Membrane processes is one of the most attractive and efficient method for removing heavy metal ions from liquid samples. One of the most promising approach in this area is the use of chelating membranes. However, they are usually based on water-soluble complexing polymers. Therefore immobilization in the membrane is necessary for application to aqueous solutions. It can be achieved by entrapping the complexing polymers in a crosslinked polymeric matrix.

Another type of membranes that can be very promising in separation of metal ions from aqueous solution are nanomaterial-based membranes. It can be expected that application of nanomaterials of large specific surface area can result in high adsorption capacity of fabricated membranes. Therefore, the aim of the project is to develop a new chelating membranes based on: (a) cellulose/silica nanoparticles composites, (b) cellulose/graphene oxide composites, (c) nanoporous alumina. Proper surface treatment of nanoparticles can improve metal sorption and enhance selectivity in filtration process. Therefore, the surface of membranes will be modified with alkoxysilane molecules containing functional groups (oxygen-, nitrogen- and sulpur-) that can efficiently bind the metal ions due to sharing an electron pair. The selected membranes will also be modified by grafting of cyclodextrins that can form inclusion complexes with several metal ions through host–guest interaction. The structure of new membranes will be investigated using microscopy techniques (scanning electron microscopy, transmission electron microscopy), X-ray diffraction and spectroscopy techniques (X-ray photoelectron spectroscopy, infrared spectroscopy, energy-dispersive X-ray fluorescence spectrometry).

In next stage of this project, the adsorptive properties of fabricated membranes toward such metal ions as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Cr(III), Cr(VI), Se(IV), Se(VI), As(III), As(V), Sb(III) and Sb(V) will be investigated. Several parameters can have impact on adsorption of metal ions on membranes. Thus, the following effects will be studied: pH, flow-rate, temperature, influence of ionic strength and organic compounds. The adsorption of metal ions will be studied using both batch experiment and on-line system. In the first mode, the prepared membranes will be placed into the solution of metal ions and stirred or shaken. In second one, the solution containing metal ions will be passed through the membrane with controlled flow-rate. To understand the mechanism of adsorption of metal ions on fabricated membranes the adsorption isotherms, kinetics and thermodynamics will be studied. Moreover, X-ray photoelectron spectroscopy measurements will be performed to investigate the nature of adsorption of metal ions onto prepared membranes. It is possible because this method is a surface-sensitive spectroscopic technique that gives information on chemical state and local bonding of atom. Therefore, the careful analysis of differences between oxygen (-OH, =C=O, O-C=O), sulphur (-SH) and nitrogen (-NH2) peaks can provide the evidence that the oxygen- sulphur- or nitrogen-containing functional groups on the surface of membranes take part in adsorption of metal ions.

The new membranes will be used for development of new analytical methodologies for determination of trace and ultratrace elements and their speciation. It is worth noting here that the application of membranes in adsorption of metal ions offers possibility of developing methods based on two analytical approaches: (a) the metal ions can be determined using atomic spectroscopy techniques after their elution, or (b) the metal ions collected onto membrane can be directly determined by X-ray spectroscopy technique. With this technique, the direct quantification of metal species held in solid materials is possible and, therefore, the elution step can be avoided. Summarizing, the metal ions will be: (a) eluted from the “classical” membranes (25-47 mm in diameter) and determined by flame-atomic absorption spectrometry (F-AAS) or inductively coupled plasma atomic emission spectrometry (ICP-OES), (b) directly determined (without elution) using miniaturized membranes (5 mm in diameter) and energy-dispersive X-ray fluorescence spectrometry (EDXRF), (c) eluted from the miniaturized membranes and determined by electrothermal atomic absorption spectrometry (ET-AAS) and total-reflection X-ray fluorescence spectrometry (TXRF). To achieve the high recovery of determined elements, several parameters will be investigated: pH, sample volume, flow-rate of sample solutions, time of stirring or shaking, eluent type and concentration, effects of coexisting ions, salinity, humic acids etc. Optimized methods will be validated (limit of detection and quantitation, selectivity, linearity and sensitivity, precision, accuracy and trueness using certified reference materials and spiked samples).

We believe that our research project will broaden fundamental knowledge on adsorption trace metal ions on membranes of different structure and functional groups. It can also be expected that application of nanomaterials (silica nanoparticles, graphene oxide and nanoporous alumina) of large specific surface area can result in high adsorption capacity of fabricated membranes. The synthesized membranes will be used for development of new analytical methodologies for determination of trace and ultratrace elements and their speciation. The project will also focus on solvent-free methodologies based on miniaturized approaches which can be considered as environmentally friendly and lie in the green analytical chemistry rules.