Uranium Wastewater Treatment using Wetland System

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The experimental study performed by wetland system using uranium contaminated water (8mg/L U, 4mg/L Mo) from the tailing pond located near uranium processing plant lead to the uranium removal rate about 95% comparing to 60 – 70% for conventional contaminated waste water treatment processes. The experiments were traced the high uranium imobilisation up to 0.4 mg/L after 80 days of process, the molibdenum and nitrates ions concentration monitoring and the optimum process parameters establishing. Using such wetland systems lead to advanced uranium waste water decontamination in accordance with the environmental quality standard.

Key words: wetland, uranium effluent, plants, contaminants

In the literature is presented a new remediation method of sites with low to moderate levels of contamination and it can be used in conjunction with other more traditional remedial methods as a finishing step. This new method is called wetland system.

The spectrum of wetland types is very wide; it ranges from constructed wetlands in a greenhouse (living machine), to natural wetland systems passing through constructed wetlands for treatment purposes, polishing wetlands, and combined sewers overflow ponds, reconstructed wetlands, etc. Wetlands constructed to treat contaminated waste waters are usually very sophisticated. They can be constructed even on dry soil where a wetland could never be imagined [1,2].

In order to provide a better design of reconstructed wetlands that matches as much as possible the needs of nature, a pronounced know-how of the natural processes of wetlands has to be provided as well as the technique of the reconstruction of natural wetlands.

To design and develop a wetland for effective wastewater treatment, it is necessary to understand the processes that occur in wetlands. Primary processes include [3]:

- uptake and transformation of nutrients by microorganisms and plants;
- breakdown and transformation of pollutants by microorganisms and plants;
- filtration and chemical precipitation through contact with substrate and litter;
- settling of suspended particulate matter;
- chemical transformation of pollutants;
- absorption and ion exchange on the surfaces of plants, sediment and litter.

In literature [4] are pointed the advantages of the constructed wetlands:

- provide a high level of treatment;
- low operation and investment costs and easy to operate;
- can be aesthetically pleasing - depending upon design, location, and type of vegetation, constructed wetlands can enhance the landscape with colour, texture, and variety in plant materials.

The paper presents the research done for the advanced uranium (U), molybdenum (Mo) and nitrates (NO_3) ions immobilization from uranium processing plant wastewater, using wetland system.

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Experimental part

The effluent used in the experiments was the uranium wastewater from the tailing pond of the uranium processing plant, with the physical-chemical characteristics presented in table 1.

The experiments were performed in a lab scale experimental module – constructed wetland system (fig. 1).

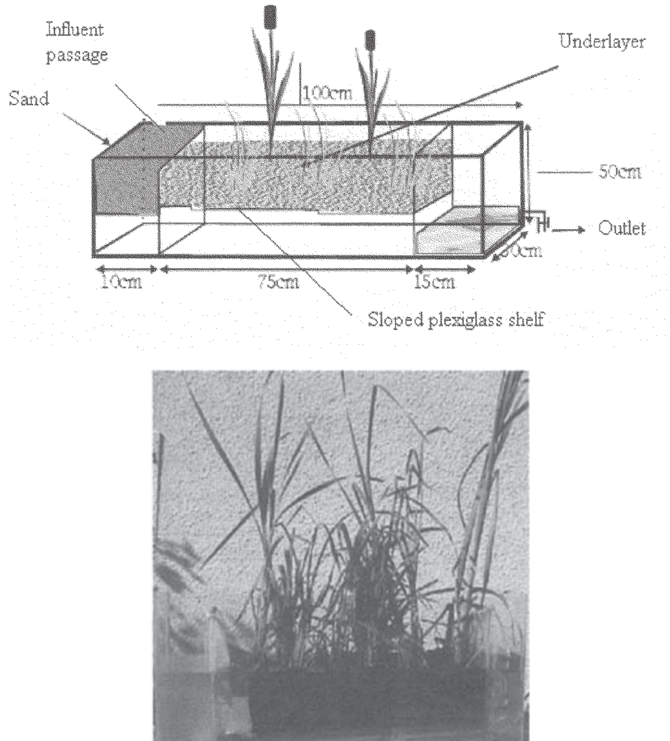

Fig. 1. Constructed wetland experimental laboratory model

The experimental module was made by plexiglas, sized: 100 cm length, 30 cm with and 50 cm high and consist in a segmental tank with three compartments. Perforated partition walls separate the designed compartments.

Table 1
CONTAMINATED WATER PHYSICAL-CHEMICAL CHARACTERISTICS

No. crt.	Elements	U.M.	Results
1	Uranium natural	mg/l	8
2	Molybdenum	mg/l	4,0
3	pH	pH units	9
4	Total suspended solid	mg/l	38.5
5	CBO_5	mgO_2/l	37
6	CCOMn	mgO_2/l	31,18
7	CCOCr	mgO_2/l	192
8	N total	mg/l	33,55
9	Nitrates	mg/l	86
10	Nitrites	mg/l	0,3
11	Sulphurs and HS	mg/l	< 0,005
12	Residue at 105^0C	mg/l	1678

The first compartment (10 x 30 x 50cm) is filling with sand for ensure a good effluent infiltration, and more than this in this compartment is realized a pre-treatment of effluent by solid suspended settlement.

The second compartment (75 x 30 x 50cm) is designed to ensure an inclination angle about 1%. The effluent passes through the wetland system walls to the third compartment, designed with a sampling system. Therefore constructed wetland substrate was built on sand, natural soil sampled from natural wetland system, peat and flower soil. This substrate provides the system with high porosity, appropriate *p*H for plant growing and vegetation establishment.

The decisive criteria in wetland plants selection were: chemical composition of waste water, water depth, temperature, system geometry. Regarding these considerations the vegetation of experimental constructed wetland was represented by the following species, which proved to be most appropriate: *Phragmites, Typha and Carex riparia.*

To increase the wetland efficiency plant rhizomes and roots were collected in the growing season (March) from uranium ore processing plant area. In this area there are natural wetlands already formed.

To reduce the risk of preferential flowing channels, vegetative species must be planted in cross line on the flowing direction, the density of vegetation is 80 – 120 plants/m^2. Dense wetland vegetation will act to slow water velocity.

The vegetation in constructed wetlands ensures:

- roots and rhizomes provide oxygen to sediments;
- submerged parts of the plants provide support for biofilms which facilitate nutrient transformations and organic flocculation, provide filtration of pollutants, enhance sedimentation;
- emergent parts of the plants provide protection from the wind and shading which decreases water temperature and algae growth.

The study of the U, Mo and nitrates accumulation by the wetland system was done during a period of 80 days at a flow rate of 20 L/day of waste water. The effluent samples were analyzed after each three days for U, Mo and N compounds.

Because the waste water *p*H is 10 before the wetland feeding the *p*H was reduced to 6.5 value.

Analytical methods used depend on the analyzed elements: atomic absorption - using an atomic absorption spectrophotometer VARIAN spectrAA-880 with appropriate lamps, colourimetry - using colourimeter type UV-Vis CECILIA 1011, volumetric and gravimetric analysis and spectral γ method by HPGe – using multichannel analyser of Ge for γ radiation (0-3MeV) –ORTEC.

The following relation calculated the rate of contaminant recovery in wetland system from the contaminated water and soil samples:

$$G_{contaminant}\ \% = \frac{C_i - C_f}{C_f}.100 \qquad (1)$$

where:

G = recovery rate (%);

C_i = contaminant concentration in the contaminated water (g/L);

C_f = final concentration (g/L).

Relative abundance of dominant species using the coverage of each species in the wetland system (percentage of coverage exceeds 100% because of overlapping vegetation layers) is calculated using the next relation:

$$\text{Relative abundance} = \frac{\text{Covering species}}{\text{Total vegetation cover}} \cdot 100 \qquad (2)$$

Results and disscussions

The model experiments were done to analyse the aquatic plants efficiency for the contaminants (U, Mo and nitrates) from uranium effluents from uranium decantation tailing pond located in the area of uranium ore processing plant.

The process of uranium accumulation in wetlands can be considered as analogous with that of ore enrichment in sedimentary type uranium deposits. In such deposits, U(VI) minerals like carnotite and tyuyamunite form and U(IV) oxide minerals such as pitchblende (UO_2:$2UO_3$) and coffinite (UO_2:SiO_2) occur in the less oxidized areas.

For effective uranium immobilization was performed the maintenance of reducing conditions within the wetland sediment, by microbial mediated reduction of uranyl ions (U(VI)) and by plants or inorganic substrates adsorption [5-7].

The main factors in uranium adsorption are: pH, kinetics, organic components and solute concentrations for sorption. Although uranium sorption on wetland sediments may be very strong, it is not an irreversible process.

The experimental results regarding the uranium efficiency removal after 80 days is represented in figure 2.

The uranium removal rate from contaminated water samples increases in time up to 95%, after only 40 days, the uranium removal efficiency is about 90%. The uranium concentration in effluent decreases after 40 days, the concentration becomes 0.39g/L value which is in

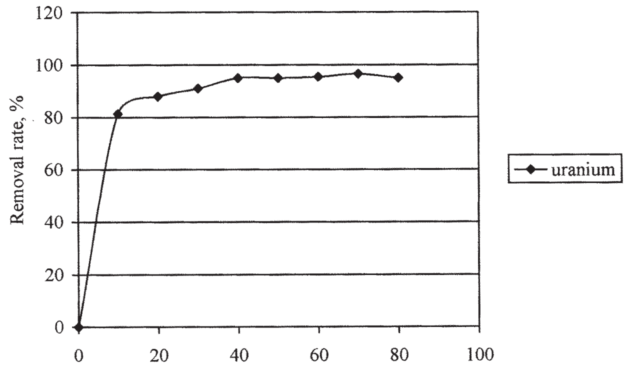

Fig. 2. Uranium removal efficiency

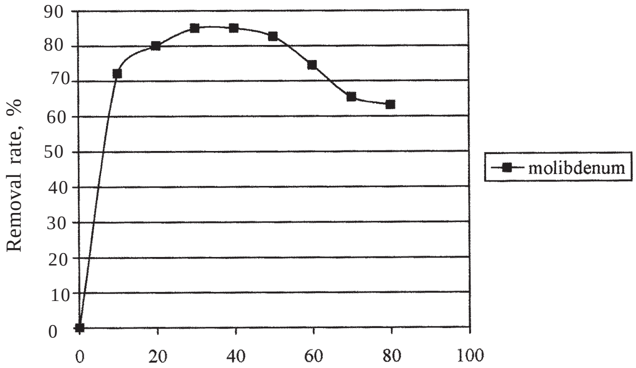

Fig. 3. Molybdenum removal efficiency

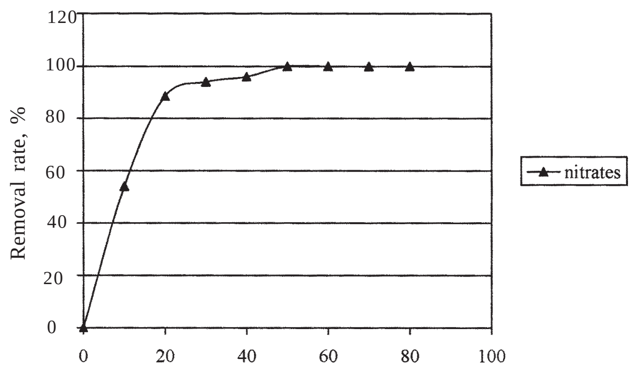

Fig. 4. Nitrates removal efficiency

accordance with environmental standards. After 80 days, the uranium concentration decreasing was not significant.

The experimental results regarding the Mo removal efficiency, after 80 days, are represented in figure 3. The Mo decreasing performed on a different mechanism, so after about 20 days the analysis shows that Mo removal efficiency is about 85%, then the removal efficiency decrease, so Mo is desorbed in the process. This phenomena may be explained by reaching the saturation due to the U-Mo bounding and correlations.

Nitrogen (N) is a key element in wetland biogeochemical cycles. Nitrogen occurs in a number of different oxidation states and numerous biological and physico-chemical processes can transform nitrogen in these different forms. The major removal mechanism for organic nitrates in wetland systems is the sequential processes of ammonification, nitrification and denitrification. Ammonia is oxidized to nitrate by nitrifying bacteria in aerobic zones. Organic nitrogen is mineralized to ammonia by hydrolysis and bacterial degradation.

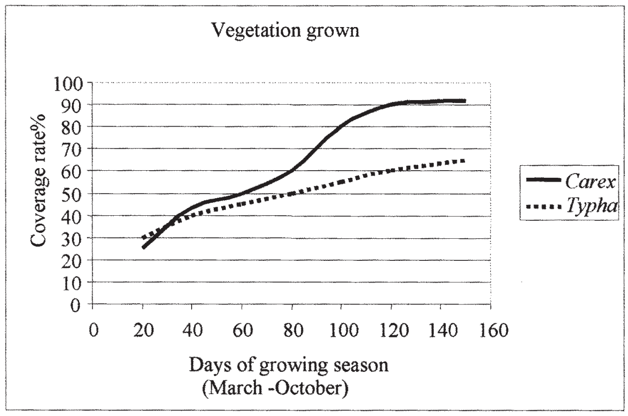

Fig. 5. Vegetation coverage rate

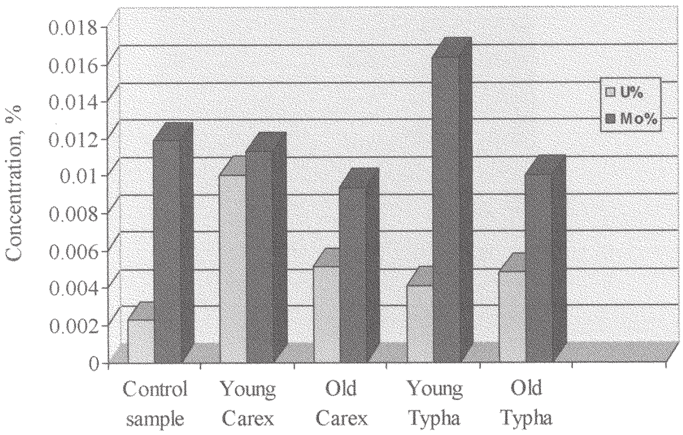

Fig. 6. Contaminants concentration (U, Mo) in vegetation

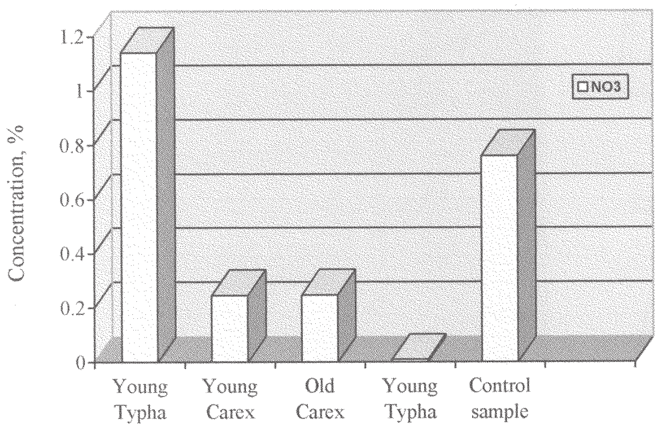

Fig. 7. Monitorization of nitrates concentration in vegetation

Nitrates are converted to nitrogen gas (N_2) and nitrous oxide (N_2O) with denitrifying bacteria in anoxic and anaerobic zones. The oxygen required for nitrification is supplied by diffusion from the atmosphere and leakage from macrophyte roots. Nitrogen is taken up by plants, incorporated into the biomass and released back as organic nitrogen after decomposition [8].

The experimental results on nitrates efficiency removal after 80 days is represented in figure 4. The effluent concentration after 40 days of process leads to values under the detection limits. The removal nitrates rate is about 85%, after only 10 days and the total nitrates removal is observed after 40 days of process development.

Wetland system plants have a high growth rate during the growing season. To obtain full coverage of wetland is required a minimum of 6 months and maximum 2 years. Plants used in experimental wetland system have achieved coverage of over 100% in a single growing season (March

Tabel 2
RECOMMENDED OPERATION PARAMETER

Factor	Exp. Range
Detention time (for soluble pollutants removal), days	10 to 14
Detention time (for suspended pollutants removal), days	3 to 5
Effluent flow, l/days	20
Water depth , m	0.2 to 0.5
Water pH	6 – 8
Aspect ratio	5:1 to 10:1
Bottom slope, %	0.5
Vegetation density	80 plants/m^2

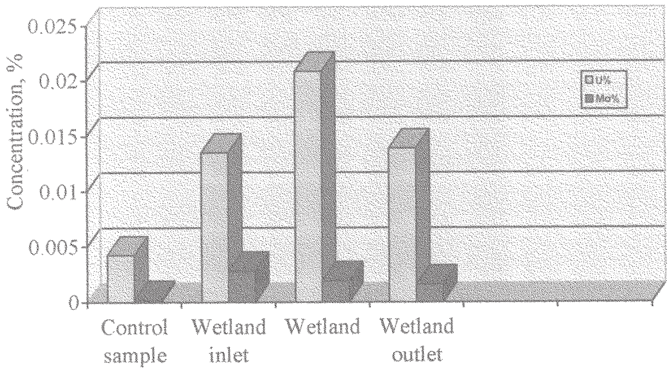

Fig. 8. Monitorization of contaminants concentration in soil

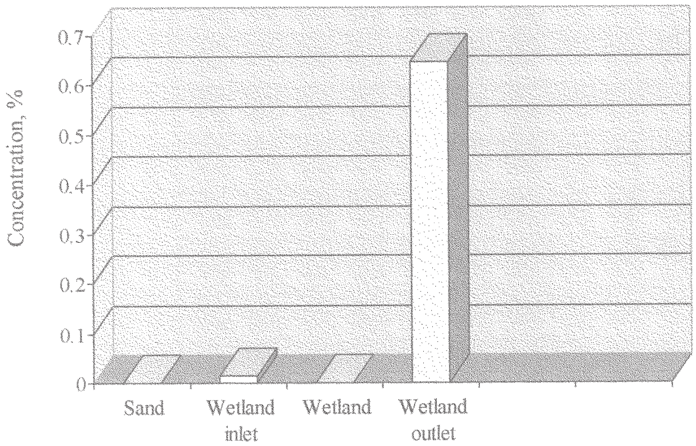

Fig. 9. Monitorization of nitrates concentration in soil

to October). Full development cycle roots - rhizomes and the system establishment require a period of 3 to 5 years. Figure 5 present the evolution of plant growth and development during the monitoring programme.

The content of contaminants (U and Mo) in plants is showed in figure 6. The contaminants concentrations in wetland vegetation are varied as a function of the stage of plant development.

The results show that the U and Mo concentration in young *Carex* plant (U = 0.01004 %) are higher than the maturity (U = 0.00514%), while *Typha* concentrated more Mo (Mo = 0.0163%) than U (U = 0.00412%).

Nitrogen content in plants is graphically presented in figure 7. Significant results were obtained for plants reached maturity. The mature *Typha* retains a large amount of nitrates, NO_3 = 1.14%, comparing with young plant with the content of about 0,01% NO_3.

Soil monitoring consists mainly in the *p*H control and sampling the existing contaminants. The soil samples are collected after the following program: preliminary characterization at the beginning, one year after the project start and approximately every three years to assess and characterize the transformations which are taking place in the soil.

The test results were plotted in figure 8. From figure it is noted that U is concentrated most in the soil wetland system (U = 0,02085%). In terms of nitrates concentration in soil (fig. 9), significant data were obtained only from samples collected at the outlet of wetland system (NO_3 = 0,6456%).

The experimental study results goes to process operation parameters recomandation resumed in table 2.

Conclusions

The present paper performed an experimental study of the radioactive contaminants accumulation process using a laboratory wetland system. The radioactive contaminants are from waste water from the uranium processing plant tailing pond. The research result has highlighted the following aspects:

- the efficiency of uranium removal increase in time and after 80 days of experiment reached values of 95%, the uranium concentration in effluent decreases after 40 days, the concentration becomes 0.39g/L value that is in accordance with environmental standards; after 80 days, the uranium concentration decreasing was not significant;
- after 20 days the analysis shows that Mo removal efficiency is about 85%, then the removal efficiency decrease, so Mo is desorbed in the process;
- the results regarding effluent concentration passed through the wetland system showed that after 40 days effluent no longer contained nitrates; the removal efficiency rate is 85%, after only 10 days;
- the plants used in experimental wetland system have achieved coverage of over 100% in a single growing season (March to October);
- the results show that the U and Mo concentration in young *Carex* plant (U = 0.01004 %) are greater than the

maturity (U = 0.00514%), while *Typha* concentrated more Mo (Mo = 0.0163%) then U (U = 0.00412%);

- significant results were obtained for plants that reached maturity; the mature *Typha* retains a large amount of nitrates, NO_3 = 1.14%, comparing with young plant with the content of about 0.01% NO_3;
- U is concentrated mostly in the soil wetland system (U = 0.02085%);
- in terms of nitrates concentration in soil significant data were obtained only from samples collected at the outlet of wetland system (NO_3 = 0.6456%);
- the optimum design factors recommended in the constructed wetlands design, are: detention time, effluent flow, water depth, aspect ratio and shape.

The experimental results certify that the application of remediation of contaminated environments using wetland system is an efficient alternative decontamination solution by environmental friendly unconventional methods.

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