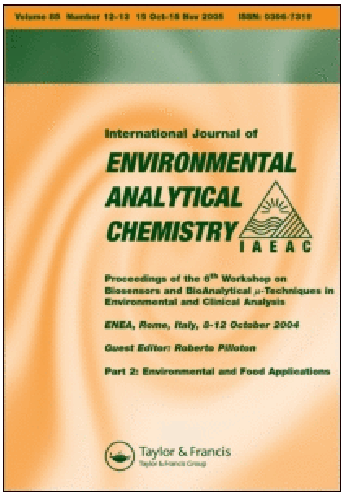

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# Extraction of Chromium from Contaminated Soils

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# EXTRACTION OF CHROMIUM FROM CONTAMINATED SOILS

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A chromium contaminated soil area was studied, in order to recover metals present as contaminants in soils, associated to the soil remediation. A leaching solution of HCl (0,1 M) and NaCl (1,9 M) was used to extract the chromium content. The concentration of chromium in the leached solutions was analysed. For each contaminated sample, the evolution with time of chromium concentrations in leaching solutions was studied. A Langmuir-type model showed a good fit to experimental data, allowing the determination of the maximum concentration of chromium that can be reached in the leaching solutions, and the time required to attain a fixed leached concentration of chromium. The influence of natural organic matter content of the soil on the leaching time was evaluated. The results obtained allows to conclude that the natural organic matter content significantly influences the extraction time, due to the metal complexation by dissolved organic matter present in leaching solutions.

*Keywords:* Chromium; leaching process; soil natural organic matter content; contaminated soil

## INTRODUCTION

Soil and groundwater pollution has became a major issue in the last few years affecting agriculture, industry, housing and involving large amounts of money and time [1].

The understanding of the processes governing the migration and plant availability of trace metals in soils is essential for predicting the environmental impact of the spreading of metals contained in wastes, and the efficiency of their recovery.

The transport of contaminants in the environment is a complex process; among other factors it involves the adsorption of these compounds by soil components such as organic materials and non-clay and clay minerals [2]. The amount of

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heavy metals retained in soil depends not only on the types of soils, but also on the different heavy metals involved. The mechanisms suggested in several studies on heavy-metal retention include precipitation as solid phases (oxides, hydroxides, carbonates), ion exchange and complexation reactions [3,4].

The binding mechanisms for metals in association with organic matter include adsorption, complexation and chelation (complexation by coordination with multidentate ligands) [5,6]. The complexes formed with monodentate ligands are less stable than those formed with multidentate ligands. As it might be expected, the natural organic component of the soil constituents has a high affinity for heavy metal cations, because of the presence of ligands or groups that can form chelates with the metals [7].

Leaching studies were carried out, in order to recover metals present as contaminants in soils, associated to the soil remediation. Laboratory leaching studies were done to extract metals with a solution of HCl (0,1 M) and NaCl (1,9 M) [8]; at the same time, the content of metal contaminant was quantified.

Ten contaminated samples were studied, considering their different level of contamination and their different natural organic matter content. All samples were characterised after previous treatment.

For each contaminated sample, the evolution with time of heavy metal concentrations in leaching solutions was studied. A Langmuir-type model showed a good fit, allowing the determination of the maximum metal concentration that can be reached in the leaching solutions, and the time required to attain a fixed leached concentration of metal:

$$\frac{C}{C_m} = \frac{t}{t+B} \qquad [1]$$

Where:

$C$ – leached concentration;
$C_m$ – maximum leached concentration;
$t$ – leaching time;
$B$ – constant.

Rearranging equation 1:

$$\frac{t}{C} = \frac{t}{C_m} + \frac{B}{C_m} \qquad [2]$$

By plotting $t/C$ against $t$, a straight line can be obtained, where the slope is $1/C_m$ and the intercept is $B/C_m$. Using experimental data, $C_m$ and $B$ values can be calculated.

The extraction behaviour of the metal contaminant in each type of soil was interpreted, considering the influence of the natural organic matter on the leaching time.

## EXPERIMENTAL

The natural soil studied was constituted essentially of decomposed organic debris. Ten samples with different contents of natural organic matter and similar mineral characteristics were collected, from different places at a forest site contaminated by the leaching of wastes from metal foundry industries, a very common occurrence in Portugal. After to be sampled, these soils that do not have organic contamination, were stored in appropriate vessels. At the laboratory, the samples were placed in a clean area to avoid any possible contamination and dried at 35°C during two weeks. After which each sample was sieved in order to get granulometric fractions of the soils with uniform physical and chemical properties; for that, a 2 mm non-metallic sieve was used. The smallest size fraction was reduced to an appropriate volume by quartering. The reduced samples were then stored in bottles for laboratory treatment.

The determinations of soil water content (W), particle density ($\rho_p$), bulk density of the disturbed soil ($\rho_a$) and porosity ($\varepsilon$) were made using the procedures described by Tan [9]. The pH was measured in a solution of 50 g of soil in 50 ml of distilled water, with a potentiometer Orion 701A model and with an 8165BN Orion electrode after 15 minutes of mixing [9]. The natural organic matter content (OM) was quantified by the Tinsley method; the carbon oxidation was made with potassium dichromate under strong acidic conditions [9,10].

The transfer of chromium from the soil to the liquid phase was done through a leaching process, at constant stirring velocity and temperature (50°C); 100 g of soil were leached with 1000 ml of a solution containing 0,1 M HCl and 1,9 M NaCl [8]. Leached samples of 20 ml were taken out at 1, 2, 6, 12, 24, 36 and 48 hours. Leached chromium was analysed by a Perkin Elmer atomic absorption spectrophotometer, model 3100.

The dissolved organic matter expressed in total carbon was determined by an Ionics Total Organic Carbon Analyser, model 1258 (West 800).

The adjustments of concentrations of dissolved organic matter were made adding organic matter extracted from the soil sample with the highest content, using dilute solution of NaOH for extraction. The adjustments of pH were made with solution of HCl 0,1 M.

All the experiences were repeated until the differences in results were smaller than 3%.

## RESULTS AND DISCUSSION

The physical and chemical characteristics of the ten contaminated samples are shown in Table I. The fit of Equation 2 for leached chromium in sample I is shown in Figure 1 as an example. The Langmuir-type model showed a good fit as can be observed in Figure 2 for chromium in sample I. As the behaviour was similar for all studied samples, it was possible to determine the maximum concentration of chromium that can be reached in the leaching solutions ($C_m$), and the time required to attain a fixed leached concentration of chromium.

TABLE I - Physical and chemical characteristics of the samples

| *Sample* | $\rho_p$ (g cm$^{-3}$) | $\rho_a$ (g cm$^{-3}$) | $\varepsilon$ (%) | *W* (%) | *pH* | *OM* (%) |
|---|---|---|---|---|---|---|
| A | 2,51 | 0,669 | 73,3 | 3,8 | 5,0 | 34,4 |
| B | 2,61 | 0,790 | 69,8 | 3,1 | 5,1 | 32,4 |
| C | 2,53 | 0,835 | 67,0 | 3,1 | 4,8 | 33,7 |
| D | 2,53 | 0,969 | 61,7 | 2,1 | 5,0 | 26,9 |
| E | 2,71 | 0,870 | 67,9 | 2,8 | 5,3 | 34,9 |
| F | 2,99 | 0,845 | 71,7 | 3,1 | 5,2 | 40,7 |
| G | 2,65 | 0,716 | 73,0 | 3,8 | 5,0 | 38,7 |
| H | 2,65 | 0,829 | 68,7 | 3,3 | 5,0 | 37,9 |
| I | 2,80 | 0,720 | 74,2 | 3,7 | 5,2 | 41,6 |
| J | 2,60 | 0,841 | 67,8 | 3,1 | 5,5 | 38,6 |

The maximum leached concentrations are listed in Table II for all studied samples. All the metallic contaminant species present in the soil must be removed to the liquid phase when leaching is carried out at enough low pH [3,5]. Therefore, the leaching solutions were selected in order to guarantee a pH compatible with the complete removal of the metallic contaminant species, since the initial aim was their recovery. Thus accordingly, through the maximum concentration of chromium in the leaching solutions, it was possible the calculation of chromium content of soil samples ($m_m$). These values are also expressed in Table II.

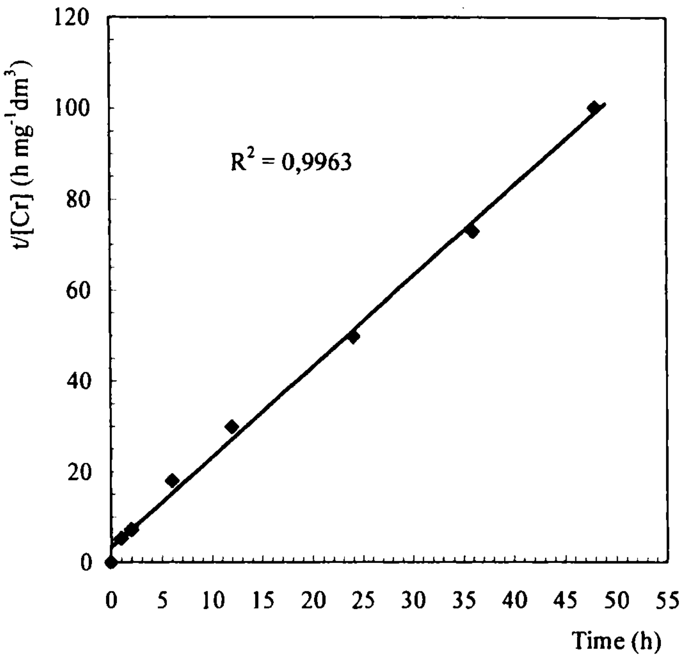

FIGURE 1 Fit of Equation 2 for leaching experimental data in sample I

TABLE II – Maximum leached concentration of chromium ($C_m$) and chromium content of soil samples ($m_m$)

| *Sample* | *A* | *B* | *C* | *D* | *E* | *F* | *G* | *H* | *I* | *J* |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_m$ (mg dm$^{-3}$) | 1,44 | 0,636 | 0,494 | 0,746 | 0,647 | 0,589 | 0,370 | 0,444 | 0,501 | 0,507 |
| $m_m$ (mg kg$^{-1}$) | 14,4 | 6,36 | 4,94 | 7,46 | 6,47 | 5,89 | 3,70 | 4,44 | 5,01 | 5,07 |

The influence of the natural organic matter content on the leaching time was analysed. The time needed for extraction of 95% of the maximum concentration that can be reached in the leaching solutions was determined through Equation 2 and plotted against natural organic matter content. The result of this study is illustrated in Figure 3. It shows that leaching time decreases with increasing of organic matter content. However, the pH and the chromium contents were different from sample to sample, which influences the leaching time.

Aiming to analyse the effect of natural organic matter content for fixed pH conditions, the samples should be leached beginning with similar chromium content. Therefore, the samples with higher amount were submitted to a previous

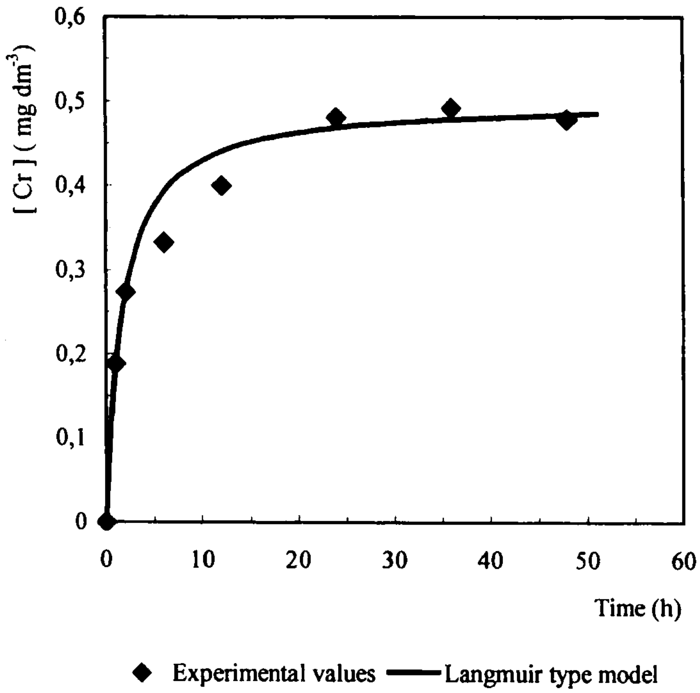

FIGURE 2 Fit of Langmuir-type model for leaching experimental data in sample I

extraction, till reach a chromium level similar to the sample with the lowest content of contaminant (sample G – 3,7 mg $kg^{-1}$). After that, the leaching was processed reproducing the conditions of pH and organic matter correspondent to the results expressed in Figure 3. During the previous extraction of chromium, some natural organic matter content was also extracted. In order to reproduce the desired conditions of pH and organic matter, the amount of organic matter extracted was added to the leaching solution, adjusting pH.

For some selected samples, Table III shows the natural organic matter content of the soils, the pH and the dissolved organic matter (DOM) at the end of leaching, and the maximum leached concentration.

According to pH values expressed in Table I, the studied soils are acidic; for this type of soils, the more effective adsorbents for metallic cations are the natural organic substances present in soils [11]; this natural organic matter significantly affects the adsorption of trace metals contaminants [12]. It is known that higher organic content in the soils also results in higher adsorption capacity. Nevertheless, the rate of leaching is affected more by the leaching conditions than by the capacity of the soils for the adsorption of metals [11].

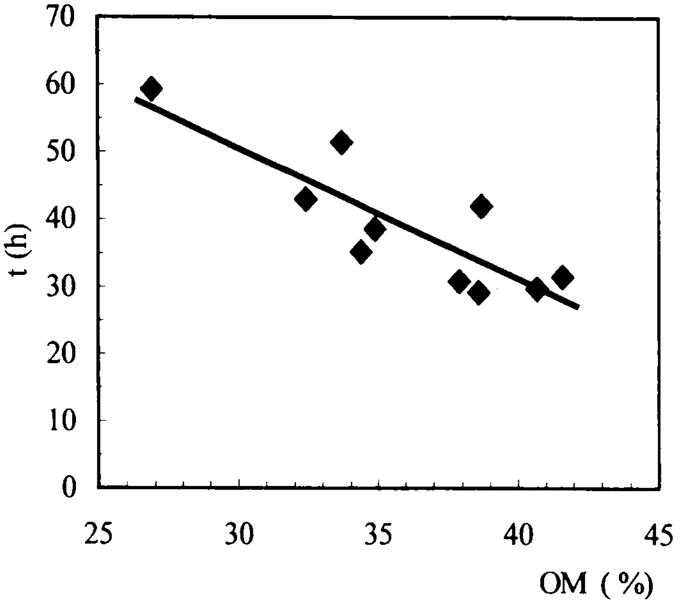

FIGURE 3 Influence of natural organic matter content on the leaching time (95% of maximum leached concentration)

The formation of complexes between heavy metals and ligands in aqueous phase, i.e. speciation, results in a competition between the ligands and the adsorption capacity of soils. The presence of chloride in leaching solutions induces the formation of metal-chloride complexes that are soluble and not adsorbed into the soil surface. As a consequence, the sodium chloride present in leaching acidic solutions enhances the transport of heavy metals to the liquid phase, which is related with: a) a decrease in activity due to sodium chloride, b) the competition from sodium cations for adsorption sites and c) the complexation of metal cations as negative and neutral chloride complexes.

The leaching process allows the transport of natural organic matter into the liquid phase as well, decreasing the organic-based surface adsorption sites and enhancing the possibility of metal complexation by the dissolved organic matter [11].

This hypothesis was tested comparing results obtained for different concentration of dissolved organic matter in the leaching solutions. For that, the samples treated to have the same initial chromium amount were also extracted using leaching solutions with adjusted concentrations of dissolved organic matter. This adjustment was done adding organic matter to the samples with lower concentration, in order to reproduce the concentration of the leaching solution with the highest level of dissolved organic matter (sample J – 17,9 (C) mg dm$^{-3}$). The pH and the dissolved organic matter at the end of leaching, and the maximum leached concentration are compared in Table III with those obtained without adjustment of dissolved organic matter. The time required to reach 95% of the maximum leached concentration is compared in Figure 4, for leaching without and with adjustment of dissolved organic matter.

TABLE III – Parameters to analyse the effect of natural organic matter content on the leaching time

| *Sample* | *OM (%)* | *Without dissolved organic matter adjustment* | | | *With dissolved organic matter adjustment* | | |
|---|---|---|---|---|---|---|---|
| | | *pH* | *DOM (C) (mg dm$^{-3}$)* | *$C_m$ (mg dm$^{-3}$)* | *pH* | *DOM (C) (mg dm$^{-3}$)* | *$C_m$ (mg dm$^{-3}$)* |
| D | 26,9 | 2,5 | 9,41 | 0,372 | 2,5 | 18,0 | 0,369 |
| B | 32,4 | 2,5 | 13,0 | 0,371 | 2,5 | 17,6 | 0,378 |
| J | 38,6 | 3,0 | 17,9 | 0,367 | 3,0 | 17,9 | 0,367 |
| G | 38,7 | 2,5 | 14,7 | 0,370 | 2,5 | 18,4 | 0,367 |
| F | 40,7 | 2,5 | 16,2 | 0,368 | 2,5 | 18,2 | 0,373 |
| I | 41,6 | 2,1 | 15,0 | 0,373 | 2,1 | 17,2 | 0,362 |

The results show that without dissolved organic matter adjustment and constant pH, the dissolved organic matter increases with increasing of organic matter content of the soils (samples D, B, G and F). According to other authors, it was also observed that pH influences the concentration of dissolved organic matter [11]. Samples with similar organic matter content have higher concentration of dissolved organic matter for higher pH (samples G and J). The effect of pH is also noted for samples F and I. As pH is lower for leaching of sample I, the dissolved organic matter is smaller even for a slightly higher organic matter content.

It can be considered that the adjustment of dissolved organic matter did not influence the maximum leached concentration of chromium. These results were expected, because if leaching is carried out at enough low pH, all the metallic species present in the soil must be removed to the liquid phase [3,5].

For the samples without adjustment of dissolved organic matter, Figure 4 shows that higher concentrations of dissolved organic matter in the leaching solutions correspond to lower leaching times. It should be noted that even for samples with similar natural organic matter content (samples J and G), the leaching time is lower for sample J, because its higher pH induces a higher concentration of dissolved organic matter.

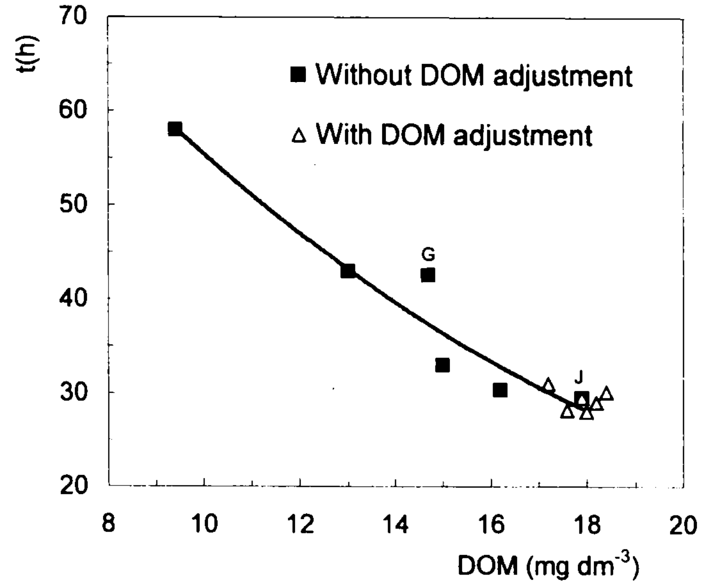

FIGURE 4 Influence of dissolved organic matter on the leaching time (95% of maximum leached concentration)

These results were confirmed comparing times expressed in Figure 4 for leaching without and with adjustment of dissolved organic matter. As it can be observed, when concentrations of dissolved organic matter were increased to be similar in all the samples, the leaching time became also similar.

It can be concluded that the increasing of dissolved organic matter significantly decreases leaching time due to the metal complexation by dissolved organic matter present in the leaching solutions. According to experimental results, dissolved organic matter helps the role of chlorides, decreasing surface adsorption sites and increasing metal complexation.

Other research confirm the same trend for lead, copper and zinc with the same experimental conditions [13].

It should be enhanced that the leaching methodology assayed allows the recovery of metals present as soil contaminants, associated to the soil remediation in what concerns to metal content reduction. Nevertheless, it should be emphasized that from the financial point of view, the advantages of this methodology depend greatly on the goals desired; the metallic content of the soil, the importance of the recovery of the metals and the environmental exigencies are fundamental parameters to be considered.

## CONCLUSIONS

A Langmuir-type model showed a good fit for leaching studies, allowing to determine the maximum concentration of chromium that can be reached in the leaching solutions, and the time required to attain a fixed leached concentration of chromium.

The results obtained enables to conclude, that natural organic matter content of the soils significantly influences leaching time through the effect on dissolved organic matter transferred to the liquid phase. When pH is similar, samples with higher content of organic matter have higher concentration of dissolved organic matter. Increasing of pH increases the transfer of organic matter to the liquid phase. Increasing of dissolved organic matter decreases leaching time due to the metal complexation by the dissolved organic matter.

The leaching methodology assayed, allows the recovery of metals present as soil contaminants, associated to the soil remediation in what concerns to metal content reduction.

### *Acknowledgements*

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