TRABAJO FIN DE MASTER EN

INGENIERÍA QUIMICA "PRODUCCIÓN Y CONSUMO SOSTENIBLE"

Curso: 2011-2012

TITULO DEL TRABAJO FIN DE MASTER

Aplicación de la tecnología de electroxidación al tratamiento y reutilización de agua en la acuicultura. Estudio de la formación de subproductos.

TITLE IN ENGLISH

Electroxidation technology applied to water treatment and reuse in aquaculture. Study of by-products formation.

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Santander a, 10 de Julio de 2012

Electroxidation technology applied to water treatment and reuse in aquaculture. Study of by-products formation.

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Aquaculture, as a technique for growing aquatic plants and animals, is an important source of high protein foods, and hence economical profits [1]. On the other hand, aquaculture has a negative effect in environmental due to its wastewater rich in nitrogen compounds and organic matter [2].

Electrochemical oxidation with boron doped diamond (BDD) electrodes is a potential technology to remove pollutants from water, including total nitrogen ammonia the main aquaculture seawater contaminant. Previous studies in the research group have developed applications in treatment of leachate [3], wastewater [4] and waste streams in aquaculture [5]. Concerning the latter application and as a result of this electrochemical oxidation, bromide contained in seawater is turned into bromate, a carcinogenic chemical. An investigation about the generation of this hazardous by-product is required, so formation pattern of bromate during aquaculture seawater electroxidation with boron doped diamond (BDD) electrodes was evaluated in this work.

In order to determine generation of bromates, several experiments were carried out with water from a fish-culturing facility located in Cantabria at different current densities (10 and 50 A m^{-2}) and constant temperature (25ºC). Ion chromatography was used for bromide, bromate and chloride quantification and spectrophotometry for total ammonia nitrogen (TAN) determination.

As a result, electrochemical oxidation technology using boron doped diamond (BDD) electrodes was successfully tested as an efficient alternative to treat aquaculture seawater removing total ammonia nitrogen (TAN), being 4 mg/l the maximum concentration of bromate achieved in the range of current densities applied. It has been found current density has a large effect on % TAN removal and time needed to reach it. Bromate formation is influenced by current density too, and its formation begins when total ammonia nitrogen (TAN) has been practically eliminated.

Keywords: Electroxidation, by-product, bromate, BDD anode

References

1. FAO Fisheries and Aquaculture Department, World aquaculture 2010. Technical Paper 500/1 (2011).

2. M. Martinez-Porchas, L.R. Martinez-Cordova, World aquaculture: Environmental impacts and troubleshooting alternatives, The Scientific World Journal 2012 (2012).

3. G. Pérez, J. Saiz, R. Ibañez, A.M. Urtiaga, I. Ortiz, Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates, Water Res. 46 (2012) 2579-2590.

4. G. Pérez, P. Gómez, R. Ibañez, I. Ortiz, A.M. Urtiaga, Electrochemical disinfection of secondary wastewater treatment plant (WWTP) effluent, Water Science and Technology 62 (2010) 892-897.

5. V. Díaz, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, Kinetics of electro-oxidation of ammonia-N, nitrites and COD from a recirculating aquaculture saline water system using BDD anodes, Water Res. 45 (2011) 125-134.

Acknowledgements

Financial support of projects CTQ2008-00690 (Spanish Ministry of Education, Culture and Sports (MECD) and Cantabria Regional Society R+D+i S.L. (IDICAN)) and CTQ2011-23912 (Spanish Ministry of Economy and Competitiveness (MINECO)), is gratefully acknowledged. The collaboration of Tinamenor S.L. is also acknowledged. R. Sanz would like to thank MECD for the grant to realize the Chemical Engineering Master "Sustainable Production and Consumption" at University of Cantabria.

Chemical Engineering Master's Degree
“Sustainable Production and Consumption”

Electroxidation technology applied to water treatment and reuse in aquaculture Study of by-products formation

Advisors: Dra. Raquel Ibañez, Dra. Inmaculada Ortiz

Dpto. Ingeniería Química y Quimica Inorgánica, UC

Rubén Sanz Garrido

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Approach

- Aquaculture
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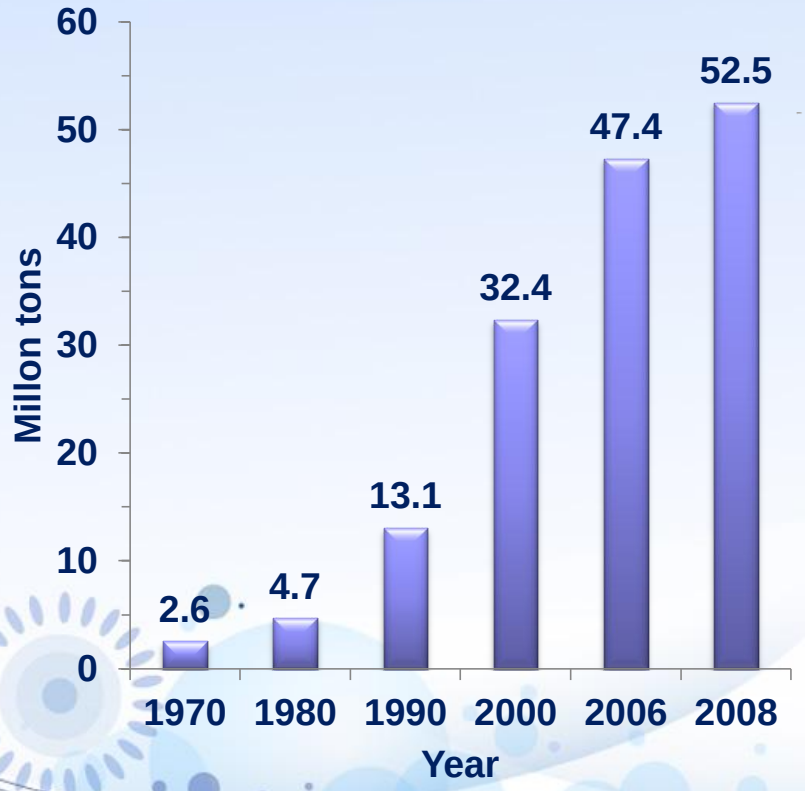
Aquaculture

The rearing of aquatic animals or the cultivation of aquatic plants for food



FAO Fisheries and Aquaculture Department, **World aquaculture 2010**. Technical Paper 500/1 (2011)

Aquaculture

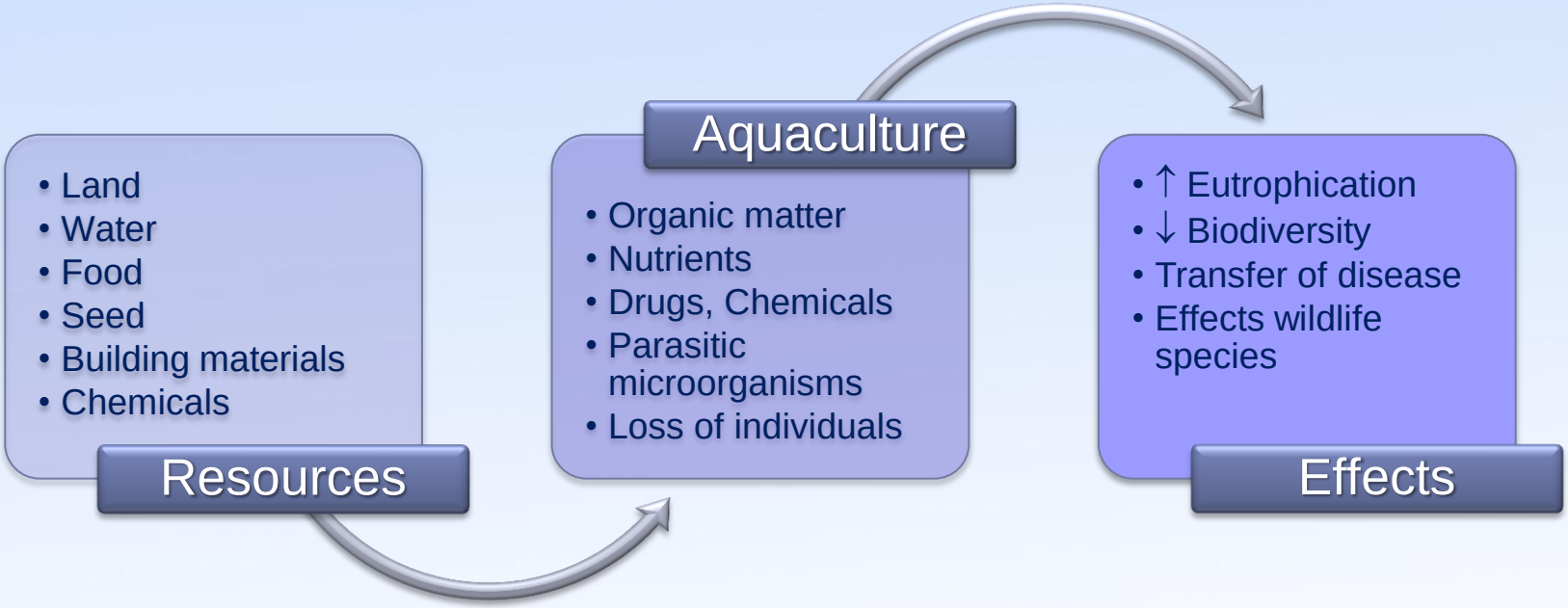
The rearing of aquatic animals or the cultivation of aquatic plants for food

- **59.9 % production**
- **30.7 % value**

- **32.3 % production**
- **56.0 % value**

FAO Fisheries and Aquaculture Department, **World aquaculture 2010**. Technical Paper 500/1 (2011)

Aquaculture



RAS → Recirculation loop → Treatment → Recycling & Reuse → ↓ Impact

Disinfection By-Products (DBP's) → Bromate → Carcinogenic

M. Martinez-Porchas, L.R. Martinez-Cordova, **The Scientific World Journal** 2012 (2012).

Background

Advanced Oxidation Processes (AOPs) - In-situ production of highly reactive agents to remove organic and inorganic materials in water and waste water by oxidation.

Sosprocan SPAS Procesos Avanzados de Separación

Landfill leachate

Waste water

Aquaculture

Chlorination
Ozonization

Electroxidation

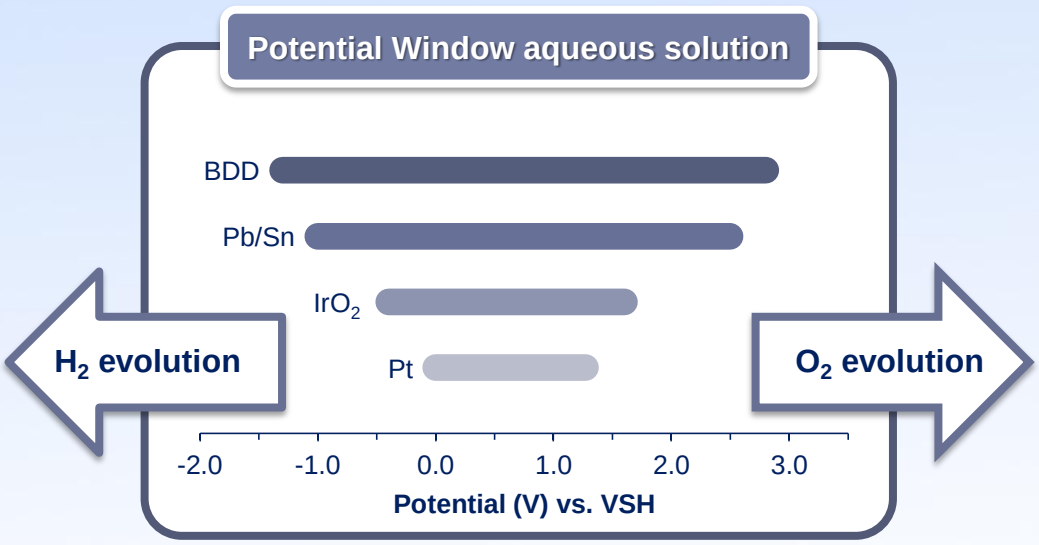
Handling
Transporting
Producing

Photovoltaic power supply
Less maintenance
More cost-effective
No transport
No storage

G. Pérez, J. Saiz, R. Ibañez, A.M. Urtiaga, I. Ortiz, **Water Research**. 46 (2012) pp. 2579-2590.
V. Díaz, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, **Water Research**. 45 (2011) pp. 125-134.
D. Ghernaout, M.W. Naceur, A. Aouabed, **Desalination.** 270 (2011) pp. 9-22.

Background

Boron doped diamond (BDD) electrodes



Corrosion stability in very aggressive media

Inert surface

Low adsorption properties

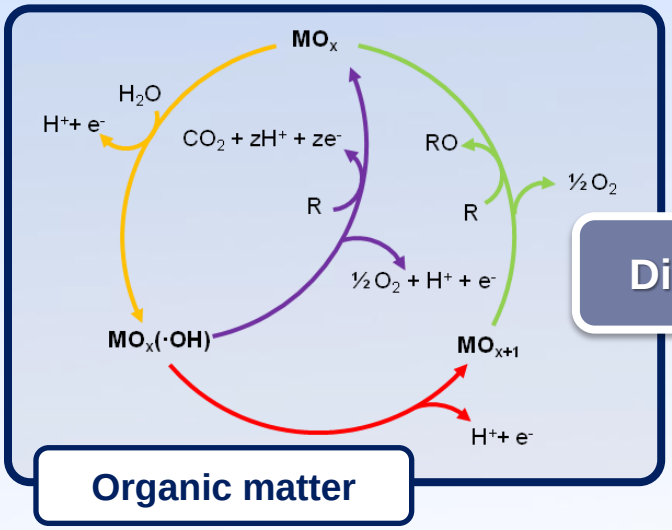
Resist deactivation

M. Panizza, G. Cerisola. **Chemical Reviews**, 109 no. 12, (2009) pp. 6541-6569.

I. Tröster, et al. ***Diamond and Related Materials***, 11 (2002) pp. 640-645

Background

Reaction mechanisms



Direct

Chloride

$$Cl^- \xrightarrow{2e^-} Cl_2 \xrightarrow{6e^-} HClO/ClO^- \xrightarrow{2e^-} ClO_3^- \xrightarrow[\cdot OH]{2e^-} ClO_4^-$$

(Cl_2 → ClO_2^- via ·OH; ClO_2^- → ClO_3^- via ·OH)

Bromide Bromate

$$Br^- \xrightarrow{2e^-} Br_2 \xrightarrow{6e^-} HBrO/BrO^- \xrightarrow{2e^-} BrO_3^-$$

(Br^- → Br^0 via ·OH; Br^0 → BrO^0 via ·OH; BrO^0 → BrO_2^- via ·OH; BrO_2^- → BrO_3^- via ·OH)

Indirect

Ammonia

$$2\,NH_4^+ + 3\,HClO \rightarrow N_2 + 3\,Cl^- + 5\,H^+ + 3\,H_2O$$

$$2\,NH_4^+ + 3\,HBrO \rightarrow N_2 + 3\,Br^- + 5\,H^+ + 3\,H_2O$$

Bromide Bromate

$$HClO + Br^- \rightarrow HBrO + Cl^-$$

$$2\,HClO + HBrO \rightarrow BrO_3^- + Cl^-$$

Byung Soo Oh, et al. **Science of the Total Environment**, 408 no. 23 (2010), pp. 5958-5965

, M. E. Henry Bergmann, T. Iourtchouk, J. Rollin. **Journal of Applied Electrochemistry**, 41 no. 9 (2011), pp. 1109 - 1123

Aim

To evaluate formation pattern of bromate during the electrochemical oxidation with boron doped diamond (BDD) electrodes

To study the influence of current density variation, 10 or 50 A/m^2, in Total Ammonia Nitrogen (TAN) removal and bromate formation

To develop analytical methods required for the quantitative determination of the species of interest: chloride, bromide and bromate

Experimental methodology

- Starting material
- State of the Art Revision
- Experimental Setup
- Analytical Techniques

Starting Material

Tinamenor S.L. fish farm located in Pesues, on the coast of Cantabria

Fish

Mollusks

Parameter	Value
pH	7
Conductivity (mS/cm)	46
Salinity (‰)	29
COD (mg O_2/l)	52
TAN (mg/l)	0.8
NO_2^- (mg/l)	77
NO_3^- (mg/l)	174
Cl^- (mg/l)	17170
SO_4^{-2} (mg/l)	2489
Br^- (mg/l)	60

V. Díaz, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, **Water Research**. 45 (2011) pp. 125-134

State of the Art Revision

Keywords

- Ammonia
- Aquaculture
- BDD
- Bromate
- Bromide
- By-product
- Determination
- Disinfection
- Electrochemical oxidation
- Electrode
- Electrolysis
- Electro-oxidation
- Oxidation
- Seawater

Database

THOMSON REUTERS
WEB OF KNOWLEDGE℠

SciVerse
Scopus
ScienceDirect

Aquaculture
21812 results

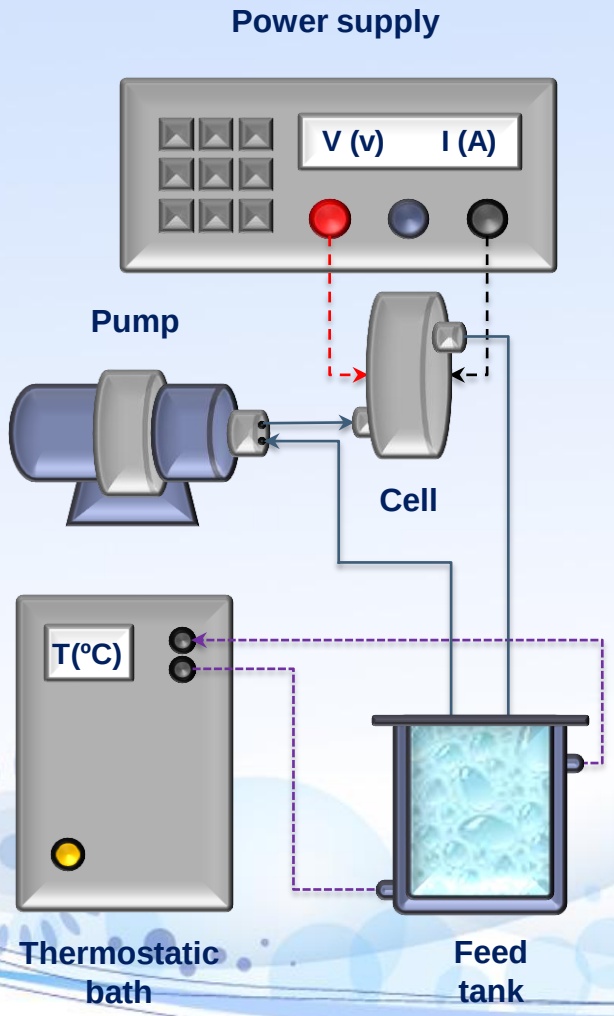
Seawater
2938 results

Oxidation
234 results

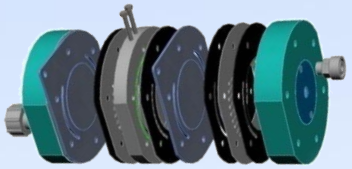
Treatment
- Chlorination (16)
- UV (37)
- Ozonization (11)
- Electro-oxidation Electrolysis (10)

Bromate
- UV
- Ozonization

Experimental Setup



Diacell 201 PP



- Boron doped diamond (BDD) on silicon anode and cathode
- 2 compartments
- Electrode surface = 70 cm^2 each
- Interelectrode gap = 1 cm

Operation conditions

- Flow rate = 6 l/min per cell compartment
- Seawater volume = 2 l
- Temperature = 25 ± 2 ºC
- Current density
  J = 10 A/m^2
  J = 50 A/m^2

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Analytical Techniques

Ionic Chromatography

Dionex 120 IC
IonPac AS-HC column
Eluent Na_2CO_3 9 mM
Flowrate 1 ml/min
Pressure 2000 psi

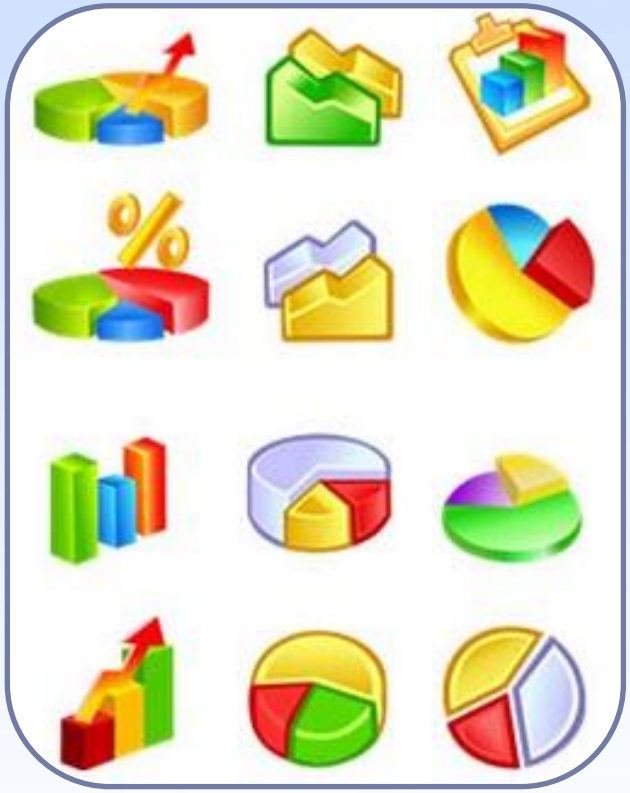
Cl^-
Br^-
BrO_3^-

OnGuard II Ba/Ag/H

Spectrophotometry

Spectroquant Pharo 100

Total Ammonia Nitrogen (TAN)



Results & Discussion

- State of the Art Revision
- Analytical Techniques
- Experimental Results

State of the Art Revision

Electrolysis
37.874 results

By-products
485 results

Bromate
15 results

Seawater
2 results

Journals

- Aquacultural Engineering
- Catalysis Today
- Chemical Reviews
- Desalination
- Diamond and Related Materials
- International Journal of Electrochemical Science
- Journal of Chromatography
- Journal of Hydrogen Energy
- Journal of Separation Science
- Science of the Total Environment
- Separation and Purification Technology
- The Scientific World Journal
- Water Research

Bromate Analytical techniques

- Iodometry
- Spectrophotometry
- Ion chromatography
- Gas chromatography - mass spectrometry
- Capillary electrophoresis

Furthier Investigation

- Formation bromate
- Aquaculture seawater electroxidation

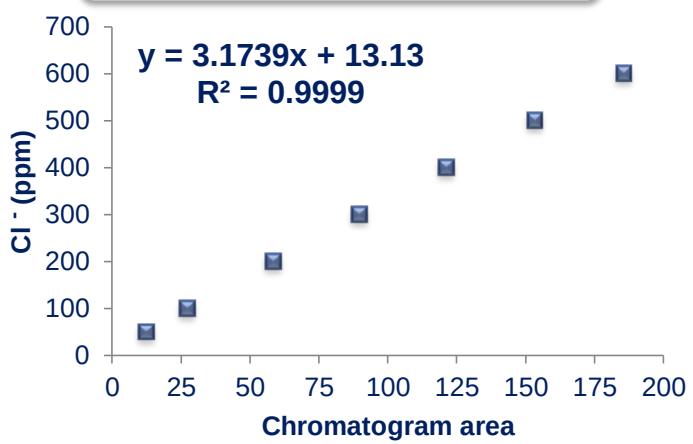
Byung Soo Oh, et al. **Science of the Total Environment**, 408 no. 23 (2010), pp. 5958-5965
J. Echardt, A. Kornmueller, **Water Science and Technology** 60 (2009) pp. 2227-2234

Analytical Techniques

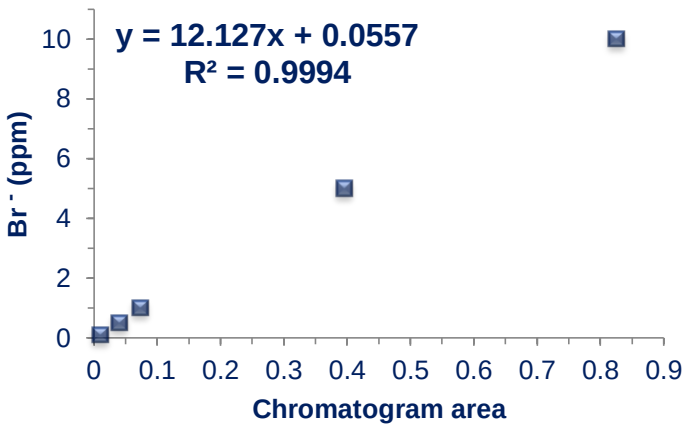
Ionic Chromatography Calibration

	Lower	Upper
Cl^- ppm	50	600
Br^- ppm	0.1	10
BrO_3^- ppm	0.05	0.5

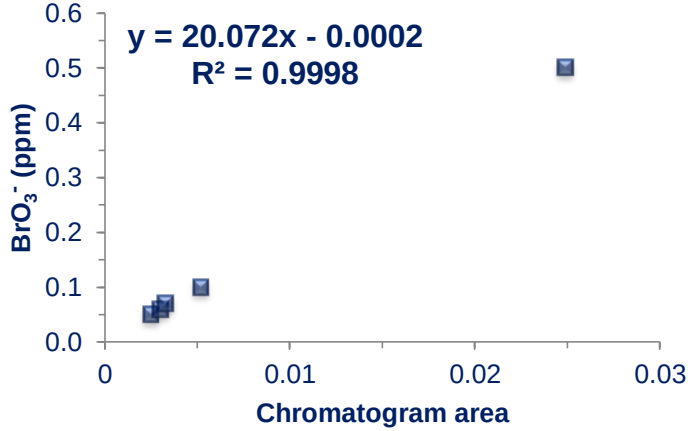
Chloride



Bromide

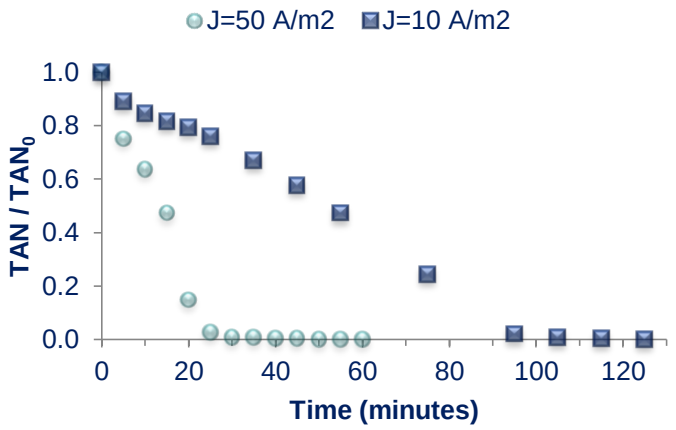


Bromate

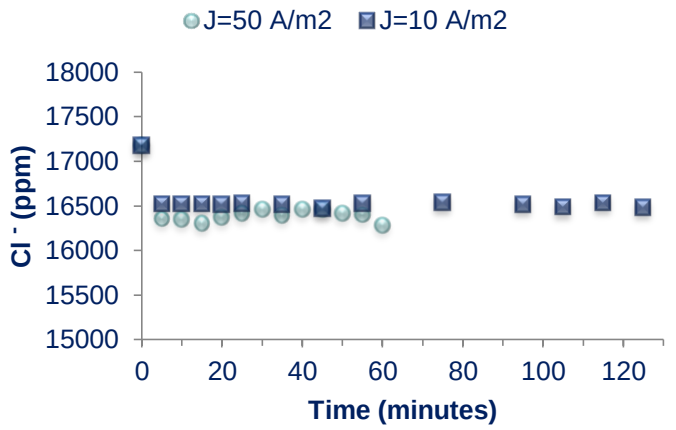


Results & Discussion

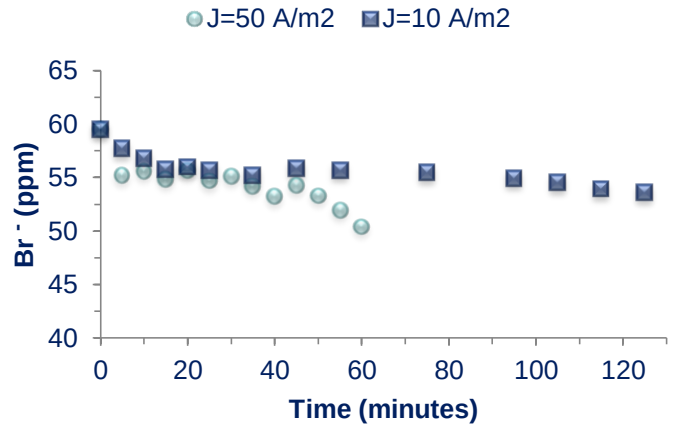
Total Ammonia Nitrogen (TAN)



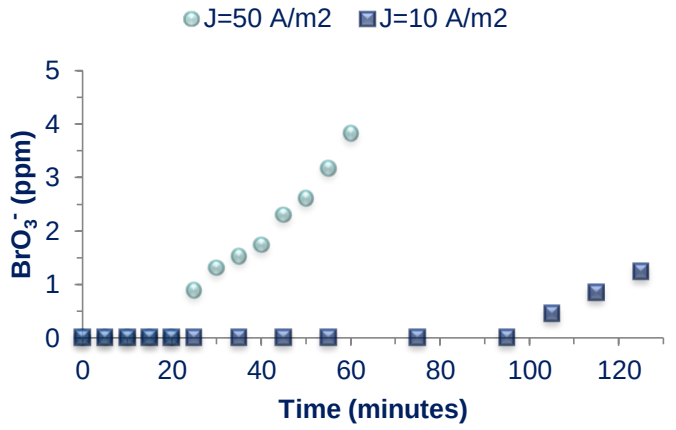
Chloride



Bromide



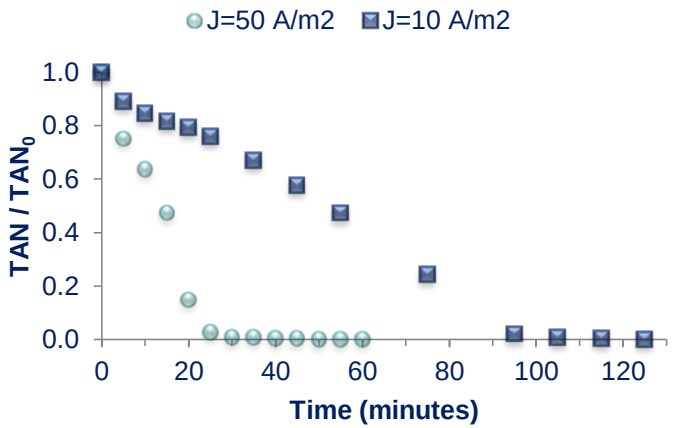
Bromate



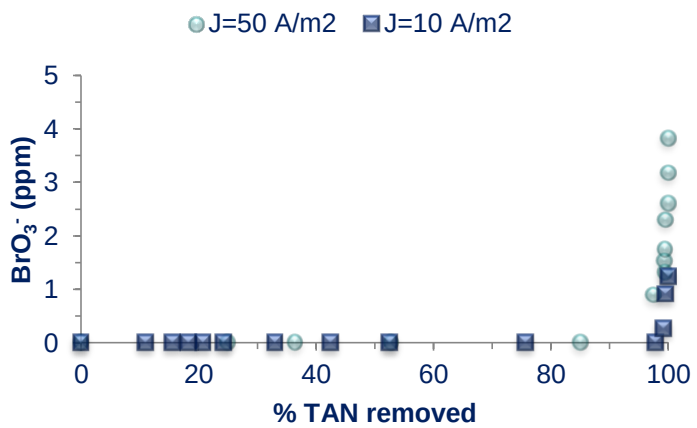
Chemical Engineering Master's Degree "Sustainable Production and Consumption"

Results & Discussion

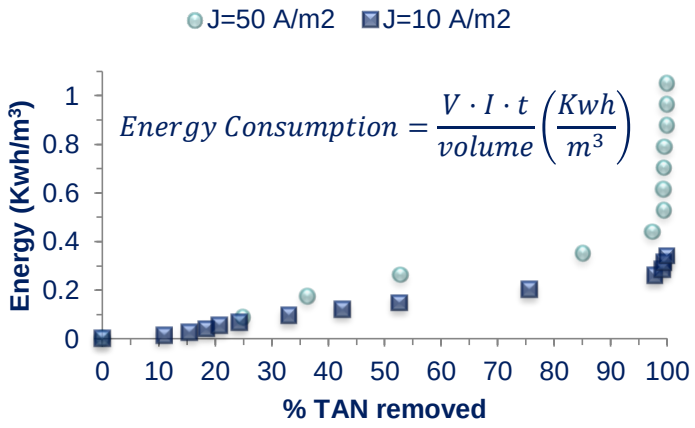
Total Ammonia Nitrogen (TAN)



Bromate vs. %TAN removed

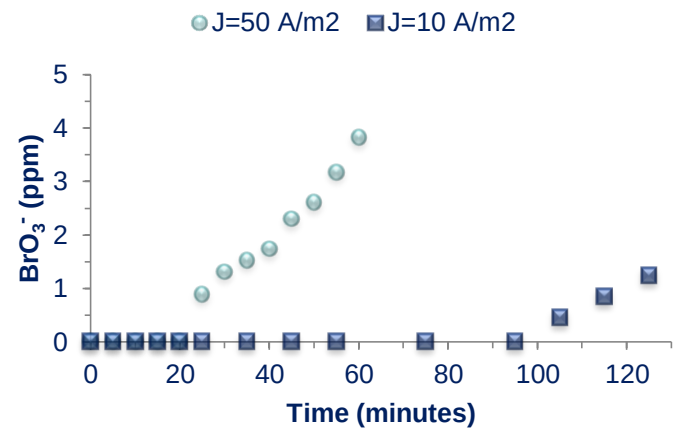


Energy Con. vs. % TAN removed



$$Energy\ Consumption = \frac{V \cdot I \cdot t}{volume}\left(\frac{Kwh}{m^3}\right)$$

Bromate



Conclusions

Conclusions

Electrochemical oxidation technology using boron doped diamond (BDD) electrodes has been successfully tested in total ammonia nitrogen (TAN) removal aquaculture seawater

The current density has a large effect on %TAN removal and the time needed to reach it

Bromate formation is also influenced by the current density and its formation begins when TAN has been practically eliminated

Thank you for your attention

MASTER EN INGENIERÍA QUÍMICA CURSO 2011-2012
"PRODUCCIÓN Y CONSUMO SOSTENIBLE"

ELECTRO-OXIDATION TECHNOLOGY APPLIED TO WATER TREATMENT AND REUSE IN AQUACULTURE. STUDY OF BYPRODUCTS FORMATION

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Scope

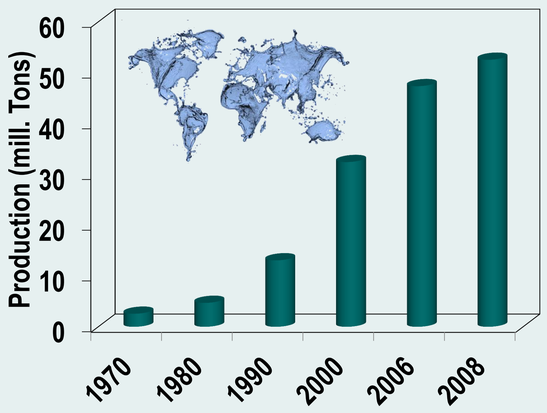


Fig. 1 Evolution in aquaculture production

Aquaculture world production reached 52,5 million tons in 2008 (Fig.1) including fish, crustaceans, mollusks and other aquatic animals for human consumption [1].

The raise of this activity has produced an increase in their impact on the environment due to the large amounts of water needed and the wastewater produced rich in nitrogen compounds, phosphorus and organic matter [2].

Electrochemical oxidation technology using boron-doped diamond (BDD) electrodes (Fig.2) can be applied to remove pollutants generated in this activity, total nitrogen ammonia (TAN) and organic matter, however the generation of toxic by-products, specifically bromate, for cultured fish has to be taken into account [3].

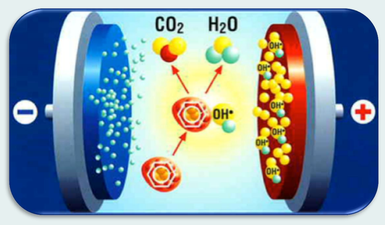


Fig. 2 BDD electrode

Experimental

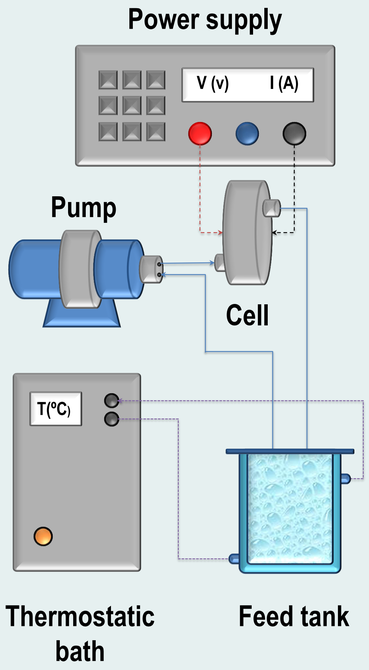


Fig. 3 Experimental setup

Diacell 201 PP

- 2 compartments (fig.4)
- Boron doped diamond (BDD) on silicon anode and cathode
- Each electrode surface = 70 cm^2
- Interelectrode gap = 1 cm

Operation conditions

- Flow rate = 6 l/min per compartment
- Seawater volume = 2 l
- Temperature = 25 ± 2 ºC
- Current density
  J = 10 A/m^2
  J = 50 A/m^2

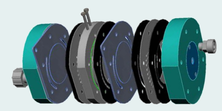


Fig. 4 Cell Detail

Aim

To evaluate formation pattern of bromate during the electrochemical oxidation with boron doped diamond (BDD) electrodes

To study the influence of current density variation, 10 or 50 A/m^2, in Total Ammonia Nitrogen (TAN) removal and bromate formation

To develop analytical methods required for the quantitative determination of the species of interest: chloride, bromide and bromate

Analytical methods

Ionic Chromatography

Table 1 Concentration limits

	Lower	Upper
Cl^- ppm	50	600
Br^- ppm	0.1	10
BrO_3^- ppm	0.05	0.5

Table 2 Calibration Equations

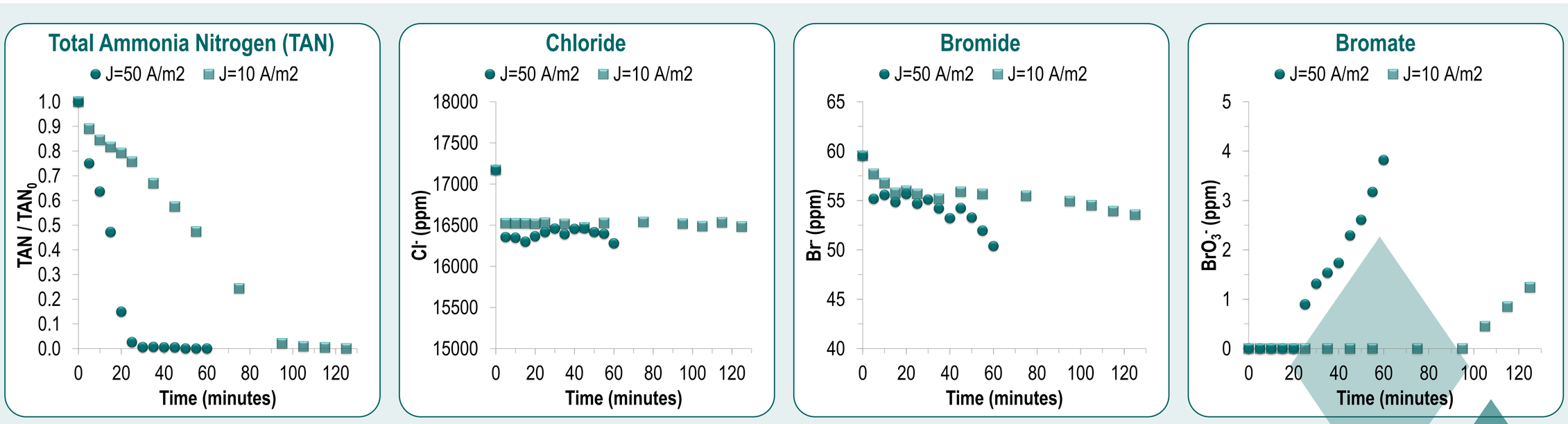
	R^2
$[Cl^-] = 3.17 \cdot CA + 13.13$	0.999
$[Br^-] = 12.13 \cdot CA + 0.06$	0.999
$[BrO_3^-] = 20.07 \cdot CA - 2 \cdot 10^{-4}$	0.999

CA = Chromatogram Area

Spectrophotometry

Total Ammonia Nitrogen (TAN)

Results



Conclusions

Total Ammonia Nitrogen (TAN) removal

- Electrochemical oxidation technology, using boron-doped diamond (BDD) electrodes, has been proved an efficient technology to seawater TAN removal

Current density effect

- The higher current density is:
  the lower time needed to TAN removal
  the higher bromated concentration is reached

Bromate formation

- begins when TAN concentration reaches values near to zero
- rate is lower at lower current densities

References

[1] FAO Fisheries and Aquaculture Department, **World aquaculture 2010**. Technical Paper 500/1 (2011)
[2] M. Martinez-Porchas, L.R. Martinez-Cordova, **World aquaculture: Environmental impacts and troubleshooting alternatives**, The Scientific World Journal 2012 (2012).
[3] V. Díaz, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, **Kinetics of electro-oxidation of ammonia-N, nitrites and COD from a recirculating aquaculture saline water system using BDD anodes**, Water Res. 45 (2011) 125-134.

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