In-situ electrochemical regeneration of particulate active carbon for combined adsorption and degradation of herbicides

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Background

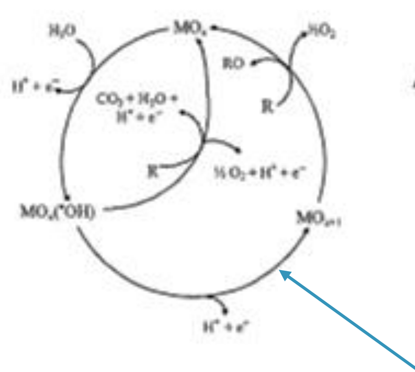
Several review papers report the occurrence of so-called micropollutants caused by agrochemicals in different water bodies . The ever-increasing accumulation of herbicides into the environment has caused various problems and as a result the European Union has defined the maximum residue limits (MRLs) for phenoxy acid herbicides:

- Drinking water: 0.1 µg/L

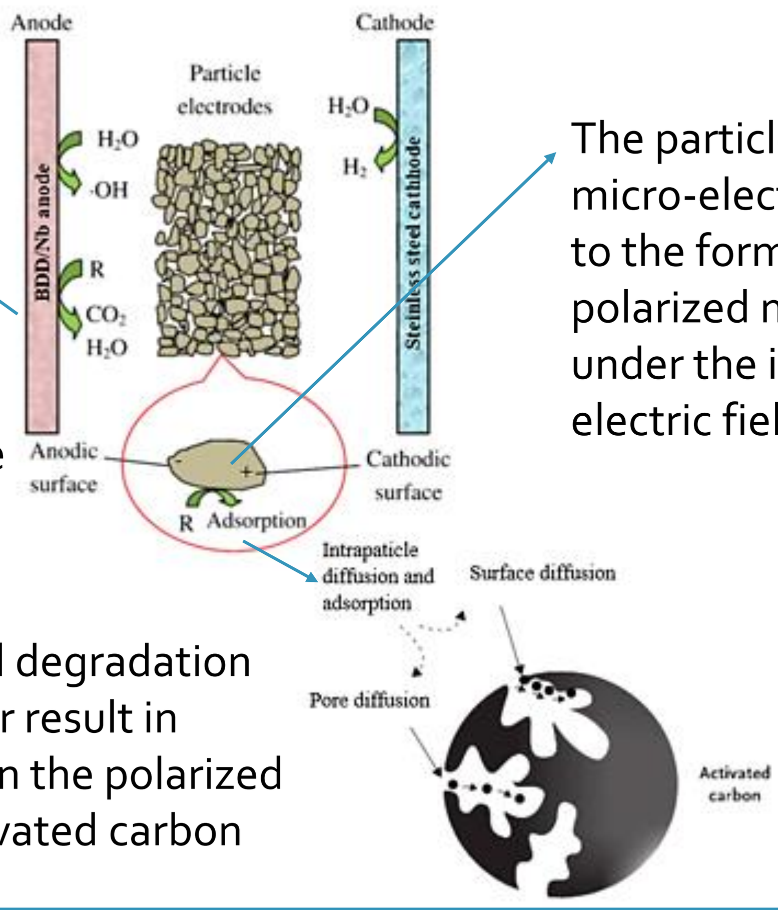
Strategy

Combined electrochemical degradation and active carbon adsorption technology (3D-BDD/Nb anode system) targeting low concentrations of phenoxy acid herbicide micropollutants.

Scheme of the direct electrochemical oxidation of organic compounds on active and nonactive anodes. From Comninellis, C. Electrochim Acta, 1994, vol. 39, pp. 1857-1862 →



Electrochemical oxygen transfer reaction. An BDD anode has a non-active behaviour and favour complete oxidation of the organics to CO_2.



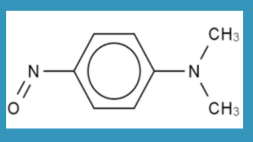
The particle operates as micro-electrolytic cells due to the formation of polarized microelectrodes under the influence of the electric field.

The combination of electrochemical degradation and active carbon adsorption further result in electrosorption, electro-oxidation on the polarized carbon and regeneration of the activated carbon

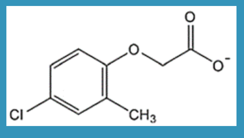
Materials and methods

The setup

RNO

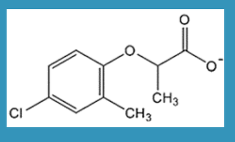


MCPA



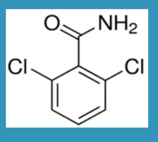
solubility 825 mg/L

MCPP



solubility 900 mg/L

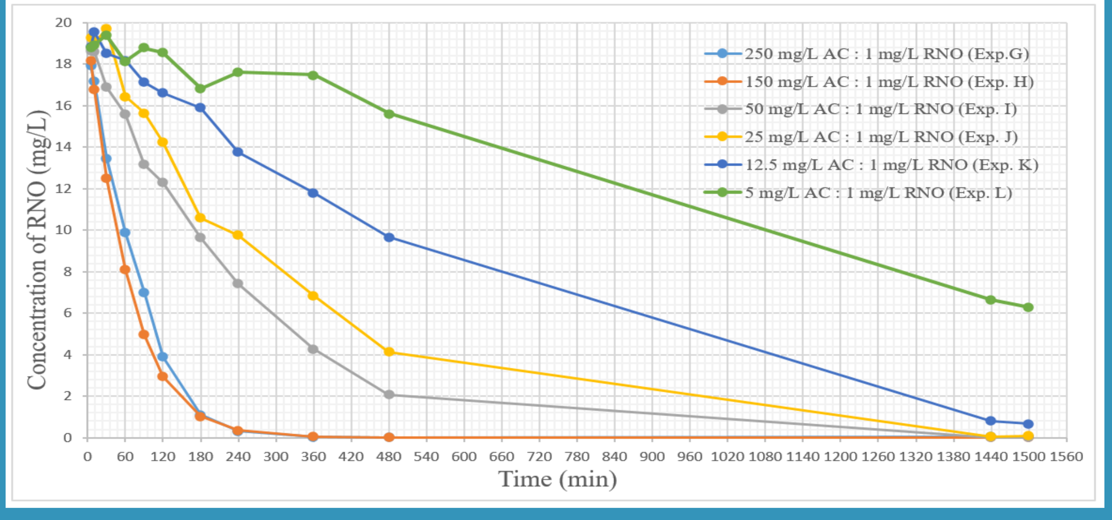
BAM



solubility 2700 mg/L

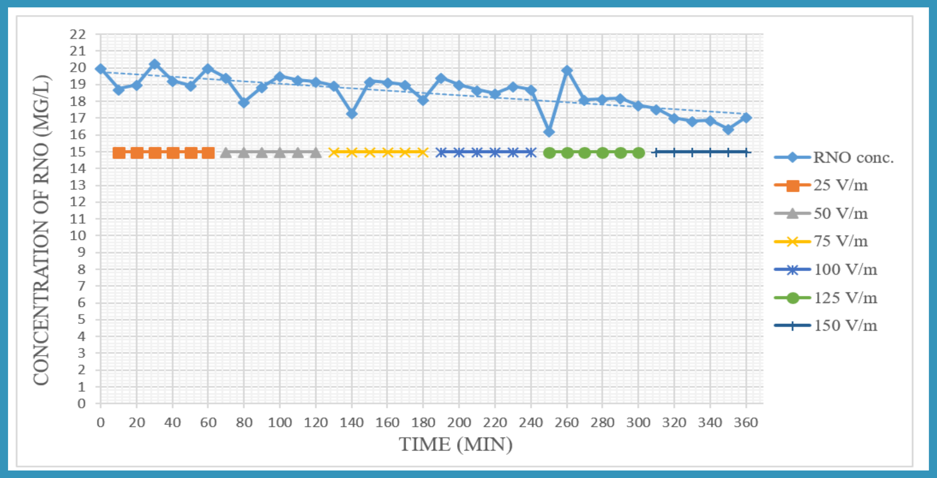
RNO studies

Test on activated carbon and RNO ratios



5 mg/L AC : 1 mg/L RNO

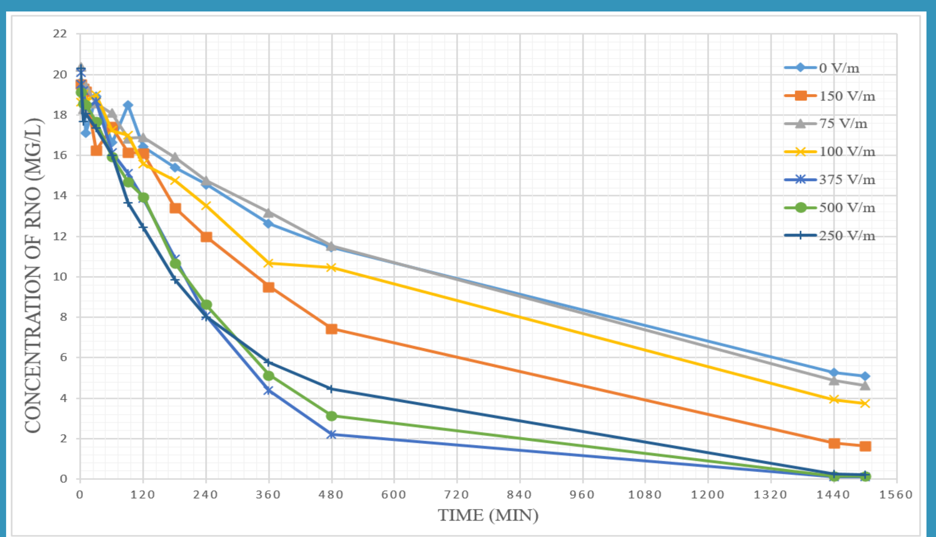
Direct oxidation



Concentration evolution for direct oxidation. The different colours represent an exact electric field strength. The increase in electric field strength did not significantly increase the surface oxidation.

3D electrochemical process

Concentration evolution of the three-dimensional electrode experiments with RNO solution. An increase in the electric fields strength has a positive influence on the degradation.



Efficiency considerations

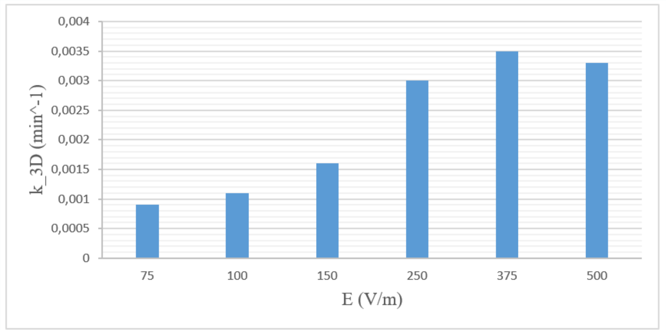
$$r_{RNO} = \frac{d[RNO]}{dt} = -k * [RNO]^x * [AC]^y * [OH\cdot]^z$$

$$= -k^{'} * [RNO]^{x=1}$$

$$k^{'} = k * [AC]^y * [OH\cdot]^z$$

Pseudo-first-order model:

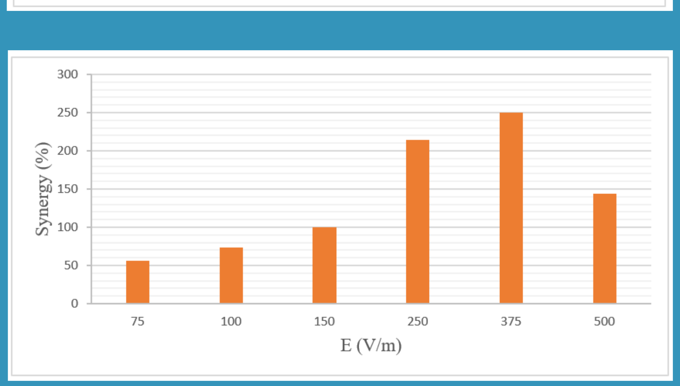
$$\frac{d[RNO]}{dt} = -k_{obs} * [RNO]^1$$



Comparison of the degradation parameters of RNO as a function of the electric field strength.

$$Synergy = \frac{k^{'}_{3D}}{k_{AC} + k^{'}_{(\cdot OH)}} > 1$$

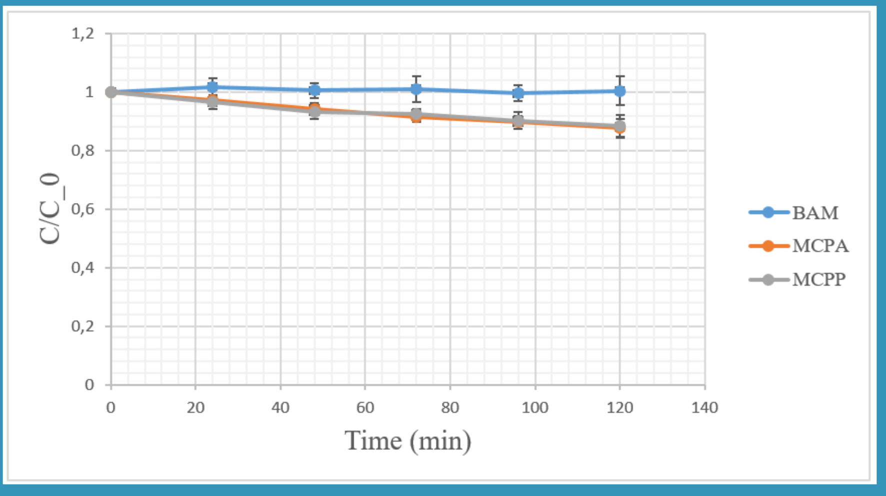
$$synergy(\%) > 100\%$$



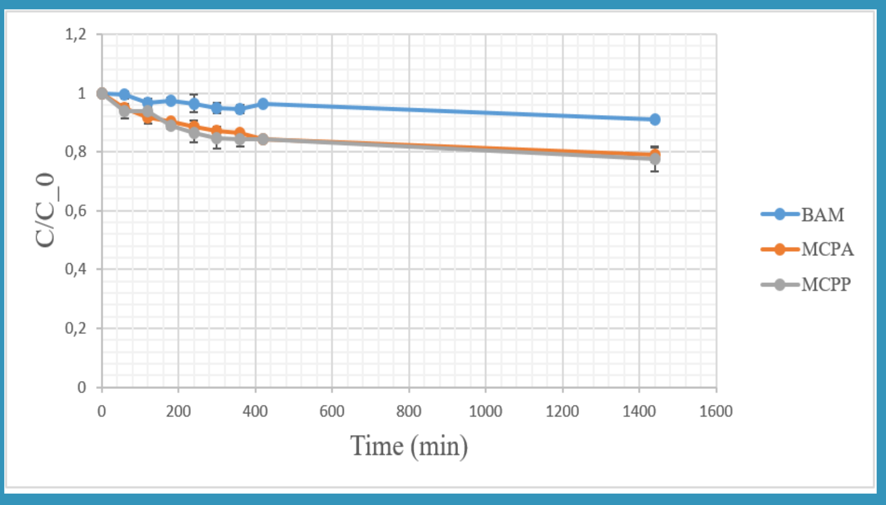
Synergy was obtained over 150 V/m, which implied that other reactions might occur in the system besides those in AC and 2D-BDD/Nb anode systems.

Phenoxy acid herbicide studies

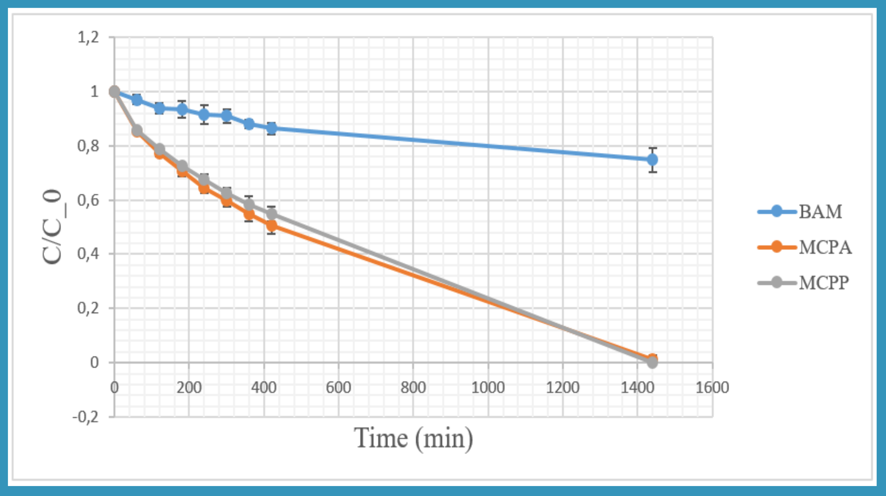
Test on a 10 mg MCPP and 50 mg MCPA and BAM solution



Relative concentration of direct oxidation with an electric field strength of 375 V/m.



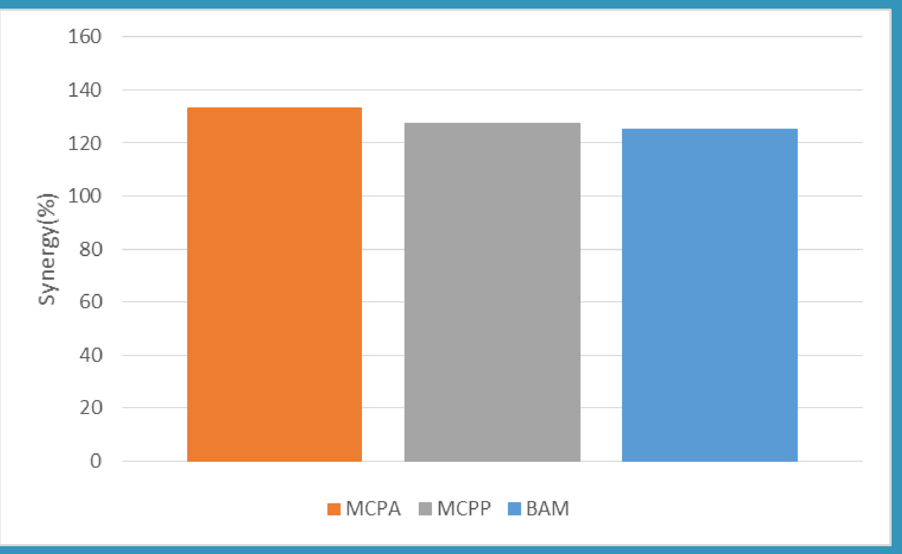
Relative concentration evolution of adsorption.



Relative concentration evolution of the 3D-BDD/Nb anode system with an electric field strength of 375 V/m..

Synergy

The synergy(%) indicate that the uptake removal is substance dependent (solubility) and initial concentration dependent



Conclusion

- A combining adsorption and electrochemical degradation system can be used as a water treatment for micropollutants, represented by the herbicides (MCPA, MCPP and BAM), removal.
- Synergy is obtained.
- The removal uptake is negatively correlated with the herbicide solubility with water and positively correlated with the initial concentration.

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