azide (NaN<sub>3</sub>) and

0.01 M CaCl<sub>2</sub> to restrain the microbial activity and to maintain the ionic strength.

The dried contaminated soil (2 g) was mixed with the solvents in the ratio of 1:5 (soil: solution) [12]. Dark glass bottles were sealed with Para-film and agitated on a horizontal reciprocating shaker at a constant speed of 200 rpm at room temperature (25 °C). For evaluating the real competitive removal of heavy metals, experiments were conducted without pH adjustment and only the final pH of the solvent was measured. Mixture solutions were collected in different time intervals (3, 6, 24, 30, 48 and 72 h) and centrifuged at 6000 rpm for 15 min. Finally, the sample was analyzed for the desorbed heavy metals and phenanthrene concentration.

### 2. 4. Analytical Methods

Soil samples were air-dried and digested in accordance with EPA method 3050B to determine the heavy metals concentration (Pb, Zn, and Ni) by Flame Atomic Absorption Spectrophotometry (WFX-210). The removal efficiency was calculated by the ratio of the final extracted concentration of contaminant (Q<sub>t</sub>) in the supernatant to the initial concentration of contaminant (Q<sub>0</sub>) in soil.

Phenanthrene in aqueous solution was extracted using liquid-liquid extraction (LLE) [20]. 5 mL of the supernatant was placed into a conical glass centrifuge and 15 ml dichloromethane was added to the solution. The mixture was gently shaken with hand for 5 min and after that, the cap was opened in order to release the gas. The tube resealed and was placed on a shaker at 250 rpm for 24 h. Finally, the liquid phase was directly injected by 1µl glass syringe to the GC-FID (Beifen-3420A) equipped with the SGE-BP5 capillary column. The ratio of phenanthrene concentration in the solution to the initial concentration of phenanthrene in the soil would give the removal efficiency of phenanthrene.

The surface morphology of samples was characterized by scanning electron microscopy (SEM) (Hitachi-SU3500) equipped with energy dispersive spectrometer (EDS) and back-scattered electron detector (BSE). X-ray diffractometer (XRD) (Bourestnik-Dron8) with X'Pert HighScore1.0 software was used to determine the mineralogical composition of the samples.

### 2. 5. Kinetic Modeling

Five kinetic equations, including empirical power function, Lagergren pseudo-first model, pseudo-second order equation, parabolic diffusion and Elovich model, were used to evaluate the results of desorption experiments. Fractional power function is expressed as follows:

$$q_t = kt^v \quad (1)$$

where k (kg mg<sup>-1</sup> h<sup>-v</sup>) is the rate constant of power function, q<sub>t</sub> (mg kg<sup>-1</sup>) is the amount of contaminant

released after time  $t$  (h) and,  $v$  is the constant of power function which is  $0 < v < 1$  [21]. The linear form of Lagergren pseudo-first-order model is as follows [11]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $q_e$  is the equilibrium amount of contaminant desorbed from the soil and  $k_1$  ( $\text{h}^{-1}$ ) is the Lagergren rate constant. The linear plot of  $\ln(q_e - q_t)$  against  $t$  (h) gives the values of  $q_e$  and  $k_1$  from the intercept and slope of the graph. One linear form of pseudo-second-order model is according to the Equation (3) [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $k_2$  ( $\text{kg mg}^{-1} \text{h}^{-1}$ ) is the rate constant of pseudo-second order equation. The linear plot of  $t/q_t$  versus  $t$  (h) would give the values of  $q_e$  and  $k_2$  in the pseudo-second-order equilibrium from the slope ( $1/q_e$ ) and intercept ( $1/k_2 q_e^2$ ) of the graph [23]. The parabolic diffusion model shows that diffusion control phenomenon is a rate-limited process [21]. This model has been applied to soil media, which can be expressed as follows:

$$q_t = k_p t^{1/2} + I \quad (4)$$

The parabolic constant,  $k_p$  ( $\text{mg kg}^{-1} \text{h}^{0.5}$ ) and the  $I$  constant, respectively are obtained from the slope and intercept of the plot  $q_t$  versus  $t^{1/2}$ . The simplified form of Elovich equation is formulated as follows [24]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

in which  $\alpha$  ( $\text{mg kg}^{-1} \text{h}^{-1}$ ) and  $\beta$  ( $\text{kg mg}^{-1}$ ) as Elovich constants are determined by plotting  $q_t$  against  $\ln t$ .

## 2. 6. Statistical Methods

In this study coefficient of determination ( $R^2$ ) and root-mean-square deviation (RMSD) were used to evaluate the fit of kinetic equations to the experimental results. RMSD is basically used to measure the differences between experimental data ( $q_{t,\text{exp}}$ ) and values predicted by the kinetic model ( $q_{t,\text{pred}}$ ) in a series of time ( $n$ ) [25]. The RMSD value is obtained based on the following equation [26]:

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^n (q_{t(\text{pred})} - q_{t(\text{exp})})^2}{n-2}} \quad (6)$$

If the RMSD was a small value, the kinetic model would be correspondent to the experimental data.

## 2. 7. Quality Control

A certified soil sample was used to check the accuracy and calibration of the atomic absorption spectrophotometry. Also, experiments were carried out in duplicate and samples were read in triplicate with a standard deviation below 5%. Reagent blank was used during acid digestion and

instrument detection procedure to make sure of no cross-contamination.

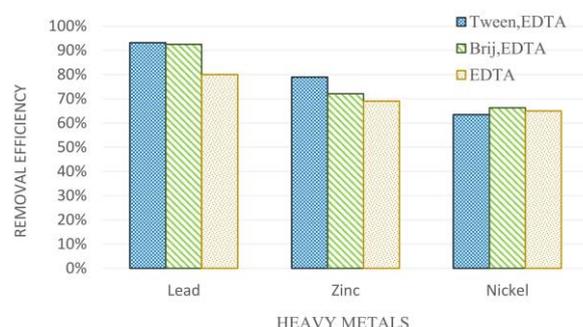
## 3. RESULTS AND DISCUSSIONS

**3. 1. Removal Efficiencies** Figure 1 depicts the removal percent of heavy metals from soil using different solvents. Desorption efficiency in batch experiments follows  $\text{Pb} > \text{Zn} > \text{Ni}$ . Lead has the highest removal efficiency in all the experiments. This result is comparable with other studies on desorption pattern of heavy metals from soil [27, 28].

The initial and final pH of the soil slurry in all experiments were about  $7.5 \pm 0.4$  that was higher than the stability constant ( $\log k$ ) of EDTA. It means that the stable complex Metal-EDTA is predominant to the Metal-OH-EDTA and Metal-H-EDTA complexes [12]. The Pb-EDTA complex has higher stability constant ( $\log k = 17.9$ ) than the Zn-EDTA complex ( $\log k = 16.5$ ) [29]. Moreover, Zn removal depends on pH fluctuations while Pb is less sensitive to pH [30]. Hence the highest Pb and Zn removal reached 93 and 79% with the mixture of EDTA and Tween 80, respectively (see Figure 1). While the Ni-EDTA complex has a high stability constant of 18.56 [31], the highest removal efficiency of 66% was obtained for Ni.

Due to the dominant  $\text{SiO}_2$  structure of the soil (Table 2), Ni likely appears in the residual fraction that decreases Ni availability [32]. Also, the residual fraction is less extractable by EDTA than the exchangeable and carbonate fractions [33]. Surfactants in combination with EDTA, particularly yield more removal efficiency for Pb compared to just EDTA, with a difference of more than 10% removal. Surfactants enhance the remediation of heavy metals in the soil when combined with a ligand that forms a micelle complex [3].

Tween 80 and Brij 35 had a maximum efficiency of 22 and 19% phenanthrene removal, respectively. Clay minerals dominate the intra-particle diffusion that propels the laborious desorption of phenanthrene [10].



**Figure 1.** The removal efficiency of heavy metals in different batch experiments after 72 h

Some previous studies ascertained that in soil-water systems Tween 80 has the capability to extract phenanthrene better than Brij 35, which is in line with our results [12]. Previous experiments evidence that soil properties control the sorption and desorption of PAHs from soil samples. Moreover, PAHs removal from soils with longer aging time is less than those with a short aging time [19]. The lower phenanthrene removal efficiency in this study (<25%) compared to other reports [12] could be related to the aging time (30 days) and high buffering of the soil studied.

**3. 2. Desorption Kinetics** Kinetic models were used to investigate the desorption mechanism over a certain time scale. Rate constants, correlation coefficient ( $R^2$ ) and RMSD were obtained for five kinetic models, fractional power function, Lagergren pseudo-first-order, pseudo-second-order, parabolic diffusion and Elovich (Table 3).

The order of fitted kinetic model for phenanthrene on the basis of  $R^2$  and RMSD followed by parabolic diffusion > pseudo-second order > fractional power function > Elovich > pseudo-first order. The relationship between  $q_t$  for phenanthrene and  $t^{1/2}$  yielded

a linear plot with the highest  $R^2$  (>0.95) and the lowest RMSD (<6.0), which ascertained the validity of the parabolic diffusion law [21]. The best fitness of parabolic diffusion kinetic model indicates that the desorption behavior of phenanthrene during 72 h from the soil appeared to be diffusion controlled [21]. This confirms and might be the reason for the slow removal of phenanthrene from the soil studied by all solutions containing Tween 80 and Brij 35 surfactants.

The most appropriate kinetic model for heavy metals (Pb, Zn, Ni) removal by both solutions used is pseudo-second order equation according to statistical evaluation. Desorption capacity value ( $q_e$ ) from the pseudo-second-order equation is well adjusted to the experimental values obtained. Shirvani et al. [34] also reported that desorption of cadmium from fibrous silicate clay minerals using different reagents (acetate, citrate and desferrioxamine B) fitted a pseudo-second order model. Table 4 compares some previous kinetic studies results on desorption behavior of contaminants. Previous studies reported that pseudo-second-order equation was suitable for the simultaneous desorption of phenanthrene and Pb from a natural soil (Table 4) [11, 12].

**TABLE 3.** Statistical values and desorption kinetic parameters of phenanthrene, Pb, Zn, and Ni

Equation	Parameter	Tween 80 / EDTA				Brij 35 / EDTA			
		PHE	Pb	Zn	Ni	PHE	Pb	Zn	Ni
Pseudo-first order	$q_e$ (mg kg <sup>-1</sup> )	425.89	309.85	544.84	328.95	416.42	259.82	610.51	320.02
	$K_1$ (h <sup>-1</sup> )	$3.3 \times 10^{-3}$	$22.6 \times 10^{-3}$	$17.6 \times 10^{-3}$	$7.4 \times 10^{-3}$	$2.5 \times 10^{-3}$	$18.1 \times 10^{-3}$	$15.5 \times 10^{-3}$	$7.8 \times 10^{-3}$
	$R^2$	0.964	0.521	0.731	0.728	0.908	0.703	0.661	0.879
	RMSD	21.50	1042.89	485.94	294.19	32.11	1102.41	413.19	304.52
Pseudo-second order	$q_e$ (mg kg <sup>-1</sup> )	169.50	1111.11	833.33	370.37	107.53	1986.95	769.23	384.61
	$K_2$ (kg mg <sup>-1</sup> h <sup>-1</sup> )	$1.05 \times 10^{-4}$	$5.7 \times 10^{-4}$	$2.0 \times 10^{-4}$	$7.4 \times 10^{-4}$	$4.04 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.5 \times 10^{-4}$	$7.5 \times 10^{-4}$
	$R^2$	0.836	0.999	0.996	0.997	0.956	0.999	0.988	0.996
	RMSD	6.86	19.88	42.11	32.15	7.03	64.89	59.32	25.54
Fractional power function	$\nu$	0.76	0.13	0.34	0.19	0.57	0.11	0.48	0.16
	$K$ (kg mg <sup>-1</sup> h <sup>-<math>\nu</math></sup> )	4.24	655.52	202.65	166.93	7.92	717.12	114.68	191.01
	$R^2$	0.947	0.887	0.937	0.783	0.898	0.883	0.910	0.976
	RMSD	7.21	62.23	82.91	33.35	7.25	56.48	124.41	9.77
Parabolic diffusion	$I$	-13.05	52.72	211.05	187.54	1.12	774.07	115.89	202.43
	$K_p$ (mg kg <sup>-1</sup> h <sup>-0.5</sup> )	13.01	57.725	74.657	22.35	10.023	48.821	80.995	21.627
	$R^2$	0.983	0.728	0.841	0.750	0.960	0.765	0.803	0.933
	RMSD	4.93	84.42	93.74	37.27	5.91	77.44	115.94	16.73
Elovich	$\alpha$ (mg kg <sup>-1</sup> h <sup>-1</sup> )	12.79	22577.42	302.58	1133.06	10.00	101143.30	168.81	1980.19
	$\beta$ (kg mg <sup>-1</sup> )	0.048	0.008	0.006	0.020	0.038	0.010	0.005	0.021
	$R^2$	0.966	0.970	0.942	0.837	0.937	0.885	0.931	0.987
	RMSD	12.27	52.96	233.65	30.05	9.44	50.35	257.64	7.37

**TABLE 4.** Compilation of desorption kinetic studies in contaminated soils

References	Contaminant	Soil type	Kinetics used	Contact time (h)	Best kinetic
Kandpal et al. [35]	Cu, Cd, Ni, Zn	Acidic and neutral soil	First order	72	First order
Shirvani et al. [34]	Cd	Silicate clay minerals	Pseudo-first- and pseudo-second-order, Elovich, power function, parabolic diffusion	24	Pseudo-second order
Wang et al. [11]	Phenanthrene, Pb	Spiked natural soil	Pseudo-first and pseudo-second order	24	Pseudo-second order
Fonseca et al. [12]	Phenanthrene, Pb	Natural soil	Power function, pseudo-second order	24	Power function, pseudo-second order
Sadegh-Kasmaei and Fekri [36]	Cu, Cd	Agricultural soil	Zero-, first-, second-, and third-order, Elovich, parabolic diffusion, Power function	48	Power function and Elovich
Wei et al. [37]	Pyrene	Kaolin, montmorillonite	First order (simple and two compartment)	48	First order
Li et al. [8]	Cd	Tourmaline	Pseudo-first- and pseudo-second-order	24	Pseudo-second order
Inyang et al. [24]	Cd, Pb	Kaolin, Na-montmorillonite	Elovich, first- and second-order, parabolic diffusion	48	Elovich
Mohammadi et al. [22]	Phenanthrene, anthracene, Pb, Zn, Ni	Kaolin	Pseudo-second order, power function, Elovich, parabolic diffusion	72	Pseudo second order (except anthracene), Elovich (anthracene)
Gharibzadeh et al. [38]	Phenanthrene	Spiked natural soil	Pseudo-first- and pseudo-second-order, power function	24	Pseudo-second order
This study	phenanthrene	Spiked natural soil	Pseudo-first- and pseudo-second-order, Elovich, power function, parabolic diffusion	72	Parabolic diffusion (phenanthrene), pseudo second order (Pb, Zn, Ni, phenanthrene)

Similar to our findings some other researchers reported that the sorption/desorption of phenanthrene and heavy metals (such as lead, arsenic, and cadmium) does not follow a pseudo-first order model over the entire range of contact time [11, 39]. Over a long contact time, the contaminants may first physically adsorb onto the surface of the soil particles and organic matter but then some chemical bonds may form between the contaminants and soil organic matter over time. For the desorption, contaminants on the surface of the particles may release faster while longer time is needed for the contaminants in stronger and/or deeper chemical bonds within the soil minerals and organic matter to be removed. This may affect the kinetic modeling of multiple contaminants such as PAHs, over the entire contact time. That is why some previous researchers reported a two phase desorption kinetics of desorption [37, 40]. The majority of Pb probably exist in available forms (exchangeable and carbonate fraction) [41]. For the first hours, Pb desorption gradient is sharper follows the high stability of the Pb-EDTA complex ( $\log K = 17.9$ ) and more Pb availability. We observed that although Ni-EDTA complex had a higher stability than Zn-EDTA,

after a time the Ni diagram went over the Zn.  $Ni^{2+}$  has a higher crystal field stabilization energy and mostly incorporates in the recalcitrant fractions [42]. It makes Ni less available to form a complex with EDTA and to leave the solid fractions.

The desorption rate of heavy metals and phenanthrene as a function of contact time are presented in Figure 2. The  $Q_s/Q_0$  fraction is the ratio of contaminant concentration at time (t) to the initial concentration in soil. Desorption rates of Ni, Zn and Pb were fast for the first 24 h and then declined and reached a plateau in the last 48 h of the experiment. Heavy metals from loosely bound phases are easily desorbed compared to the resistant phases [12, 35, 36].

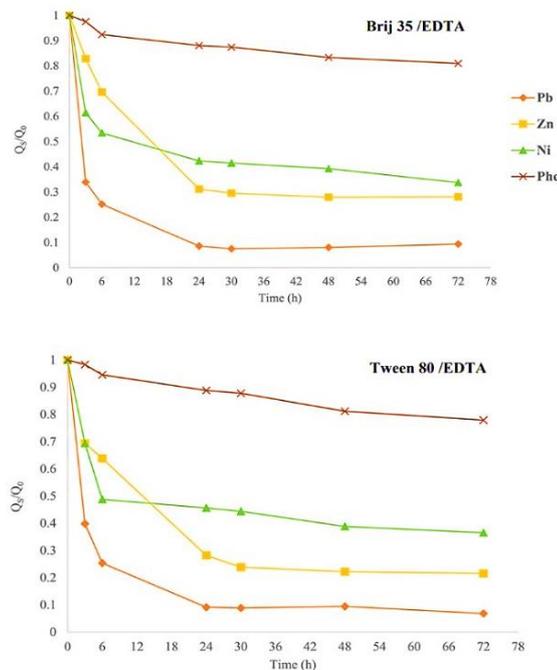
In contrast, the phenanthrene desorption was slow compared with heavy metals desorption during the assays; however, the desorption rate for the first 6 h had a steep slope. Several authors observed the same trends by using various solutions and materials [12, 35].

Several factors cause the low desorption of phenanthrene. For instance, Gao et al. [43] indicate that the aging of soil involves phenanthrene diffusion into micro-pores and reduces the phenanthrene desorption.

Not only intra-particle diffusion but also cation- $\pi$  interaction and surfactant adsorption to the soil might intensify the low rate desorption of phenanthrene. In the soil-water system, a specified amount of surfactant would inevitably adsorb to the soil and would lead to the re-adsorption of PAHs to the soil surface [3]. Consequently, for the selection of a surfactant Zhou and Zhu [14] proposed that both the solubilizing capabilities for PAHs and the sorption of surfactant on soil should be considered.

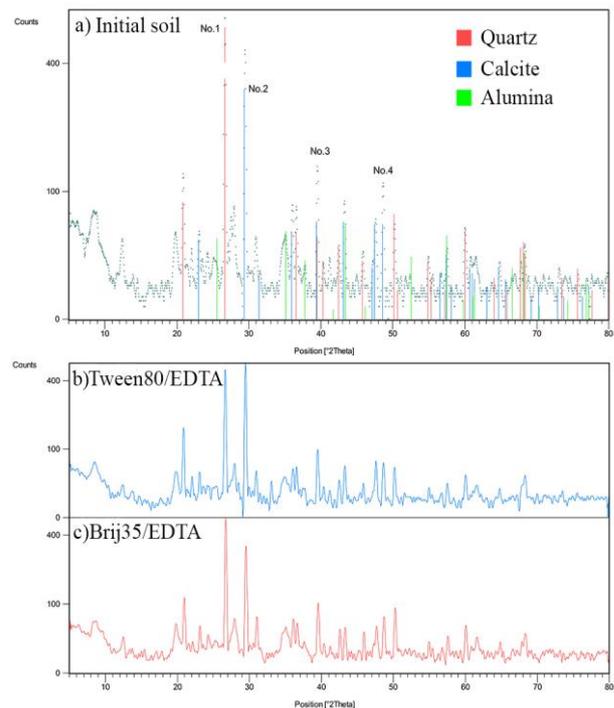
A number of assays have focused on the adsorption of nonionic surfactants [3, 6, 7]; however, few data have been focused on Tween 80 and Brij 35. On the other hand, binding of heavy metals ( $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ) in the soil-water system could create a hydrophobic circumference and facilitate the cation- $\pi$  binding of PAHs which influences the sorption affinity of PAHs [1].

**3. 3. Soil Mineralogy** The soil samples were analyzed by SEM and XRD to better understand the physical and morphological characteristics of the soil. The diffraction pattern for the initial spiked soil was compared to the decontaminated soils treated with the mixed solutions of Tween 80/ EDTA and Brij 35/ EDTA (Figure 3). Quartz, Calcium oxide, and Aluminium oxide are respectively the dominant minerals in the soil. Peak height and d-spacing for four

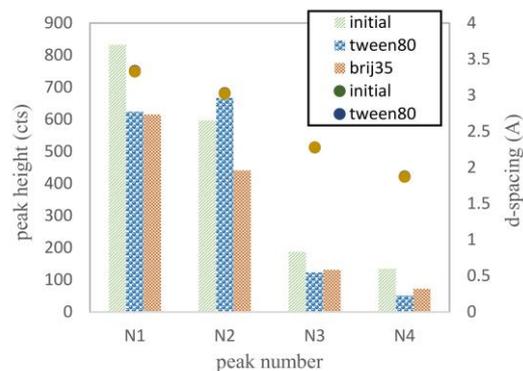


**Figure 2.** Desorption profile of heavy metals and phenanthrene versus time ( $Q_s/Q_0$ : the ratio of contaminant concentration at time (t) to the initial concentration)

specific peaks (No. 1 to No. 4) were evaluated to see whether any changes engendered after the experiments. According to the Bragg equation, peak position changes directly depends on d-spacing [44]. As shown in Figure 3 before and after soil treatment, the diffraction patterns were analogous and d-spacing values overlapped for each of the four peaks (Figure 4) which means no significant alteration occurred in soil structure. However, a decrease in determined peak heights (Figure 4) occurred through the possible dissolution of minerals.



**Figure 3.** X-ray diffraction pattern of the dominant minerals in the initial spiked soil (a), decontaminated soil using Tween 80/EDTA (b), and Brij 35/EDTA (c)

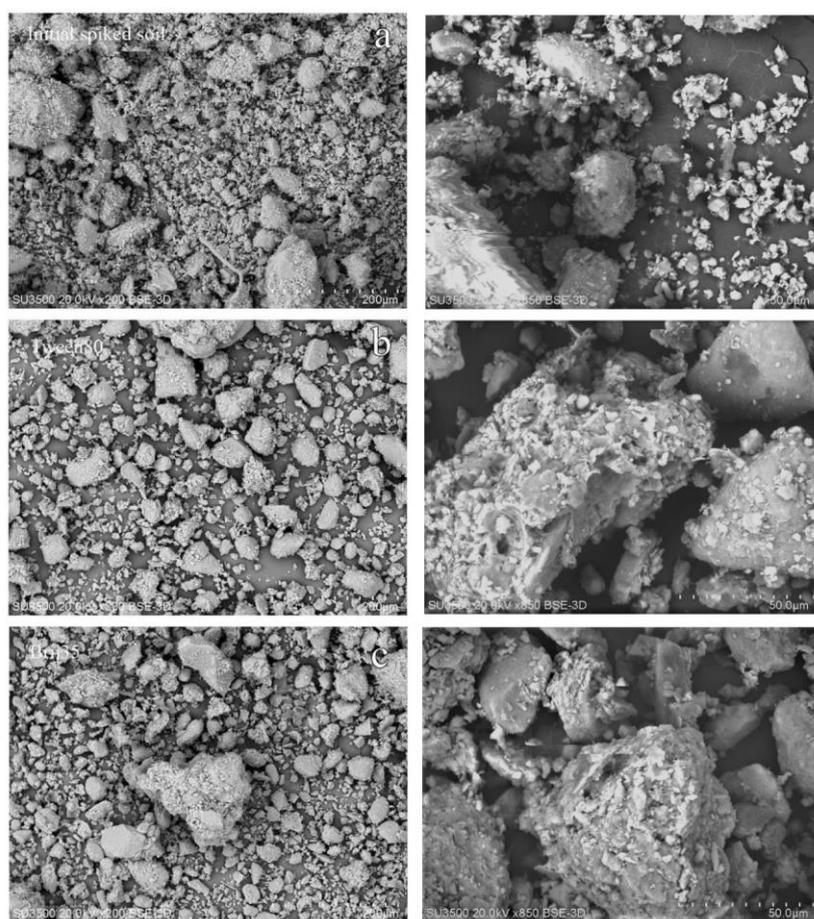


**Figure 4.** X-Ray diffraction analysis: comparison of peak height (left y-axis) and d-spacing values (right y-axis) for four specific peaks (shown in Figure 3a) in the initial spiked soil and final decontaminated soils

The decrease in peak height was also observed by Roach et al. [44] after the electrokinetic remediation. In the case of using Tween 80/ EDTA, we observed an increase in peak height which belongs to calcite mineral (peak no. 2). In fact, Tween 80 affects the growth of  $\text{CaCO}_3$  crystals to some extent [45] and may result in changing the peak intensity.

In all EDS analyses, atoms of silica, aluminum, iron and oxygen were detected which are the usual

composition of aluminosilicate minerals. Figure 5 shows the soil differences before and after the experiments scanned with BSE detector (200 $\mu\text{m}$ ). The bright areas in the initial soil indicate the atoms with a higher atomic number. After decontamination of soil, the brightness intensity on mineral surfaces decreases that approves the heavy metals removal (Figures 5b and 5c).



**Figure 5.** SEM images of (a) the initial soil, (b) soil decontaminated with Tween 80/ EDTA and (c) Brij 35/ EDTA

#### 4. CONCLUSION

This study aimed to assess the desorption kinetic and simultaneous removal of heavy metals (Pb, Zn, and Ni) and phenanthrene from natural high buffering soil using nonionic surfactants (Brij 35 and Tween 80) combined with EDTA as a chelating agent. The highest removal efficiency was observed for Pb followed by Zn and Ni. For phenanthrene in the clayey soil with high buffering capacity, the nonionic surfactants yield the maximum removal efficiency of 22%.

Tween 80 combined with EDTA, gives better solubility and extraction of heavy metals (especially Pb) and phenanthrene, compared to Brij 35. The desorption rate of heavy metals (Pb, Zn, Ni) was well described by pseudo-second order and Elovich models, while phenanthrene desorption was well described by parabolic diffusion and pseudo-second-order models. The fast desorbing fraction of heavy metals occurred in the first 24h contact time. At the end of the experiments, no significant alteration occurred in the soil structure. However, peak heights decreased due to the dissolution of minerals.

## 5. ACKNOWLEDGMENT

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## Desorption Kinetics of Heavy Metals (Lead, Zinc, and Nickel) Coexisted with Phenanthrene from a Natural High Buffering Soil

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این مطالعه با هدف بررسی واجذب رقابتی فلزات سنگین (سرب، روی، نیکل) و فناترن در طول زمان از خاکی طبیعی با ظرفیت بافری بالا انجام شده است. دو نوع سورفکتانت غیر یونی (Brij 35 و Tween 80) به همراه نمک دی‌سدیم اتیلن دی‌امین تتراسات (Na<sub>2</sub>-EDTA) به عنوان محلول‌های شوینده استفاده شد. به منظور ارزیابی داده‌های واجذب زمانی آلاینده‌ها، از پنج مدل سینتیکی استفاده گردید: معادلات توان تجربی، شبه درجه یک، شبه درجه دو، الویج و انتشار پارابولیک. بهترین راندمان حذف با استفاده از ترکیب Tween 80/EDTA بدست آمد که ۹۳٪ سرب از خاک حذف شد. واجذب رقابتی نیکل و روی تحت تأثیر کمپلکس پایداری‌شان با EDTA تغییر می‌کند. علاوه بر این، با توجه به ویژگی‌های خاک مورد مطالعه، فرایند واجذب فناترن دشوار و کند صورت گرفت. بهترین سینتیک‌های واجذب بر اساس معادلات انتشار پارابولیک (برای فناترن) و شبه درجه دو (فلزات سرب، روی و نیکل) حاصل شد. در سیستم آب-خاک-سورفکتانت استفاده شده، تغییرات ساختار خاک رخ نداد؛ با این حال Tween 80 کریستال‌های کلسیم کربنات در خاک را در حین فرایند واجذب تحت تأثیر قرار می‌دهد.

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