BIOREMEDIATION OF MINE WATERS FROM A URANIUM DEPOSIT

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Abstract

Polluted waters generated in a uranium deposit in Western Bulgaria were treated by means of a natural wetland located in the deposit. The waters had pH in the range of about 5.5 – 7 and contained uranium, radium, manganese, iron and sulphates as main pollutants. The wetland was characterized by an abundant water and emergent vegetation and a diverse microflora. *Typha latifolia, Typha angustifolia* and different algae were the prevalent plant species in the wetland. The water flow rate through the wetland varied from about 0.2 to 0.5 l/s reflecting residence times of about 15 – 40 hours. An efficient removal of pollutants was achieved in the wetland during the different climatic seasons even during the cold winter months at temperatures near 0^oC. The removal was connected with different processes but the microbial dissimilatory sulphate reduction and the sorption of pollutants by the organic matter (living and dead plant and microbial biomass) played the main role. The removal of manganese was connected with the prior bacterial oxidation of Mn^{2+} to Mn^{4+}.

Introduction

The uranium deposit G located in Western Bulgaria for a long period of time was a site of intensive mining activities. These activities were ended in 1990 but since that time the underground mine and some dumps consisting of mining wastes are sources of polluted waters. These waters have pH usually in the range of about 5.5 - 7 and contain uranium, radium, manganese, iron and sulphates as main pollutants. In 1991 a portion of polluted waters was directed to a small ravine located in the deposit. A natural wetland characterized by an abundant water and emergent vegetation and a diverse microflora was located in the ravine and an efficient clean-up of the polluted waters was performed during their course through the wetland. This natural clean-up process was monitored for a period of about ten years. Detailed studies on the influence of different environmental factors on this clean-up and on the mechanisms of pollutants removal were also carried out. Some data about these studies are shown in this paper.

Materials and Methods

The wetland covered an area of about 250 m^2 (approximately 70 m long and 3-4 m wide). *Typha latifolia*, *Typha angustofolia* and *Juncus bulbosus* were the prevalent plant species in the wetland but some representatives of the genera *Phragmites*, *Scirpus*, *Eleocharis*, *Potamogeton*, *Utricularia*, *Carex* and *Poa* as well as different algae were also well present. Data about the microflora of the wetland are shown in Table 1.

Table 1. Microflora of the mine waters and the natural wetland

Microorganisms	Samples		
	Mine waters before treatment	Waters from the wetland	Sediments from the wetland
		Cells/ml (g)	
Aerobic heterotrophic bacteria	$10^1 – 10^4$	$10^4 – 10^8$	$10^2 – 10^6$
Cellulose – degrading aerobes	$0 – 10^2$	$10^2 – 10^6$	$0 – 10^3$
Fe^{2+} - oxidizing chemolithotrophs (at pH 2)	$0 – 10^3$	$0 – 10^2$	$0 – 10^1$
Fe^{2+} - oxidizing heterotrophs (at pH 7)	$0 – 10^2$	$10^3 – 10^6$	$10^1 – 10^4$
Mn^{2+}- oxidizing heterotrophs (at pH 7)	$0 - 10^2$	$10^3 - 10^6$	$10^1 – 10^4$
$S_2O_3^{2-}$ - oxidizing chemolithotrophs (at pH 7)	$10^3 – 10^7$	$10^4 – 10^7$	$10^2 – 10^5$
Anaerobic heterotrophic bacteria	$10^1 – 10^3$	$10^2 – 10^6$	$10^4 – 10^7$
Cellulose-degrading anaerobes	$0 – 10^1$	$10^1 – 10^4$	$10^2 - 10^5$
Sulphate-reducing bacteria	$0 – 10^3$	$10^2 – 10^6$	$10^4 – 10^7$
Fe^{3+} - reducing bacteria	$0 - 10^2$	$0 - 10^2$	$10^2 – 10^5$
Mn^{4+} - reducing bacteria	$0 – 10^2$	$0 - 10^2$	$10^2 - 10^4$

The bottom of the wetland was located on impermeable intrusive rocks with a very low hydraulic conductivity.

The water flow rate through the wetland varies from about 0.2 to 0.5 l/s reflecting residence 0.2 times of about 15-40 hours.

The quality of the waters was monitored at different sampling points located in the wetland. The parameters measured in situ included: pH, Eh, dissolved oxygen, total dissolved solids and temperature. Elemental analysis was done by atomic absorption spectrophotometry and induced coupled plasma spectrophotometry in the laboratory. The radioactivity of the samples was measured, using the solid residues remaining after their evaporation by means of a low background gamma-spectrophotometer ORTEC (HpGe-detector with a high distinguishing ability). The specific activity of Ra^{226} was measured using a 10 l ionisation chamber. The total β-activity was measured by a low background instrument UMF-1500 M.

Elemental analysis of solid samples from the bottom sediments and the plant biomass in the wetland was performed by digestion and measurement of the ion concentrations in solution by atomic absorption spectrophotometry and induced coupled plasma spectrophotometry. Mineralogical analysis was carried out by X-ray diffraction techniques. The mobility of the pollutant was determined by the sequential extraction procedure (1).

The isolation, indentification and enumeration of microorganisms were carried out by methods described elsewhere (2 - 5).

Results and Discussion

An efficient clean-up of the polluted waters took place in the wetland and the residual concentrations of pollutants in the wetland effluents were decreased below the relevant permissible levels for waters intended for use in the agriculture and/or industry (Table 2).

Table 2. Data about the mine waters before and after their treatment in the natural wetland

Parameters	Before treatment	After treatment	Permissible levels for waters used in agriculture and industry
Temperature, ^{o}c	(+0.1) – (+19.8)	(+0.1) – (+21.5)	-
Ph	5.5 - 7.1	7.1 - 7.9	6 - 9
Eh, mV	(+315) – (+512)	(+281) – (+344)	-
Dissolved o_2, mg/l	1.2 – 3.7	2.3 – 4.1	2
Total dissolved solids, mg/l	891 - 2141	451 - 1032	1500
Solids, mg/l	37 - 123	28 – 82	100
Organic carbon, mg/l	0.9 – 2.8	14 – 28	20
Sulphates, mg/l	442 - 1094	203 - 464	400
Uranium, mg/l	1.7 – 5.3	< 0.1	0.6
Radium, Bq/l	0.55 – 1.70	< 0.1	0.15
Total β-activity, Bq/l	1.25 – 2.80	< 0.5	0.75
Manganese, mg/l	4.4 – 24	0.1 – 0.9	0.8
Iron, mg/l	48 - 154	0.5 – 1.7	5

The removal of uranium and sulphate as well as of a significant portion of iron was connected with the process of microbial dissimilatory sulphate reduction taking place in the anoxic zone of the wetland. The sulphate-reducing bacteria were a quite diverse population in the wetland. The representatives of the genera *Desulfovibrio* and *Desulfobulbus* were the most numerous among these bacteria. The precipitation of uranium was connected with its reduction from the hexavalent to the tetravalent state caused by the hydrogen sulphide produced by the sulphate-reducing bacteria. This microbial metabolite reduced the ferric ions to the ferrous state and then precipitated Fe^{2+} as the insoluble FeS. Portions of tri-and pentavalent arsenic were also precipitated as the relevant insoluble sulphides. The sulphide forms of the pollutans were present in the relevant oxidisable mobility fractions and were refractory to chemical and microbial resolubilization, especially under the conditions typical for the anoxic bottom zone of the wetland.

The removal of manganese and of a portion of iron was connected with their prior oxidation to Mn^{4+} and Fe^{3+}, followed by precipitation as MnO_2 and $Fe(OH)_3$, respectively. This heterotrophic bacteria (mainly such related to the genus *Metallogenium*) able to oxidize Fe^{2+} and Mn^{2+} at slightly acidic and neutral pH. A portion of As^{3+} was oxidized to As^{5+} by some bacteria related to the genus *Pseudomonas* . The As^{5+} ions were then precipitated mainly as hydroxide and sulphide compounds or were adsorbed by the $Fe(OH)_3$ and by the organic matter (living and dead plant and microbial biomass) and clays present in the wetland.

Table 3. Removal of pollutants from the mine waters in the natural wetland

Pollutant	Pollutant removed, g/24 h	
	During the warmer months	During the cold winter months (at 0 – 5^{o}C)
Uranium	64 – 180	32 - 77
Manganese	145 – 611	92 - 203
Iron	1415 – 4316	910 - 2107
Sulphates	8404 – 18740	4105 - 9925

Apart from the arsenic, most of the radium as well as portions of the other metals were also removed by the above-mentioned sorption mechanisms (Table 3). The adsorbed ions were present as the exchangeable mobility fractions of the relevant element. Some algae (mainly such related to the genera *Volvox Pediastrum*, *Eudorina*, *Volvox*, *Melosira* and *Scenedesmus*) and microorganisms (mainly such related to the genera *Aspergillus*, *Penicillium*, *Pseudomonas* and *Bacillus*) were very efficient sorbents of pollutants. The content of uranium in some specimens of algae was as high as 270 mg/kg dry biomass, and that of radium exceeded 500 βq/kg. Negative effects of the pollutants on the growth and activity of the indigenous plant and microbial communities were not observed. At the same time, however, the contents of uranium and radium in some clay specimens exceeded 1000 mg and 1000 Bq per kg dry clay.

The efficiency of the water clean-up markedly depended on the ambient temperature (Table 4). However, good results were achieved even during the cold winter months (December-February) at temperatures close to 0^0 C. Since the environmental conditions during the winter are not favourable for the microbial and plant growth and activity, the role played by some sorbents, mainly be dead plant biomass and clays, was essential for the removal of pollutants.

Table 4. Content of pollutants in different plant species from the natural wetland

Pollutant	Typha latifolia		Typha angustifolia		Juncus bulbosus	
	I	II	I	II	I	II
Uranium, mg/kg dry	95 – 405	ND	41 – 114	ND	71 – 224	ND
Radium, Bq/kg dry	75 – 245	ND	45 – 125	ND	60 – 175	ND
Manganese, mg/kg dry	82 – 375	10	59 – 240	8	95 – 305	12

Notes: I – Data about plant specimens grown in the wetland;
II – Data about plant specimens grown in an non-polluted wetland;
ND = not detected.

The results obtained during this study showed that the treatment of acid waters polluted with radioactive and heavy metals, arsenic and sulphates can be efficiently carried out by natural wetlands with a proper size and located in regions with suitable geological and hydrogeological conditions.

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