

LEAD REMOVAL FROM CONTAMINATED SOIL BY ELECTROKINETIC REMEDIATION TECHNIQUE

Nice Mika Sakamoto Kaminari, nice.kaminari@gmail.com

Renata Bachmann Guimarães Valt, revalt@bol.com.br

Haroldo de Araújo Ponte, hponte@ufpr.br

Maria José Jerônimo de Santana Ponte, mponte@ufpr.br

Federal University of Parana, Laboratory of Environmental Technology (LTA), PO Box 19011, ZIP CODE 81531-990, Curitiba, PR, Brazil

Abstract. *There are many places in the world, where the soil has been seriously contaminated due to inappropriate disposal practices, industrial activities and pollutants. The polluted soil becomes a threat to the environment due to toxic substances present as heavy metals. It is important to consider that these metals, besides causing damage to the environment, also offer serious risks to human health. Alternative techniques are developed to remove these contaminants from soil. The electrokinetic remediation technique has been considered promising because it has excellent potential for restoration of sites contaminated by heavy metals. The electrokinetic remediation process consists of applying a low intensity direct current through the ground between two or more electrodes. Thus, the objective of this research is to evaluate the lead ions removal efficiency using the electrokinetic remediation of contaminated soil. The variables chosen were following: the applied potential, the remediation time and amount of kaolin contained in the soil. In order to verify the influence of these variables was used the full factorial design to obtain the desired response (removal efficiency) as empirical function.*

Keywords: *electrokinetic remediation, heavy metal removal, full factorial design.*

1. INTRODUCTION

Soil contamination by heavy metals, mainly by lead, can occur in several ways: natural, geological and also through activities performed by human activities (mining, industry and transport). Unfortunately the industrial activity coupled with the increase of municipal waste dump, has brought a considerable increase in the amount of metals in soil (Mavropoulos, 1999). This results in reduction of crop fields and agricultural contamination of water sources (Chaves, 2008).

Levels of lead in soil are in the range of 10 to 70 mg / kg (Who, 1995). According Larini (1993), the lead content in soil varies from region to region, where levels are higher in industrial areas than in isolated areas

There are several technique for soil remediation as: precipitation, incineration, phytoremediation, electrochemical processes, etc. All based on two processes in situ and ex situ.

The electrokinetic remediation is an in situ technique consists of applying a direct current of low intensity (mA/cm²) or applying a potential between the electrodes located on the soil. The contaminants are mobilized in the form of charged species, particles or ions. Applied current mobilizes species electrically charged particles and ions in the soil. One consequence of this technique is the occurrence of parallel reactions such as reduction of hydrogen or oxygen generation, reducing the process efficiency.

The success of electrokinetic remediation depends on the mineralogical structure of the soil. Several studies (Hamed et al. 1991; Pamukcu and Whittle, 1992, Acar et al. 1993; Tondorf and Hick, 1994, Iryoda, 2008, Guaracho et al., 2009) have shown that the electrokinetic remediation process is applied to clays with low sorption and buffering capacity (Hamed et al., 1991). Several studies were conducted using the electrokinetic remediation of soils contaminated with lead, copper and cadmium (Hamed et al. 1991; Pamukcu and Whittle, 1992, Acar et al. 1993; Tondorf and Hick, 1994), obtaining satisfactory results.

The aim of this study is to evaluate the efficiency of removal of lead ions using the technique of electrokinetic remediation in contaminated soils. The variables that will be studied are: concentration of kaolin in soil contaminated with a solution of lead nitrate (2000 ppm), applied potential and time of remediation. In order to verify the influence of these variables was used the full factorial design to obtain the desired response (removal efficiency) as empirical function.

1.1. Soil

According to Vieira (1988), the soil is defined as an unconsolidated surface consists of layers that are deferred by the physical nature and chemical, mineralogical and biological, which develop with time under the influence of climate and biological activity itself. Therefore, the mineralogy is the factor that controls the shape, grain size and the physical and chemical properties of soil. These particles are composed mostly of crystalline minerals, which may be clay minerals or not clay.

The kaolinite is a clay mineral commonly found in tropical and subtropical soil (Bortoluzzi et al., 2007). This mineral has particular importance with regard to problems of soil contamination due to its physical-chemical characteristics and how they interact with contaminants, interfering significantly in the transport and remediation

A soil sample obtained in Maringá - PR was examined in the study of Costa (2002), indicating that the percentage composition of kaolinite is in the range of 60%, as shown in Tab. 1.

Table 1. Percentage composition of clay soils in the region of Maringá – PR (Costa, 2002)

| Composition (%) | Soil types | | |
|--------------------------------|------------|--------|----------|
| | Latosol | Neosol | Vertisol |
| Fe ₂ O ₃ | 16 | 14 | 6 |
| Gibbsite | 6 | 6 | 0 |
| Kaolinite | 68 | 65 | 54 |
| Clay (2:1) | 10 | 15 | 40 |

Kaolin is a material / ore formed by a group of hydrated silicates of aluminum, mainly kaolinite and halloysite

The structure of kaolinite has a great advantage in many cases due to its high chemical stability and low coefficient of expansion. So when it interacts with other elements in the soil contributes to the mechanical stability of the soil.

However, the interactions of heavy metals (cations) with kaolinite can affect its structure, its influence on mechanical and chemical properties such as the ability to increase their size, compression capability and behavior of the double layer.

2. METODOLOGY

For this study was designed as Yeung (1997) and set up an experimental unit represented schematically in Fig. 1.

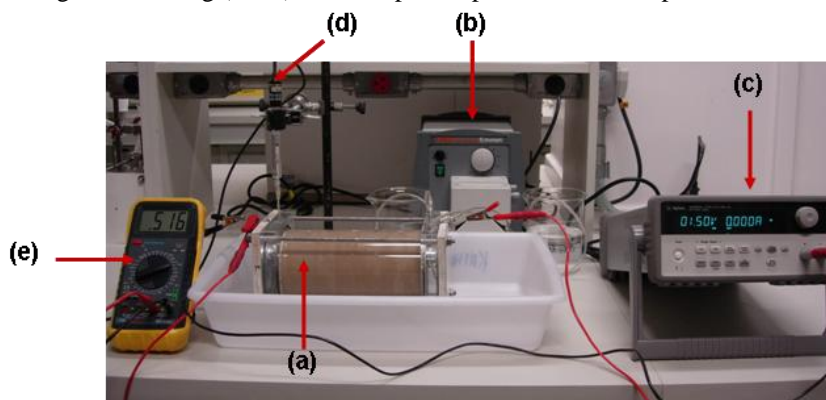


Figure 1. Experimental unit: (a) electrokinetic reactor, (b) peristaltic doser pump, (c) Power supply, (d) reference electrode, (e) multimeter

The analyses of the concentration were performed in the spectrophotometer (model UV FEMTO 600 Plus). The voltammetric study was realized in the PGZ 301 potentiostat Voltalab of Radiometer Voltmaster 4 Analytical and software coupled to a microcomputer. We used an electrochemical cell composed of the following electrodes: auxiliary electrode screen of platinum, reference electrode Hg/Hg₂Cl₂/KCl Sat (SCE) and working electrode (304 stainless steel, graphite, Pb/Sb and Ti/Ru- Ir). The solution used for voltammetric analysis was 0.1 M NaNO₃ (supporting electrolyte).

The bed consisted of sand and kaolin, sand was chosen because of its ability to be an inert soil. The kaolin clay was chosen because it comprised about 95% of tropical soils and also due to their physical and chemical characteristics that interact with the contaminants, significant effects on the transport and remediation (Iryoda, 2008).

The sand was left to rest for 24 h in a 10% H₂SO₄ solution and 10% HCl solution to remove the influence of any organic contaminant present. Then, it was washed again with deionized water and dried in a sand bath for 48 h to remove moisture.

The three steps used in the experimental design included statistical design experiments, estimation of coefficients through a mathematical model with response prediction, and analysis of the model's applicability. The experiment was conducted with one response variable in a full factorial design. Removal efficiency (R) was selected as dependent variable in the experiment. Three independent parameters were chosen as variables: kaolin concentration; applied potential; and time remediation. Eleven experiments are needed to estimate the coefficients of removal efficiency using multiple linear regression analysis. All experiments were performed in duplicate.

Removal efficiency (R) was calculated based on the follow equation.

$$R = \frac{(C_i - C_f)100}{C_i} \tag{1}$$

where:

- R = Removal efficiency (%);
- C_i = Initial Concentration (ppm);
- C_f = Final Concentration (ppm).

3. RESULTS

The polarization curves of anodic and cathodic (Fig. 2) were performed with a scan rate of 1 mV / s, which is the recommended speed for electrochemical systems. The curves were performed in solutions of 0.1 M NaNO₃.

The anodes tested were graphite, stainless steel 304 and Ti/Ru-Ir; the cathodes tested were Pb/Sb and stainless steel 304.

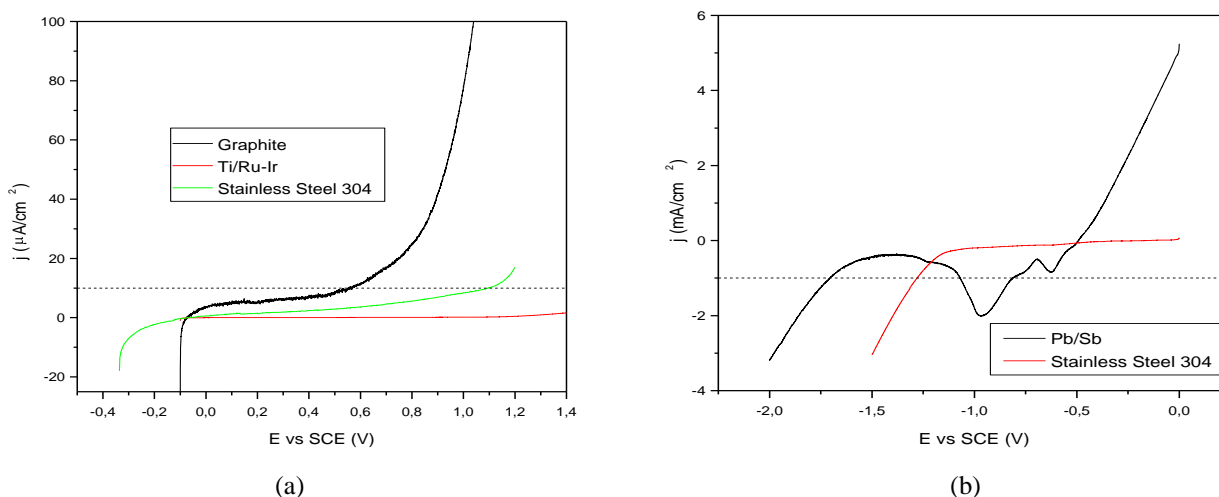


Figure 2. Polarization Curve: (a) anodic, (b) cathodic

Through Fig 2 (a) the electrode Ti/Ru-Ir showed higher potential for the oxidation of oxygen (ROO) and Pb / Sb electrode with higher potential for reduction reaction of hydrogen (RRH). So choosing these materials for the anode and cathode respectively. These two reactions are the parallel reactions that occur simultaneously at the anode and cathode.

The experimental design was used to test the efficiency of removal of lead (R) (Tab.2). The coded values are presented in Tab. 3, these values were previously analyzed and tested to be adopted.

The Ti/Ru-Ir electrode showed higher potential for the oxygen oxidation reaction (ROO) (Figure 2a) and Pb/Sb electrode showed the greatest potential for hydrogen reduction reaction (RRH) (Figure 2b). So choosing these materials for the anode and cathode respectively. These two reactions are the parallel reactions that occur simultaneously at the anode and cathode.

Table 2. Experimental Design

| Experiments | Potential (E) | Kaolin (C) | Time (t) | R (%) |
|-------------|---------------|------------|----------|-------|
| 1 | -1 | -1 | -1 | 78,15 |
| 2 | 1 | -1 | -1 | 89,29 |
| 3 | -1 | 1 | -1 | 82,50 |
| 4 | 1 | 1 | -1 | 61,42 |
| 5 | -1 | -1 | 1 | 95,25 |
| 6 | 1 | -1 | 1 | 72,58 |
| 7 | -1 | 1 | 1 | 91,05 |
| 8 | 1 | 1 | 1 | 94,45 |
| 9 | 0 | 0 | 0 | 80,05 |
| 10 | 0 | 0 | 0 | 79,96 |
| 11 | 0 | 0 | 0 | 79,99 |

Table 3. Values of coded levels

| Variable | -1 | 0 | 1 |
|------------------|----|----|----|
| Time (hours) | 2 | 3 | 4 |
| Potential (Volt) | 5 | 7 | 9 |
| Kaolin (%m/m) | 20 | 40 | 60 |

The variables that influence the response (removal of lead) can be viewed on the Pareto chart (Fig. 3).

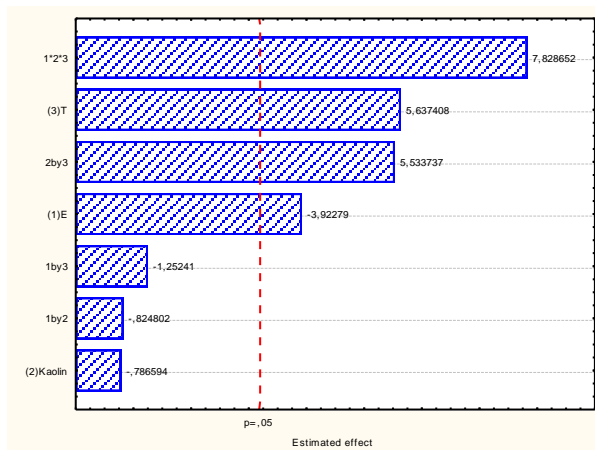


Figure 3. Pareto Chart

Using the least squares method and with the statistical software the removal of lead can be represented by Equation (2) with determination coefficient (R^2) of 95.95%

$$R = 82,24 - 7,3E + 10,49t + 10,3C.t + 14,57E.C.t \tag{2}$$

The p-value in the Analysis of Variance (ANOVA) was less than 5% of the computed F-values (F_c) obtained for R was greater than the F-value in the statistical table (F_t) (Tab.4), indicating that the model was significant at a high confidence level (95%). The p-value probability was also relatively low ($p < 0.05$), indicating the model's significance.

Table 4 – The Analysis of variance (ANOVA) for equation 2

| Source | Sum of Square | Degree of Freedom | Mean Square | F_c |
|---------|---------------|-------------------|-------------|-------|
| Model | 963,47 | 4 | 240,87 | 35,42 |
| Residue | 40,65 | 6 | 6,8 | - |
| Total | 1004,12 | 10 | - | - |

$$F_t = 4,53$$

The Fig. 4 shows the behavior of the removal efficiency (R) versus time (t) and potential (E), keeping constant the concentration of kaolin in the minimum level (20%) this was the optimum condition where we got the greater efficiency of removal of lead (95.25%).

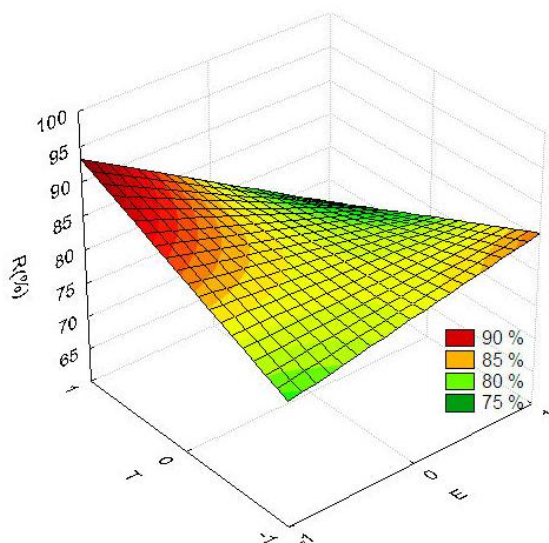


Figure 4. Removal efficiency as a function of time and keeping potential concentration of kaolin by 20%.

4. CONCLUSIONS

The present results were satisfactory, because it provided a good analysis of the interference of variables in the electrokinetic remediation of lead. Through statistical analysis we realized that all three variables influence in lead removal. Among the electrodes studied Ti/Ru-Ir and Pb/Sb showed high potential of ROO and RRH are therefore chosen as anode and cathode, respectively.

With these electrodes the optimum condition was obtained in experiment 5, with 20% kaolin, 4 hours of remediation and 5.0 V potential, with 95.25% of removal efficiency. The values are in agreement with the literature, in which the amount of kaolin had a significant effect of reducing lead removal, as also observed in these experiments.

The electrokinetic remediation proved to be an efficient process with great potential for application in the removal of contaminants in mixtures of sand and kaolin. This efficiency is demonstrated by the influence of migration, by reducing the concentration of lead ion in relation to cases involving only flow without applied potential.

5. ACKNOWLEDGEMENTS



4. REFERENCES

- Acar, Y.B. and Alshawabkeh, A.N. "Principles of electrokinetic remediation", *Environ. Sci. Technol.*, Vol. 27, No 13, pp. 2638-2647.
- Bortoluzzi, E.C. and Pernes, M., Tessier, D., 2007, "Interstratificado caulinita-esmectita em um argissolo desenvolvido a partir de rocha sedimentar do sul do Brasil", *Revista Brasileira de Ciência do Solo*, Vol. 31, pp.1291-1300.
- Chaves, E.V., 2008, "Absorção de metais pesados de solos contaminados do aterro sanitário e pólo industrial de Manaus pelas espécies de plantas Senna multijuga, Schizolobium amazonicum e Caesalpinia echinata", 87p. Tese (Doutorado em Biotecnologia) Universidade Federal do Amazonas.
- Costa, A.C.S., Almeida, V.C., Lenzi, E. and Nozaki, J., 2002, "Determinação de cobre, alumínio e ferro em solos derivados do basalto através de extrações sequenciais", *Quim.Nova*, Vol. 25, pp. 548-552.
- Guaracho, V.V., Kaminari, N.M.S., Ponte, M.J.J.S., Ponte H.A., 2009, "Central composite experimental design applied to removal of lead and nickel from sand", *J. Hazard. Mater.*, No. 172, pp. 1087-1092.
- Hamed, J., Acar, Y.B. and Gale, R.J., 1991, "Pb (II) removal from kaolenite by electrokinetics" *Journal Geotech Eng*, Vol. 17, pp. 241-271.
- Hicks, R.E. and Tondorf, S., 1994, "Eletrorestoration of metal-contaminated soils", *Environ Sci Technol*, Vol. 28, pp. 2203-2210.
- Iryoda, K.I., 2008, "Estudo da influência da caulinita na remediação eletrocinética em solo contaminado com chumbo", 71p. Dissertação (Mestrado em Engenharia de Materiais e Processos) – Setor de Tecnologia, Universidade Federal do Paraná.

- Larini, L., 1993, "Toxicologia", Editora Manole, Segunda Edição.
- Mavropoulos, E., 1999, "A hidroxiapatita como absorvedor de metais", 105p. Dissertação - Fundação Oswaldo Cruz, Escola Nacional de Saúde Pública.
- Pamukcu, S. and Wittle, J.K., 1992, "Electrokinetic Removal of Selected Heavy-Metals from Soil", Environ Prog, Vol.11, No. 3, pp. 241-250.
- Vieira, I.S., 1988, "Manual da Ciência do Solo: Com Ênfase em Solos Tropicais", Ed. Agronômica Ceres, 2 ed., São Paulo, Brasil.
- WHO - Human Exposure to Lead, 1995, In: Human Exposure Assessment Series, WHO.
- Yeung, A.T., Scott, T.B., Gopinath, S., Menon, R.M. and Hsu, C., 1997, "Design, fabrication and assembly of an apparatus for electrokinetics remediation studies". Geotechnical Testing Journal, Vol. 20, pp. 199-210.

5. RESPONSIBILITY NOTICE

The authors are the only responsables for the printed material included in this paper.