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Electrocatalytic Oxidation of Organic Pollutants: Kinetic Considerations for Environmental Applications

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- INTRODUCTION
- ENVIRONMENTAL ELECTROCHEMISTRY
- ELECTROCHEMISTRY OF OXYGEN TRANSFER
- NEW DEVELOPMENTS
- CONCLUSIONS

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ELECTROCHEMISTRY

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… Electrochemistry is about reducing tensions, as the French call the voltage, and being aware of current events …

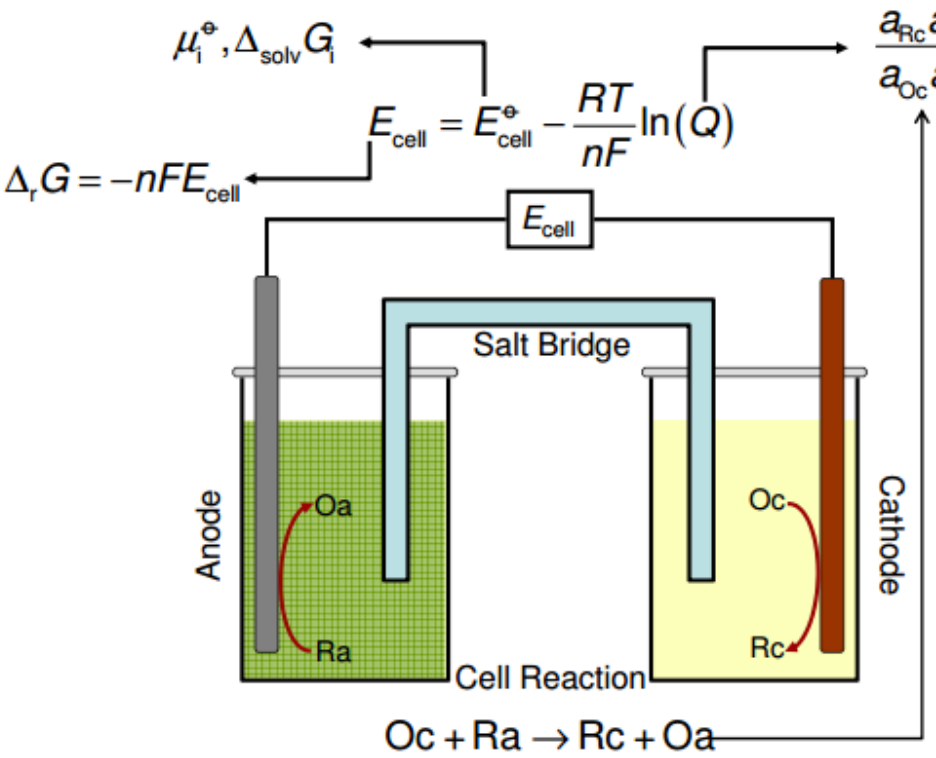

Fig 1. Electrochemical cell

Thermodynamics

Kinetics:

dn/dt = i / (nF)

1 molecule is around 0.1 nm, and under 1 V implies:

100 MV/cm of potential gradient!

ELECTROCHEMICAL OXYGEN TRANSFER REACTION (EOTR)

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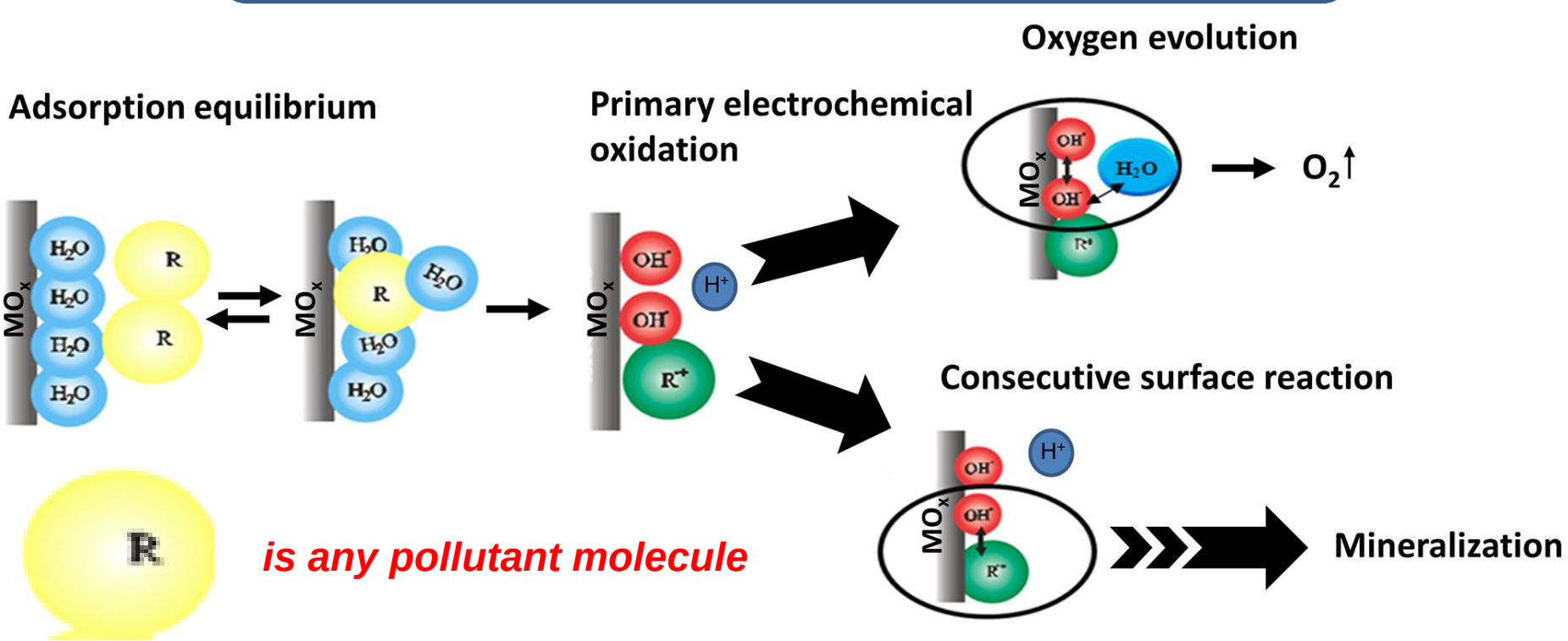

How does affect the molecular structure of the organic compound?

Fig 2. Key steps for environmental goal using EOTR.

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THE CHARGE TRANSFER INTERMEDIATE!

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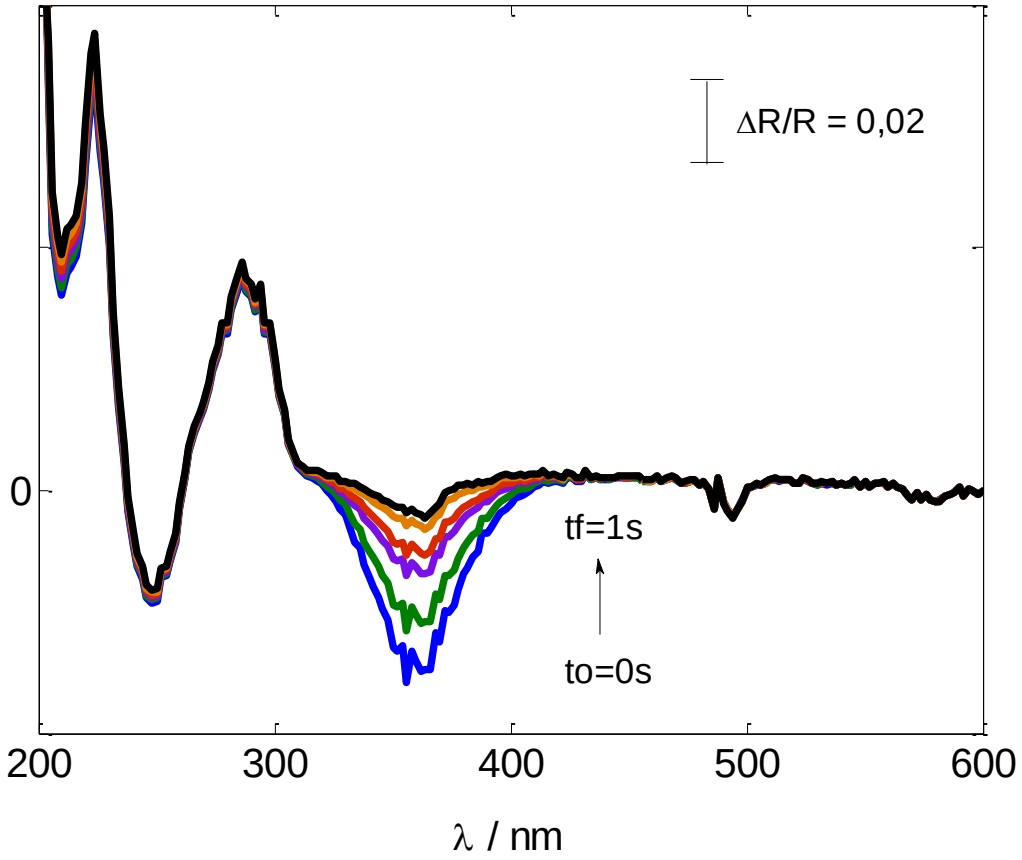

Fig 3. Spectroelectrochemical observation of the charge transfer intermediate.

Case: *p*-metoxiphenol on PbO_2-Bi

From the temperature dependence we obtained the free energy of activation! $\Delta^{\ddagger}G$

account the driven force!

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MATHEMATHICAL MODEL OF THE ELECTROCHEMICAL PROCESS

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Convective - diffusive equation

$$\frac{dc_j}{dt} = D_j \nabla^2 c_j - v.\nabla c_j$$

$$\begin{cases} y \to \infty; & c = c_0 \\ y = 0; & r\big|_{q} = j\big|_{q} \end{cases}$$

Langmuir – Hinshelwood equation

$$r = \frac{kKc}{1 + Kc}$$

Levich diffusion length

$$\delta = 1.61 D^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^{\frac{1}{6}}$$

Current equation (new reaction rate model)

$$i = \frac{nFS}{2K\left(1.61 D^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^{\frac{1}{6}}\right)} \left\{ KDc_0 + kK\left(1.61 D^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^{\frac{1}{6}}\right) + D - \left[\left(1.61 kKD^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^{\frac{1}{6}} + D - Dc_0 K\right)^2 + 4KD^2 c_0 \right]^{\frac{1}{2}} \right\}$$

From appropiate kinetic experiments the characteristic constants (k and K) can be evaluated!

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VOLCANO PLOT AND LINEAR FREE ENERGY CORRELATIONS

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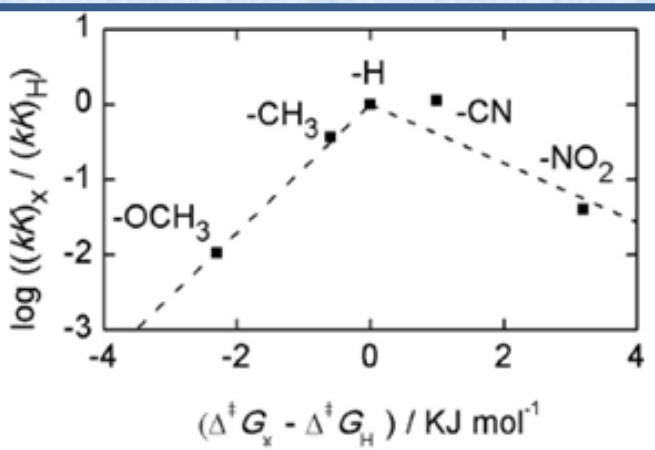
Phenolic family:

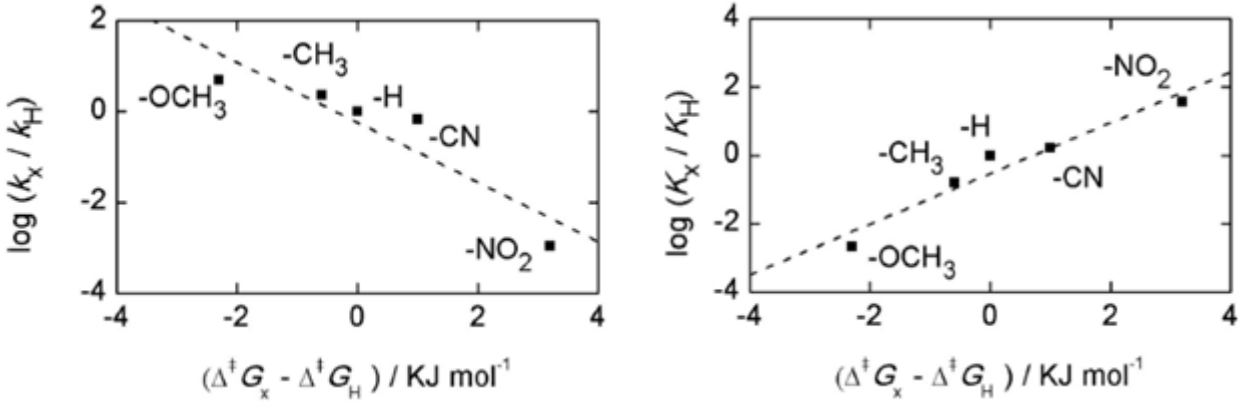
p-nitrophenol,
p-cyanophenol,
Phenol,
p-methylphenol,
p-methoxyphenol



The stability conditions at the interface can be redefined!

Fig 5. Volcano plot on PbO_2-Bi

kinetics



thermodynamics

Fig 6. Structure – reactivity relationships on PbO_2-Bi

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CONCLUSIONS

1) **A new structure – reactivity relationships have been envisaged.**

2) **The charge transfer reaction rate and the adsorption properties at the electrode are decoupled using a new kinetic model.**
The transport phenomena with surface reaction model.

3) **The chemical kinetic of an organic compound family can involves a volcano plot in the EOTR.**

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THANK YOU

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Research interests:

Fundamental Electrochemistry
Physical Chemistry
Energy and Environment
Chemical Sciences

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OBSERVATIONS AND POSIBILITIES

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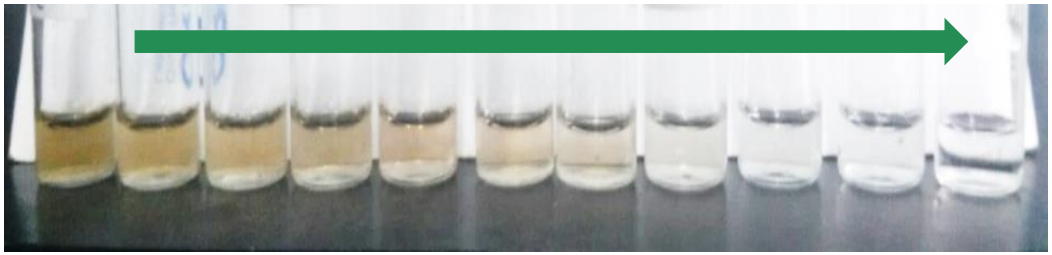
Fig A1. Petroleum residual dissolve with surfactant in water media

ELECTROLYSIS TIME



Satisfactory results in many water polluted systems:

- Insecticides, pesticides, herbicides

- Phenols, poly aromatic heterocyclic compounds, chlorinated compounds

- Municipal wastewaters: urea, surfactant, e-coli

- Highly polluted biphasic media (oil from petroleum wastes / water)

EXPERIMENTAL VALIDATION FOR PHENOLIC COMPOUNDS

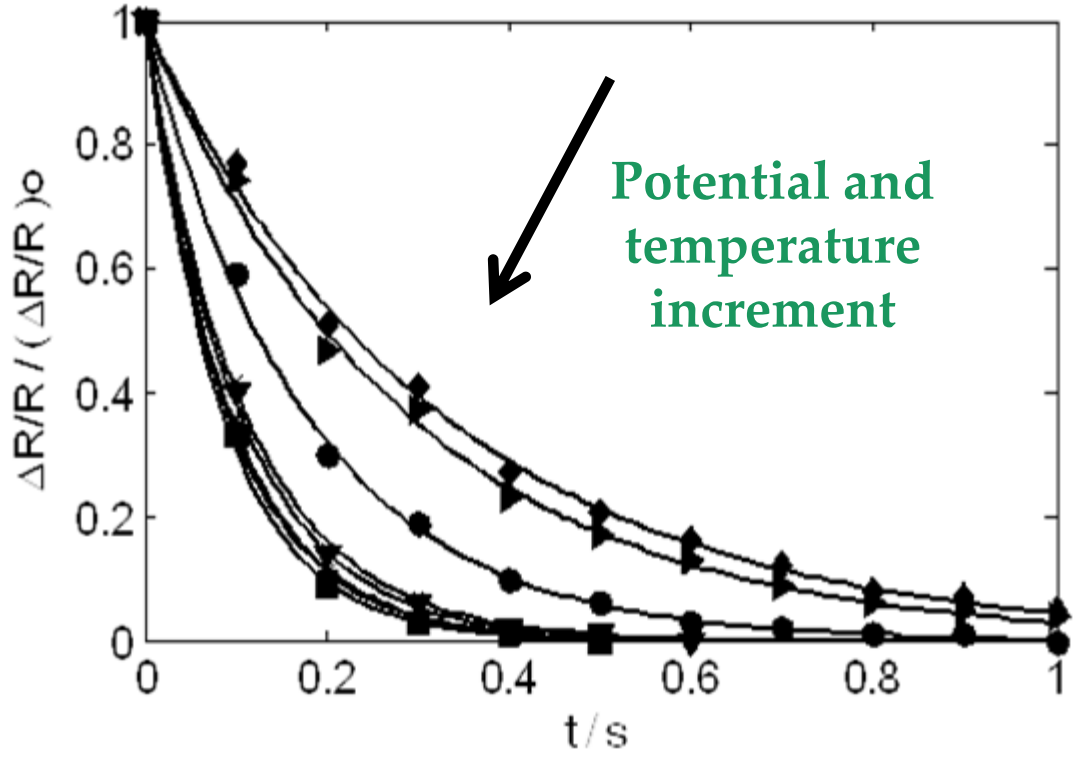


Fig A2. Spectral signal decay as a function of experimental parameters

EXPERIMENTAL VALIDATION FOR PHENOLIC COMPOUNDS

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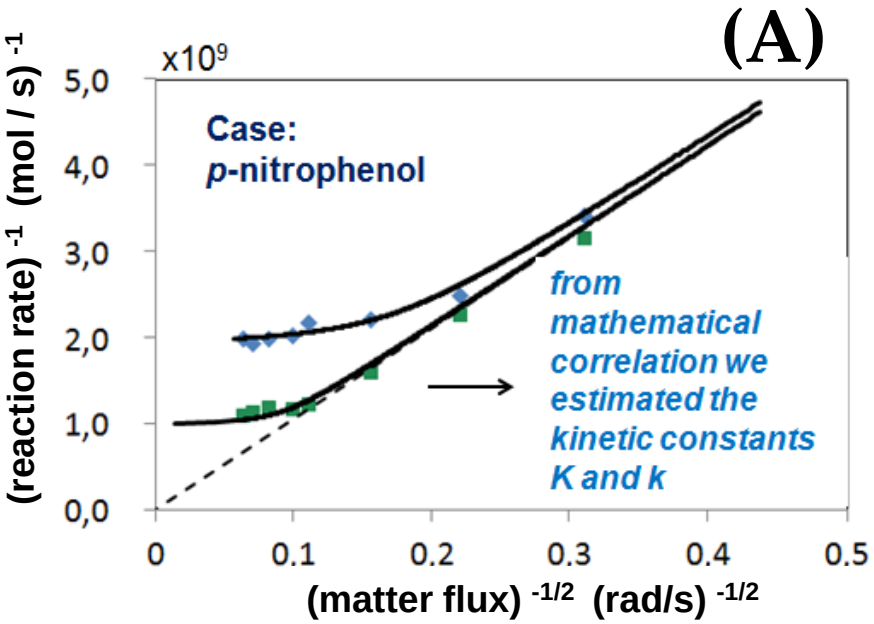

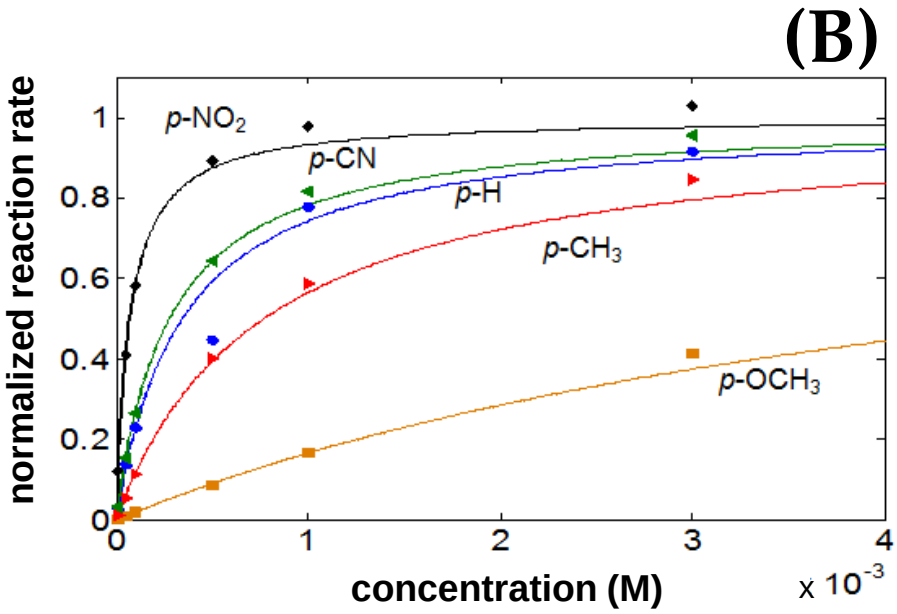

Fig A3. (A) (reaction rate) $^{-1}$ vs. (matter flux) $^{-1/2}$ plot for two electrodes. (B) Reaction rate results envisage the structure – reactivity relationships

K and k accounts the chemical effects

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Phenolic family:

***p*-nitrophenol, *p*-cyanophenol, phenol**

***p*-methylphenol, *p*-methoxyphenol**

EXPERIMENTAL VALIDATION FOR PHENOLIC COMPOUNDS

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a) PbO_2-Bi

b) SnO_2-Sb

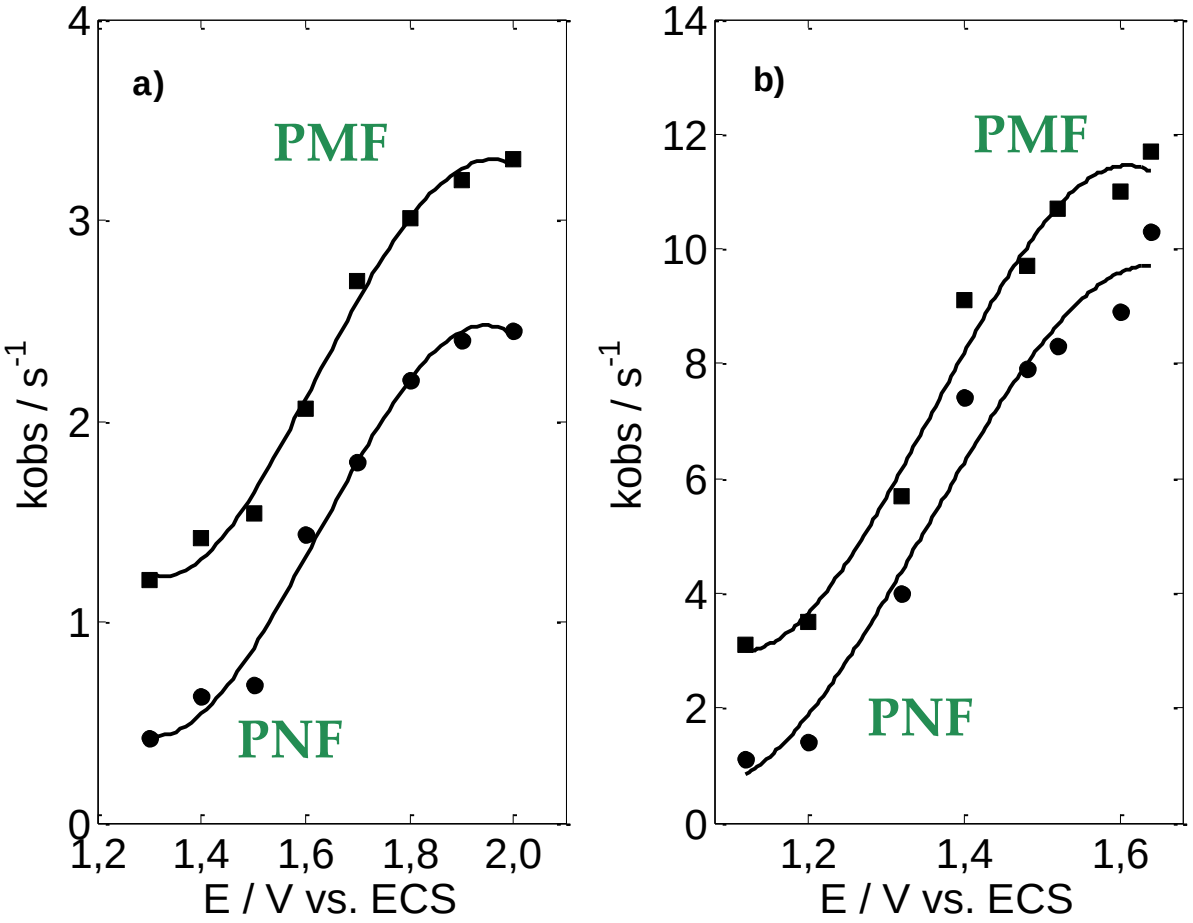

Fig A4. Potential effect.