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Master of Science HES-SO in Life Sciences

# Use of molecular sponge to extract other precious metals in wastewater

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## DESCRIPTION

Metalor Technologies is a worldwide company specialised and leader in precious metals refining. Their customers come from different areas such as jewellery and watchmaking industry. For a factory, recovery and recycling of wastewaters is always a big issue. Everyday, about 70 $m^3$ of acidic wastewaters have to be recycled in their plant at Marin-Epagnier which represents 100'000 $m^3$ per year. The recovery of precious material and the neutralization of those wastewaters are essential and a wastewater treatment plant is in place. They use different techniques to recover all metals present. The first one is cementation to recover precious metals and hydroxides precipitations to remove all remaining metals. Finally, the solution is neutralized and can be treated as classic wastewater at Marin-Epagnier STEP.

Although these techniques are very efficient for many precious metals such as Ag, Au, Pd and Pt, they are less efficient for Rh, Ru and Ir also known as OPM. They are commonly used in car industry as catalytic converters or on spark plugs and in chemistry as catalysts.
Because of their bad recovery during cementation step, the economic impact is huge and depends on the fluctuation of precious metals costs. The biggest struggle for Metalor is the entire loss of Ir every year.

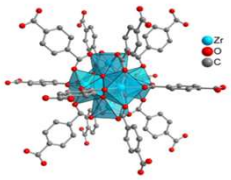
The problematic of the project is the bad recovery of OPM during the cementation step. The idea is to implement a new step to selectively recover these metals and especially Ir. To do that, the concept of a molecular sponge which is called metal-organic framework was attractive. Previous studies were made based on the scientific paper and then the patent from Daniel T. Sun et al where they used a Fe-based MOF to recover traces of Au in water.

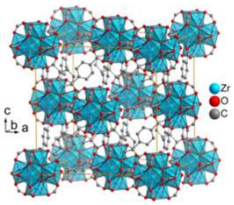
Zr-based MOF which show a high chemical and physical stability were chosen because of the acidity of wastewaters. Other techniques were tested too such as IL, resins and polymers.

## OBJECTIFS

The main objective was to develop a process that can efficiently and selectively recover OPM from wastewaters, with effort on Ir. The objectives of the project are described below:

- Synthesis and characterization of different MOF UiO-66 derivatives
- Screening of multiple MOF commercially available for potential OPM adsorption
- Optimization of the ICP method for the determination of metals in wastewater
- Adsorption tests with different parameters (temperature, concentrations of precious and common metals, composition)
- Adsorption of Ir on anion exchange resin activated by $Cl_2$
- Synthesis and characterization of hydrophilic ionic liquids (IL) for precipitation of Ir
- Precipitation tests using IL

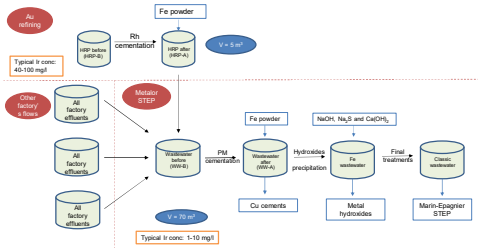



Structure of MOF UiO-66 showing the cluster and the full porous structure

## RESULTS

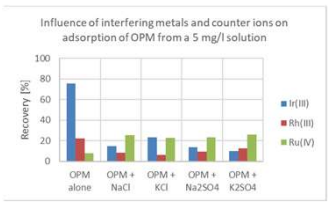
To better understand how the different effluents are connected in the factory, the scheme below was drawn.



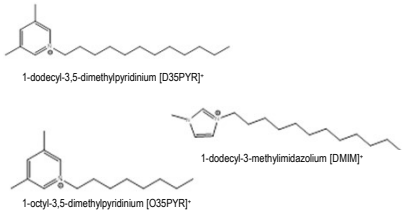

***Scheme of effluents from Metalor factory***

MOF UiO-66 derivatives were synthesized and characterized by analytical techniques such as FTIR, PXRD or SEM-EDX. Adsorption of OPM in real wastewaters was tried, however, the presence of interfering metals such as $Na^+$ had a bad influence due to their smaller atomic radius they were adsorbed faster into the pores. Furthermore, MOF were destroyed in acidic media even at pH=2.5.

Hydrophilic pyridinium and imidazolium based IL for the selective precipitation of Ir(IV) was done. The selectivity was lost when concentrations of Rh(III) and Ru(IV) were above 1.5 mg/l which is the case in the sample HRP. This sample was chosen instead of wastewaters for its high concentration of OPM (90% of Ir from the factory come from this effluent) and its lower volume (5 $m^3$ instead of 70 $m^3$).

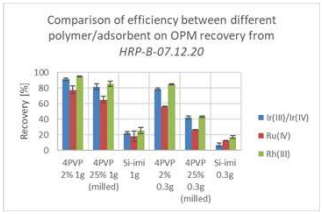



***Influence of interfering metals on OPM adsorption using MOF***

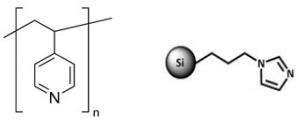



***Structures of IL cations, conter ion: $Br^-$***

Finally, polymers were tested on HRP effluent. 4PVP 2% cross-linked with divinylbenzene was the most efficient for OPM recovery.




***Comparison between polymers for OPM adsorption from HRP effluent, 3% & 1% m/v***




***Structures of polymers***

## CONCLUSION

Different techniques such as MOF, IL and polymers were tested for the recovery of OPM from industrial wastewaters. MOF were not effective for this purpose due to their lack of stability in acidic media and the presence of interfering metals in wastewaters. However, other ligands such as thiol or pyridine based could be tested. IL were very interesting and selective for Ir(IV) recovery in wastewaters. The loss of selectivity in HRP effluent was not expected and problematic. In addition, the quantity of IL needs to be controlled due to their inner toxicity.

The most efficient technique was the use of 4PVP 2% cross-linked with divinylbenzene even though it is not selective to OPM. Several parameters need to be tested to optimize its use at real scale such as quantity and recycling. Other polymers derived of 4PVP could be tested such as poly(2-vinylpyridine) or 4PVP copolymer.

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