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Sequential chemical extraction of copper from clay: an overview

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Abstract
In general, the total content of heavy metals and trace elements in soils is useful, but the speciation (bioavailability) is also in need for agricultural purpose, for example. The present paper studies the efficiency of some soil remediation treatments on soils polluted, especially with copper, by using sequential chemical extraction (SCE). Usually, SCE is fractioned, according to Tessier, in five fractions: exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound and residual. Copper (Cu) is one of the contaminants found in many soils around the world. In small concentration, it is an essential microelement for plants and organisms, but in high concentrations, it is harmful for the entire ecosystem. Because the concentrations of Cu are associated with soil texture and several other parameters, many remediation soil treatments are based on organic mixture, by converting the element into a less exchangeable form, and thus less bioavailable. In this study, the efficiency of organic amendments such as organic matter (OM), zero-valent iron with organic matter (OMZ), dolomite (DL) and organic matter with dolomite (OMDL) are investigated. These treatments were applied on soils affected by Cu pollution. The results indicated that OMDL and OMZ treatments had the best efficiency on Cu pollution, by enhancing the stability of the element, decreasing the level of bioavailability.

Keywords: soil pollution, sequential chemical extraction (SCE), heavy metals, organic soil treatments.

1. INTRODUCTION

Soils are known to retain many types of organic and inorganic pollutants. It is important to know the total content of heavy metals from soils, but in some study cases, it is recommended to find out the speciation of these metals, also known as bioavailability. Metals have different mobilities and levels of bioavailability and these two characteristics are connected. If the mobility is high, this will increase the potential plant intake, affecting indirectly the human and animal health.

Copper (Cu) is one of the most common contaminants in many soils around the world. Many studies had reported high concentrations of Cu in: vineyard soils due to the use of copper-based fungicide in Brazil [1], in New Zeeland [2] where the wood was treated against insects and fungal, with a specific product based on Cu, Cr, and As. In time, due to this type of treatments and the lack of legal regulations, the soil accumulated high concentrations of copper.

Another source of pollution with Cu, is the industrial sludge that may contain a various number and quantity of pollutants that tend to leach to surface and ground water [3, 4].

Other sources of copper that can be taken into account are mining, plastic industry, agriculture (fertilizers, pesticides, and as feed additive in livestock and poultry nutrition) and automobile industry [5, 6].

The most important problem that can occur in copper polluted soils is the bioavailability of the element to the living organisms and the leach to the surface and ground water. For plants and organisms, Cu is an essential micronutrient. In excess, it affects nitrogen and protein metabolism, causing chlorosis of leaves and disturbing the mineral uptake, producing also damages to cell membrane that will lead to cell death [7]. In soils, in normal concentrations, Cu is bound to organic matter and presents no risk for living beings. But, if the concentrations exceed the alert thresholds, the soil becomes toxic and unfertile [8]. According to [9], the average level of copper in the European soil is about 68 mg kg^{-1}, and to [6] in the Earth crust, concentrations can vary between 25 and 75 mg kg^{-1}. It is found in the composition of a large number of minerals [5].

In general, soil pollution is affecting large surfaces of land. In this case, the old methods of excavation and burial of the contaminated soil are not practical. Recently, there were developed alternative methods of stabilization that are less invasive, with smaller costs and predictable results. These methods use natural amendments in order to fix the contaminant in soils, thus the stabilization succeeded if the pollutant concentrations were constant over the time [10]. Usually, the contents of Cu are associated with soil texture and several other parameters, in particular pH and organic matter. As a consequence, many remediation treatments are based on organic mixture, that are converting the element into a less exchangeable and thus, less bioavailable forms.

Studies have shown that immobilization of heavy metals by stabilization amendments represents a promising method in order to restore the contaminated lands.

The element's bioavailability is the most important risk factor, explaining that a metal becomes harmful when the organisms absorb it in high concentrations. Currently, there are no known methods that can be used to determine the bioavailability for every type of organisms. But this characteristic is bound to the level of solubility and mobility of each element, so there were developed a number of methods known as sequential chemical extraction (SCE). SCE is used to determine the elemental concentration and its behavior in different environmental conditions. These methods helped some countries, such as Sweden (Council Directive 1999/31/EC, Sweden) to regulate their legislation regarding elemental pollution, by adding the soluble part of the element and not the total obtained concentration of it. Following this direction, also new and promising remediation technics of polluted soils were developed [11].

For this study, the efficiency of the stabilization amendments was determined by sequential chemical extraction (SCE). Usually, SCE is applied on a soil sample, starting with the weakest reagent, and ending with the strongest one. According to Tessier, it has five fractions: exchangeable (FI), carbonate bound (FII), Fe and Mn oxide bound (FIII), organic matter bound (FIV) and residual (FV). In general, metals of anthropogenic origin are found in the first four fractions and in the last fraction, there can be found those from the parent rock [12, 13].

The first step removes the most mobile elements by using a salt solution. The protocol continues in order to decrease the mobility by step FII, the carbonate bound, where acid solutions are used. Step FIII, representing metals bound to Fe and Mn oxides, can be obtained by using a solution that can dissolve insoluble sulfides salts. For metals that are bound to the organic matter, F IV, the remaining soil must be oxidized. The last fraction, FV, is formed by the metals that are incorporated into the crystal structure, and represents the most stable and thus, difficult to extract. For this step, stronger acids are usually used [14].

In [15], SCE was applied to study the leaching behavior of Cu. The source of the contaminant was the sludge and wastewater obtained from Cu production. The experimental procedure consisted in dividing all the present metals from soils into fractions. In this paper, only three phases were studied, namely: deionized water, dissolved organic carbon solution and stimulating acidic rain. In conclusion, the last step released a very high concentration of Cu, that also presented an enhanced mobility. Cu released from the sludge tends to concentrate in the upper layer of the soil column.

2. EXPERIMENTAL

Site description and sample collection

The soil samples were collected from a field experiment, located in France. On this site, the wood has been treated for many years with copper sulfate, or arsenate copper chromate in order to prevent its degradation as a consequence of the insects and fungi activities.

Because anions are usually more mobile than cations, As and Cr concentrations found in soils were smaller (26.3 respectively 31 mg kg^{-1}), but Cu tended to accumulate until it reached values equal to 2600 mg kg^{-1}. The soil requires environmental assessments if Cu concentrations exceed 60 mg kg^{-1} as [1] recommended.

This experiment adopted two phases. The objective of the phase was to immobilize the pollutants with the help of organic amendments, and phytoremediation was used as a second phase. Phytoremediation is based on the fact that plants developed two strategies in order to tolerate heavy metals. They are known as: metal exclusion and metal accumulation. Through exclusion, plants avoid excessive metal uptake and restrict its transport to the shoots. In this case, heavy metals tend to accumulate in their roots. Metal accumulation plant strategy entails the transport of heavy metals from roots in order to accumulate them in shoots [16]. For this research, plants that adopted the exclusion strategy with the aim of minimizing the danger of transferring the contaminants to other ecosystems and lowering the level of soil erosion were used. Examples of plants that were used: *Populus nigra*, *Salix Viminalis*, *Salix caprea*, *Amorpha fructicosa*, *Agrostis delicatula*, *A. capillaris*, *A. castellana*, *A. gigantea*, *Cytisus Striatus*, *Dactilys Glomerata* and *Holcus lanatus*. The final purpose was to obtain a fully dynamic and independent ecosystem [10].

Sequential Chemical Extraction protocol

The first phase consisted in applying on some experimental soil squares different types of amendments such as: plants, organic matter (OM), dolomite (DL), organic matter and dolomite (OMDL), organic matter and zero-valent Fe (OMZ), basic sludge (BS). The final goal was to determine the level of element stabilization for each applied treatment, and the fraction in which Cu became instable. For this study, the soil samples were analyzed by applying a particular protocol of sequential chemical extraction (SCE). The analysis began with 0.2 g of clay, sequential treated with the reagents presented in Table 1. Additionally, the fraction for which the extraction is executed, is also presented. Because the SCE was applied on clay the last fraction, the residual one was excluded. Before each step, the samples were washed with H_2O.

Table 1. Reagents used for SCE

Reagent	Fraction
NH_4NO_3 1M buffered at pH 7 with NH_3	Exchangeable
CH_3COOH 1M pH=5.5	Oxidizable/Carbonate
$Na_4P_2O_7$ 0.1M pH 10 (3 times)	Organic matter and sulfides
H_3NOHCl 0.5M	Fe/Mn (oxy)hydroxide
CH_3COONH_4 1M	Fe (oxy)hydroxides

After each extraction step, the tubes were centrifuged for 20 min at 7000 rotation/minute. The measurements of Cu concentrations were performed by using Atomic Adsorption Spectrometer (AAS) Contra 300 with flame. AAS is one of the most used analytical methods for the speciation of heavy metals [17].

Clay extraction protocol

For clay extractions 200 g of soil were used. The soil was sieved using a 2 mm sieve, mechanically dispersed in distillated water and shaked for 24h. The clay fraction was obtained by sedimentation. The samples were centrifuged at 5000 rotation/minute for 10 minutes and the solid fractions were put to dry at 40^0 C for 24 h. The final amount of clay varied from 0.200 to 0.912 g.

3. RESULTS AND DISCUSSION

Table 2 presents the percent of Cu concentrations on each fraction and the mobility index values for each applied treatment. After the SCE protocol was applied on soil clays, the results were compared according to the applied treatment. The total Cu concentration, obtained after the sequential extraction protocol, varied in values from 2790.22-3872.68 mg kg^{-1}.

Table 2. The percent of Cu concentrations on each fraction and the mobility index values for each applied treatment

Treatment	**Percent of Cu concentration on each fraction**	**Mobility index** (%)	**Total concentration of Cu (mg kg^{-1})**
UNT	FIV (49.91%)>FIII (30.82%)>FII (17.34%)>FI (1.93%)	19.27	3187.04
OM	FIV (54.47%)>FIII (34.63%)>FII (9.39%)>FI (1.51%)	10.9	3827.66
DL	FIV (55.63%)>FIII (22.94%)>FII (19.70%)>FI (1.74%)	21.43	3872.68
OMDL	FIV (58.52%) >FIII (29.71%)>FII (9.87%)>FI (1.89%)	11.77	2790.22
OMZ	FIV (63.91%) >FIII (21.10%)>FII (13.92%)>FI (1.08%)	15	3872.68

The metal concentration that is available for plants, can be found by calculating the *mobility index* presented in Formula 1, [18]:

$$MI = \frac{FI + FII}{FI + FII + FIII + FIV} \quad (1)$$

Regarding the first two fractions, the total metal concentrations are considered to be available for plant uptake, presenting a high mobility. Under normal conditions, the elements obtained for Fe and Mn oxides, organic matter and residual phases, are more stable in soils [19].

In this study, the mobility index for Cu, obtained from untreated soil is 19.27 (%). In general, for unpolluted soils, Cu has a mobility index smaller than 10 [Wong et al., 2002]. In total, the first two fractions were 19.27 %, which is smaller than the third fraction (30.82 %). This indicates that half of the total Cu concentration is likely to reach to the plants that are growing on site.

The soil treated with OM, presented a smaller Cu mobility index (10.9 %). This value, is the smallest one compared to the others obtained by applying other treatments. This indicates that, the organic matter treatment can be successfully used in Cu pollution. The first two fractions, also presented a small decrease in value, compared to UNT soil. In this case, fraction three presented a higher value for Cu extraction.

For DL treatment, the mobility index had the highest value (21.43 %). In this case DL is not recommended to be used as a treatment in the case of Cu pollution.

The OMDL and OMZ treatments presented a better value in the first two phases for the index of mobility. But by using OMZ treatments, in the case of Cu pollution, it was obtained the most stable FIV fraction (63.91 %) of Cu.

4. CONCLUSIONS

A particular SCE protocol was applied on treated clay, obtained from a soil previously polluted, under industrial conditions, with high concentrations of Cu. The amendments used in this case were OM, DL, OMDL and OMZ. The obtained solutions were analyzed by AAS, which was a sensitive and precise technique, used many times for this type of experiments. The results underline the fact that a high concentration of Cu was present in exchangeable and organic fraction. This indicates an anthropogenic source of pollution. These two phases were especially put under observation, in order to conclude the efficiency of the treatments. In this case the smallest sum for Cu concentrations was obtained for OM, OMDL and OMZ treatments. The organic matter properties of stabilizing Cu in soil by forming stable complexes presented one of the reasons that these treatments were very efficient. The treatment with Fe grit (pure Fe^0) was also used in another study [20] where it reduced the leaching with 91% for Cu in a sandy, acidic soil. The DL treatment did not present the same efficiency.

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