Gold extraction from different minerals is possible by using hydrometallurgical processes, although the traditional method is the cyanide extraction. Starting with the beginning of the XX century this method was unanimously accepted around the world [1].

Main disadvantage of such process is represented by higher toxicity of the cyanide, which can pollute the groundwater as a consequence of accidental leaking, representing a real threat to human health. Because of that it is really important to develop and implement new and clean technologies for gold production and recovery, like adsorption, thus avoiding the appearance of other residual contaminants. Materials with adsorbent properties used for gold recovery can be: active carbon particles [2], mesoporous adsorbents [3], chitosan, or chemical modified oxides [4, 5].

Field of materials engineering should consider aspects of antibacterial and bactericidal properties in the design of new materials for advanced biomaterial systems with medical applications [6].

Last decades brought a larger use of gold in fields like electronic or medical devices. Gold usage has a long history, for example it was used as medicine (Chrysotherapy) since antiquity. Gold has been used to treat diseases such as small pox, syphilis, skin ulcers and measles [7, 8]. Its usage as medicine shows several benefits such as: stress and anxiety reduction, depression recovery, increased determination, increase of the intelligence coefficient until 20 units on Stanford-Binet scale, toning weakened organs, consequently improving the well-being of subjects. Since 70’s gold was included into the category of modern drugs used to ensure a good health of the joints especially in serious diseases such as rheumatoid arthritis [9]. At physical level gold is acting over the endocrine system and especially over the pituitary gland. Materials containing gold particles can be used in medical imaging and as well as into the cancer therapy [10]. Also, an enhanced and harmonized function of the endocrine gland which balancing secretion of different peptides - hormones, neurotransmitters - having a reviving and rejuvenating role was observed. Some tests proved that gold drugs strengthen the bone system and improve the sexual function. On cardiac level - was noticed that gold present a good efficiency into the equilibration of cardiac function, myocardial toning, adjusting heart rate, adjusting blood pressure, sanguine flow, elimination of cardiomyopathy and heart failure [11-13]. A big number of experimental studies proved that gold particles and gold ionic form present good antimicrobial and antibacterial effects [14]. It was proved that the cationic form of gold presents a moderate toxicity and the anionic form present zero toxicity [15].

Gold is probably the oldest metal used as delivery vehicle for gene therapy, and one of the most advanced agents in all drug pharmacopoeias, its administration to humans being both deliberate and unintentional. The widest clinical application of gold (in rheumatoid arthritis) derives from a premise that was totally flawed. It has been used clinically to perform immune suppression but has caused toxicity.

Despite the many known advantages of gold applications into different various economic areas, there is a serious concern about the toxicity of such materials on living organisms. The toxicity of gold, unlike most drugs, is not predictably related to the levels it achieves in body tissues. As a result, gold pharmacology and toxicology is remarkably complex. Recent laboratory findings on gold metabolism have highlighted the important metabolic differences between the three oxidation states (0, I and III). When placed in the context of a wealth of clinical experience, these findings provide useful information on its toxicology and mechanisms that involve the seemingly paradoxical behaviour of gold [16].

Toxic effect of gold materials onto the living organisms depends on the availability of materials. Bioavailability of gold particles is determined by adsorption, which depends on the particle size and superficial load. If materials exhibit a good bioavailability, they can also induce teratogenic effects [15].

In most cases, the toxicity tests of different materials are made using in vivo test on the cells cultures. Thus, the goal of this study was to determine the minimum concentration at which gold ions become toxic for bacterial cultures. Based on these results same amount of gold was adsorbed onto the surface of Amberlite XAD7
Experimental part

Material and methods

Microbiological behaviour of Au(III). Toxicity tests

For the establishment of the microbiological behaviour of Au(III), toxicity tests were performed using Au(III) solutions with concentrations of 50 mg/L: 33 mg/L: 25 mg/L: 10 mg/L: 5 mg/L and 2.5 mg/L obtained by dilution of a stock solution containing 100 mg Au(III)/L. Toxicity tests were performed on heterotrophic bacteria cultures obtained from Bega River. Bacteria cultures were obtained on a solid non-selective growth medium - Plate Count Agar, making two types of cultures: test cultures (3 repeats) – using test solutions with gold content and control cultures - without test solution. Inoculations method was performed by incorporation into Plate Count Agar growth medium, in sterile Petri dishes, which were incubated at 303 K for 48 h. In sterile Petri dishes 1 mL of test solution, 1 mL of bacterial inoculum and 10 mL of Plate Count Agar growth medium were introduced. In control cultures, instead of the test solution, 1 mL of sterile distilled water was used.

Synthesis and characterization of the MD7-G-Au material

In order to prepare the polymeric material with gold ions content used during antibacterial tests, Amberlite XAD7 resin (Sigma-Aldrich, Merck) was used as solid support. A well known amount of polymeric resin was functionalized with L – glutamic acid (Merck, Germany) which is acting as extractant. A proper amount of extractant was dissolved in distilled water and mixed with support into the ration support: extractant = 10:1. This mixture was kept in contact for 24 h at 298 K. Filtered and dried into the oven at 323 K for 24 h. Further, this functionalized resin was used for gold recovery from cyanuric baths with initial gold concentration of 2 g/L, cyanide matrix being broken with aqua regia. In order to determine the amount of gold that can be loaded onto the Amberlite XAD7-L-glutamic acid (MD7-G) surface, the efficiency of the adsorption process of gold ions on its surface has been pursued. For this, the gold initial concentration was varying in the range 2.5 mg Au(III)/L and 150 mg Au(III) /L. Adsorption process was conducted at pH 4 in a thermostatic shaker at 298 K, and 200 rpm for 2 h.

In samples, after filtration, the Au(III) residual concentration was determined by atomic adsorption spectroscopy, using the atomic adsorption spectrophotometer, Varian SpectraAA 280 FS.

Obtained material was characterized by the energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM).

Superficial charge of the material it is a key factor for adsorptive processes, so is important to determine the pZC. For these studies 0.1 M NaCl solution, varying pH in the range 1-14, using buffer solutions were used. Thus, 0.1 g MD7-G material over which 25 mL of NaCl was added and kept in contact for 1 hour in a julabo SW23 water bath at 298 K.

Results and discussion

Microbiological behaviour of the Au(III). Toxicity tests

In first stage, minimum concentration for which gold becomes toxic for bacterial cultures was determined. Experimental studies regarding gold toxicity on heterotrophic bacterial cultures are depicted into figure 1 (A to D).

After 48 h incubation, a very good bacteria growth was observed for the control culture (fig. 1 A). In test cultures, bacteria growth at 2.5 mg Au(III)/L and 5 mg Au(III)/L concentrations was observed (fig. 1 C, D). Starting with 10 mg Au(III)/L, no bacteria growth was observed (fig. 1 B).

Synthesis and characterization of the MD7-G-Au material

MD7-G-Au synthesis method

A schematic representation of the MD7-G-Au material synthesis is presented in figure 2.

pZC of MD7-G material

For materials with good adsorbent properties, knowing the acid-base properties has an important role to play in their use. Thus, when the H+/OH ions can determine the potential at interface, this can be expressed as a zero electrical charge point, in terms of pH. We can affirm that the material pZC is the pH value at which the material surface has a net charge. The pZC determination by the equilibrium method was performed[17-19]. For any initial pH value, in the range 1-14, the material has buffering capacity. In figure 3 the pZC for MD7-G material is presented.

In the initial range pH, 4-8, the final pH remains constant, which allows us to affirm that the material pZC is 4. The pH

Fig. 1. Bacteria growth after 48 h incubation in control culture and tests culture
range 4-8 can be considered the equilibrium domain for the material. Produced adsorbent material has a pZc interval form 4 to 8, which allows the use of this material in adsorption processes at pH 4-8. For this pH value, both cationic and anionic species can adsorb on the material surface. For pH values below the pZcone, material surface will be positively charged due to H⁺ protons adsorbed, favouring the adsorption of anionic species. For pH values above the pZcone, the material surface will be negatively charged due to OH⁻ adsorbed hydroxyl ions, favouring the adsorption of cationic species.

Au (III) loaded efficiency
Due to its antibacterial and antimicrobial effect, the gold amount existing in the biological environments is very important. The higher the gold amount is, the more benefits are, in terms of destroying bacteria.

The gold amount dependence loaded through adsorption on the MD7-G material surface of efficiency with which it manages to retain it is shown in figure 4. It can be seen that with the increase in the gold concentration into the solution increase the gold load on the MD7-G synthesized material surface, increasing its efficiency of retaining gold. However, over 100 mg of Au (III)/L the material’s efficiency decreases, so that for further studies regarding antibacterial effect behaviour were used gold doped materials obtained for maximum efficiency.

Characterization of the MD7-G-Au material
Energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM)
For morphological and elemental analysis of MD7-G-Au in powder form, we used the scanning electron microscopy method, SEM and the energy dispersive X-ray spectroscopy, EDX.

The analysis was performed to prove the presence of gold particles in the synthesized material. The obtained results are presented in figure 5 and figure 6. From the presented dates it can be observed the gold presence onto MD7-G-Au material surface.
Infrared spectroscopy (FT-IR)

In order to highlight the groups specific to Au (III) doped MD7-G material, FT-IR spectroscopy was used. The specific spectrum of the material is shown in figure 7.

From the FT-IR spectrum it can be observed that around the wavelengths of 1469 and 1389 cm\(^{-1}\), vibrations specific to the aliphatic C-H group occur, and at 1700, 1200 and 1300, and at the 1100 cm\(^{-1}\), vibrations specific to the bond C=O. All of these vibrations being specific to the Amberlite XAD7 support, most of being powerful one[20, 21].

It is also observed that around the wave number 1500-1600 cm\(^{-1}\) vibrations specific to the NH\(_2\) groups from the extractant molecules[22,23], which reveal the functionalization of the polymer support with the amino acid specific groups. It can be observed that around 1600 cm\(^{-1}\) and 3400 cm \^-1\ are vibrations specific to Au (III) particles [24].

Antibacterial activities of the MD7-G-Au

Taking into account the necessity to produce new antimicrobial products (for example dyes easy to use in hospitals) was tested the antimicrobial effect of the MD7-G-Au produced material. During these tests, into the bacterial cultures the MD7-G-Au materials with different gold content were placed. Analysing obtained experimental data it was noticed that the MD7-G-Au material becomes toxic for bacterial cultures when tested sample contain 0.25 % Au (III). Into the figure 8 the experimental data obtained for type 1 test culture, where the MD7-G-Au material with 0.25% Au(III) which was placed in five areas on Plate Count Agar growth medium and type 2 test culture, the MD7-G-Au material with 0.25% Au (III) was mixed with 1 mL bacterial inoculum and 10 mL of Plate Count Agar growth medium are presented.

After 48 h incubation, a very good bacteria growth was observed in the control culture (fig. 8 A-C). In type 1 test culture, bacteria growth was observed just in marginal area of the growth medium where there is no the MD7-G-Au material (fig. 8 A). In type 2 test culture, no bacteria growth was observed (fig. 8 B).

In conclusion, the toxicity of MD7-G-Au material is obvious (fig. 9).

In type 1 test culture (fig. 9 A), all areas with MD7-G-Au material with 0.25% Au(III) are inhibitory for bacteria growth. In type 2 test culture, where the MD7-G-Au material with 0.25% Au(III) are evenly distributed in the growth medium, there is a general inhibition of bacteria growth (fig. 9 B).

Conclusions

Present study proved the antibacterial effect of gold particles found into the solutions containing Au(III) ions and also in case of gold particles loaded onto the functionalized Amberlite XAD7 resin with L-glutamic acid. Based on experimental data it was proved that no bacterial growth is observed when the gold concentration into the solution is 10 mg Au(III)/L. When the MD7-G-Au material was used the antibacterial effect was obvious when the gold concentration had a value of 0.25% Au(III).

In type 1 test culture, where the MD7-G-Au material with 0.25% Au(III) which were placed in five areas on Plate Count Agar growth medium, has been observed an inhibitory effect for bacterial growth on all areas covered with the MD7-G-Au material.

In type 2 test culture, the MD7-G-Au material with 0.25% Au(III) mixed with 1 mL bacterial inoculum and 10 mL of Plate Count Agar growth medium, has been observed an inhibitory effect for bacterial growth on all areas covered with the MD7-G-Au material.

Based on the obtained experimental data one can conclude that the MD7-G-Au material can be used into the production of different dyes used into the construction of smart building adaptable at climatic changes.
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