Micro-pollutants, Oxidants, Catalysts and the Water Matrix: A Harmonic Quartet or the War of the Roses?

Mantzavinos D.[1*]

[1] Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, GR-26504 Patras, Greece

*corresponding author: e-mail: mantzavinos@chemeng.upatras.gr

Abstract

Advanced oxidation processes (AOPs, e.g. heterogeneous and homogeneous photocatalysis, electrochemical oxidation, ozonation, ultrasound irradiation, Fenton and alike reactions, and many more) have been investigated for the treatment of emerging pollutants over the past 20 years (Klavarioti et al., 2009). In particular, the occurrence of persistence micro-pollutants in various water matrices, such as pharmaceuticals and personal care products, raises serious environmental concerns since these xenobiotics can re-enter the water cycle, i.e. escaping intact from the conventional wastewater treatment plants and finally ending up in surface and ground waters (Verlicchi et al., 2012).AOPs can effectively degrade organic pollutants typically found in environmental matrices (secondary treated effluents, surface waters, ground waters) at concentrations ranging from the ng/L to low mg/L level. This said, the specific treatment cost (i.e. the cost per unit mass of removed pollutant and/or per unit volume of effluent), as well as the environmental footprint are generally high; both are usually related to the treatment performance, which, in turn, depends on the specific treatment conditions and the quality of the water matrix.

Keywords: competition; matrix; performance; synergy; wastewater

1. The Intriguing Role of the Water Matrix

As a rule of thumb, treatment efficiency decreases with increasing water matrix complexity. This is due to the fact that the target pollutant is likely to compete with the non-target constituents of the matrix (e.g. organics, inorganics and microorganisms) for the precious oxidant species, as well as (in the case of heterogeneous processes) for the active sites of the catalysts/activators. This behavior is illustrated in Figure 1, where the pseudo-first order kinetic constant of sulfamethoxazole (SMX) degradation, by means of solar photocatalysis over WO_3/TiO_2 suspensions, decreases as the matrix shifts from ultrapure water (UPW) to drinking water (DW: containing bicarbonates and other ions) to secondary treated wastewater (WW: containing residual organics and various ions) (Ioannidou et al., 2017). On the other hand, the exactly opposite behavior occurs when magnetic carbon xerogel decorated with iron and cobalt (CX/CoFe) activates sodium persulfate (SPS) to degrade bisphenol A (BPA); the extent of BPA conversion (Figure 2) increases as the matrix shifts from UPW to wastewater (Outsiou et al., 2017).

2. Discussing the Ramifications

It is evident that various complicated interactions may occur amongst the (i) target pollutants and microorganisms, (ii) non-target matrix species, (iii) oxidants, and (iv) catalysts/activators. The net effect of all these contributions, which can be synergistic, simply additive or even antagonistic, will eventually dictate degradation kinetics (and possibly mechanisms); moreover, the relative contribution of each individual effect may depend on the specific treatment system in question and, for a certain system, on the specific operating conditions. This kind of interactions have not been investigated systematically so far and this remains an open research question that, in turn, raises several other scientific and technological questions, as follows:

(i) What makes a treatment technology technically and economically viable and sustainable even for the less privileged communities? Would this require minimization of human and natural resources utilization without compromising treatment efficiency? How can a sanitary illusion be avoided?

(ii) What compromises efficiency? The obvious answer is that efficiency has to do with the "operating" conditions, but is this enough? Can the matrix itself be the one and only critical factor determining the interactions amongst the various parties involved? Can all these interactions be quantified, modelled or predicted, as well as related to efficiency?

(iii) How can the need to eliminate antibiotic resistance bacteria and antibiotic resistance genes compromise efficiency and possibly move the challenge beyond the matrix effect and the decontamination in terms of emerging micro-pollutants? In other words, is public health protection far more demanding than environmental protection to eventually determine efficiency?

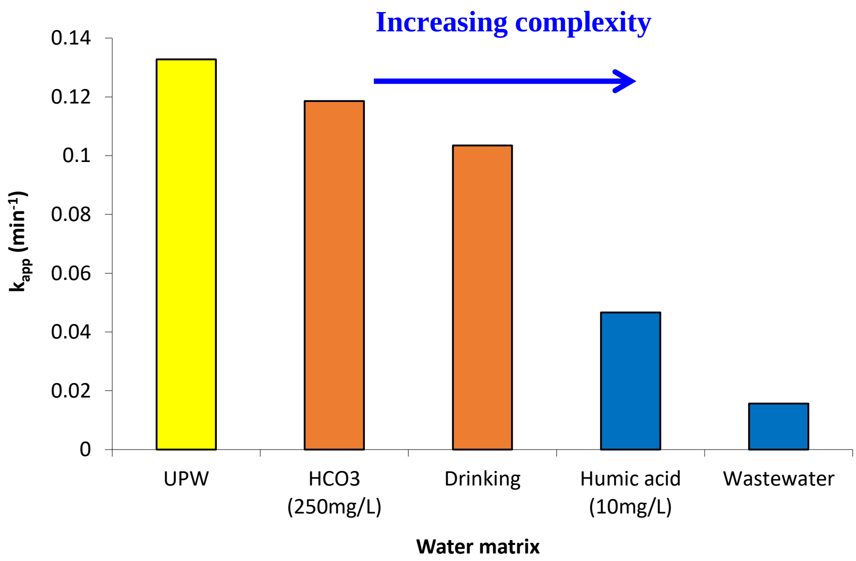

Figure 1. The effect of water matrix on SMX degradation by solar photocatalysis over WO_3/TiO_2 suspensions

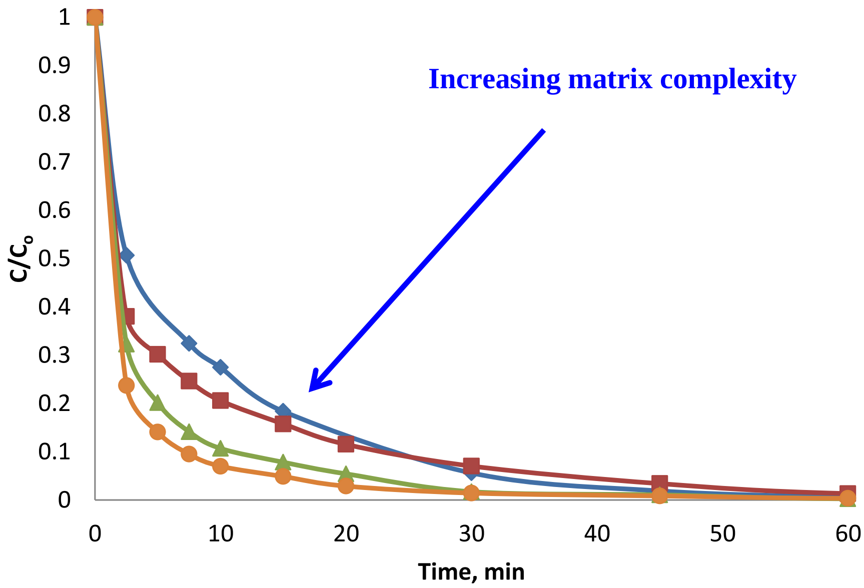

Figure 2. The effect of water matrix on BPA degradation in the presence of SPS and CX/CoFe xerogel in UPW (ciel line), DW (dark red line), surface water (green line), WW (amber line)

References

Ioannidou E., Frontistis Z., Antonopoulou M., et al (2017), Solar photocatalytic degradation of sulfamethoxazole over tungsten-modified TiO_2, *Chemical Engineering Journal*, **318**, 143-152.

Klavarioti M., Mantzavinos D. and Kassinos D. (2009), Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, *Environment International*, **35**, 402-417.

Outsiou A., Frontistis Z., Ribeiro R.S., et al (2017), Activation of sodium persulfate by magnetic carbon xerogels (CX/CoFe) for the oxidation of bisphenol A: Process variables effects, matrix effects and reaction pathways, *Water Research*, **124**, 97-107.

Verlicchi P., Al Aukidy M. and Zambello E. (2012), Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A review, *Science of the Total Environment*, **429**, 123-155.