

Sorption ability of the composite sorbent for water treatment from radioactive elements

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Abstract. The goal of research is to develop the composite sorbent with application of various metal oxides nanoforms and nonpathogenic mold fungi mycelium modified by these nanoforms. This article describes the producing method of the composite sorbent and the research results of the sorbent sorption ability while the sorption process conditions are changed.

1. Introduction

Nuclear energy makes possible to avoid an energy crisis by using the energy released at certain atomic nuclei reactions. However, with the development of nuclear energy and its related industries, environmental pollution by radioactive ions has become a serious environmental issue, which carries a potential threat to human health as the long-lived radionuclides do not decompose. Instead, they tend to accumulate, can be easily transported over long distances and often included in the biological cycle of matter. Up to 80% of anthropogenic radioactive pollution arrives in the Earth aquatic environment, turning it into the most powerful depot of radionuclides.

The major problem in the technologies development for the radioactive substances disposal from the environment is the invention of materials that can irretrievably, effectively and abundantly absorb radioactive ions from water.

In the last years in many countries research on new class sorbent development is actively progressing. These sorbents should constitute of biological substances or include them as the main element – biosorbents. For example, they can be produced from microbe mass or fungi which are microbiological industry wastes. Apart from that, application of different metal oxides nanoforms as a sorbent is viewed as promising.

The prerequisites for metal oxides nanoforms using as component of composite sorbent are hypotheses on fact that - the metal nanoparticles can be used as matrices for immobilization of plutonium, technetium, uranium and transuranic elements due to the ability to absorb radioactive ions while the deformation process of the nanomaterial takes place [1]. As a result, the absorbed radionuclides are permanently enclosed in the sorbent structure [2].

The prerequisites for nonpathogenic mold fungi mycelium using as component of composite sorbent are hypotheses that state - the main characteristics of metal nanoparticles deposited on the growing mycelium of fungi are not differed from the nanoparticles properties suspended in the solution. At the same time there was no any preliminary modification of the particles or mold for the adsorption of nanoparticles on the surface of the growing mycelium. While deposition of the nanoparticles on the mold there was no any aggregation with each other [3].



2. Materials and methods

For the research model uranyl nitrate solutions with various initial concentration of $(\text{UO}_2)^{2+}$ were used. As the nanosized components of composite sorbent the titanium dioxide nanotubes, obtained by low-temperature sintering of electroexplosive nanopowders and the nanopowders of cupric oxides, obtained by electrical explosion of cupric wire in air were used. The titanium dioxide nanotubes were visualized using scanning electronic microscope Hitachi S-3400N with the additional attachment for microanalysis which was used for fluorescent-spectral analysis of nanomaterials. The length of the nanotubes was varied from 300 nm to 600 nm, the diameter was about 8 nm and the thickness of the walls about 2.5 nm.

As the biological component for sorbent development the mycelium of non-pathogenic mold fungi *Aspergillus niger* was used due to its natural occurrence and because this filamentous fungi exhibits a high tolerance to environmental conditions [4].

2.1. Cultivation of microorganisms

For the cultivation the inoculating of microorganisms nutrient medium "Nutrient broth dry" (the volume is 100 ml, pH 5) was produced by Pasteur loop aseptically. Cultivation of microorganisms was carried out in 250 ml round-bottomed flask at 37°C in a thermostat until the surface protection film fungi certain size (2-3 mm) will appear.

After that the flasks were placed on a shaker and were incubated under constant stirring with heating (350 rev/min) for 7 days. The growth of microorganisms was recorded visually (appearance of the film, blurred the medium, sediment appearance, pH change). Upon completion of cultivation mycelium of nonpathogenic mold fungi was washed three times by distilled water.

2.2. Deposition of nanomaterials on the mycelium of nonpathogenic mold fungi

Firstly, 100 ml of distilled water and samples of nanomaterials (TiO_2 , CuO) were added to separate 250 ml flask. It is known that nanoscale materials form poorly stable suspensions [5]. High ability of nanoparticles to agglomerate in an aqueous medium does not allow reaching the maximum surface and, consequently, the maximum sorption ability of the material. The ultrasonic dispergation was used for agglomerates to breaking it up.

Secondly, into each flask 1 g (wet weight) of washed mycelium was added and then the flasks were closed with gauze-cotton plugs and were stirred in the shaker (350 rev/min) for 24 hours.

2.3. The uranyl ions sorption process

The research of the uranyl ions sorption process was carried out under static conditions at the indoor temperature. In all experiments the volume of the solution was 5 ml and the weight of composite sorbent sample was 1 g. The time of contact of the sorbent with the solution was from 1 to 14 days. Upon completion of the sorption solution was separated from the solids by centrifugation or filtration. The series of experiments were carried out to study the changes in the sorption properties of the composite sorbent depending on the variation of the sample mass of nanomaterial, the pH of the solution, as well as the time and temperature conditions of the sorption process.

Measurements of solution were performed at 130-ionomer and glass electrodes ESL-63-07. The pH measurement error was 0.05. Containing of uranyl ions in solution was estimated by luminescent method on spectrofluorimeter «Fluorat-02 Panorama» using standard routine.

Sorption capacity was evaluated by the degree of adsorption:

$$S = \frac{C_{in} - C_{fin}}{C_{in}} \cdot 100\% \quad (1)$$

where C_{in} and C_{fin} - initial and final uranium concentration, mg/L.

3. Results and discussion

3.1. Change in the pH of the solution

The experiment was conducted at the initial uranium concentration 1.212 mg/L. It was noted that the optimal pH value is from 4 to 5. It can be explained by the fact that in the acidic environment (pH = 2) uranyl ions compete with protons for binding sites on the surface of the sorbent. When pH=7, uranyl ions can contact not only with surface of the sorbent, but with hydroxide ions (Figure 1).

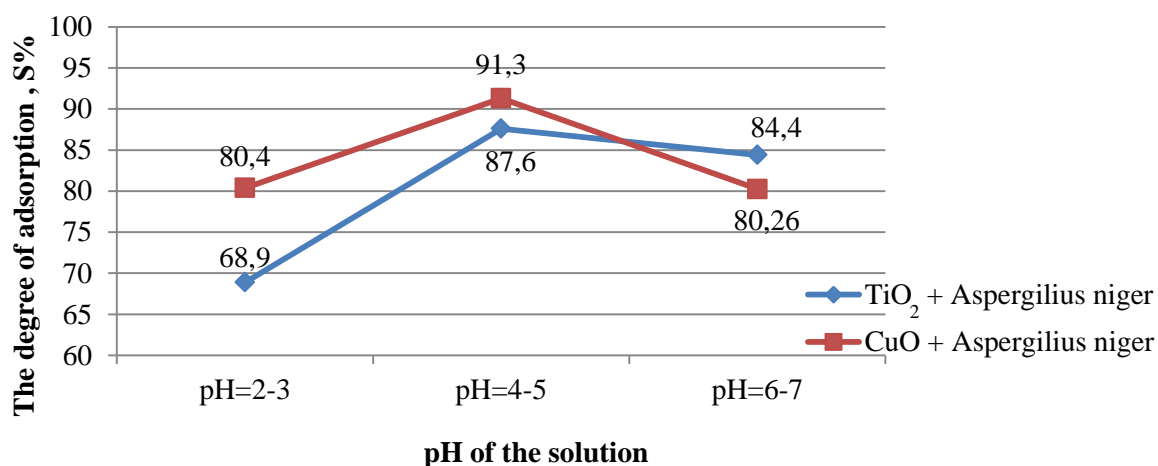


Figure 1. Dependence the degree of adsorption of uranyl ionson pH of the solution.

3.2. Change in the time of the sorption process

The experiment was conducted at the initial uranium concentration 1.17 mg/L. It was established that the maximum value of the degree of adsorption reached after one day and it is practically unchanged for the next two weeks (Figure 2).

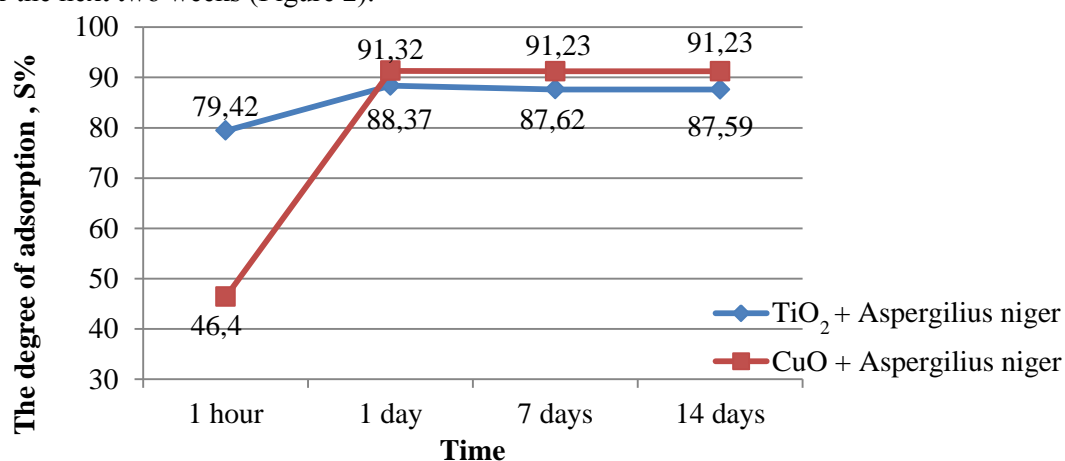


Figure 2. Dependence the degree of adsorption of uranyl ions on time.

3.3. Change in the temperature conditions

The experiment was conducted at the initial uranium concentration 1.17 mg/L. It was noted that the temperature difference has a little influence on the degree of adsorption value (within 10%). It can be explained by the fact that mycelium wall is highly dense, that does not change its structure depending on the temperature, and the degree of adsorption value is practically unchanged (Figure 3).

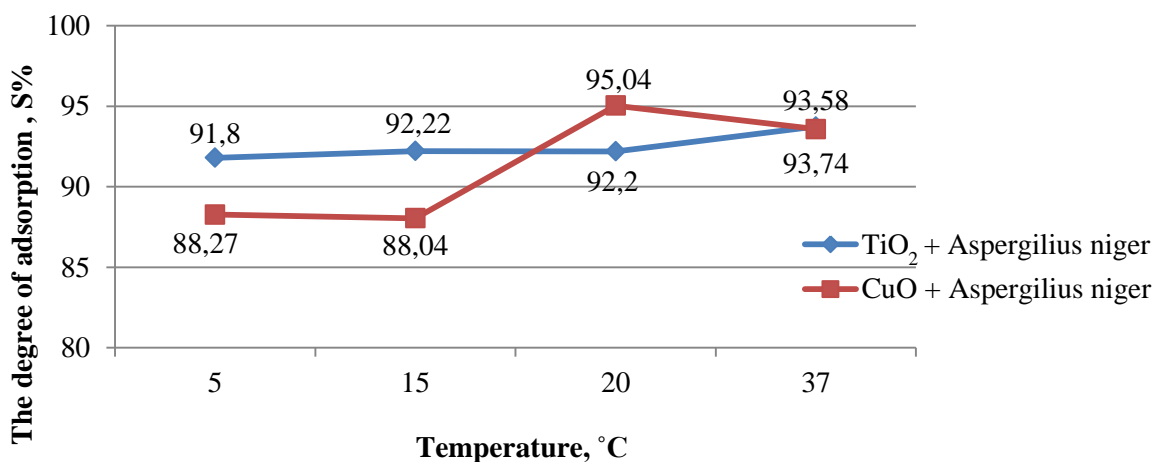


Figure 3. Dependence the degree of adsorption of uranyl ions on temperature conditions.

3.4. Change in the nanomaterial sample mass

The experiment was conducted at the initial uranium concentration 0.4 mg/L. In the study of the influence of nanomaterial sample mass on the absorption of uranyl ions it was founded that the optimal ratio nanomaterial:mycelium was the ratio of 1:100 (Figure 4), as thus binding sites of uranium ions on the surface of the mycelium is available that increases the efficiency of the sorbent.

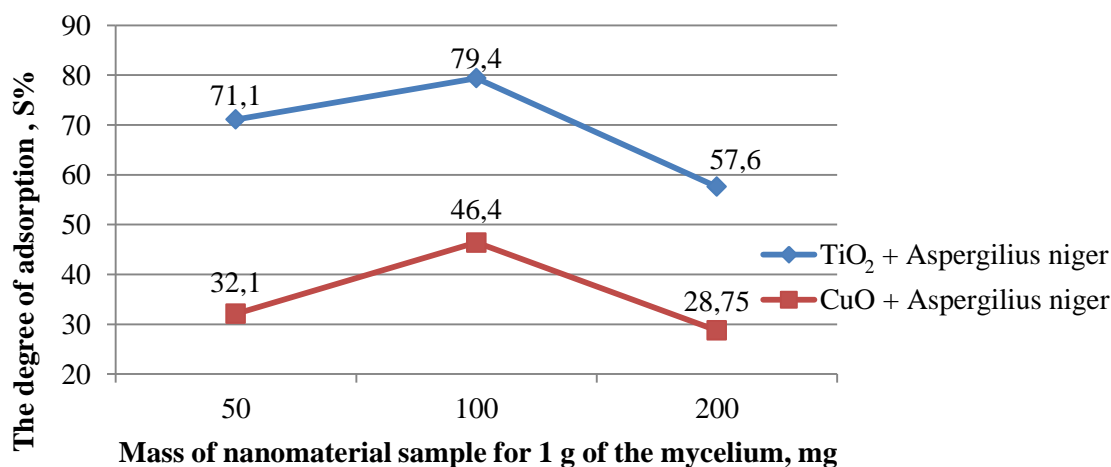


Figure 4. Dependence the degree of adsorption of uranyl ions mass on nanomaterial sample.

These results may indicate that at ratio nanomaterial:mycelium 1:200, the mycelium adsorbs uranium predominantly and the degree of adsorption is 57.6% for titanium dioxide nanotubes and is 28.75% nanopowders of cupric oxides. Raising of sorption with increasing sample mass of nanomaterial (ratio 1:100) leads to increasing the degree of adsorption to maximum value.

With further increasing in shot of nanomaterial (up to 1:50) the sorption degree is reduced to 71.1% for TiO₂ and to 32.1% for CuO. In this case, it can be assumed that the sorption takes place predominantly through the nanomaterial rather than mycelium as they mostly cover the sorption surface of mycelium and thereby reduce its contribution to the sorption process.

Due to visual inspection using a light microscope (40X increase) it was noted that the deposition of nanoparticles on the mycelium surface does not lead to deterioration of the mold growth or a change in its cultural properties. It proves that the formation of the hybrid matrix is not attended by the nanoparticles adhesion. The resulting composite material is a tubular mold mycelium, wrapped in

several layers of nanoparticles. Figure 5 shows images of *Aspergillus niger*: before (a) and after (b) cultivation with titanium dioxide nanotubes.

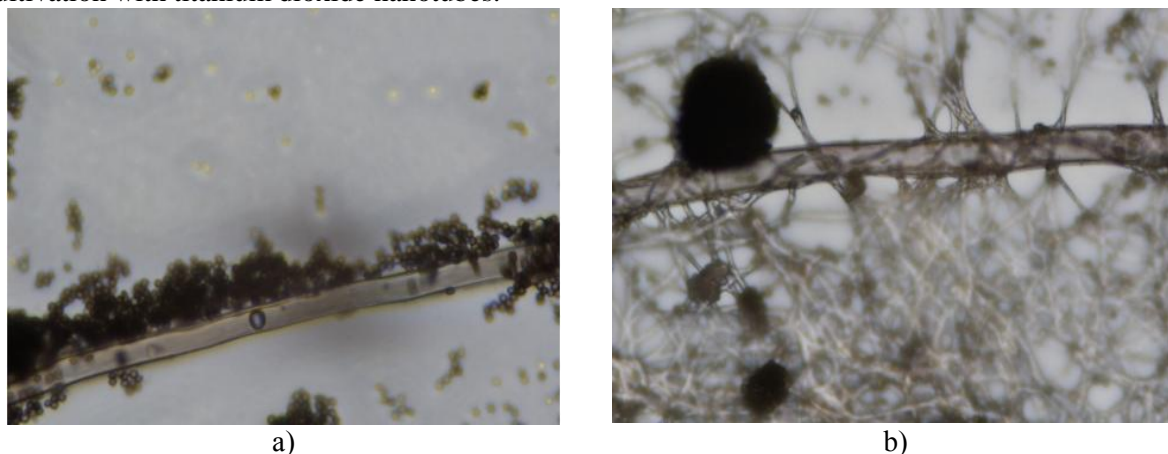


Figure 5 Images of *Aspergillus niger*: before (a) and after (b) cultivation with titanium dioxide nanotubes.

Due to separation of the metal nanoparticles, fungal matrixes preserve all the properties of the initial nanoparticles. The absence of aggregation contributes to the significant increasing of the modified mycelium activity in comparison with the nanoparticles suspended in the solution. Also an important advantage of mold matrices using is the fact that the composite sorbent is separated easily from the reaction mixture.

4. Conclusion

Due to application of non-pathogenic fungi as the active matrix for deposition of metal oxides nanoforms on the mycelium of nonpathogenic mold fungi it is assumed to be safe and simplified process for operation and utilization of composite sorbent in comparison with using separate nanosorbents. The optimal conditions to provide high sorption ability of the composite nanobiosorbent for water treatment from radioactive elements were founded.

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