Composite "track-etched membrane modified with metal–organic frameworks" for heavy metal adsorption

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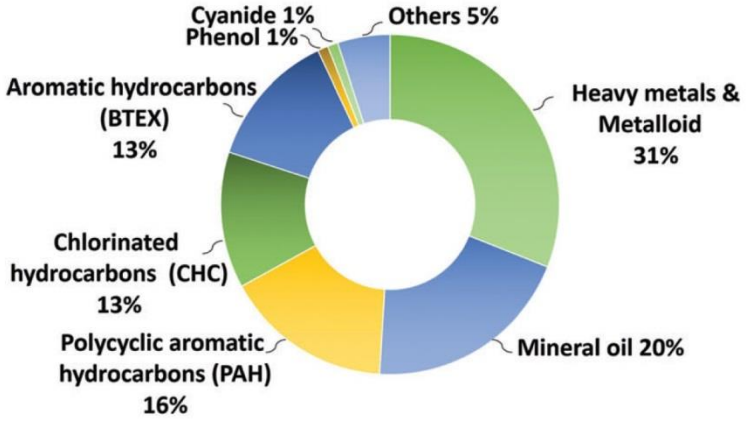
In the last time, the problem of water purification from dangerous substances is becoming more and more acute. A particular difficult problem in water purification is that associated with removal of heavy metal ions.

Adsorption has become a well-known, effective and economical method to remove heavy metals.

The creation of solid adsorbents with high capacity and stability in the aquatic medium is a very important task.

One of the promising types of adsorbents is **metal-organic frameworks (MOFs)**.



Normalized composition of water pollutants

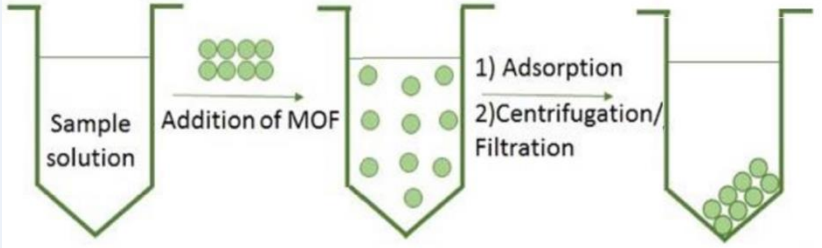
[S. Bolisetty et al. // Chem. Soc. Rev., 2019, 48, 463-487]

MOFs are crystalline materials consisting of an infinite network of metal-ions, or metal-ion clusters, bridged by organic ligands through coordination bonds into porous two- or three-dimensional extended structures.

In our work:

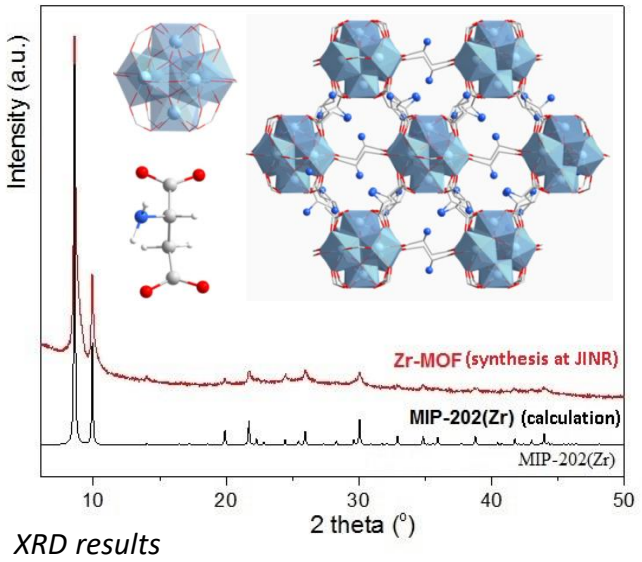
1. **Ni-MOF** $\{[Ni(L\text{-trp})(bpe)(H_2O)]\cdot H_2O\cdot NO_3\}_n$ (*L*-trp = *L*-tryptophan, bpe = 1,2-bis(4-pyridyl)ethylene) and **Zr-MOF** MIP-202(Zr), based on *L*-aspartic acid, were synthesized.
2. The properties of Ni-MOF and Zr-MOF in the process of ruthenium sorption from aqueous solutions of ruthenium chloride were investigated.
3. A track-etched membrane, modified with chitosan, was studied as a substrate for the Ni-MOF. The membrane was received from Flerov Laboratory of Joint Institute for Nuclear Research.

The possibility of efficient and convenient extraction of the adsorbent from the solution is significant



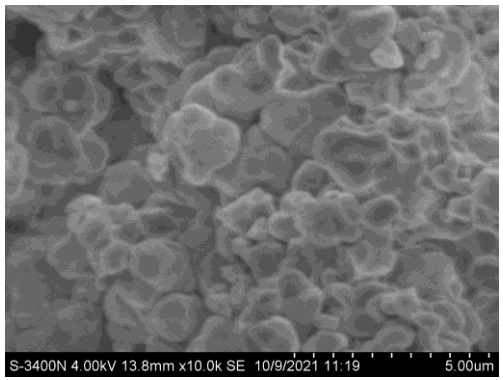
Usual variants of the adsorbent extraction from the solution

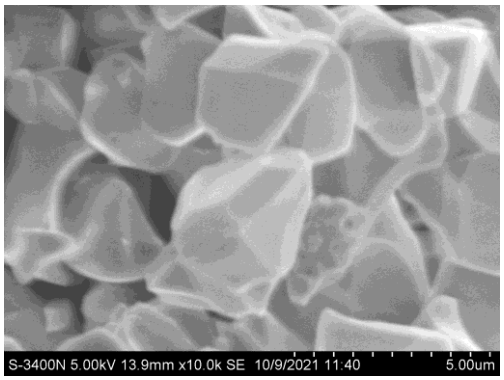
Synthesis of MOFs



XRD results

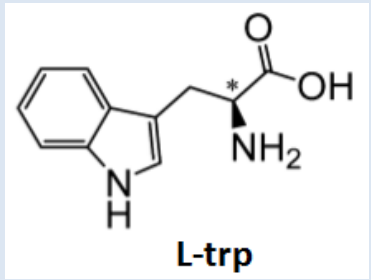
$ZrCl_4$, *L*-asp → (*120-160˚C 1.5-3 h.*, H_2O) → Zr-MOF

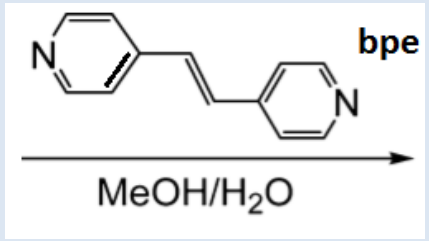


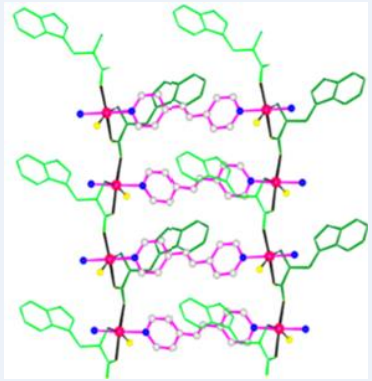


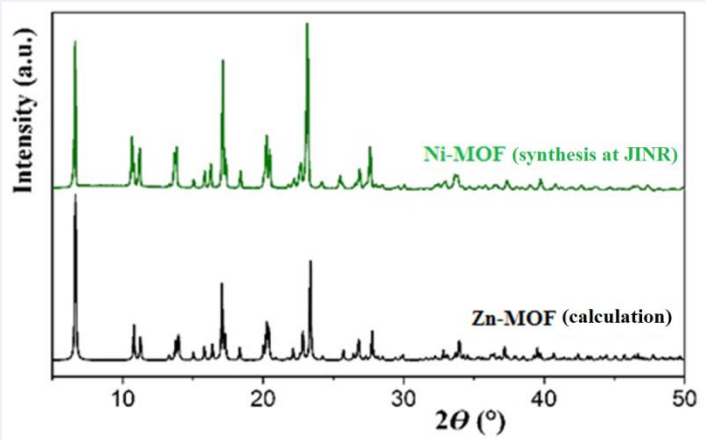
- ***A procedure for the synthesis of MOF MIP-202(Zr) with different particle sizes has been developed***

$Ni(NO_3)_2 \cdot 6H_2O$ + L-trp + bpe, $MeOH/H_2O$ (*50˚C 48 h.*) → Ni-MOF



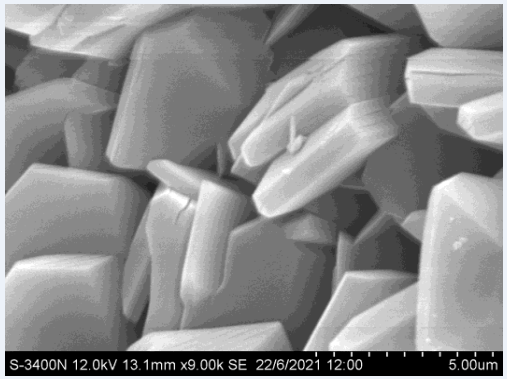






- ***Crystal structure of Ni-MOF is identical with the structure of a similar Zn-based compound described in the literature***

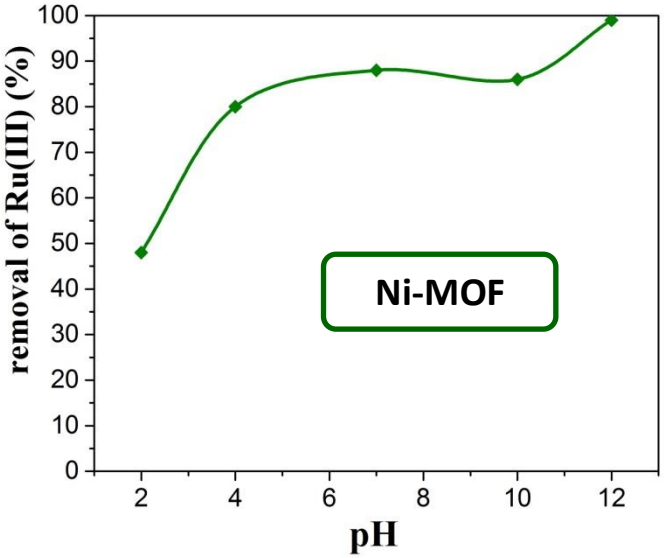
[O.Yu. Ivanshina, I. Zuba, S.V. Sumnikov, A.A. Nabiyev, and A. Pawlukojć. // AIP Conf. Proc. (2021) 2377, 020001]

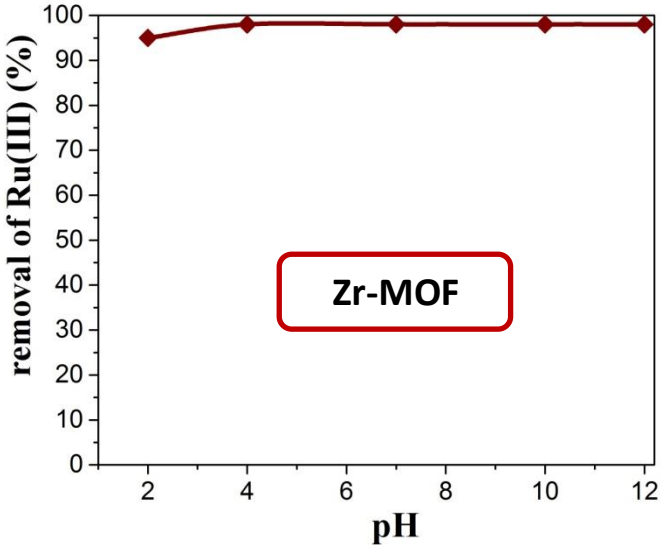


Study of ruthenium sorption on MOFs

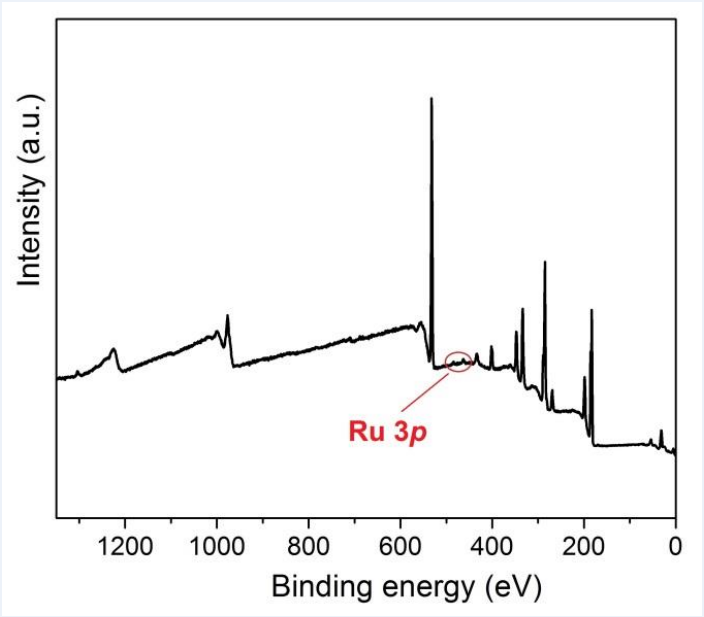
Sorption conditions

- 50 mg of MOF
- 10 mL solutions of hydrochloric acid or sodium hydroxide
- 5 µg mL^{-1} Ru^{3+}
- 24h shaking (room temperature)
- MOF separated from solutions by filtration
- UV-Visible spectrophotometry detection

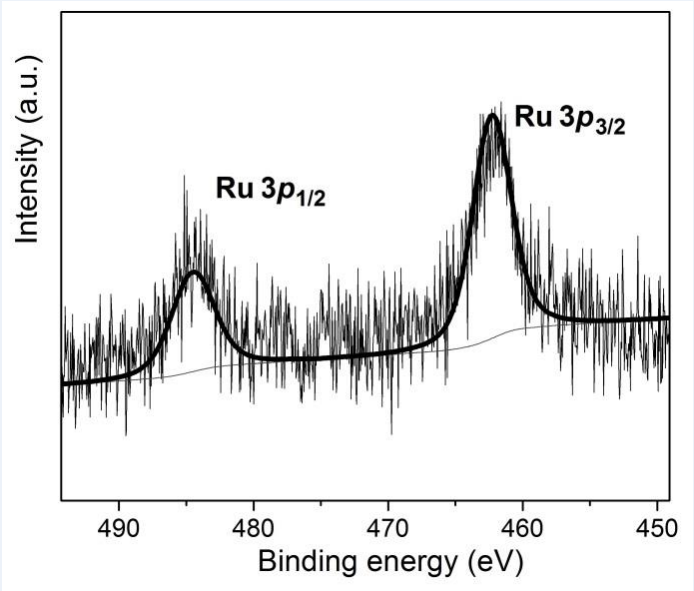




XPS measurement of MIP-202(Zr) powder after adsorption process with Ru(III) were performed to evidence the ruthenium sorption:



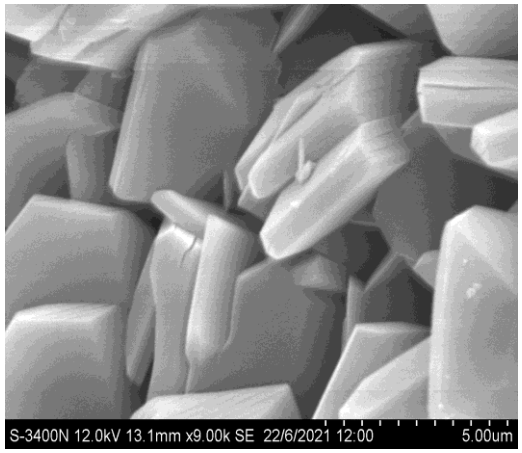
The wide-scan XPS spectrum

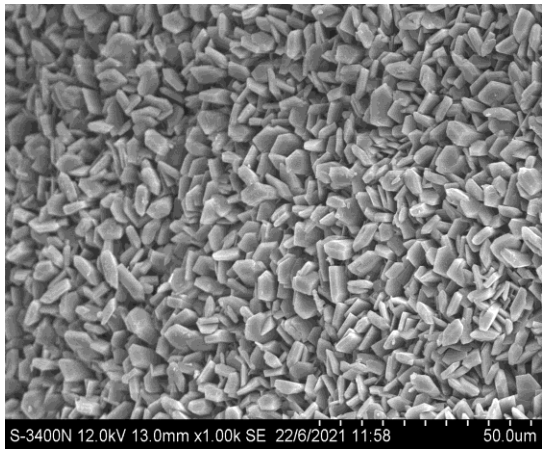


Regional *XPS* spectra Ru 3*p*

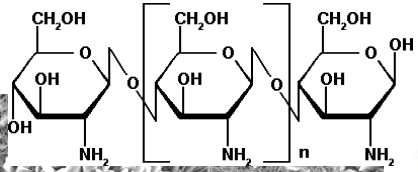
Composite “track-etched membrane modified with chitosan and Ni-MOF”

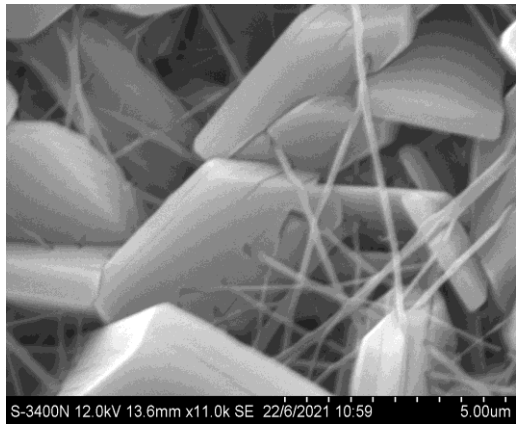
The method of self-assembly of the adsorbent on a substrate was chosen in our work. The synthesis of Ni-MOF takes place under mild conditions that do not destroy either the membrane or the chitosan fibers.

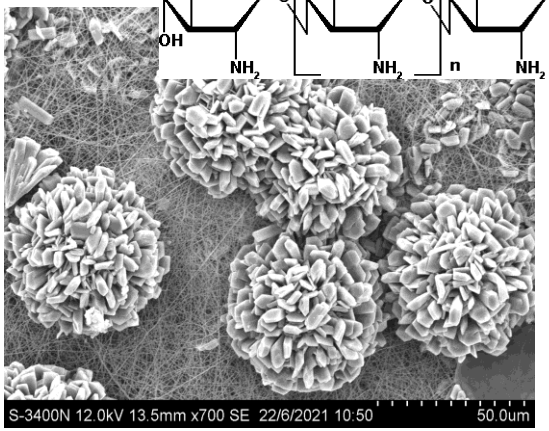




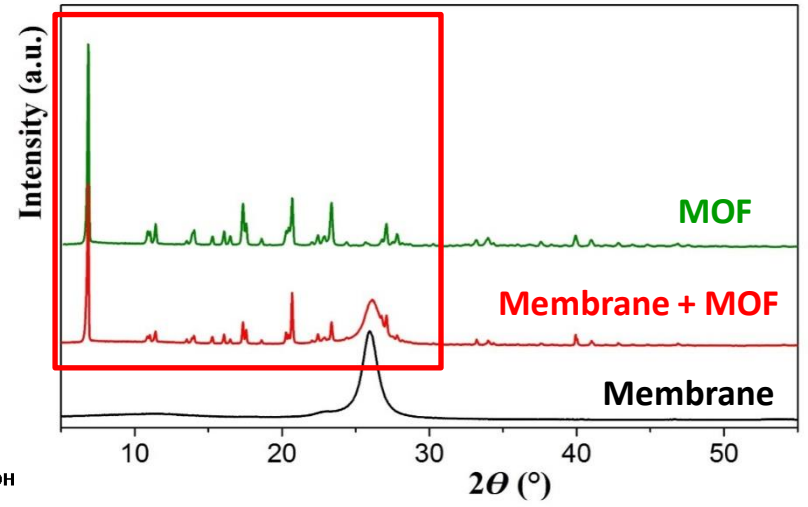
Pure Ni-MOF

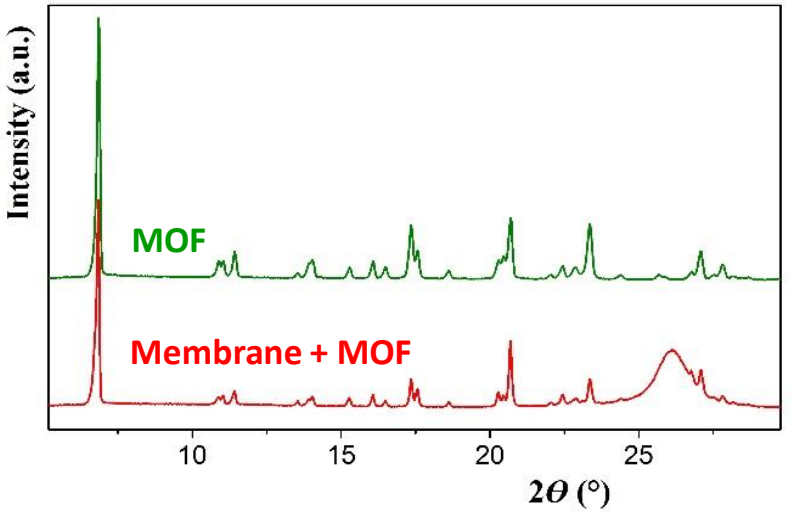






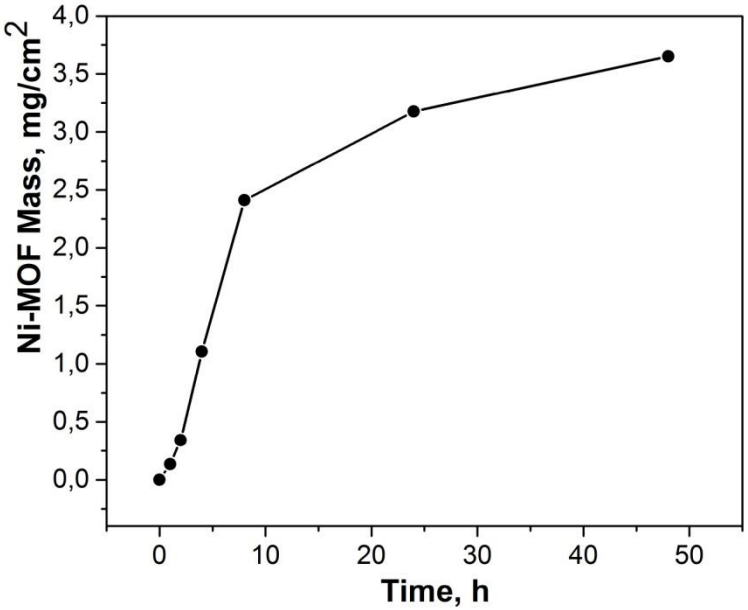
Poly(ethylene terephthalate) (PET) track-etched membrane (from FLNR JINR), modified with chitosan + Ni-MOF





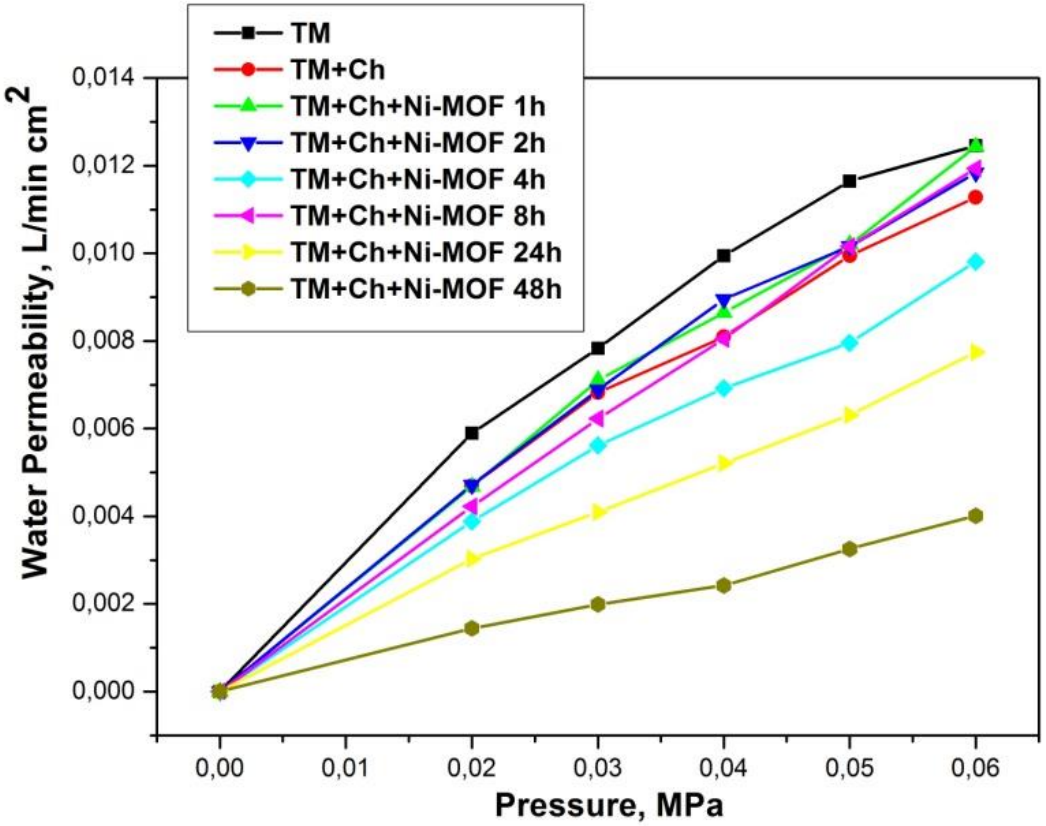
- ***Only in the presence of chitosan MOF particles firmly adhere to the substrate***
- ***Microstructure and crystal structure of pure Ni-MOF and Ni-MOF supported on the membrane are identical***

Dependence of Ni-MOF mass on the membrane from the time of synthesis



Water permeability was investigated for the obtained series of samples.

("TM+Ch+Ni-MOF 24h" means that time of Ni-MOF self-assembly on track-etched membrane modified with chitosan was 24 hours.)



- ***The optimal deposition time for Ni-MOF on the track-etched membrane (TM) modified with chitosan (Ch) was 24 hours.***

Our plans

- Studying of the adsorption properties of the obtained membranes coated with Ni-MOF particles.
- The study of the mechanism of adsorption of heavy metal ions on MOF.

Raman, IR and X-ray photoelectron spectroscopy can help to suggest how the adsorption process proceeds.

- Creation of composites “track-etched membrane modified with chitosan and Zr-MOF”

In case of good adsorption properties of the obtained membranes coated with MOF particles, these composites can become a basis of filters for water purification from heavy metals.

Thank you very much for your attention!