Description of the proposal

Metals constitute a group of chemicals whose presence in aquatic ecosystems pose a risk to human health, as well as the wellbeing of many other living organisms (Sun et al. 2008). The most important anthropogenic sources of metals are associated with mining, burning of fossil fuels, nuclear weapons and nuclear fuel production, manufacturing of fertilizers, metal plating and alloying, and wood preservation among others (Mirazimi et al. 2015; Dwivedi et al. 2010). Industrial wastewaters contain different types of inorganic and organic pollutants in either soluble or insoluble forms (Javanbakht et al. 2014). Coagulation-precipitation, ion exchange, complexation, reverse osmosis, chemical oxidation or reduction, and sorption are techniques commonly applied for metal removal. The main disadvantages of these methods are their high energy consumption, high operational cost, generation of large amount of sludge and in some cases secondary pollution, low efficiency especially at metal concentrations 1–100 mg/L (Yan et al. 2010; Sulaymon et al. 2013).

Application of biological objects for the removal of metal, defined as biosorption and bioaccumulation, has been recommended as a simple, economic, efficient, and environmentally friendly technique (Javanbakht et al. 2014). Biosorption is a metabolically-passive physicochemical process of pollutant removal, while bioaccumulation is a two-step process, which includes biosorption and transport of pollutant inside cells (Chojnacka 2010). Thus, in bioaccumulation, more binding sites are available for metal binding and lower residual concentrations can be reached. Non-living biomass, naturally abundant biomass types and/or industrial biomass waste can be used as biosorbents. Such types of biomass do not require maintenance and nutrition and do not produce toxic effects on microorganisms and their sorption capacity (Javanbakht et al. 2014; Chojnacka 2010). Bioaccumulation, however, can occur only by living cells and thereby complicates the process (Javanbakht et al. 2014; Chojnacka 2010). Biosorption and bioaccumulation of various metal ions by different types of microorganisms: fungi, bacteria, microalgae, have been reported in the literature (Safonov et al. 2015; Zinicovscaia et al. 2015; German et al. 2003).

Lithium is used in many items, such as high-performance grease, heat-resistant ceramics, flux for welding, batteries, harmaceuticals and is also required for use in a nuclear fusion furnace (Tsuruta 2005). Fluoride is a common contaminant in a variety of industrial wastewaters. Therefore, the recovery of lithium and fluorine ions is an important subject.

Neutron activation analysis (NAA) technique used in Frank Laboratory for Neutron Physics JINR to determine the efficiency of metal removal by biological objects is not suitable for determination of abovementioned environmental contaminants.

In completion to INAA, Particle Induced Gamma-ray Emission (PIGE) applied at the 3 MV Tandetron of IFIN-HH proved to be a suitable technique to determine Li and F contents in thick target environmental and biological samples. As for example, PIGE with 3 MeV proton beam was able to determine F and Li in tree leaves thick samples at a sensitivity level of mg/kg d.w. (dry weight). In addition, Na, P, and Mg levels in this type of samples were found to be of tenth ppm for Na, as well as of 0.5 % for P and Mg (Pantelica et al. 2017).

The environmental and biological samples to be investigated are prepared as **pellets of homogeneous fine powders (thick targets).**

The purpose of the present project is to study the effectiveness of lithium and fluorine bioaccumulation and biosorption from batch systems and wastewater by cyanobacteria *Spirulina platensis* and to choose which process is more suitable for industrial application. The effectiveness of metals uptake will be traced using high sensitive analytical technique PIGE.

PIGE technique with 3 MeV protons beam is based on the nuclear reactions (p,p′γ), (p,γ), (p,αγ), or (p,nγ). For PIGE at the 3MV Tandetron of IFIN-HH, a GEM10P4-70 detector (relative efficiency of 10 % at the 1332 keV of ^{60}Co), placed at 45° with respect to the beam direction and the target support was employed.

In the case of Li, F, Na, Mg, and P analysis, the (p,p′γ) type of reaction on the target isotopes ^{7}Li, ^{19}F, ^{23}Na, $^{24,25}Mg$, and ^{31}P, respectively, is used. In addition, the $^{7}Li(p,n\gamma)^{7}Be$ and $^{23}Na(p, \alpha\gamma)^{20}Ne$ reactions are considered.

Main gamma-ray lines of interest for this type of biological samples: 477.6 keV for ^{7}Li, 197.1 for ^{19}F, 440 keV for ^{23}Na, 1368.6 keV for ^{24}Mg, and 1266.1 keV for ^{31}P.

The project aims at achieving the following **objectives**:

1. to investigate metal accumulation at different metals concentrations in solution;
2. to study metal biosorption in dependence of different physico-chemical parameters (pH, metal concentration, incubation time, sorbent dosage and temperature)
3. to calculate adsorption models, thermodynamics and kinetic models of the process
4. to study the effect of co-ions on studied ions uptake.
5. to study the process of metal removal from industrial effluents
6. to determine sample elemental content and effectiveness of metal uptake by PIGE and PIXE techniques
7. to determine functional groups responsible for metal binding using FTIR technique
8. to process experimental data obtained
9. to disseminate the obtained results by means of ISI journals, international conferences and congresses

Estimated results: A rich set of data concerning optimal parameters (pH, concentration, incubation time, sorbent dosage and temperature) for metal removal will be obtained. Study of the spirulina biosorption and bioaccumulation properties represents theoretical and practical interest, as it will allow to develop a cheap, environmentally friendly methodic of metal removal from industrial effluents and production of cheap biosorbents.

Dissemination:

We take into consideration minimum one paper submitted to a renowned ISI journal as well as an oral presentation to an International Conference.

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