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Drugs Trapping by natural matrices, observation of the environment and leaching experiment

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Pharmaceutical products (PPs) represent nowadays a common pollution in aquatic environments. The PPs consumption have increased decade after decade all over the world leading to a pollution of numerous water compartments whereas no efficient water treatment has been done. Indeed, actual Waste-Water Treatment Plants (WWTPs) show limited solution in the removal of emerging organic micro-pollutants. A complete improvement of water treatment could be realistic if the associated treatment costs are controlled. Results of such unsuitable treatment drives to a constant overflow of numerous micro-pollutants, including PPs in natural waters. Today, this spillage has well-documented consequences on the biota, the human health, various ecosystems and shows a severe environment impact in general (Fent et al., 2006).

Drugs concentrations vary between $\mu\text{g.L}^{-1}$ and some ng.L^{-1} . The entire aqueous environments are actually contaminated as shown by the abundant and various scientific publications on this subject. Namely, effluents of WWTP's (Kostich et al., 2014), river waters (Loos et al., 2009), groundwater (Lapworth et al., 2012), marine waters (McEneff et al., 2014) and sediments (Petrović et al., 2001).

The ability of sediments and more particularly organic matter (OM) and the clay fraction to trap some drugs has been highlighted with the warning study on hormones. From the numerous studies led on this environmental problematic, mineralogy of clay and the nature of organic matter are the main actors for the sequestration/adsorption of emerging organic pollutants (Stein et al., 2008).

Therefore, two different natural matrices were chosen in this study: sewage sludge of a rural phytoplanted filter and natural sediments in an urban system.

Two analytical methods were applied in order to investigate the presence of drugs in the matrices of the organic mud deposits. (i) Py-GC-MS of insoluble OM to get an idea on the compositions of the natural and anthropogenic sources of the organic matrix and (ii) a light Methanol/Water (1:1) extraction followed by GC-MS and HPLC-MSMS analysis to focus on drugs composition associated to the organo-mineral compounds of the sludge deposit.

Our analytical results show that drugs at different levels contaminate both of these two natural matrices. Drugs found in sewage sludge are most concentrated in influent as Salicylic Acid and Acetaminophen, whereas some pharmaceuticals, resistant to sewage treatment, as Oxazepam and Ketoprofen, were identified in sediments. These resistant pharmaceuticals were also detected in river water (Joigneaux, 2011).

This study focused on the role of clays to trap pharmaceuticals. Chemical and physical analyses (TOC, granulometry, and powder X-ray diffraction) were performed to emphasize the occurrence of clays and organic matter associations, to characterize the clay minerals, and to identify the possible relation between the sorption of emerging pollutants and the physicochemical properties of clays.

Batch experiments and percolation experiments using oedometer cells were performed in order to simulate the natural conditions and to better understand the clay-pollutants interactions. Batch interactions give a long time interaction and regular volume, whereas percolation experiments permit a higher solid to liquid ratio and a runoff simulation. Both tests were performed on standard mixtures and natural water effluents (Fig.1).

The sorbent composition is a pure Na-swelling-smectite for batch interactions and a mix between sand and clay (95%-5%, respectively) for percolation experiments. The low proportion of 5% clays was enough to lead to an important decrease of the hydraulic conductivity of the material, from 10^{-6} for pure sand to 10^{-9} m s^{-1} for the 5% swelling clay-95% sand mixture, but this value stays consistent with WWTP's installations.

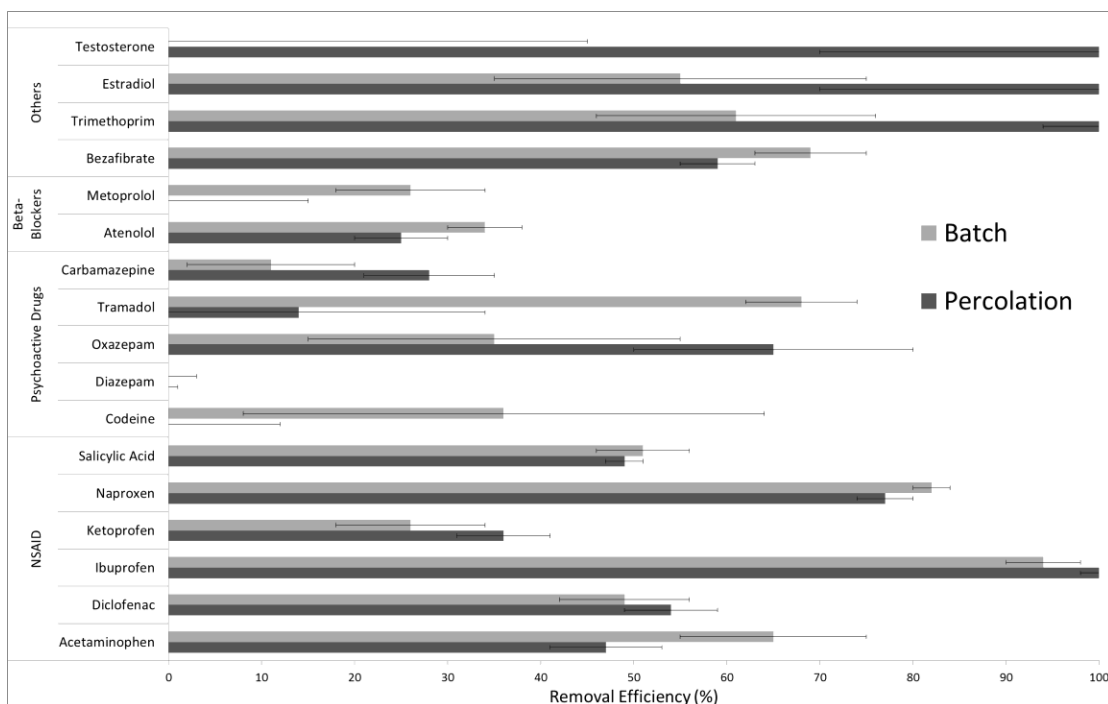


Fig.1. PPs Trapping with swelling clay by two experiments, Batch and Percolation experiments, on waste-water effluents (NSAID : Non Steroidal Anti-Inflammatory Drug)

If results with one by one standard experiments at high concentration are known and the impact of clay was proved (Çalışkan Salihi and Mahramanlioğlu, 2014), studies on natural water with low concentrations and complex compositions seem to be new and give us promising results.

Our results show that pollutants have the same affinity with clay in batch than during percolation. Indeed, the two ways gives us similar results and permit good association between clays and drugs. (i) Some compounds are refractory to sorption like diazepam and carbamazepine (ii) but most of them are predominantly removed by clays. In this experimental device, clays bring a significant added benefit compared to a rural planted filter. The remaining question concerns the duration of the efficiency of our filter, which will be saturated by organic materials. Long-time percolation experiments were carried out to understand this phenomenon and their potential releases. The final purpose is to create a WWTP compatible system with obligations adjoining as cost, water-flow and hydrodynamic properties.

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