

# UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

Dipartimento di Ingegneria Idraulica, Geotecnica ed Ambientale



Department of Civil and Environmental Engineering  
University of Washington

## **STUDIES OF RAPID IODINE REACTIONS WITH NATURAL ORGANIC MATTER USING THE METHOD OF ROTATING RING-DISK ELECTRODE**

Relatore

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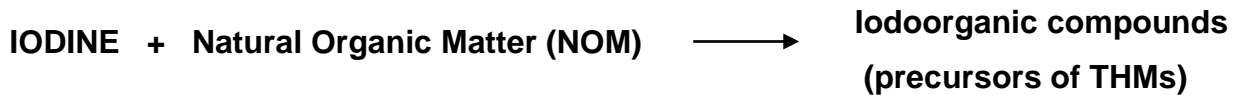
Candidato

Francesco Infante

Matr. 324/244

ANNO ACCADEMICO 2011 – 2012

## STATEMENT OF THE PROBLEM



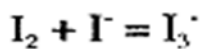
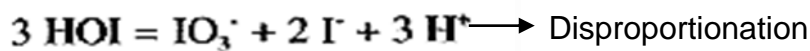
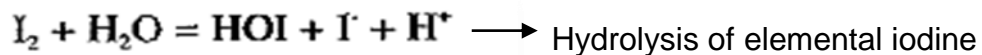
Iodo-trihalomethanes (I-THMs) are by-products of the oxidative treatment of iodide containing drinking waters. Several oxidants/disinfectants such as  $O_3$ ,  $Cl_2$  or chloramines oxidize  $I^-$  to hypoiodous acid (HOI) in a fast reaction. Subsequently, HOI can react with NOM under formation of I-THMs

(e.g.  $CHI_3$ )



**Bad taste      Odor**

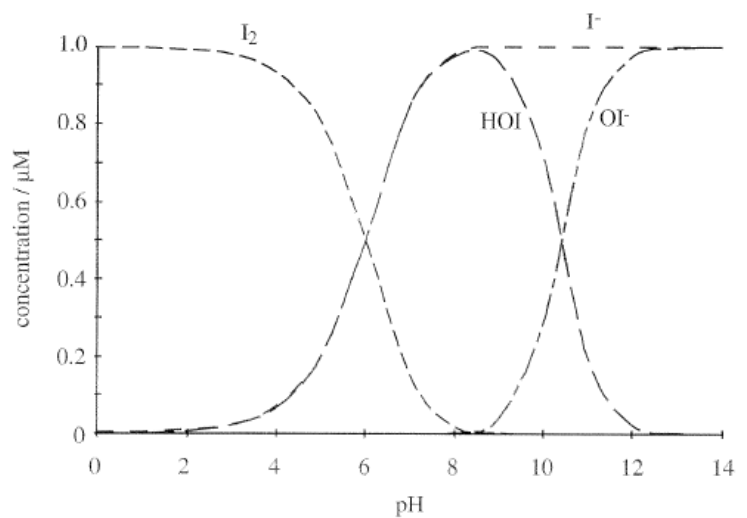
## TYPICAL $I_2$ REACTIONS IN WATER



HOI       $5.5 < pH < 10.4$

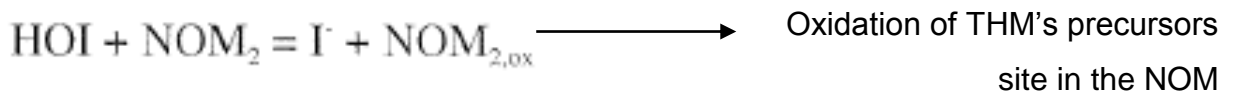
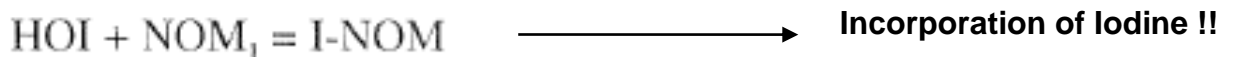
$OI^-$        $pH > 10.4$

These limits depend on the concentration of  $I_2$



## WHAT HAPPENS IF I ADD NOM?

Consumption of HOI is observed. It is caused by these reactions:



## GOAL OF THIS STUDY

Investigation of the reaction kinetics of iodine species, especially HOI,  
with Aldrich Humic Acid and Suwanne River NOM  
with respect to the formation of iodine-containing DBP's.

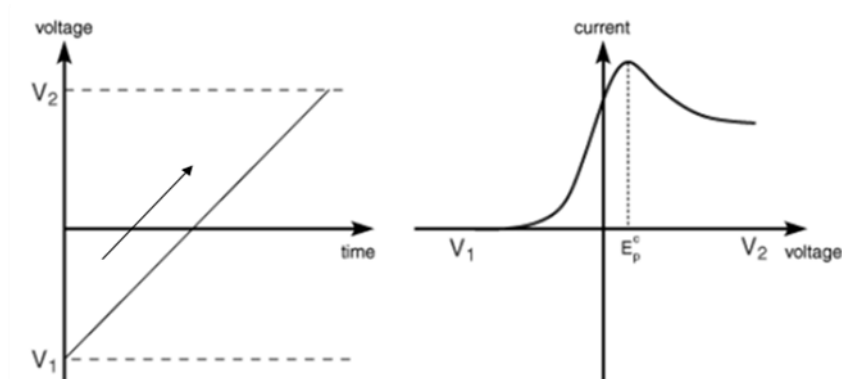
## METHODS

- 1 . Voltammetric Analysis
- 2 . Electrolysis Experiments (current vs time)

by using the **rotating ring-disk electrode (RRDE)**

### Principle of a voltammetric analysis (Linear Potential Scan)

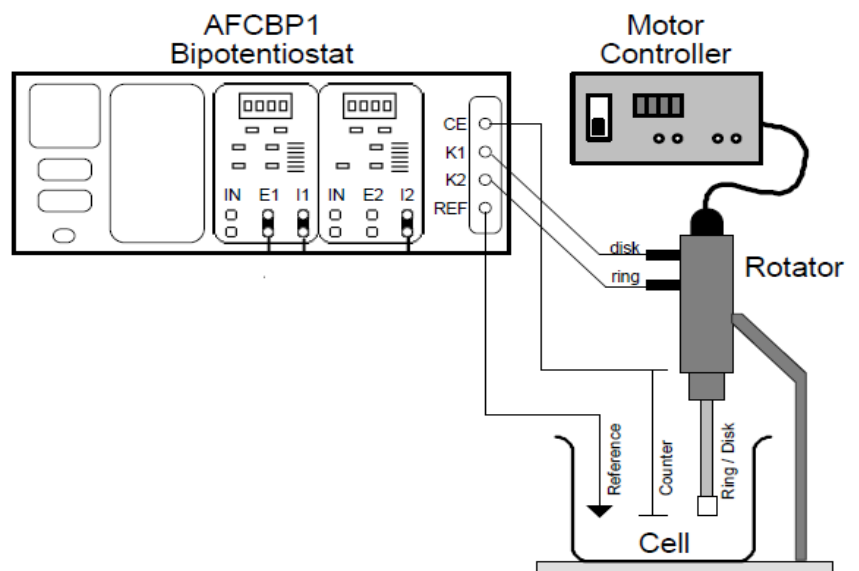
The voltage is scanned from a lower limit to an upper limit and the current response is plotted as a function of voltage obtaining a voltammogram (current vs potential)



## EXPERIMENTAL APPARATUS

It includes the following items:

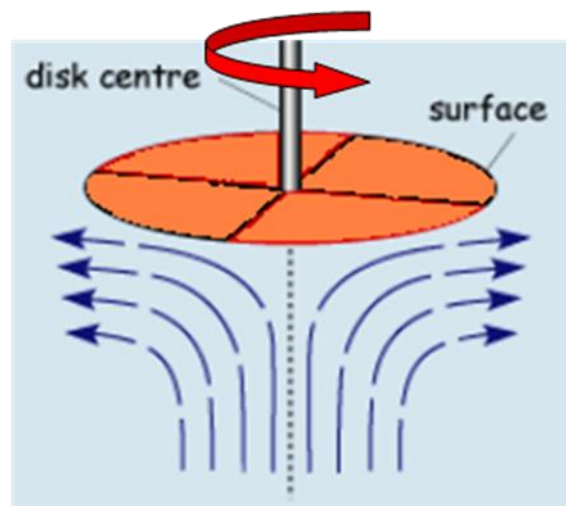
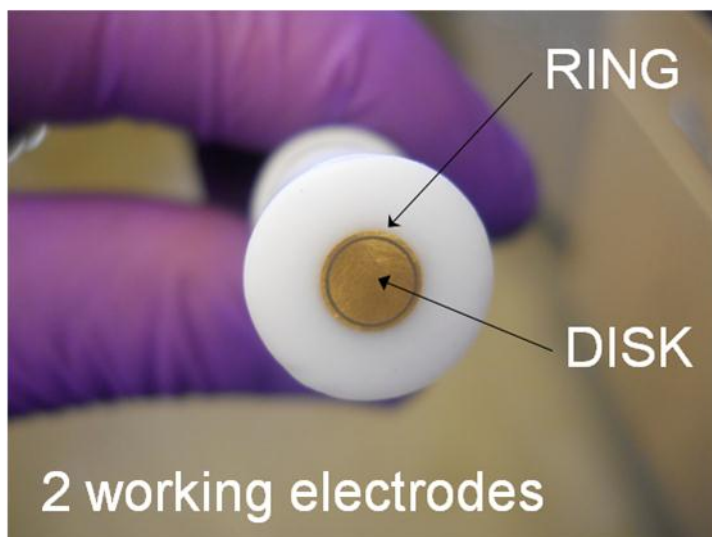
- voltammetric cell
- working electrode(s) (gold)
- counter-electrode
- reference electrode
- bipotentiostat
- rotator and speed controller



- PC with software

## WHY DO WE USE A ROTATING RING-DISK ELECTRODE?

In a stagnant solution the mass transfer of iodine species from the bulk to the electrode surface is leaded by diffusion then the measured current due to their oxidation or reduction decreases over time. Ensuring stirred condition in the cell, this mass transfer is leaded both by diffusion and convection then measured current is constant



## PROCEDURES

**PHASE 1** : RRDE voltammetry in order to define :

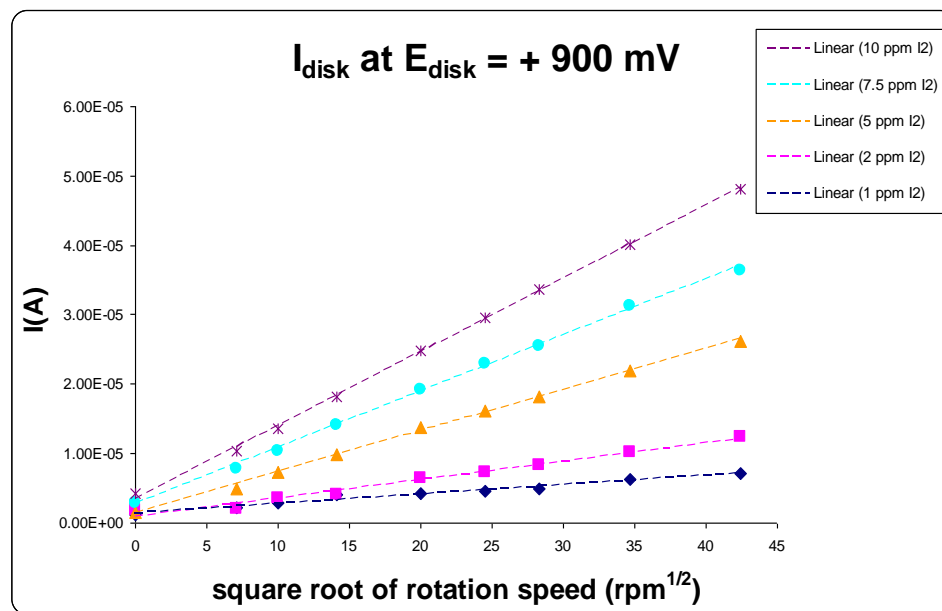
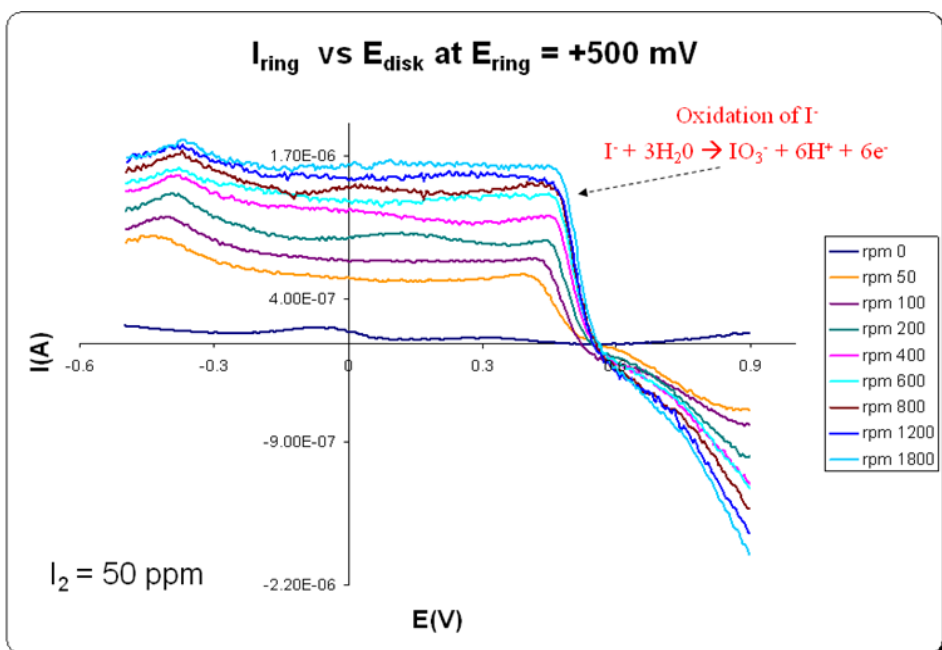
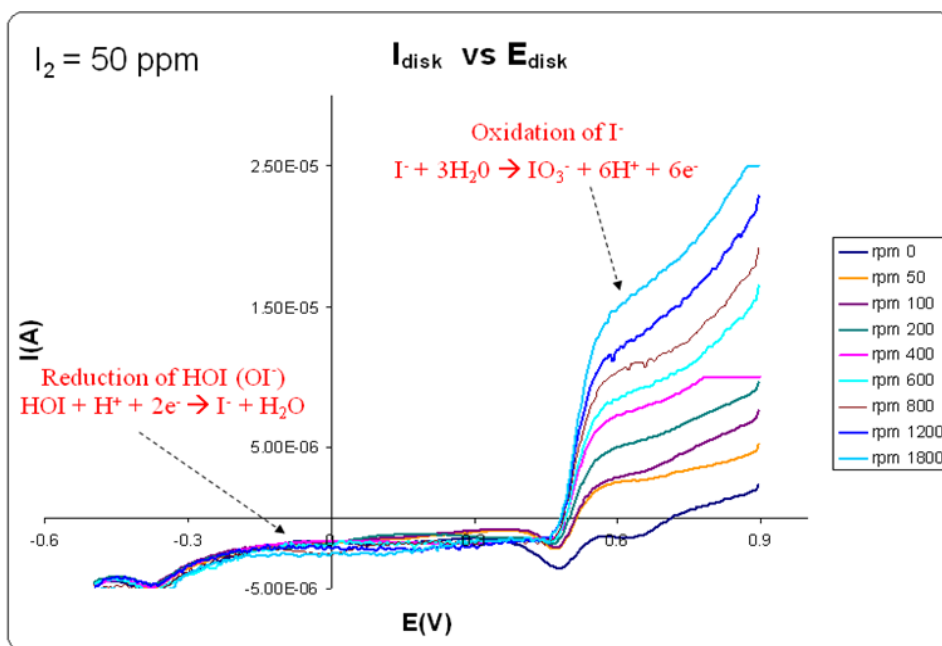
- $E_{\text{ring}}$
- $E_{\text{disk}}$
- Rotation speed  $\omega$  (rpm)
- Target Concentration of  $\text{I}_2$

Parameters to be used in  
electrolysis experiments

**PHASE 2** : Electrolysis of solutions adding before  $\text{I}_2$  and after NOM and varying for each experiment:

- Concentration of AHA (and SRNOM)
- pH

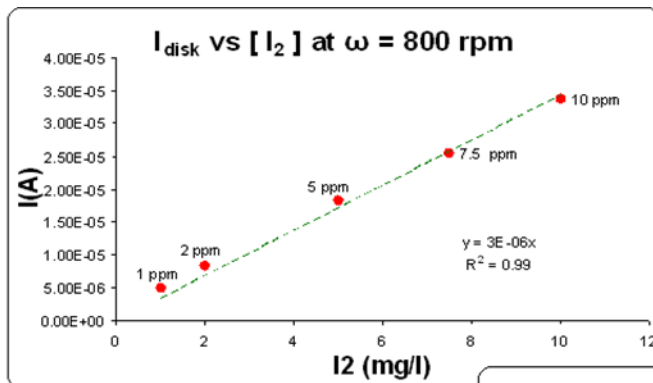
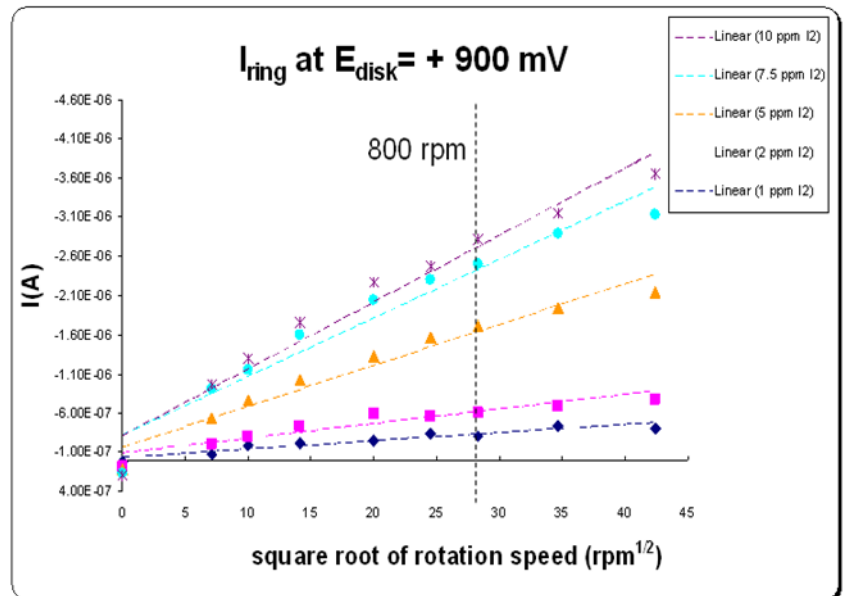
## RESULTS PHASE 1 (VOLTAMMETRY)



Proportionality between current and the square root of rotation speed is described by this law:

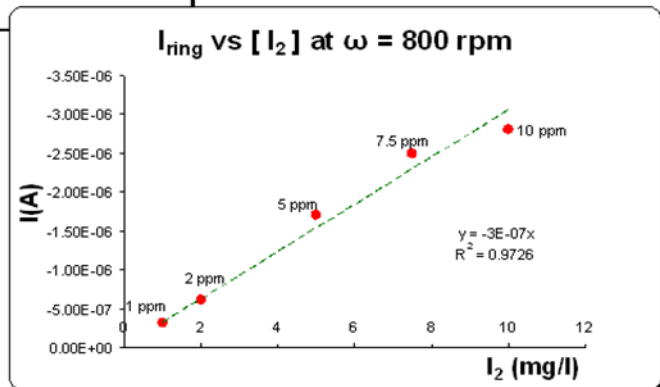
$$i_l = \alpha \omega^{1/2}$$

(Levich)



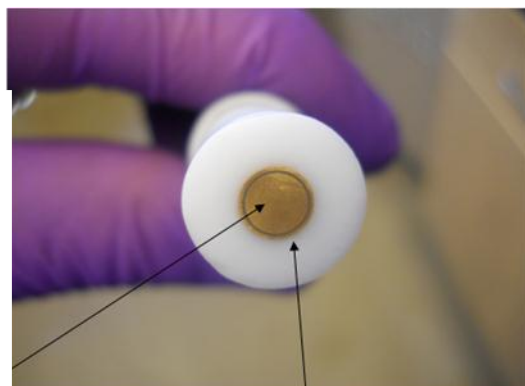
$$i_l = \alpha C_{\text{bulk}}$$

$$I_2 = 7.5 \text{ mg/l}$$



**PHASE 1 COMPLETED**

- $E_{\text{ring}} = 500 \text{ mV}$
- $E_{\text{disk}} = 0 \text{ mV}$
- Rotation speed  $\omega = 800 \text{ rpm}$
- $I_2 = 7.5 \text{ ppm}$

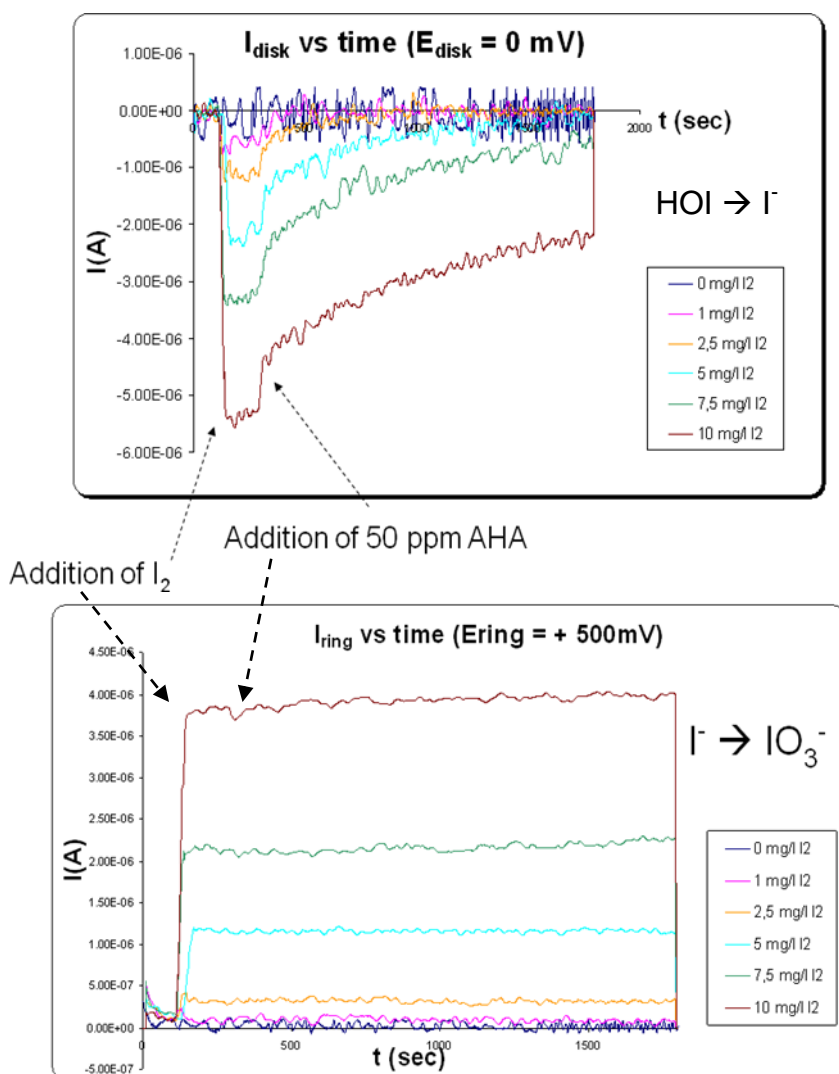


Reduction on the disk :  
 $\text{HOI} \rightarrow \text{I}^-$

Oxidation on the ring :  
 $\text{I}^- \rightarrow \text{IO}_3^-$

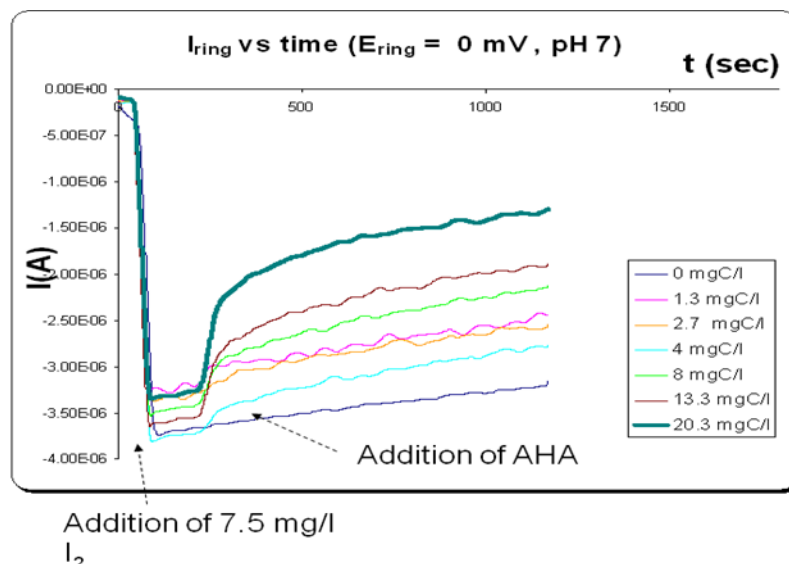
## RESULTS PHASE 2 : ELECTROLYSIS EXPERIMENTS

Test fixing [AHA] varying  $[I_2]$



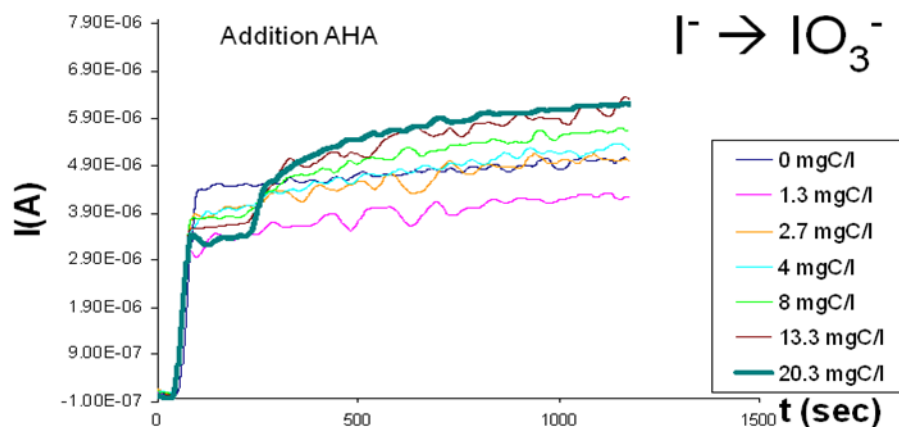
Notice : before continuing electrolysis experiments potential values of working electrodes were switched in order to reduce noise in the current signal. For this reason reduction on the disk and oxidation on the ring will be observed.

Test fixing  $[I_2]$  varying [AHA]

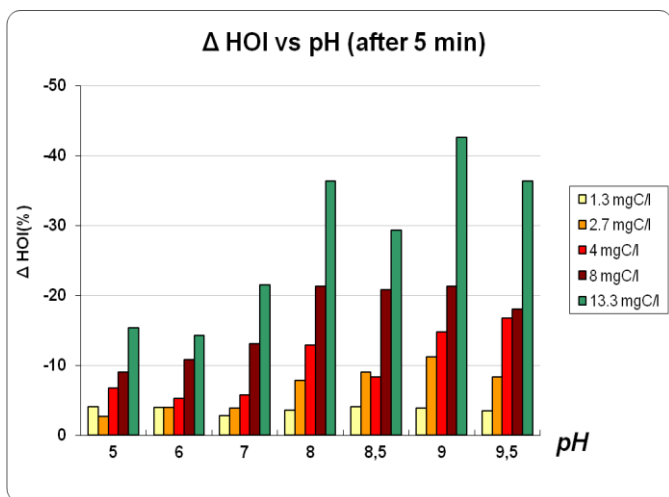


Addition of 7.5 mg/l  $I_2$

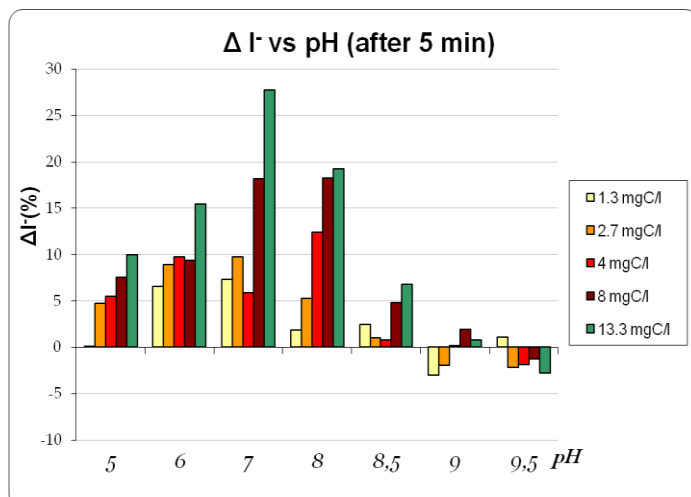
$I_{\text{disk}}$  vs time ( $E_{\text{disk}} = +500$  mV, pH 7)



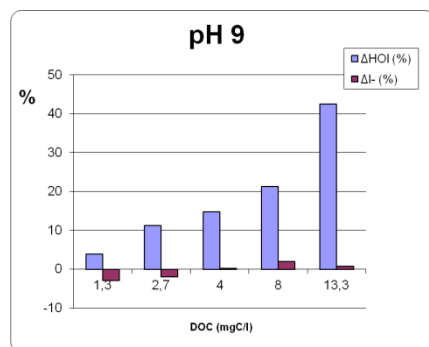
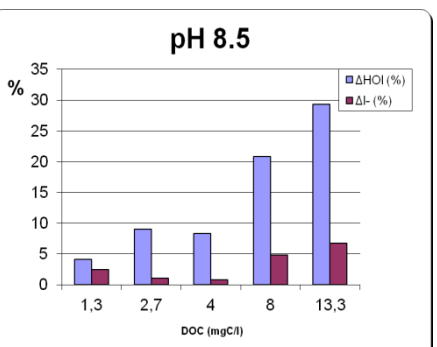
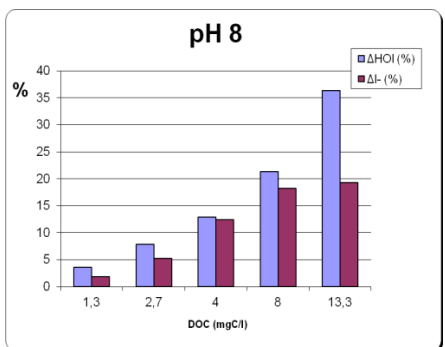
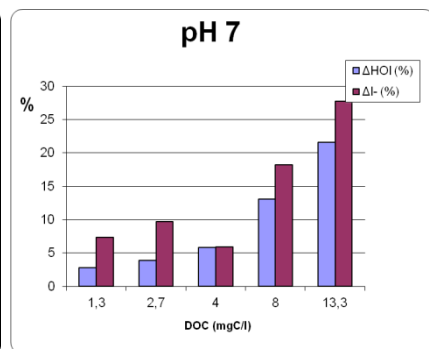
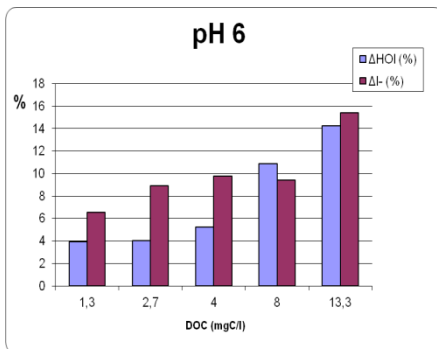
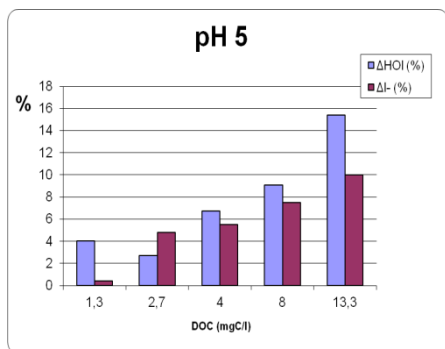
## Consumption of HOI



## Yield of $I^-$



## Comparing at different pH

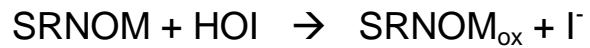




## Test with SRNOM (Suwanne River NOM)

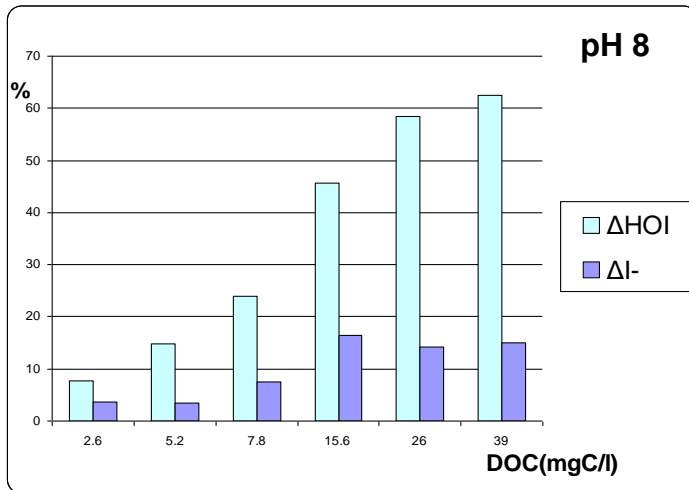


**iodination !!**

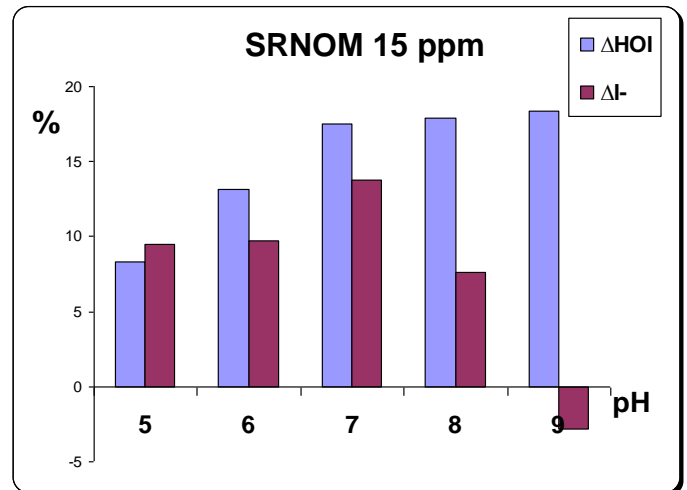


yield of iodide

### Consumption of HOI and yield of $\text{I}^-$



### Comparing at different pH



## SUMMARY AND CONCLUSIONS

For both organic species iodine incorporation appears strongly dependent from pH : while HOI consumption increases with DOC concentration at each pH, an unexpected behavior concerning the yield of  $I^-$  is observed : it increases until pH 7 then it starts to decrease rapidly to even slightly negative values at pH around 9.

In particular Iodine incorporation:

- has an irregular trend at different pH : it doesn't represent a risk at pH 6-7 while it occurs both at pH around 8-9 and 5 with respect to any AHA concentration;
- increases with SRNOM concentration at pH 8;
- is more and more high with increasing of pH from 6 to 9 with respect to a fixed SRNOM concentration (15 mg/l).

Since pH of natural waters typically ranges from 6 to 8, the simultaneous presence of both HOI and NOM brings unavoidably to iodination of the latter and consequently the yield of I-THMs after disinfection treatment represents a real risk.

Although we identified this phenomenon as leading cause of formation of iodoorganic compounds, the formation of I-THMs in drinking water is however highly influenced by the oxidant used during the disinfection treatment.