

INVESTIGATION OF HEAVY METALS DESORPTION ENHANCEMENT PROCEDURES IN LOW-PERMEABILITY CONTAMINATED SOILS

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Abstract: A significant amount of hydrocarbon contaminants (therefore heavy metal components) has remained in the soil due to careless industrial activities. Effective remediation is difficult, especially in low-permeability soils because it is extremely difficult to get desorption. A lot of research has been conducted on extreme soil acidification, batching of oxidants, air-fluid injection and electrokinetic treatment, there were successful but due to the risk from extreme loads, these methods can only be used solely in controlled ex-situ environments. This paper investigates an eco-friendly in situ treatment with carbamide peroxide in low-permeability silty clay. After several repetitions, the result of tests proved Cu component was fully adsorbed on clayey-silt among applied concentration and circumstances which applied, while two other components were partially adsorbed. Moreover, the experiments carried out to enhancement of desorption proved to be successful for Cu, Zn and Mn with carbamide peroxide.

Keywords: *low-permeability, adsorption, enhancement of desorption, remediation*

1. INTRODUCTION

Based on evidence from the past years, it can be concluded that environmental remediation of hydrocarbon and heavy metal contamination in low-permeability soils is not effective. One of the reasons is adsorption, in which continuous contaminant supply is ensured through rediffusion to groundwater. The purpose of our research is to determine that adsorbed contaminants can be get solution with this increase the degree of desorption. Soil contaminants can fall into the environment from different anthropogenic activities (oil industry, chemical industry, heavy industry). Moreover, near hydrocarbon compounds, heavy metals can be considered the other main contaminant group, which is one of today's remediation problems.

2. MATERIALS AND METHODS

2.1. Studied heavy metals

Some refined petroleum derivatives like fuels contain potentially toxic elements and heavy metals (Table 1). Akpoveta and Osakwe (2014) demonstrated that fuels contained several heavy metals as detailed below. This paper investigates the process of Zn, Mn, and Cu heavy metal adsorption in low-permeability clay then introduces measured results aimed at the enhancement of desorption.

Table 1
Heavy metals content of fuel

Fuel type	Zn (mg/l)	Cu (mg/l)	Cr (mg/l)	Pb (mg/l)	Cd (mg/l)
benzene	1.43	1.74	0.54	0.24	1.68
kerosene	2.63	1.98	0.33	0.41	1.33
diesel oil	2.87	1.77	0.86	1.01	1.50

2.2. Adsorption

The reversible sorption of contaminants on the surface of soil is called adsorption. During adsorption, several interfacial equilibrium processes take place simultaneously at the phase boundary resulting in material accumulation. Atoms and molecules that are located on the surface of the soil just meet their particles on one side, while on the opposite side, they encounter contaminant phase particles. The balance of adsorbed and desorbed material quantities is described by the following equation

$$dV \frac{\partial C}{\partial t} * \theta = -\rho_b * dV \frac{\partial C_c}{\partial t} \quad (1)$$

where C is pore fluid concentration (mg/l), C_c is contaminant concentration in soil, ρ_b is soil density, θ is water content, V is full volume. If chemical equilibrium has been established the concentration of the adsorbed component can be calculated using the following relationship

$$C_c = K_d * C \quad (2)$$

where K_d is the distribution coefficient (L/g).

Equation (2) shows the relationship between the concentration of pore fluid and the contaminant, which is determined by a sorption isotherm. In addition, equation (2) also depends significantly on temperature, thus to rule out temperature dependence, the relationship between the concentration of the pore fluid and the adsorbent is taken at a constant temperature.

Adsorption from the solution is influenced by the quantitative ratio of the adsorbent and adsorbate. According to Kroecker's equation (Kroecker, 1892), in a solution of known volume and concentration, the specific adsorbed amount decreases as the mass of the adsorbent increases. In case of contact between the

solution and solid adsorbent, after a sufficiently long time, the adsorption equilibrium is established. The time required to reach equilibrium depends on the quality of the adsorbent and the adsorbate as well as the structure of the adsorbent. After equilibrium has been established, the adsorbent can be separated from the solution then equilibrium concentration can be measured using a carefully selected method. At constant temperature, this equilibrium can be described by adsorption isotherms. The obtained results determine the points of the sorption isotherm whose points we can fit into curves to get the Freundlich and Langmuir isotherms, which are most often used.

2.3. Parameters affecting adsorption

Adsorption is controlled by several influencing factors. The effect of ionic strength for cation adsorbing is multifaceted. According to the research of Weng and Huang (2004), the cation binding on a negatively charged surface decreases with the increase in the ionic strength of the solution, which reduces the cation activity of the adsorbent. A higher temperature range increases the proportion of particles that have sufficient energy to overcome the activation energy barrier necessary for sorption processes; furthermore, the mobility of ions also increases with increasing temperature. According to Fick's first law, diffusion is proportional to the concentration gradient of the sorption system which is an extremely important factor, since adsorption is in most cases a diffusion-controlled process. It follows from the above that the number of cations fixed by the soil increases at higher temperatures. The solubility of pollutant components can be influenced by the redox potential significantly. In highly reductive ($-100\text{mV} >$) conditions, the mobility of individual cations can be decreased. Furthermore, time as an adsorption factor also affects the amount of bound adsorbent significantly.

The chemical reaction is significantly influenced by soil pH. In an acidic environment, the degree of cation adsorption decreases while the solute concentration of toxic heavy metals and/or organic hydrocarbon contaminants can increase. Furthermore, there are some other parameters (e.g., CEC, SOM) affecting the sorption processes, but these are not detailed in this article.

2.4. Analytical solution for 1D column model

The spread of water-soluble contaminants is determined by two main processes; advection which is physically or chemically dissolved substances mass flow in pores. The other one is dispersion, which is the pollutant means its spatial dispersion. Ogata and Banks solve the ADE (advection-dispersion, diffusion) equation given below

$$D * \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R * \frac{\partial C}{\partial t} \quad (3)$$

with the following boundary and initial conditions: $t = 0 - 150$ minutes and $C = C_0$ ($x = 0$) then $t > 150$ minutes, $x = 0$, $C = 0$. Here C is the concentration (ML^{-3}), x is

the distance (L), R is the retardation factor, D is the effective dispersion/diffusion (L^2T^{-1}), v is the flow velocity (LT^{-1}) and C_0 is the initial concentration (ML^{-3}). For ADE equation the Ogata-Banks' analytical solution is

$$C = C_0 * \frac{1}{2} \operatorname{erfc} \left(\frac{R*x-v*t}{2\sqrt{D*R*t}} \right) + \frac{1}{2} e^{\frac{v*x}{D}} * \operatorname{erfc} \left(\frac{R*x+v*t}{2\sqrt{D*R*t}} \right) \quad (4)$$

2.4.1. Advection

The advective contaminant-flux equation is the product of the average flow velocity and the concentration given in Equations (5)-(7)

$$F_x = \frac{dM_x}{dy dz dt} = v_x * C \quad (5)$$

$$F_y = \frac{dM_y}{dx dz dt} = v_y * C \quad (6)$$

$$F_z = \frac{dM_z}{dy dx dt} = v_z * C \quad (7)$$

where M is the chemical amount of the contaminant, n_e is effective porosity and velocity v is

$$v = -\frac{K}{n_e} \frac{dh}{dx} \quad (8)$$

2.4.2. Diffusion

The mass flow resulting from spatial chemical potential differences is called diffusion (Fick's first law). Diffusion resulting from concentration differences is called ordinary diffusion. Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration. As Fick's I. law gives the diffusive flux

$$F_D = D_{eff} * \frac{dC}{dx} \quad (9)$$

The diffusion coefficient depends on the materials, temperature, electrical fields.

2.4.3. Hydrodynamic (or mechanical) dispersion

Hydrodynamic (or mechanical) dispersion is caused by local micro-changes in the size and direction of the flow velocity within the porous medium. Dispersion causes transport (or spreading) of the solute plume ($D = D_{eff} + D_{mech}$). Dispersion reflects the fact that not everything in the porous medium travels at the average water flow

speed. Some path is faster, some slower, some longer, some shorter. This results in a net spreading of the solute plume that looks very much like a diffusive behavior. From Ogata-Banks equation one can obtain

$$D * \frac{\partial^2 c}{\partial x^2} \quad (10)$$

2.4.4. Retardation

When solutes flow through a porous medium they can interact with the solid phase. They can sorb and desorb. The net result is a process called retardation that effectively slows the transport of a solute through a porous medium. The value of R depends on the solute, water chemistry and geochemical make-up of the porous medium. From a mathematical perspective it can be thought of as a rescaling in time.

2.5. Sorption tests

Adequate model material was acquired from the settlement of Aszód, Hungary. These soil samples were investigated by soil-mechanics tests and laser scattering particle size analysis, as pale-brown clayey-silt.

2.5.1. Dynamic sorption - Column test

The experiment was performed with Cu, Zn and Mn ions that can simulate competitive sorption and to evaluate and investigate these heavy metals retention and transport under saturated flow conditions. The pH value of the contaminant solution was set to 7.7 and the experiment was made at 20 °C temperature. The steady-state flow was assured by an HPLC pump. The cylindrical column was made of steel, 250 mm in length and 10 mm in inner diameter and was closed by two steel caps. The column was filled with a mixture of clayey-silt (10%) and quartz sand (90%). The mixing was needed because the permeability of clayey silt is too low, thus that would have resulted that the fluxation (through column) would have taken too much time. The stock-solution was made of 1000 ml distilled water wherein dissolved 0,616 g of Mn, 0,786 gr of Cu and 0,879 gr of Zn. Immediately the system was compiled, a solution of heavy metals was injected upwards into the system at a constant flow rate (1 cm³/s) until 150 minutes. Samples of 5 ml were collected from the effluent with an auto-sampler at every 5 minutes time interval, it resulted 30 pieces of samples at the first section of test. Second interval was holding 50 minutes which resulted 10 samples. In interval the column-system was leached with distilled water to isolate the effect of treatment which is on third interval. At the third interval applied carbamide-peroxide (0,186 g/250 ml distilled water) as an oxidizer can observe its desorption affect. The outlet samples Zn, Mn and Cu concentrations were measured using Agilent Spectroscopy (MP-AES).

3. RESULTS AND DISCUSSION

Several quantitative methods are suggested to be used to analyze adsorbates. During this research the Agilent MP-AES Spectrometer was used to determine the concentration of Zn, Mn and Cu components used in column experiment. The Agilent Spectroscopy (MP-AES) is an analytical technique designed with a higher sensitivity that detects sub ppb levels and runs on air instead of combustible gases. The Agilent MP Expert software is used to automatically optimize the viewing position and the nebulization pressure for each wavelength selected to maximize sensitivity. We performed a total of three series of measurements with the same parameters, so that we can adequately support the obtained results. Unfortunately, the 2nd measurement was not successful due to other reasons, thus this measurement is not presented in this paper, we only deal with the results of the 1st and 3rd measurements.

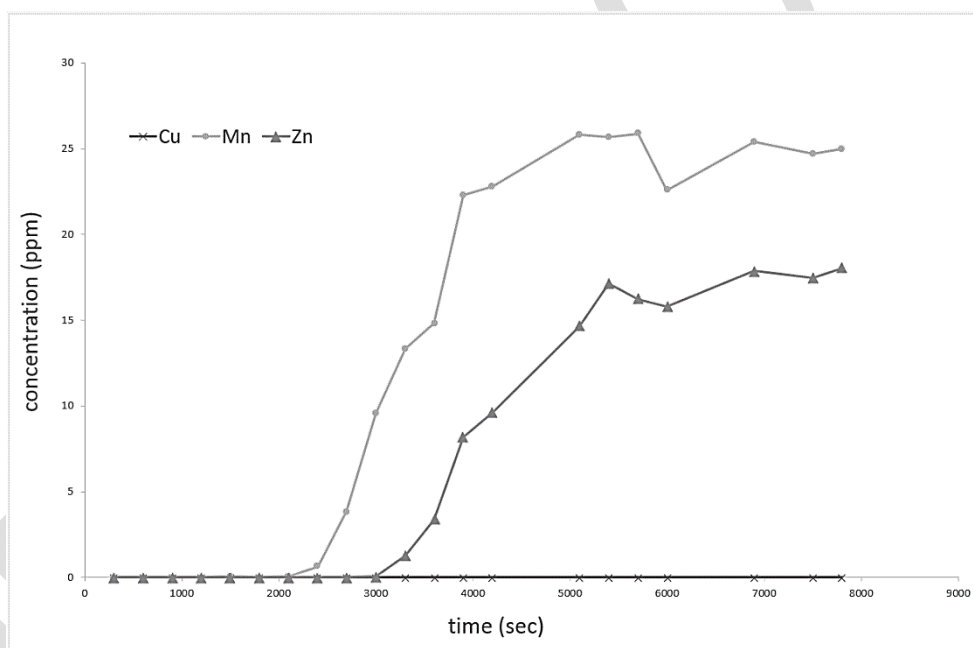


Figure 1

Breakthrough curve of the 1st competitive adsorption-test

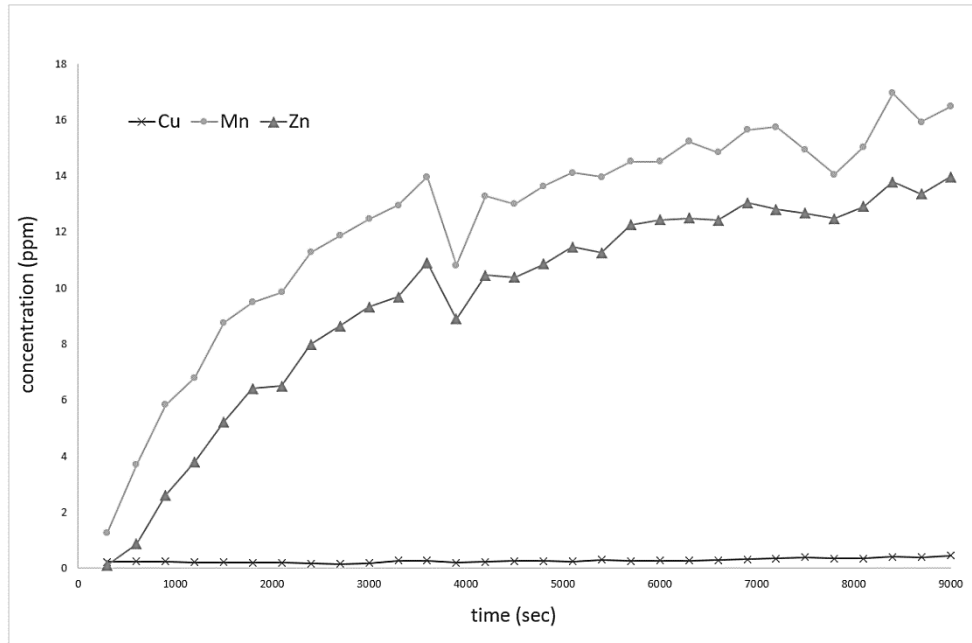


Figure 2
Breakthrough curve of the 3rd competitive adsorption-test

The breakthrough curves are presented in Figures 1-2, where the performance of the column system can be estimated. On the score of results, one can see the saturation concentrations. Moreover, the analytical solution suggested by Ogata and Banks was used to solve the advection-dispersion equation for Zn-Mn-Cu competitive adsorption. By applying the inverse modelling we can determine the retardation factor R and diffusion value. Finally, we can see the curves had a similar breakthrough time, but the third measurement series has a longer breakthrough and saturation time. The input data of the model are shown in Table 2.

Table 2
Initial values of the input parameters

Model input data	Value
v (cm/s)	0,019
x (cm)	25,0
A (cm ²)	0,786

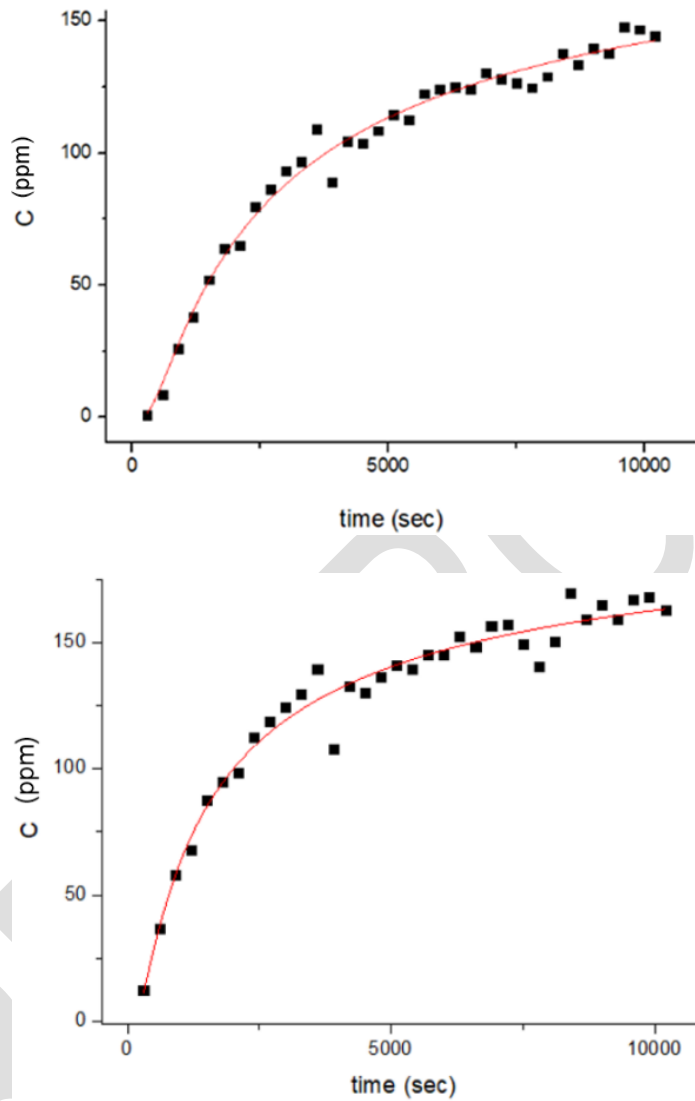


Figure 3

Zn (upper) and Mn components Ogata-Banks fitting curves

The plots given in Figure 3 show a good agreement with the column experimental data in the case of Cu and Zn components ($R^2 > 0.97$). In virtue of results Mn has the biggest adsorption factor on clayey silt. Furthermore, uninterpretable result was got for Cu, which means that it was fully adsorbed by clayey silt. Finally gotten dispersivity values are suitable.

Table 3
Obtained results from 3rd column test

Metal	Estimated			Measured		
	D (cm ² /s)	R (-)	R ² (-)	v (cm/s)	x (cm)	C ₀ (ppm)
Zn – 3 rd	2.24091	15.38587	0.98595	0.019	25	200
Mn – 3 rd	2.0261	7.53195	0.97024	0.019	25	200
Cu – 3 rd	-	-	-	0.019	25	200

During column tests we can observe that the adsorption of the manganese and zinc components already separated each other at first, moreover we can see that the retardation factor of Manganese is twice of Zinc. Finally, we increased desorption by using oxidizer aggregate, is carbamide peroxide. It is a soft-oxidizing agent of which 10 gr was dissolved in 200 ml distilled water as “treatment solution”. During the desorption test, we can observe when the treatment solution washed all column the effluent concentration was being increased in a little period (20 minutes) then rising stopped then followed by a slight decreasing phase (treatment session) (Figures 4-5).

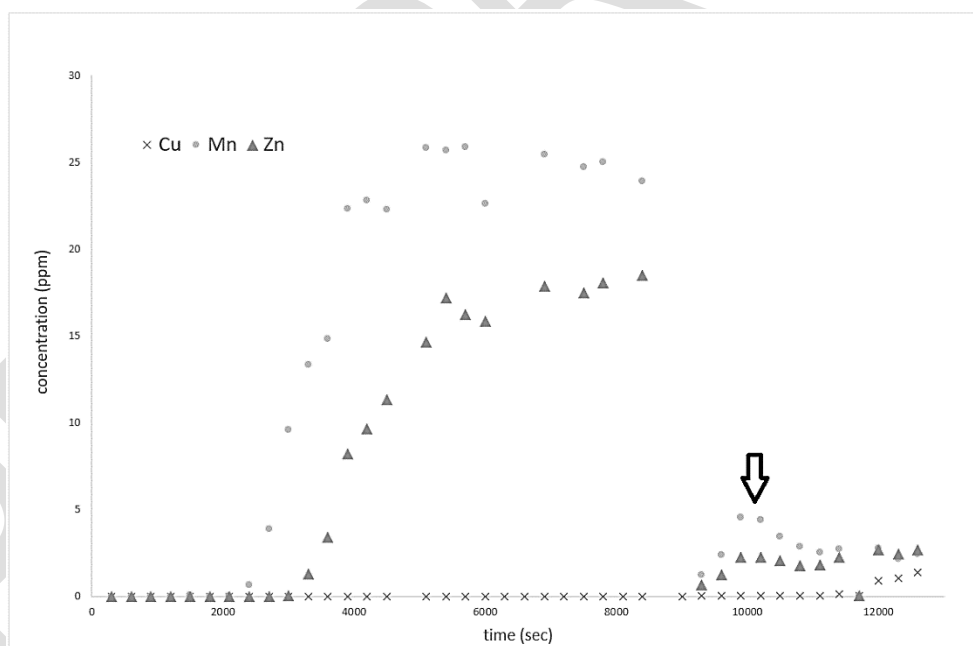


Figure 4
Concentration changes as a result of carbamide-peroxid treatment (1th)

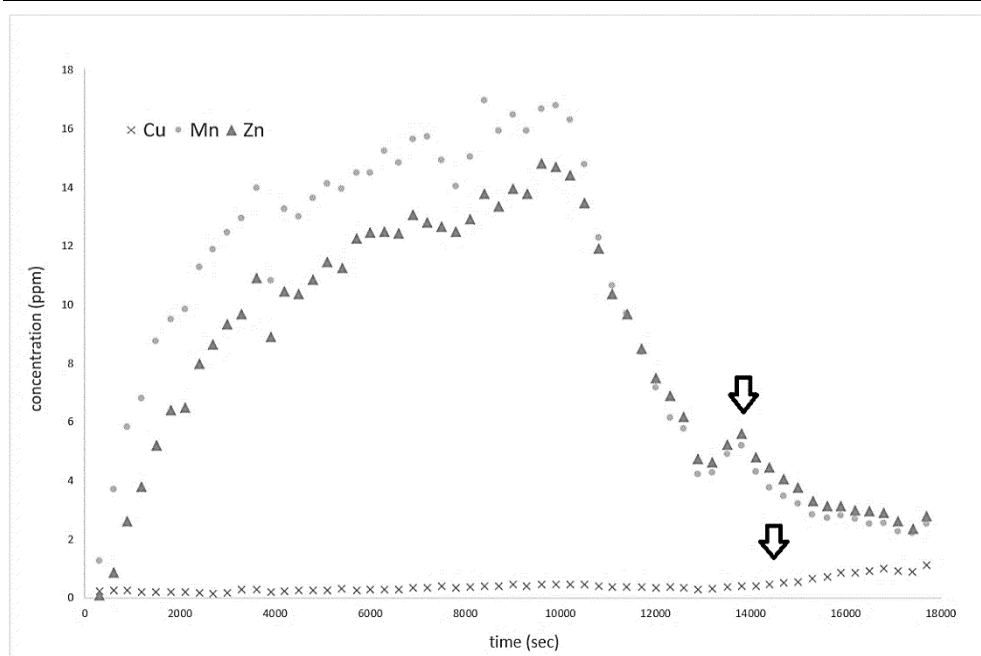


Figure 5
Concentration changes as a result of carbamide-peroxid treatment (3rd)

4. CONCLUSIONS

In virtue of investigations Cu component was fully adsorbed on clayey silt among applied concentration and circumstances which applied. The experiments carried out to enhancement of desorption proved to be successful for Cu, Zn and Mn, which have not yet been proven with the present results, but it seemed to be encouraging. We believe that the treatment with carbamide-peroxid has a measurable effect, which can be effective in increasing desorption at a higher concentration and by changing other conditions. We are continuing our research using other possible oxidizing agents and using another potential treatment (e.g., temperature, aggregates, pH, electricity).

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