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O solo, recurso estratégico para uma sociedade sustentável

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Short-term evolution of physico-chemical properties of Technosols made from contaminated soils by pyritic sludge

Evolución a corto plazo de las propiedades fisicoquímicas de Tecnoles elaborados a partir de suelos contaminados por lodos piríticos

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Abstract

The aim of this study was to evaluate, at short term, the physico-chemical and biological quality of residually contaminated soils after the Aznalcóllar mine spill and treated with "tailor-made Technosols". Two Technosols with different properties (T4 and T6) were used as treatments. Both are composed of *ex-situ* contaminated soil and two wastes from mining (sludge rich in iron oxyhydroxides and marble sludge); and T4 by a waste from agro-industry (solid olive-mill by-product) and T6 by one from urban activity (vermicompost from gardening). After 6 months of application, samples of Technosols and treated contaminated soils were characterised (soil properties, total, soluble and available concentrations of potentially harmful elements (PHEs), and toxicity bioassay with *Lactuca sativa* L.) and compared with baseline conditions. Some soils in the Guadamar Green Corridor presented a significant environmental and human health risk due to their extreme characteristics (pH<4, low fertility and multielemental contamination). After only six months, the application of Technosols on these soils has led to a significant improvement in their physico-chemical and biological properties (pH neutralisation, reduction of mobility PHEs and enrichment in organic carbon). So, in the long term, soil remediation through the Technosols is expected to be effective and proven in future studies.

Keywords: Soil remediation, metal(loid)s, waste valorisation, acid neutralisation, toxicity

Resumen

Nuestro objetivo fue evaluar, a corto plazo, la calidad fisicoquímica y biológica de suelos contaminados tras el accidente de Aznalcóllar y ser tratados con "Tecnoles a la carta". Se aplicaron dos Tecnoles (T4 y T6); ambos compuestos por suelos contaminados *ex-situ* y dos residuos procedentes de la minería (lodos ricos en oxihidróxidos de hierro y lodos de mármol); y T4 también por uno agrícola (subproductos sólidos de almazara) y T6 por uno urbano (vermicompost de jardinería). Tras 6 meses, se caracterizaron los Tecnoles y los suelos contaminados tratados (propiedades del suelo, concentraciones totales, solubles y disponibles de elementos potencialmente contaminantes (EPCs), y bioensayo de toxicidad con *Lactuca sativa* L.) y compararon con las condiciones de partida. Algunos suelos del Corredor Verde del Guadamar presentaban un importante riesgo ambiental y para la salud humana debido a sus características extremas (pH<4, baja fertilidad y contaminación multielemental). La aplicación de los Tecnoles ha mejorado significativamente sus propiedades fisicoquímicas y biológicas (neutralización del pH, reducción de la movilidad de los PHE y enriquecimiento en carbono orgánico) en tan solo 6 meses. Así pues, a largo plazo, se espera que la remediación de los suelos mediante los Tecnoles sea eficaz y demostrada en futuros estudios.

Palabras clave: Remediación de suelos, metal(oid)es, valorización de residuos, neutralización de ácidos, toxicidad

Introduction

Soil contamination by potentially harmful elements (PHEs) is one of the most alarming degradation processes worldwide. Metal mining is one of the main pollutant sources, especially the mismanagement of waste derived from this activity. A notable example of the damage that can be caused by this type of contamination was the mine spill occurred in 1998 in Aznalcóllar (SW Spain), where 4.5 hm³ of acidic waters and toxic tailings were spilled into the Agrio and Guadiamar rivers (Simón, et al., 2001), eventually affecting 45 km² of soils. The consequences of this tragic environmental accident still persist to this day, with around 7% of the affected area with bare, acidic soils with high levels of some PHEs despite the implementation of one of the most ambitious soil remediation programmes ever undertaken (Martín Peinado, et al., 2015; García-Carmona, et al., 2019).

Rehabilitation of these contaminated areas is critical to prevent environmental degradation, as well as to control the exposure of human and other living organisms to PHEs (Pavel & Gavrilescu, 2008). Recently, one of the booming environmental rehabilitation technologies, based on sustainability and circular economy, is the use of waste-derived Technosols. This technology refers to those soils whose properties are characterised by their technical origin (Technosol "tailor made soils"; Macías, 2004). Technosols are produced mostly from waste and fulfill a specific function such as the acid neutralisation and immobilisation of PHEs, as well as the general soil functions. The effectiveness of this strategy in improving the physico-chemical and biological characteristics of mine tailings and leachates has been demonstrated in several studies using a wide range of different Technosols (Asemaninejad, et al., 2018; Jordán, et al., 2017; Santos, Abreu, & Macías, 2019). Likewise, Aguilar-Garrido et al. (2021) showed a high acid neutralising and immobilisation of PHEs capacity in soils affected by mining of some Technosols through laboratory assays. Therefore, here we have selected two of

the best Technosols from the previous study and applied them in an *in-situ* soil rehabilitation experiment.

The aim of this study is to evaluate, in the short term, the changes produced in the physico-chemical and biological properties of both treated contaminated soils and Technosols.

Material and methods

To remediate residually contaminated soils for more than 20 years due to the Aznalcóllar mining spill, we implemented a pilot project in the Guadiamar Green Corridor (Fig. 1). About 25 cm of two Technosols (T4 and T6) were surface applied on the contaminated soils, in triplicate. Technosols were developed by mixing *ex-situ* contaminated soils and organic/inorganic wastes from mining (sludge rich in iron oxihydroxides and sludge from the cutting and polishing of marble), urban activity (vermicompost from gardening) in T6, and agro-industry (solid olive-mill by-product) in T4, in the proportions set out in Table 1.

Table 1 – Composition of Technosols T4 and T6: % of contaminated soil and of each waste.

Technosol	PS	IO	MS	OL	VC
T4	59	2	20	19	-
T6	63	2	20	-	15

PS: contaminated soil, IO: sludge rich in iron oxihydroxides; MS: sludge from marble cutting, OL: solid olive-mill by-product; VC: vermicompost from pruning and gardening

After 1 month of incubation in the field (t_0) and 6 months of its application on the contaminated soil (t_1), composite samples of each of the Technosols (T4 and T6; depth: < 25 cm), and of the contaminated soil treated below each Technosol (T4-SC and T6-SC; depth: 25 cm - 30 cm) were collected. These samples were analysed to examine for changes in soil properties (pH and EC in 1:2.5 and 1:5 soil:water extract, respectively; organic C; calcium carbonate; total N and Fe; available P; cation exchange capacity; and basal heterotrophic respiration (ISO 17555, 2002)). The mobility and bioavailability of PHEs was also assessed by determining the multi-elemental concentration in the total

fraction (X-ray fluorescence with NITON XL3t-980 GOLDD+), water-soluble and available by EDTA extraction fractions (measured by PerkinElmer Avio® 500 ICP-OES). A bioassay with *Lactuca sativa* L. (OECD, 2003) was also carried out to evaluate the evolution of the toxicity of the soils studied. Changes in the parameters of the Technosols and the treated soils in time were evaluated using the non-parametric U Mann-Whitney test ($p < 0.05$).

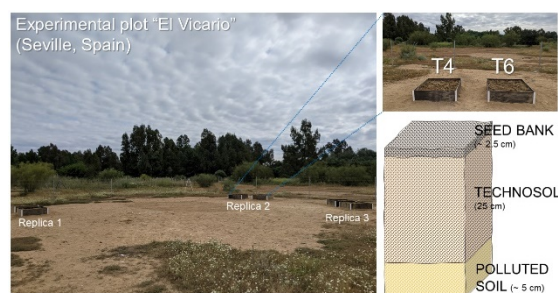


Fig. 1 – Experimental plot and scheme of the rehabilitation system based on Technosols.

Results and discussion

Technosols (T4 and T6) with a sandy loam–loam texture were highly carbonated, with pH close to neutral or slightly alkaline. They also had a high total Fe and OC content, but low CEC was measured (Table 2). These soil properties and constituents play an important role in reducing the mobility and availability of PHEs in soils, as they are potential PHEs adsorbers and acidity neutralisers (Aguilar-Garrido, et al., 2021; Merdy, Gharbi, & Lucas, 2009).

Table 2. Properties of contaminated soil and Technosols at the beginning (t_0) and 6 months after installation (t_1).

	T4		T4-SC		T6		T6-SC	
	t_0	t_1	t_0	t_1	t_0	t_1	t_0	t_1
pH	7.03 a	7.78 b	3.60 a	7.33 b	7.12 a	7.79 b	3.60 a	6.71 b
EC	3.34	3.12	2.88 b	2.72 a	3.05 b	2.73 a	2.82	2.69
OC	2.92	2.16	0.45 a	0.87 b	2.29	2.39	0.59 a	0.92 b
CO ₃	21.60	19.47	0.68 b	0.41 a	30.39 b	19.10 a	0.62	0.38
N _T	0.20 a	0.22 b	0.10	0.10	0.18	0.20	0.10	0.10
Fe _T	4.58 b	3.96 a	4.82 b	3.85 a	3.63	3.76	5.11 b	4.13 a
P _A	9.15 b	3.25 a	6.98 b	3.42 a	73.97 b	13.47 a	6.29 b	4.41 a
CEC	8.93 a	12.10 b	7.99	8.90	9.75 b	7.58 a	6.96 a	9.27 b
SR	5.30	4.64	1.61 a	4.59 b	4.80	6.38	2.16	3.69

EC: electrical conductivity (dS m^{-1}); OC: organic carbon (%); CO₃: calcium carbonate content (%); N_T: total N content (%); Fe_T: total Fe content (%); P_A: assimilable P (mg kg^{-1}); CEC: cation exchange capacity ($\text{cmol}_{(+) } \text{kg}^{-1}$); SR: basal respiration ($\mu\text{g CO}_2 \text{ g soil}^{-1} \text{ h}^{-1}$). Lower-case letters indicate statistically significant differences over time.

The contaminated soil presented the same conditions observed in previous studies such as acidic pH, low OC content, low microbial activity and nutrient poverty (Table 2); as well as high concentrations of some PHEs (e.g. As, Cu, Pb, Ni and Zn) in the total, soluble and bioavailable fractions (Table 3).

Table 3. Total, water-soluble and available concentrations of metal(loid)s (mg kg^{-1}) of contaminated soil and Technosols at the beginning (t_0) and 6 months after installation (t_1).

	T4		T4-SC		T6		T6-SC	
Total	t_0	t_1	t_0	t_1	t_0	t_1	t_0	t_1
As	215.2 b	187.0 a	274.1	189.3	187.0	183.9	288.7 b	234.1 a
Cd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	95.3	93.1	81.5	77.5	75.1	75.4	84.9	75.8
Cr	55.2	55.4	94.8	101.6	53.7	55.8	91.9	85.8
Ni	31.3	25.2	35.8 b	29.9 a	30.2	25.6	36.0	38.9
Pb	477.7 b	418.6 a	548.9	402.7	422.9	380.6	553.6	405.3
Sb	20.6	17.8	24.9	18.1	16.3 b	<LOD a	22.8	21.4
Zn	168.1	151.9	144.9	167.1	156.9	167.8	129.0	134.1
Water-soluble								
As	0.23 a	0.51 b	0.20 b	0.17 a	0.37 a	0.59 b	0.20	0.16
Cd	0.008	0.004	0.221 b	0.000 a	0.010 b	0.005 a	0.175	0.042
Cu	0.47 b	0.19 a	3.39 b	0.08 a	0.30 b	0.07 a	3.20 b	0.14 a
Cr	0.017 b	0.000 a	0.057 b	0.000 a	0.014 b	0.000 a	0.044 b	0.003 a
Ni	0.041 b	0.012 a	1.398 b	0.000 a	0.017 b	0.000 a	1.177	0.351
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sb	0.123	0.153	0.055	0.049	0.131 b	0.107 a	0.031	0.051
Zn	0.26 b	0.10 a	35.54 b	0.04 a	0.16 b	0.05 a	27.79	6.75
Available – EDTA extraction								
As	0.90 a	2.42 b	2.45	2.58	2.54 a	3.48 b	2.42	3.73
Cd	0.38	0.34	0.28	0.29	0.38	0.40	0.24	0.23
Cu	16.18	13.11	19.29	18.38	15.14 b	13.68 a	17.88	15.25
Cr	0.18 b	0.12 a	0.18	0.27	0.21 b	0.12 a	0.15	0.20
Ni	0.50 b	0.27 a	1.55 b	0.71 a	0.57 b	0.27 a	1.31	0.81
Pb	0.69	0.09	0.25	1.67	0.71 b	0.35 a	0.71	0.55
Sb	0.23	0.31	0.15	0.28	0.25	0.33	0.18	0.27
Zn	31.51	21.94	38.47 b	17.44 a	37.29 b	28.82 a	29.88	18.33

LOD: Level of detection. Lower-case letters indicate statistically significant differences over time.

During these 6 months, with the treatment of Technosols, the contaminated soil was reverting its adverse conditions. Most notably, the strong acidic pH condition has been neutralised. In fact, a reduction in the calcium carbonate content was observed in the Technosols, especially at T6, as a result of the reaction of the latter buffering the soil pH. Likewise, a slight enrichment in OC is occurring in the underlying contaminated soil.

Regarding the mobility and availability of PHEs in the contaminated soil, there were significant reductions in the soluble fraction of Cd, Cu, Cr, Ni and Zn in both Technosols (higher reduction in T4). While in the available fraction no major changes have been observed yet. However, the toxicity bioassay with lettuce showed that the potential toxicity in the contaminated soil is decreasing, although in the T6-treated soil it was not statistically significant (Fig.1).

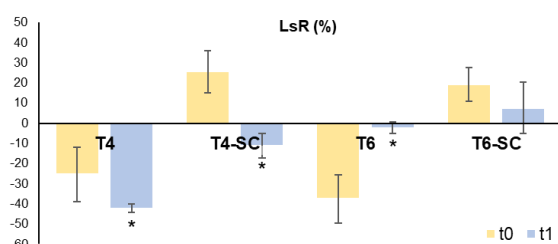


Fig. 1 – Reduction in the elongation of *Lactuca sativa* L. compared to a control (distilled water). * indicates statistically significant differences over time.

Conclusions

The application of Technosols on residually contaminated soils has led to a significant improvement in the physico-chemical and biological quality of the soils only six months later. Thus, expectations for further progress in the soil remediation process over time are high. In fact, in future studies, the development of a vegetation cover on the technosols is expected, which has not yet occurred due to the sampling times (April-October).

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