

BIOREMEDIATION OF ACID DRAINAGE WATERS BY MEANS OF A PASSIVE SYSTEM

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Abstract

Acid drainage waters polluted with radionuclides, heavy metals and arsenic were treated by means of a passive system consisting of an alkalizing limestone drain and two constructed wetlands arranged in a series. An efficient removal of the pollutants was achieved by this system during the different climatic seasons, even during the cold winter months at temperatures close to the water freezing point. The pollutant removal was due to different mechanisms but the biosorption, microbial dissimilatory sulphate reduction and chemical neutralization played the main role.

Keywords: *acid drainage; bioremediation; passive systems; constructed wetlands*

Introduction

The uranium deposit Curilo, Bulgaria, located in a short distance from Sofia, for a long period of time was a site of intensive mining activities including both open-pit and underground mining techniques as well as in situ leaching of uranium. These operations were ended twenty years ago but since that time the deposit is a permanent source of acid mine drainage waters. The generation of these waters is connected mainly with the oxidation of pyrite and other sulphide minerals present in the ore body by the indigenous acidophilic chemolithotrophic bacteria. Different methods to inhibit this activity and the subsequent generation of pollutants (Nicolova et al., 2005) or to treat portions of the polluted waters by means of different passive systems such as natural and constructed wetlands, alkalizing limestone drains, permeable reactive multibarriers and rock filters, used separately or in different combinations, were applied (Groudev et al., 2008). The present paper contains data about the treatment of a portion of the polluted waters which leave the deposit area through a small ravine and pollute some agricultural lands, small lakes and ground waters. The treatment was carried out by means of a passive system consisting of an alkalizing limestone drain and two constructed wetlands

arranged in a series. The waters had a pH in the range of about 2.5 – 4.0 and contained radionuclides (mainly uranium and radium), heavy metals (copper, zinc, cadmium, lead, nickel, cobalt, iron, manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry. The water flow rate through this system varied in the range of approximately 0.1 – 0.5 l/s, reflecting water residence time from about 75 to 15 hours.

Methods

The alkalizing drain contained a mixture of crushed limestone and rock pieces (in a ratio of about 1:2 as dry weight) with a particle size less than 12 mm. The first wetland was characterized by a subsurface water flow, a very dense water and emergent vegetation and a diverse microflora containing rich populations of different sulphate-reducing bacteria and several metabolically interdependent microorganisms (Table 1). *Typha latifolia* and *Phragmites australis* were the prevalent plant species in this wetland and their total number usually exceeded 100 plants/m². *Typha angustifolia* and representatives of the genera *Juncus*, *Eleocharis*, *Potamogeton*, *Carex* and *Poa* as well as different algae were also present. The second wetland was characterized by a relatively larger water surface but at a small depth (usually less than 10 cm). The bottom of this wetland consisted of five steps connected as cascades to enhance the natural aeration of the waters. *Typha latifolia* was the prevalent plant species in this wetland but its density was much lower (about 40 – 50 plants/m²). However, several rock pieces with sizes in the range of about 5 – 10 cm were located between the plants and their surfaces were covered by biofilms of algae and different heterotrophic bacteria (Table 1).

Table 1. Microflora of the acid drainage waters and the constructed wetlands

Microorganisms	Drainage waters before treatment	First wetland		Second wetland		
		Waters	Sediments	Waters	Sediments	
		Cells ml (g)				
Aerobic heterotrophic bacteria	10 ¹ – 10 ³	10 ³ – 10 ⁶	10 ² – 10 ⁴	10 ⁵ – 10 ⁸	10 ³ – 10 ⁵	
Cellulose-degrading bacteria	0– 10 ¹	10 ² – 10 ⁵	10 ¹ – 10 ³	10 ² – 10 ⁴	10 ¹ – 10 ²	
Fe ²⁺ -oxidizing chemolithotrophs (at pH 2)	10 ⁴ – 10 ⁷	10 ¹ – 10 ²	0– 10 ¹	0– 10 ²	0	
Fungi	0– 10 ²	10 ¹ – 10 ³	0– 10 ²	10 ¹ – 10 ³	0– 10 ¹	
Anaerobic heterotrophic bacteria	0– 10 ²	10 ² – 10 ⁴	10 ³ – 10 ⁵	10 ² – 10 ⁴	10 ³ – 10 ⁵	
Sulphate-reducing bacteria	0	10 ² – 10 ⁴	10 ³ – 10 ⁵	10 ¹ – 10 ³	10 ² – 10 ⁴	

Results and discussion

An efficient removal of pollutants was achieved by this system and their residual concentrations in the effluents in most cases were decreased below the relevant permissible levels. The efficiency of treatment markedly depended of the temperature but was efficient even during the cold winter

months, at temperatures close to the water freezing point, although at longer residence times (Table 2).

Table 2. Removal of pollutant from the acid drainage by means of the passive system

Pollutant	Before treatment, mg/l	After treatment, mg/l	Pollutant removed, g/24 h	
			During the warmer months (at 6 – 28°C)	During the cold months (at 0 – 5°C)
U	0.44 – 4.60	< 0.10	21 – 86	6.40 – 25
Cu	0.46 – 12.45	< 0.35	32 – 242	8.80 – 41
Zn	0.82 – 25.07	< 0.50	44 – 460	12 – 64
Cd	0.01 – 0.12	< 0.01	0.64 – 5.10	0.21 – 0.70
Pb	0.14 – 0.91	< 0.10	8.20 – 46	3.20 – 10
Ni	0.37 – 5.14	< 0.30	21 – 154	8.82 – 25
Co	0.32 – 4.15	< 0.30	18 – 120	7.10 – 21
Mn	0.95 – 46	< 0.5 – 2.8	53 – 590	17 – 68
Fe	77 – 925	< 1.0 – 8.2	1450 – 14870	410 – 1621
As	0.01 – 0.55	< 0.01	10 – 41	0.50 – 9.51

The removal of pollutants was due to different processes and their role varied in the different climatic seasons. The main role of the alkalizing drain was to increase the pH of the waters being treated to about 4.5 – 6.5 and in this way to facilitate the growth and activity of the plant and microbial communities inhabiting the wetlands. Furthermore, a portion of ferric ions precipitated as ferric hydroxide. This compound was an efficient sorbent for most of the other pollutants and portions of them co-precipitated in the alkalizing drain. The microbial dissimilatory sulphate reduction and the sorption of pollutants by the organic matter (living and dead plant and microbial biomass) and clay minerals played the main role in the pollutants removal in the first wetland. The heavy metals and arsenic were precipitated mainly as the relevant insoluble sulphides. The dissolved hexavalent uranium was reduced to the tetravalent state and was precipitated, mainly as uraninite (UO₂). However, portions of these pollutants as well as most of the radium were removed by sorption on the above-mentioned sorbents. The dead plant biomass was more efficient sorbent than the living plants. Larger contents of pollutants were also found inside the dead plant cells. Relatively small portions of the pollutants were accumulated inside the living plant and microbial cells. The content of uranium adsorbed on and accumulated in some specimens of algae was as high as 550 mg/kg dry biomass, and that of radium exceeded 100 Bq/kg. At the same time, the content of uranium in some clay specimens exceeded 1000 mg/kg dry clay, and that of radium exceeded 1000 Bq/kg.

The role of sorption mechanisms was particularly essential during the cold winter months when the growth and activity of the plant and microbial communities in the wetland were negligible or completely inhibited.

The effluents from the first wetland were enriched in dissolvent organic compounds and in some cases still contained iron and manganese ions in concentrations higher than the relevant permissible levels. The organics were degraded in the second wetland by the different heterotrophs and the residual amounts of iron and manganese were precipitated as $\text{Fe}(\text{OH})_3$ and MnO_2 as a result of the prior bacterial oxidation of Fe^{2+} to Fe^{3+} and of Mn^{2+} to Mn^{4+} , respectively. This oxidation was carried out by some aerobic heterotrophic bacteria producing peroxides as oxidizing agents.

Conclusions

The data from this study revealed that acid drainage waters heavily polluted with radionuclides, heavy metals and arsenic were efficiently treated by means of a passive system consisting of an alkalizing limestone drain and two constructed wetlands arranged in a series. The system was constructed in a site with suitable geological, hydrogeological and climatic conditions and the wetlands were characterized by plant and microbial communities well adapted to the local environmental conditions, including to the composition of the polluted waters. It properly sized, such water cleaning systems can operate several years and can be regarded as one of the most typical examples of sustainable development of anthropogenic ecosystems, very similar to the natural ecosystems of the same type.

References

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