Report on STM project at CNR-IRSA, Bari, 15th-28th February 2018

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Qualification: PhD in Materials Enginering **Level:** Principal Investigator

Host Institution: CNR (National Research Council) - Istituto di Ricerca Sulle Acque (Water Research Institute) - CNR-IRSA, Bari, Italy

Proposer: Dr Giuseppe Mascolo

Assisting: Dr Sapia Murgolo

Visit carried out between 15th-28th February 2018.

Title of Project: Photocatalytic testing of novel sustainable cork-derived ecoceramic photocatalysts

Report

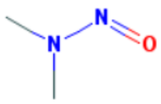
Samples were transported from Aveiro to Bari of both TiO2-based photocatalysts, and highly porous pyrolysed cork made from cork wastes, to carry out photocatalysis and absorption tests of persistent organic pollutants (POPs) in solutions of real municipal waste water. Often, a photocatalyst which works well in laboratory conditions in distilled/purified water is not effective in real waste waters, as the ions present (e.g. Na^{+}, Ca^{2+}) "poison" the activity of the catalyst by causing recombination of the reactive oxygen species created under light before they can react with the pollutants.

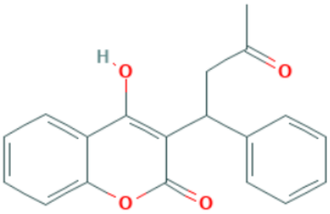
Cork is of great interest, as it is fully sustainable, as the bark is harvested without damaging the tree, which lives on to sequester CO2 for centuries. In this case, cork waste powders were used, adding a wastes valorisation aspect to the work. Cork has a highly porous 3-DOM microstructure consisting of hexagonal cells ~20 μm in diameter, but with cell walls only 1 μm thick. This structure is maintained in both the pyrolysed cork and any ecoceramics produced.

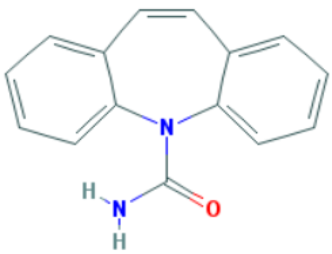
Photocatalysis tests on TiO_2

The TiO_2 samples were produced from a green sol-gel process, and were doped with 1 mol% Ag. These have been shown to be excellent photocatalysts under both UV and visible/solar light when in distilled water (*Langmuir*, 2017, 33 (20), pp 4890–4902; DOI: 10.1021/acs.langmuir.6b04474). Here they were tested in municipal waste water, with added POPs.

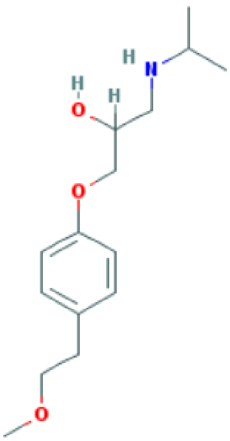
The POPs tested, and their concentrations in the waste water, were:

200 ppb NDMA – Nitrosodimethyl amine 

50 ppb Warfarin 



100 ppb Carbamazepine



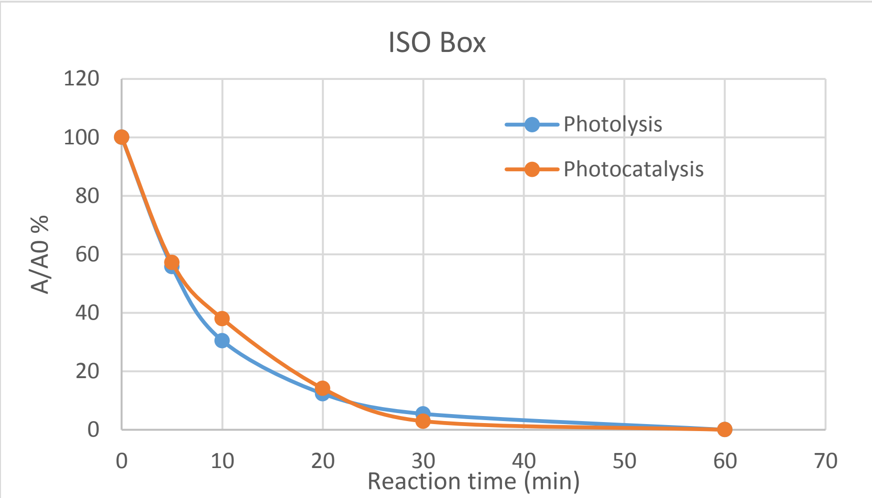
100 ppb Metoprolol

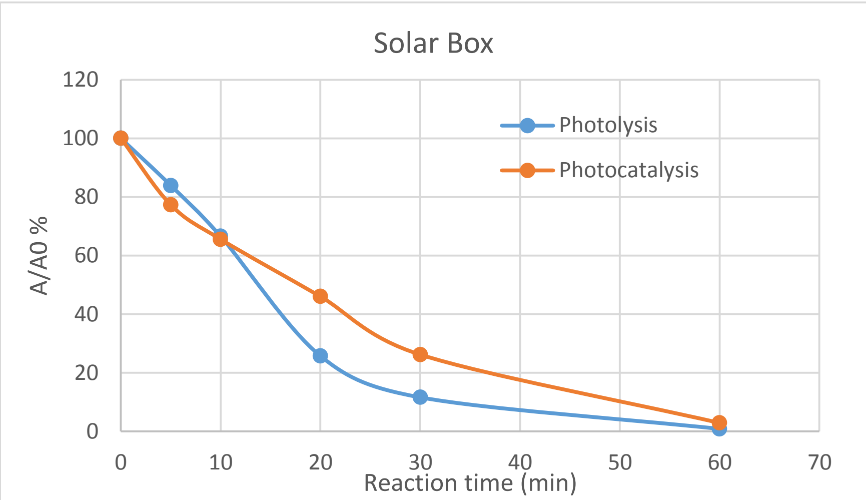
A solution of waste water spiked with these levels of POPs was prepared and used for all experiments.

Tests were carried out under UV light (254 nm, ISO box) and solar light (300-800 nm, solar box).

Firstly, photolysis was carried out on the solutions, as these POPs are known to partially degrade just under light. Then equivalent tests were carried out with 200 mg of the TiO_2 photocatalyst present. Samples were taken at 0, 5, 10, 20, 30 and 60 minute intervals, and measured by LC-MS to measure the quantity of POPs remaining.

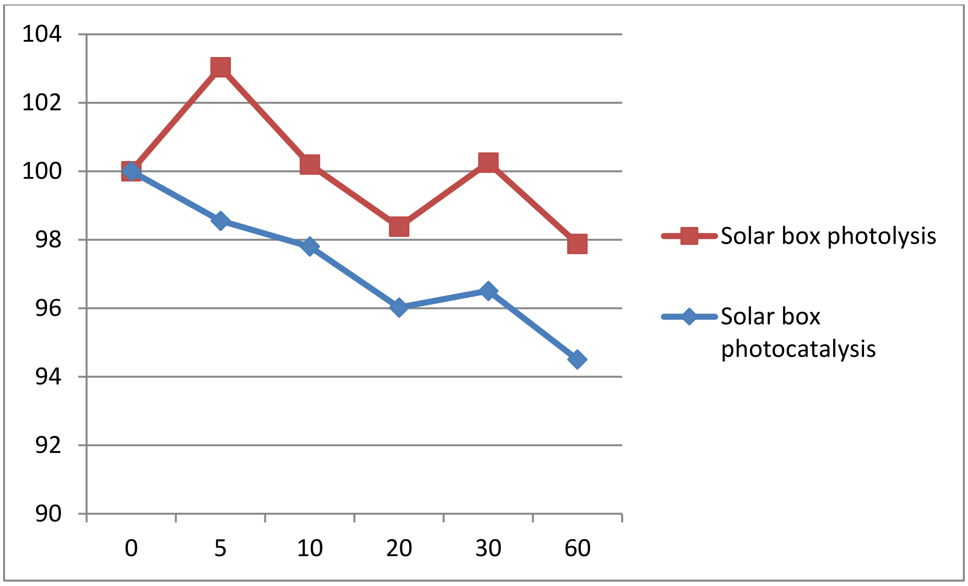
No significant difference was observed between the reduction of the pollutants with or without the photocatayst present, signifying that the photocatalysts has indeed been poisoned and rendered ineffective by the ions present in the waste water. As an example, the plots for NDMA are shown below:





It can be seen that the photocatalyst offers no advantage over pure photolysis effects under light.

No effect at al was observed for warfarin or carbamazepine, and only a very small and insignificant effect for metoprolol under visible light:

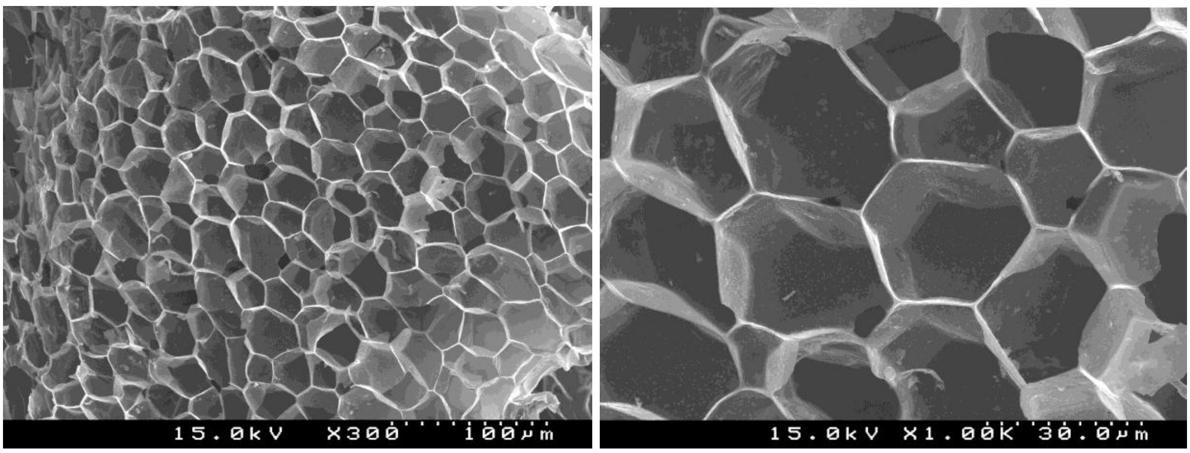


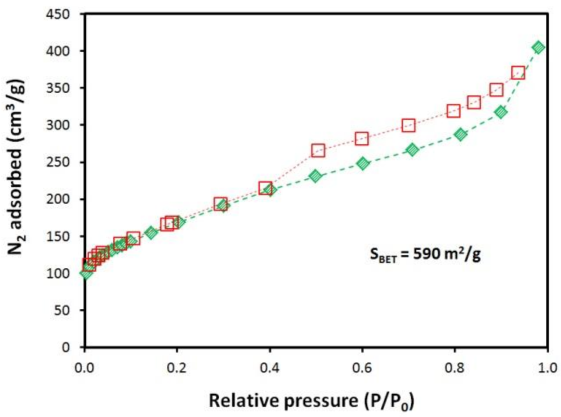
Therefore, we concluded that at present these TiO_2 photocatalysts are ineffective in real waste water, like virtually all other photocatalysts, and work will continue to try to create a photocatalyst which does work under such conditions.

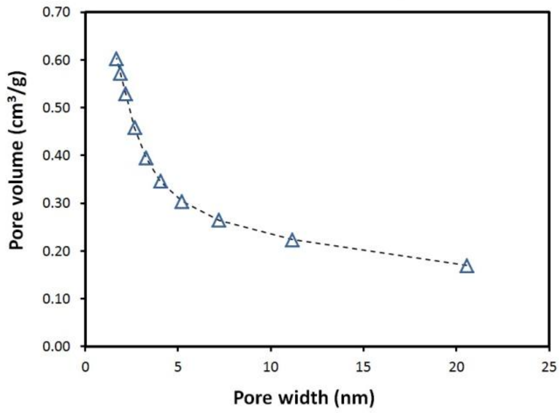
Absorption tests using pyrolysed cork powders

The same waste water spiked with POPs was used as above. Pyrolysed cork, consisting only of carbon, is not photoactive, so the presence of light was not tested.

The pyrolysed cork has a surface area of 590 m^2 g, and nanopores between 2-20 nm. It is mesoporous/macroporous, as shown by the shape of its type-IV BET isotherm, and this is because the cork cells are on the scale of 20 µm. The SEM images below show the highly porous nature of the pyrolysed cork powder, which consists of particles around 200-400 µm in diameter.



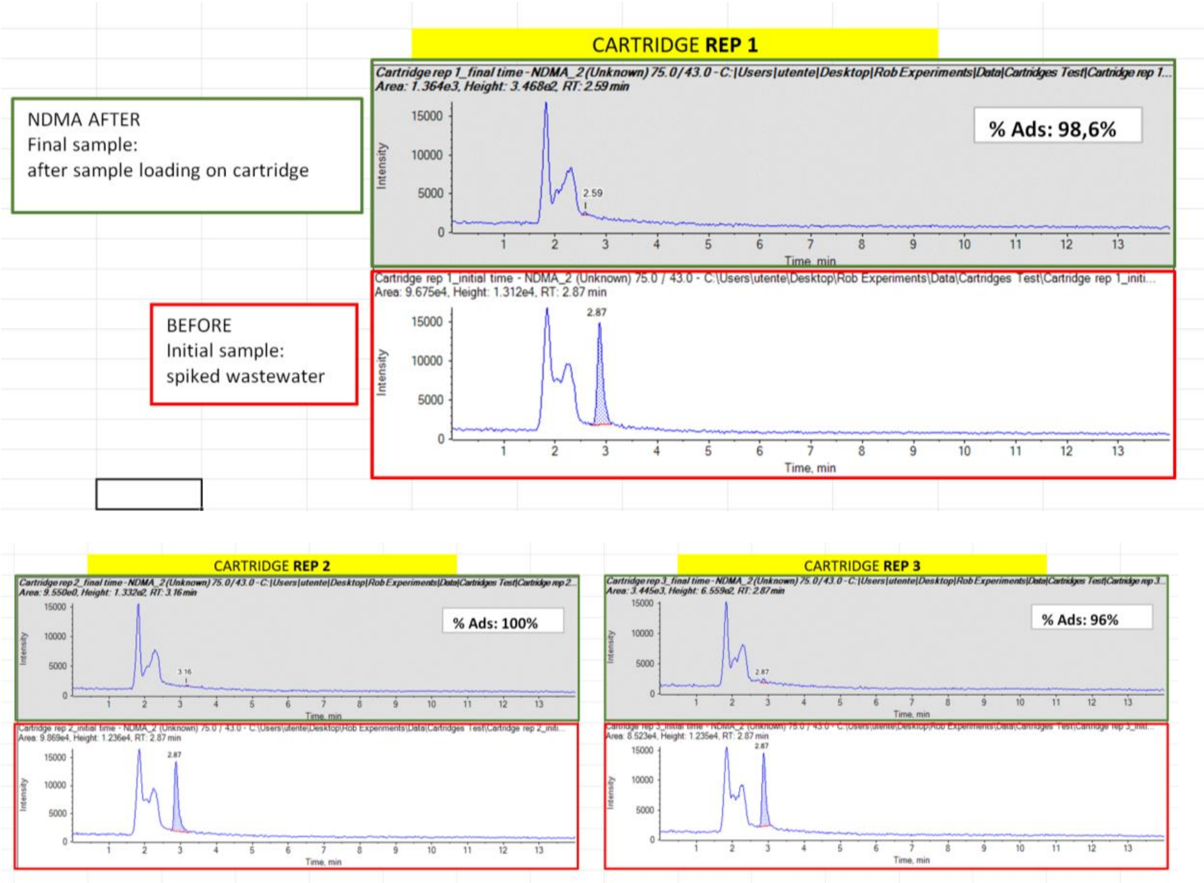




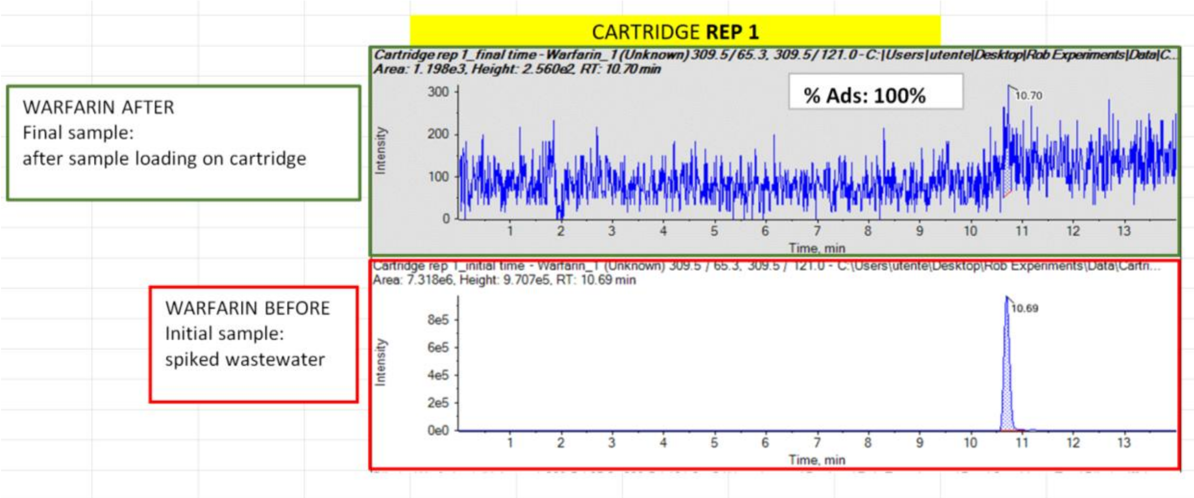
About 100 mg of cork powder was packed into a water filter cartridge with commercial end membranes, and this was tested at various flow rates between 1-2.5 ml / min, passing 50 ml of the spiked ground water through each cartridge, in the apparatus shown below:

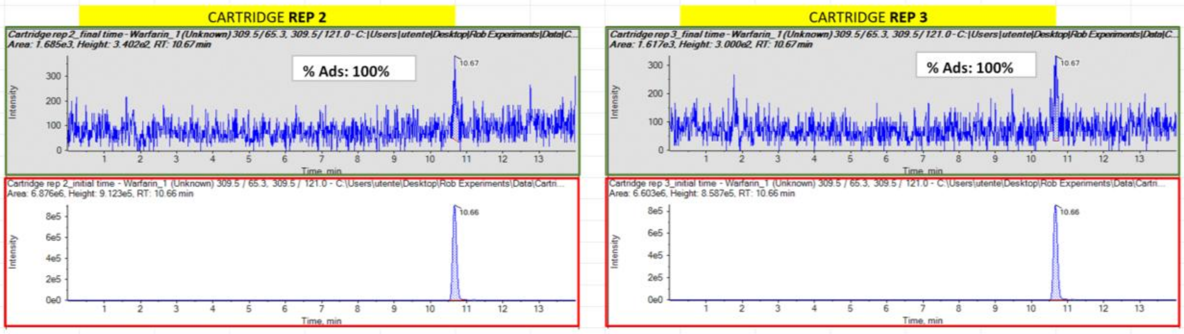
With three repetitions at around 1 ml/min, the cork showed excellent absoption of all 4 POPs.

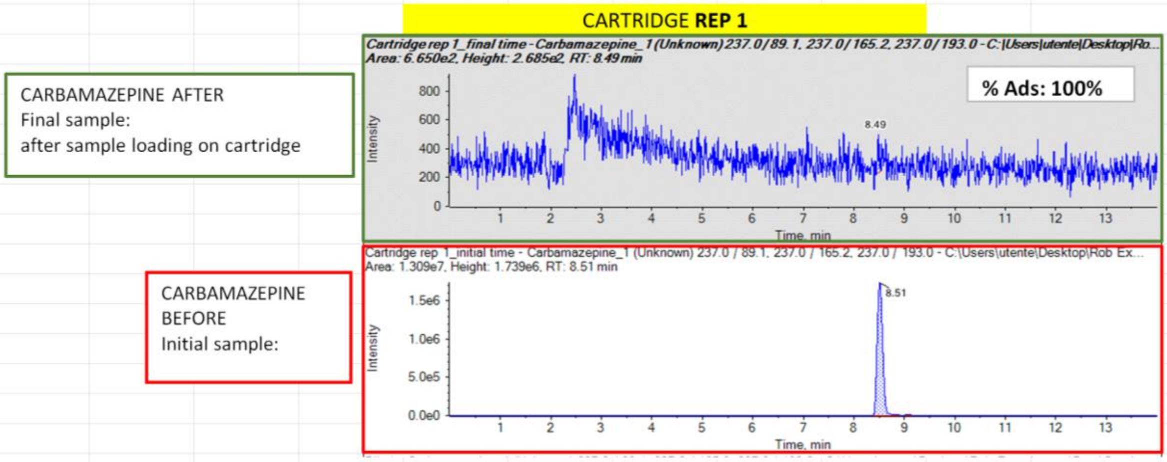
For NDMA, between 96-100% was removed in the three tests, as shown below:

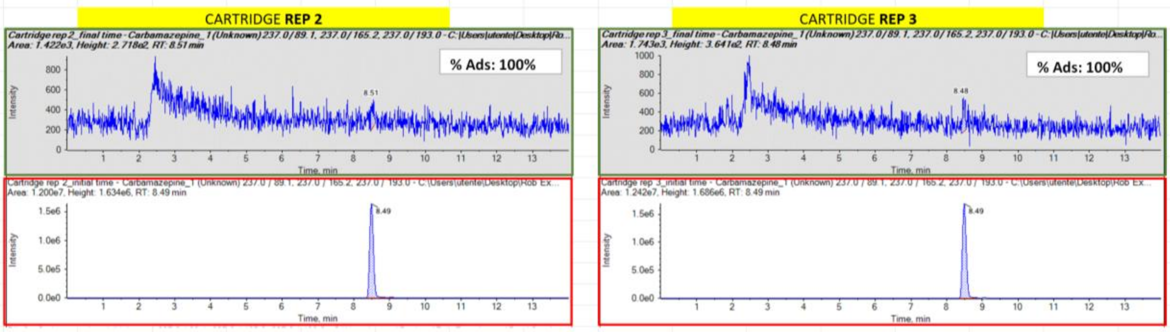


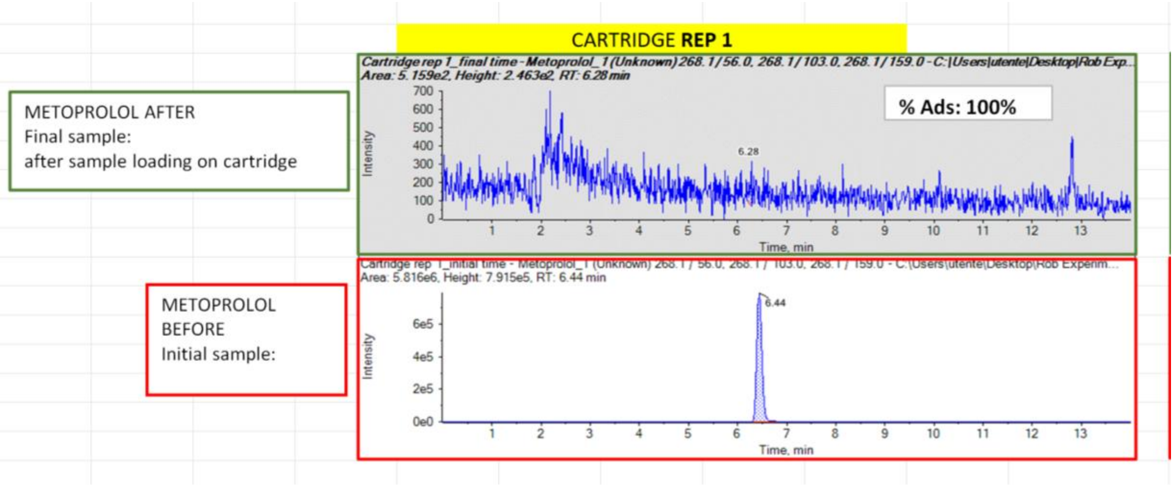
Even better results were seen for the other three POPs, with 100% removal in all cases:

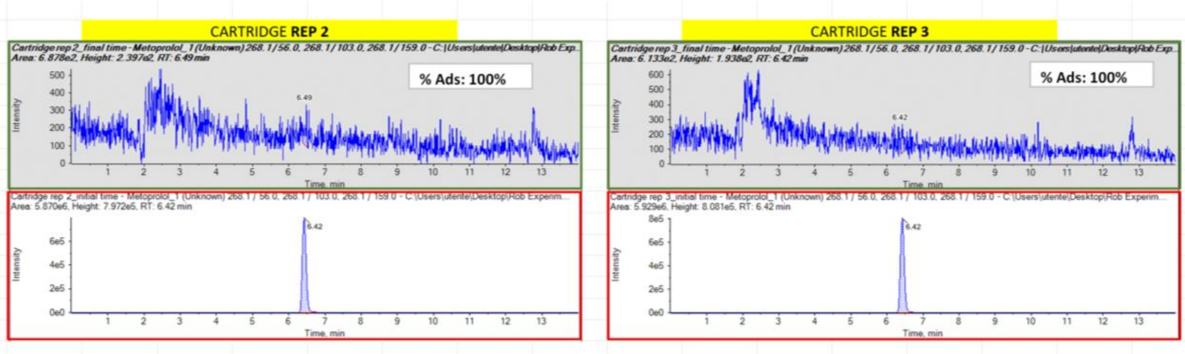



CARTRIDGE REP 2
% Ads: 100%
CARTRIDGE REP 3
% Ads: 100%

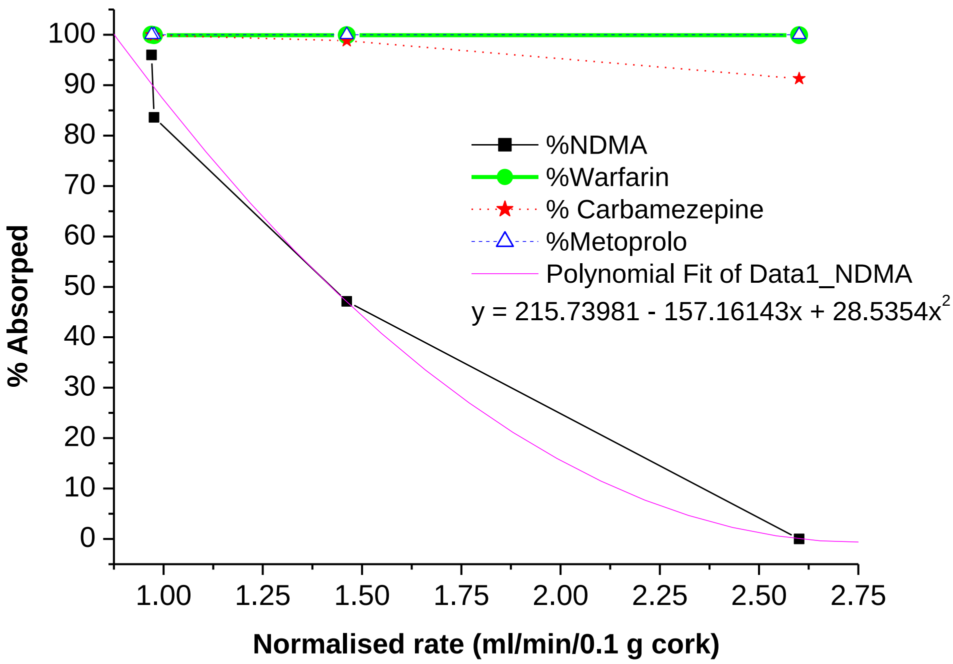

CARTRIDGE REP 1
CARBAMAZEPINE AFTER
Final sample:
after sample loading on cartridge
Cartridge rep 1_final time - Carbamazepine_1 (Unknown) 237.0 / 89.1, 237.0 / 165.2, 237.0 / 193.0 - C:\Users\utente\Desktop\Ro...
Area: 6.650e2, Height: 2.685e2, RT: 8.49 min
% Ads: 100%
Intensity
Time, min
CARBAMAZEPINE
BEFORE
Initial sample:
Cartridge rep 1_initial time - Carbamazepine_1 (Unknown) 237.0 / 89.1, 237.0 / 165.2, 237.0 / 193.0 - C:\Users\utente\Desktop\Rob Ex...
Area: 1.309e7, Height: 1.739e6, RT: 8.51 min


CARTRIDGE REP 2
% Ads: 100%
CARTRIDGE REP 3
% Ads: 100%



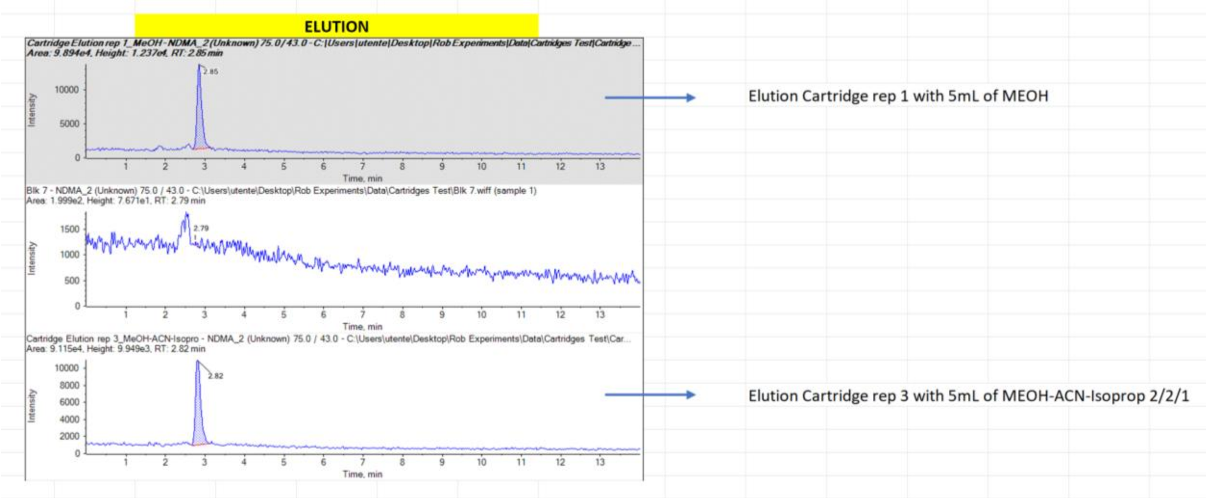


When tests were made with these POPs at faster absorption rates, it was seen that this made a huge difference in the case of the very polar NDMA, a small difference for carbamazepine, and no difference at all for warfarin and metoprolol. In the case of NDMA, only 47% was absorbed at a rate of 1.4 ml/min, and none was absorbed at all at a rate of 2.6 ml/min. Therefore, the much more polar NDMA requires a slow filtration rate to allow it to absorb onto the surface of the carbon.



Tests were also made to remove these POPs from the pyrolysed cork once absorbed, to allow recycling of the absorbant. Elution tests were made with methanol, isopropanol, acetonitrile and dichloromethane, passing 5 ml of solvent through the cartridge..

It was found that methanol could remove 100 % of the polar NDMA from the pyrolysed cork:



However, the other three POPs were much more persistent, and resisted removal with all solvents so far tested. Using a mixture of 2 ml methanol, 2ml isopropanol and 1 ml acetonitrile, 29% carbamazepine, 23% warfarin and only 1.5% metoprolol could be removed from the pyrolysed cork cartridges.

These initial results obtained for the absorption on cork are very interesting, and are already enough to publish a co-authored paper in a good journal, with a little further extra work. RP prepared a cartridge of cork for flow HPLC absorption-resorption tests with NDMA which will be carried out in the near future, and more elution tests will be carried out with other solvents (acetone, hexanol) in the coming weeks, to see if the other three POPs can be removed once adsorbed onto the pyrolysed cork.

Future collaboration will continue in this area, as well as attempts to produce a photocatalyst which is able to operate in real waste waters.

The Host

Dr Giuseppe Mascolo

The Visitor

Dr Robert Pullar