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Decreasing the contamination and toxicity of a heavily contaminated soil by in situ bioremediation

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A B S T R A C T

Experimental plot consisting of acidic leached cinnamonic forest soil heavily contaminated with radionuclides (mainly U and Ra) and non-ferrous metals (mainly Cu, Zn and Cd) was treated in situ under real field conditions using the activity of the indigenous soil microflora. This activity was enhanced by suitable changes of some essential environmental factors such as pH and water, oxygen and nutrient contents of the soil. The treatment was connected with solubilization and removal of contaminants from the top soil layers (horizon A) due to the joint action of the soil microorganisms and leach solutions used to irrigate the soils (mainly acidophilic chemolithotrophic bacteria and diluted sulphuric acid). The dissolved contaminants were transferred through the drainage soil effluents to the deeply located soil subhorizon B_2 where they were precipitated as the relevant insoluble forms (uranium as uraninite, and the non-ferrous metals as the relevant sulphides) as a result of the activity of the sulphate-reducing bacteria inhabiting this soil subhorizon. The effluents from the subhorizon B_2 containing much lower concentrations of inorganic contaminants but enriched in dissolved biodegradable organics were subjected to additional treatment in a constructed wetland for removing these residual contaminants. It was also demonstrated that an efficient treatment of the effluents from the subhorizon B_2 could be achieved by a microbial fuel cell in which the cleanup was connected with electricity generation.

1. Introduction

The contamination of soils, sediments, surface and groundwaters with uranium, its decay products and different heavy metals is a great environmental problem in countries in which mining and processing of uranium ore are applied. Such contaminants can result in radioactive and chemical exposures that directly and indirectly lead to disease.

The remediation of contaminated waters and sediments in the uranium deposits is a common practice. Various methods based on both active and passive treatment systems have been applied and in some cases the remediation is connected with the recovery of some valuable components such as uranium and some non-ferrous metals.

However, the remediation of contaminated soils located within or near the uranium deposits is a more difficult problem. Traditional efforts to manage such soils often focus on their removal by extraction followed by off-site treatment/disposal as well as on the in situ monitored natural attenuation or passive capping using the installation of clean, inert material over the contaminated soil.

In situ management of contaminated sites is potentially less expensive and less risky than ex situ management (Knox et al., 2008). In situ chemical leaching using various lixiviants (bicarbonate, mineral acids and some organic complexing agents) is applied to solubilize soil (Osiensky and Williams, 1990; Phillips et al., 1995). Such treatment is possible only in sites with suitable geologic and hydrogeologic conditions and requires the construction of collector systems that prevent the undesirable seepage of contaminated pregnant solutions into the environment. In some cases such pregnant solutions can be used as sources for recovery of uranium and other metals. A system of this type was suggested by Phillips et al. (1995) to concentrate uranium from contaminated soils by a two-stage process: firstly, extraction of uranium from the soil with bicarbonate and then precipitation of uranium from the soil effluents with U^{6+}-reducing microorganisms. In any case, the contaminated soil effluents must be subjected to cleanup before recycling or other possible use.

Another type of in situ methods is connected with the immobilization of uranium and heavy metals inside the soil by converting them into their least soluble or toxic forms or by encapsulation in solid products of high structural integrity (Mulligan et al., 2001).

Some in situ remediation methods of the above-mentioned two-types are based on the activity of some soil microorganisms able to solubilize or precipitate uranium and other heavy metals (Suzuki and

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Suko, 2006). This activity is enhanced by suitable changes in the levels of some essential environmental factors such as pH, Eh, and oxygen, water and nutrient contents in soil. These changes are achieved mainly by irrigating the soil with solutions able to solubilize and maintain the contaminants in soluble forms or to facilitate their precipitation in the soil (Groudev et al., 2005). In practice, the remediation is achieved as a result of the joint actions of the soil microorganisms and the relevant irrigating solutions.

Another group of in situ bioremediation methods is based on the ability of some plants to accumulate uranium and heavy metals from contaminated soils via their root systems (Hinchee et al., 1995). Considerable portions of the bioaccumulated contaminants are then transferred to the plant biomass located above ground. This biomass is periodically removed and burned to ashes. These ashes are suitable for disposal or can be used for recovering some valuable components.

Different variants of the above methods have been applied in several countries, mainly in Northern America and Europe. Data about the application of such a method in the uranium deposit Curilo, Bulgaria, are shown in this paper. This deposit for a long period of time was a site of intensive mining activities including both open-pit and underground techniques as well as in situ leaching of uranium. The mining operations were ended in 1990 but until three years ago large portions of the surface and ground waters and soils within and near the deposit were still heavily contaminated with radionuclides (mainly uranium and radium) and toxic heavy metals (mainly copper, zinc, and cadmium).

Some soil plots located in this area were treated in situ by means of methods based on the activity of the indigenous soil microflora (Groudev et al., 2010).

The highest concentrations of contaminants in these plots were present in the top soil horizon (A) in which some acidophilic chemolithotrophic bacteria were the prevalent microorganisms. The number and leaching activity of these bacteria were increased by irrigating the soil with diluted sulphuric acid solutions containing also ammonium and phosphate ions as nutrients for bacteria, and by increasing the permeability and aeration of the soil by periodic ploughing. The dissolved contaminants were transferred from the horizon A through the drainage effluents to the subhorizon B_2 where they were precipitated as the relevant insoluble forms (uranium as uraninite, and the non-ferrous metals as the relevant sulphides) as a result of the activity of the sulphate-reducing bacteria inhabiting this soil subhorizon. This activity was enhanced by adding dissolved organic substrates to the subhorizon B_2 through vertical boreholes. The rich-in-organic effluents containing also residual concentrations of some metals, mainly of iron and manganese, were treated by a constructed wetland for removing these contaminants. At the same time, however, it was demonstrated that the treatment can be arranged in microbial fuel cells in which the removal was connected with electricity generation.

2. Materials and methods

The soil plot used in this study consisted of a leached cinnamonic forest soil and was 240 m^2 in size. The soil profile was 100 cm deep (horizon A, 30 cm; horizon B, 50 cm; horizon C, 20 cm) and was underlined by intrusive rocks with a very low permeability. Data about the chemical composition and some essential geotechnical parameters of the soil are shown in Table 1. The contaminants were located mainly in the upper soil layers (in the horizon A).

The soil treatment was connected with the initial solubilization of contaminants. Water acidified with sulphuric acid to pH in the range of 2.8–3.5 was used as leach solution. Periodically, this solution was supplemented with ammonium and phosphate ions to maintain their concentration in the soil pore solution in the range of about 10–20 mg/l. The irrigation rate and acidity of the leach solutions were adjusted in connection with the levels of the local natural rainfall and temperature to maintain the water-filled porosity in the horizon A at about 65–70%, and the pH of soil pore solution within the range of about 3.0–3.9. This level of the soil moisture was the optimum for the activity of the aerobic microorganisms inhabiting this soil horizon. The pH of the soil pore solution was higher than the optimal values for acidophilic chemolithotrophic bacteria but was still suitable for their growth and activity. Lower pH values had a negative effect on the soil structure and composition. The upper soil layers (down to about 30 cm from the surface) were ploughed up periodically to enhance the natural aeration of these layers. The contaminants dissolved during the treatment were transferred by the drainage waters to the deeply located soil subhorizon B_2 where they were immobilized as a result of the activity of the indigenous sulphate-reducing bacteria. Water solutions of dissolved organic compounds (lactate and acetate) and ammonium and phosphate ions were injected through vertical boreholes to this soil subhorizon to enhance the bacterial activity.

Table 1
Characteristics of the soil horizon A in the plot before and after the treatment.

Parameters	Before treatment	After treatment
Chemical composition, %		
SiO_2	77.2	78.3
Al_2O_3	12.5	11.8
Fe_2O_3	2.39	1.52
P_2O_5	0.14	0.11
K_2O	2.15	1.63
N total	0.10	0.09
S total	1.72	0.71
S sulphidic	1.54	0.68
Carbonates	0.14	0.01
Humus	2.12	1.40
pH (H_2O)	4.37	3.14
Net neutralization potential, kg $CaCO_3$/t	−44.8	−20.6
Bulk density, g/cm^2	1.32	1.26
Specific density, g/cm^2	2.68	2.60
Porosity, %	51	46
Permeability, cm/h	10.7	8.6
Particle size, mm(%)		
1.00–0.25	19.4	18.5
0.25–0.01	49.1	50.4
<0.01	31.5	31.1

The effluents from the soil subhorizon B_2 were almost free of uranium, radium and toxic non-ferrous metals. These effluents still contained iron and manganese in concentrations slightly higher than the relevant permissible levels for waters intended for use in agriculture and industry and were rich-in-biodegradable organic compounds. The larger portion of these effluents were treated by a constructed wetland located near the experimental plot to remove the residual concentrations of the above-mentioned contaminants. The wetland had a rectangular shape and was 12 m long, 4 m wide and 1.0 m deep. The wetland was characterized by a mixed (surface/subsurface) water flowpath and by abundant water and emergent vegetation and a diverse microflora. *Typha latifolia* and *Phragmites australis* were the prevalent plant species in the wetland but representatives of the genera *Scirpus*, *Juncus*, *Eleocharis*, *Poa* and *Carex* and some algae were also present. The upper aerobic water zone of the wetland was inhabited mainly by different aerobic heterotrophic bacteria but the lower anaerobic soil zone was rich in anaerobic microorganisms.

A smaller portion of the rich-in-biodegradable organic compound soil effluents were directed to a microbial fuel cell in which the removal of the organic compounds was connected with the generation of electricity (Du et al., 2007; Kim et al., 2004; Pant et al., 2010).

The microbial fuel cell was a plexiglass rectangular container 50 cm high, 4 cm long, and 4 cm wide, with perforated slab graphite anode and cathode located in the bottom and in the top sections of the container, respectively. The two sections were separated by a permeable barrier of 5 cm thickness consisting of a 2.5 cm layer of glass wool and a 2.5 cm layer of glass beads. The feed stream, i.e. the wastewater from the soil cleaning, was supplied to the bottom anodic section of the container and the effluent passed through the cathodic section and exited at