INTERNATIONAL CONFERENCE

IWWATV 2015

Industrial Waste & Wastewater Treatment & Valorisation

University of Catania
Department of Industrial Engineering

Small improvements in the treatment of oily wastes from marine transportation

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The role of marine transport

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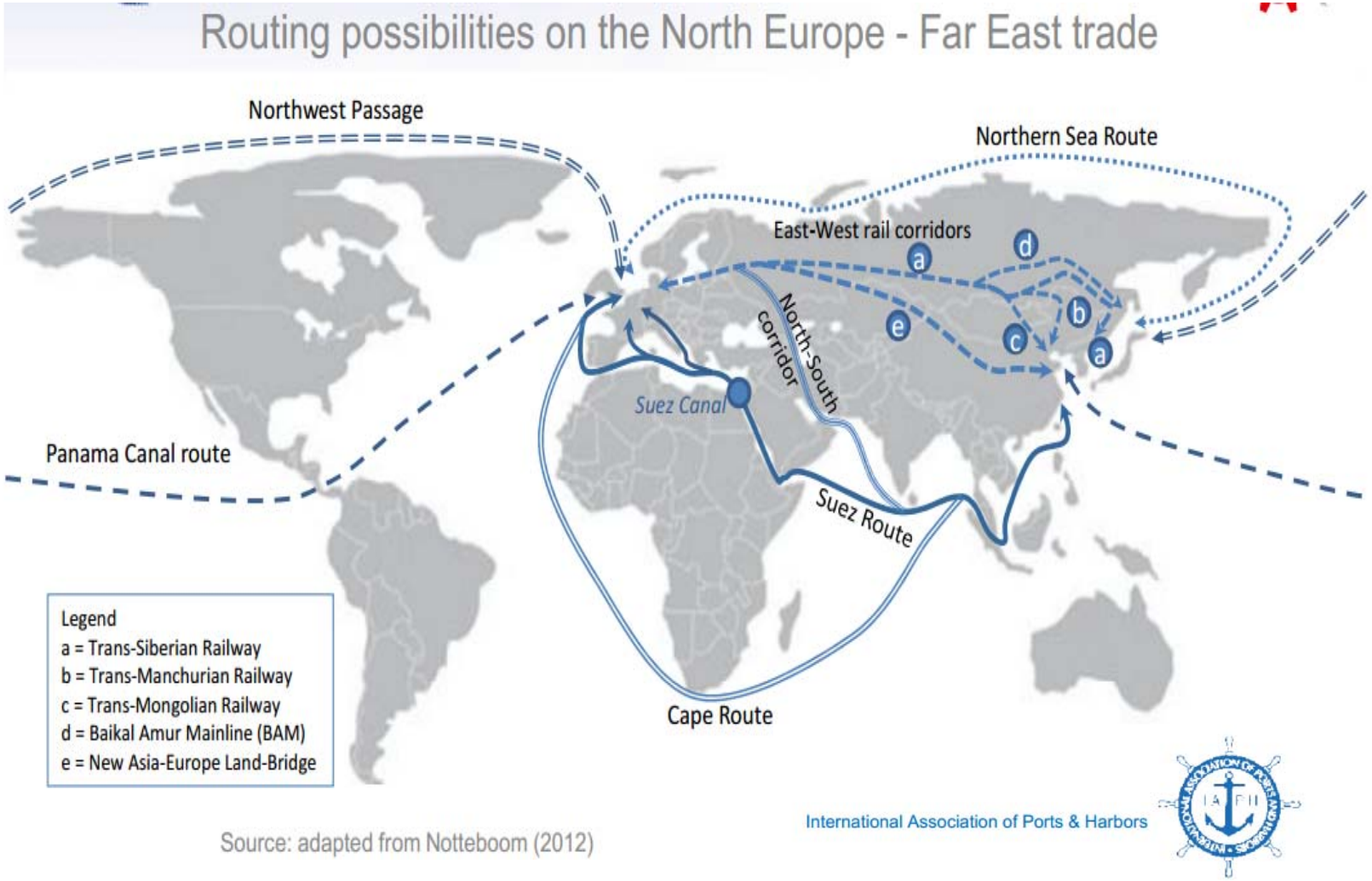
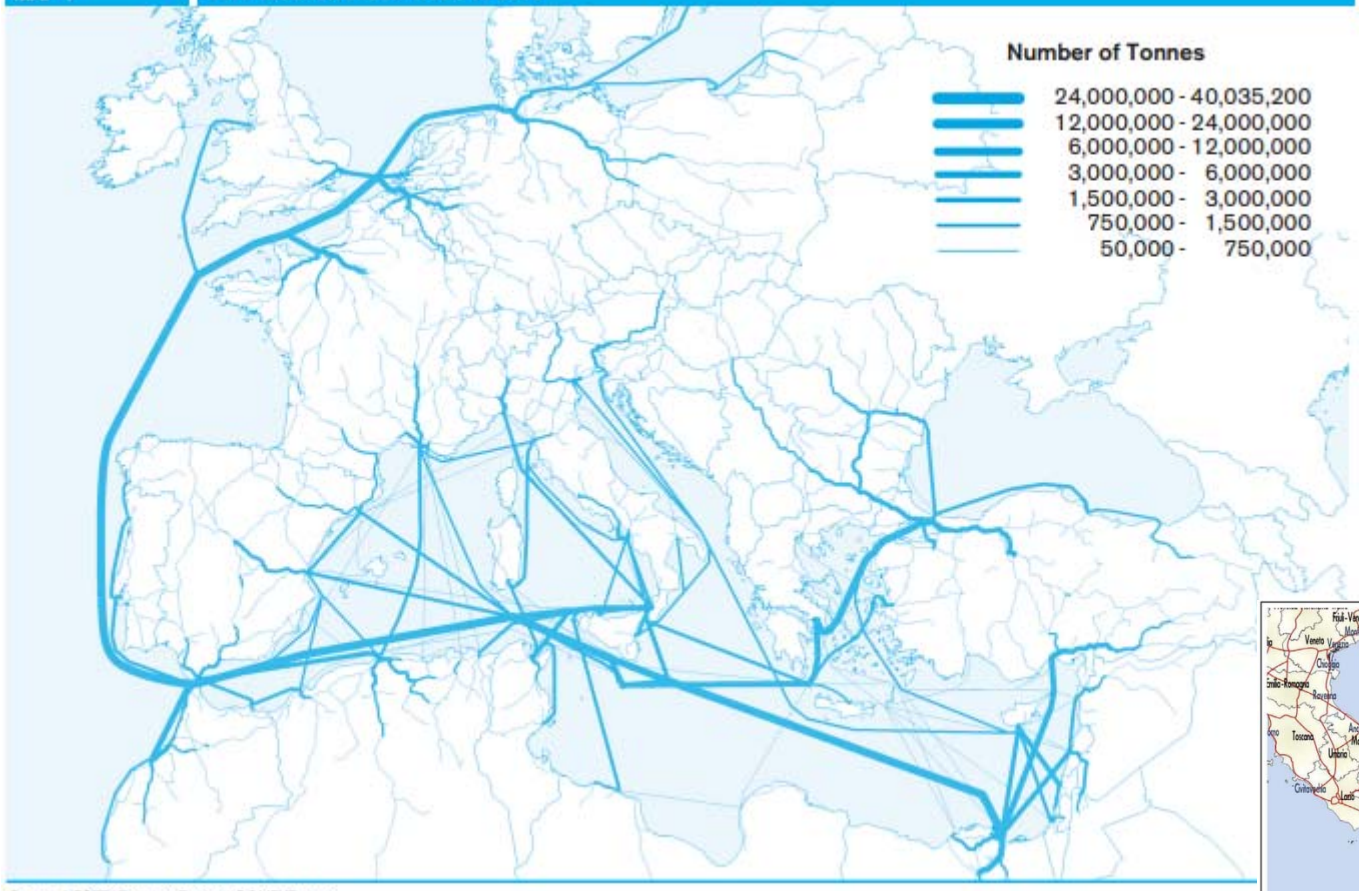


European Transport Policy

MAP 1 Intra-Mediterranean Trade in 2006



Source: NESTEAR, 2008; Eurostat COMEXT, 2006.

shipping and related maritime industries are important contributors to the European GDP

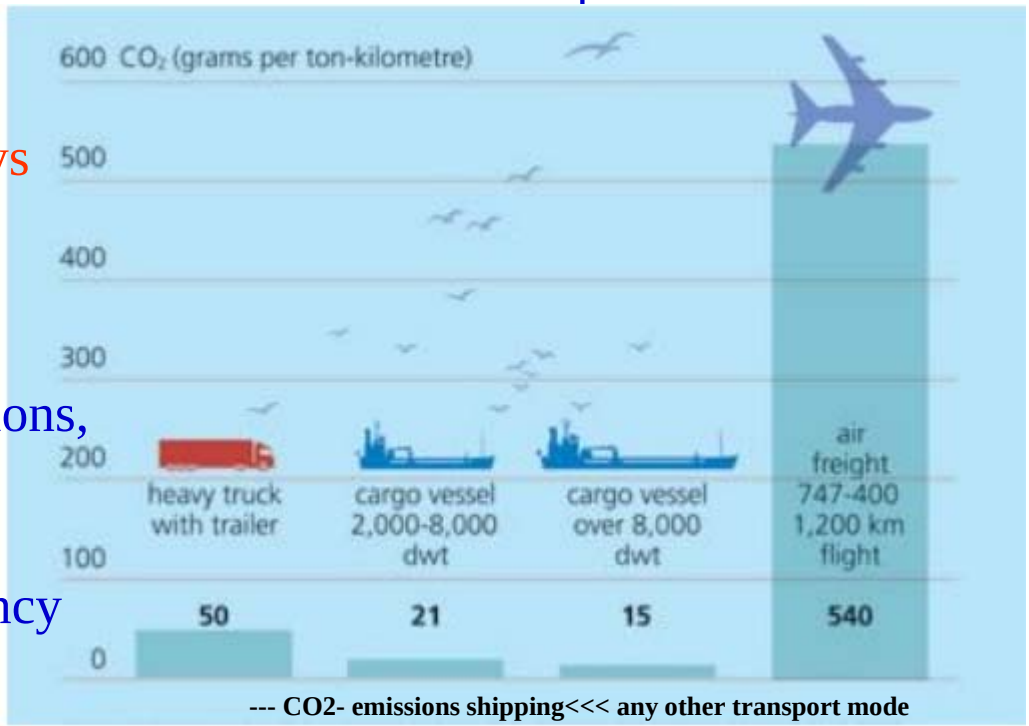
European Transport Policy

✓“underlined the importance of developing maritime transport and favor interconnection.

✓“a need for new ideas in transport logistics planning, involving not only ports and shipping operators, but the entire chain that brings goods from the factory to the final consumer. Ship services need to operate regularly to develop this concept, in order to create an alternative to road transport”.

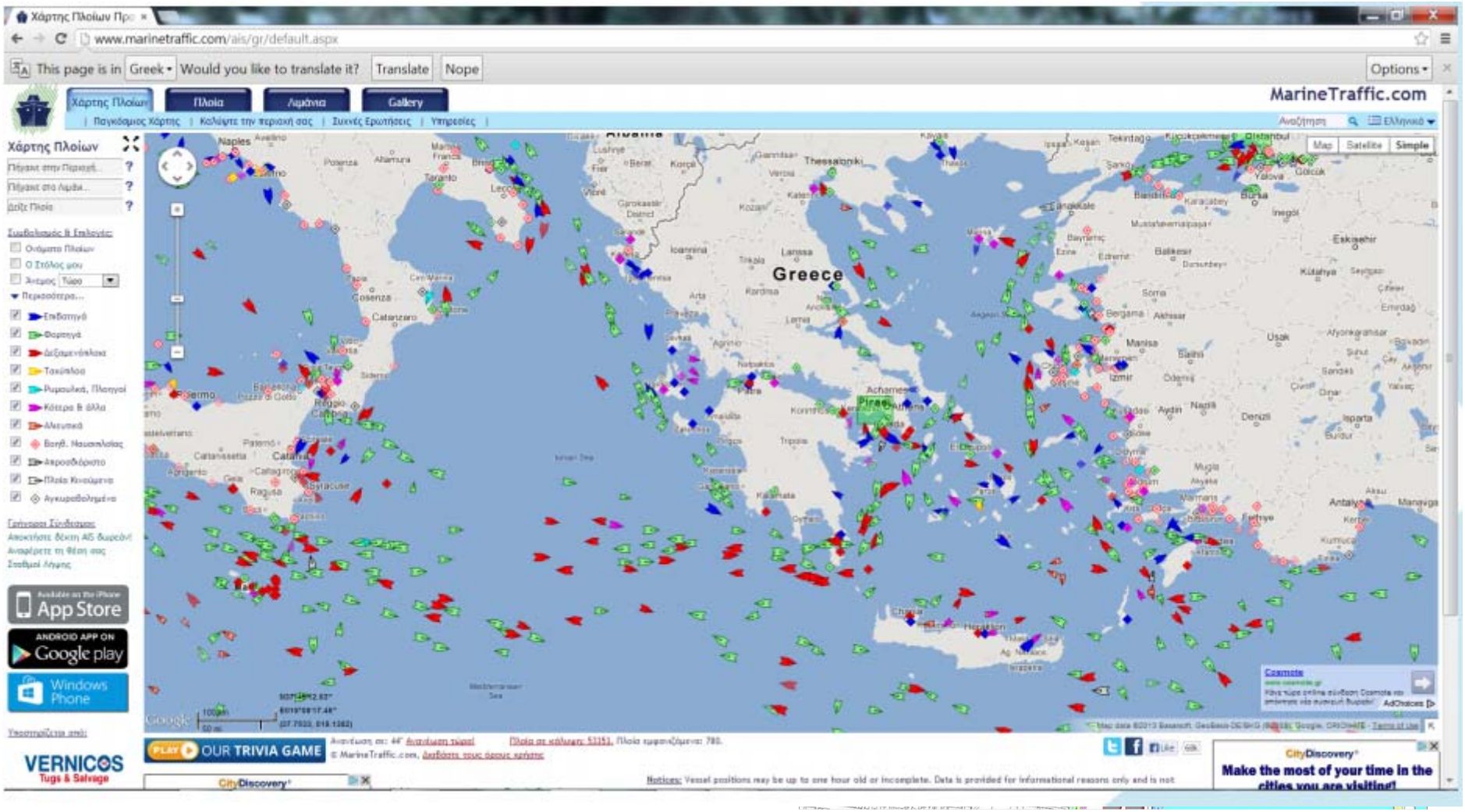
✓“the necessity to assure the sea connection”; The concept of Motorways of the Sea”.

✓“the need for favorable technical conditions, such as **quality of port services**, quality of hinterland connections, information systems and monitoring in transport logistics, and special characteristics of ship services (frequency and regularity, safety and security);



--- CO2- emissions shipping<<< any other transport mode

Marine Transport in the Mediterranean Sea



Oil Spill Risk Increase

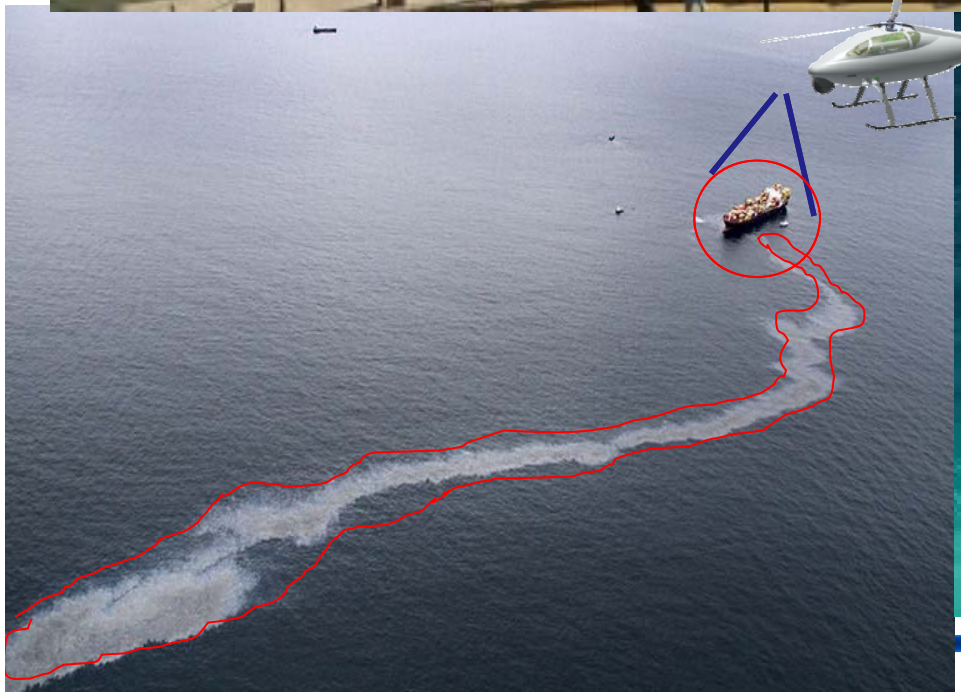
Background

Oily wastewater and oil-water emulsion are two of the main pollutants discharged to water environment, through ordinary operations These waste(water)s are generated by ships mainly in engine-rooms (bilge waters) and by washing oil tanks (slops) in amounts of millions of tons annually.

Background

These issues are particularly critical in Mediterranean Sea that has been defined as a “Special Area” by the international Law MARPOL 73/78 (IMO, 1973/1978) that strictly forbids any mineral oil or oily mixtures to be directly discharged to the sea by oil tankers. Directive 2000/59/EC and 2005/35/EC put much further pressure on the **collection by harbour authority**.

Undesiderable behaviours



Background

Slops are wash-waters originated from the cleaning of oil tankers.
Beside the presence of refractory compounds, these waters show extremely ***high salinity levels*** (***up to 25.000 p.p.m***.), that limit the possibility of discharge to sewers and address the disposal to the sea.

This severely lowers the concentrations limits for most of the "sensible" parameters, such both **COD** and **xenobiotic hydrocarbons**, thus requiring a higher level treatment.

Introduction

Many of these fluids are very stable emulsion, which make conventional treatment difficult.

The most diffused method for treatment of emulsified oily wastewater is ***de-emulsification*** followed by ***clarification***, which requires the use of a variety of chemicals such as sulphuric acid, iron and alumina sulphates, ect. Shut'ko (1986)

The water phase from chemical treatment has to be further treated. This is often achieved by ***granular activated carbon*** (**GAC**) ***filtration (Ha et al., 2000)***.

Introduction

However GAC regeneration costs so interest has risen on bioregeneration of exhaust GAC.. Little work has been done on the biodegradation and adsorption of **salty** mixtures of biodegradable and non-biodegradable SOCs

The normal bacteria which are growing in CAS or MBR cannot withstand at these adverse conditions, therefore it is necessary to be adapted (Lefebvre and Moletta, 2006).

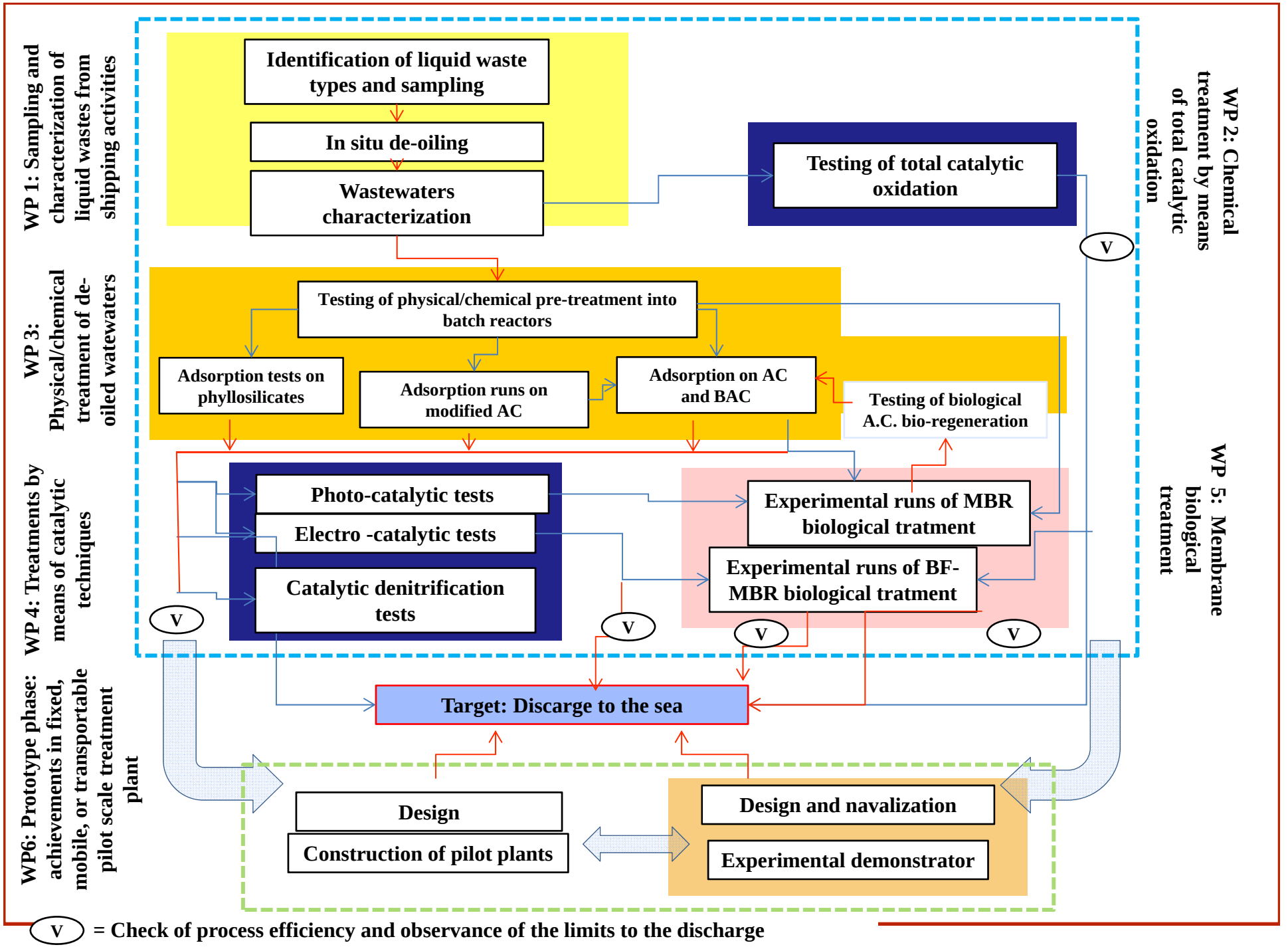
A few studies (Reid et al., 2006; Artiga et al., 2008; Llop et al., 2009; Soltani et al., 2010) have dealt with this issue (adapting the microorganism) but still a lack of information is observed for applying biological treatment for high salinity oily waters.

Research Project

1) Project PON02_00153_2939551 (Project title: **Development of innovative technologies for energy saving and environmental sustainability of shipyards and harbour areas – SEAPORT**, PON&REC 2007/2013)

2) The Italian Ministry of Education, University and Research (MIUR), through the program "Research Program of Relevant National Interest", PRIN 2010ARBLT7 (Project title: **Systems biology in the study of xenobiotic effects on marine organisms for evaluation of the environmental health status: biotechnological applications for potential recovery strategies**)

3) Project PON02_00153_2849085 (Project title: **STI-TAM Development of Innovative technologies for the treatment of fluid wastes from shipping activities and for marine environment protection, PON&REC 2007/2013)**

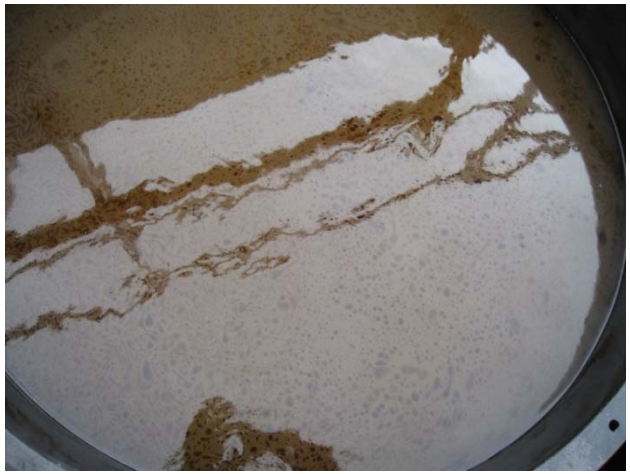

WP 1: Sampling and characterization of liquid wastes from shipping activities
Identification of liquid waste types and sampling
In situ de-oiling
Wastewaters characterization
WP 2: Chemical treatment by means of total catalytic oxidation
Testing of total catalytic oxidation
V
WP 3: Physical/chemical treatment of de-oiled watewaters
Testing of physical/chemical pre-treatment into batch reactors
Adsorption tests on phyllosilicates
Adsorption runs on modified AC
Adsorption on AC and BAC
Testing of biological A.C. bio-regeneration
WP 4: Treatments by means of catalytic techniques
Photo-catalytic tests
Electro -catalytic tests
Catalytic denitrification tests
WP 5: Membrane biological treatment
Experimental runs of MBR biological tratment
Experimental runs of BF-MBR biological tratment
V
V
V
V
Target: Discarge to the sea
WP6: Prototype phase: achievements in fixed, mobile, or transportable pilot scale treatment plant
Design
Construction of pilot plants
Design and navalization
Experimental demonstrator
V = Check of process efficiency and observance of the limits to the discharge

Pilot Plant (Cantieri navali di Augusta)

Wastewater sampling and on site pre-treatment

Wastewater sampling and in situ pre-treatment

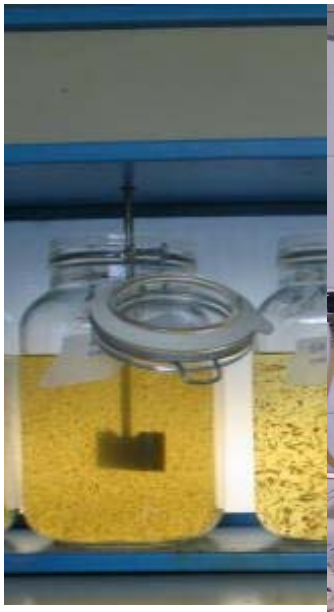
Wastewater sampling and in situ pre-treatment



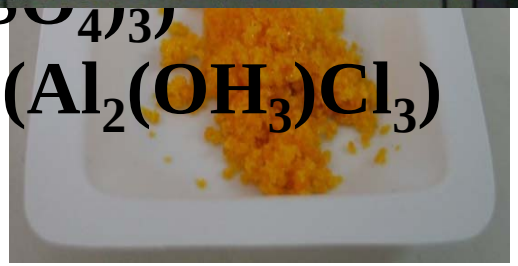
Wastewater sampling (Dockyard)

Experimental Activities

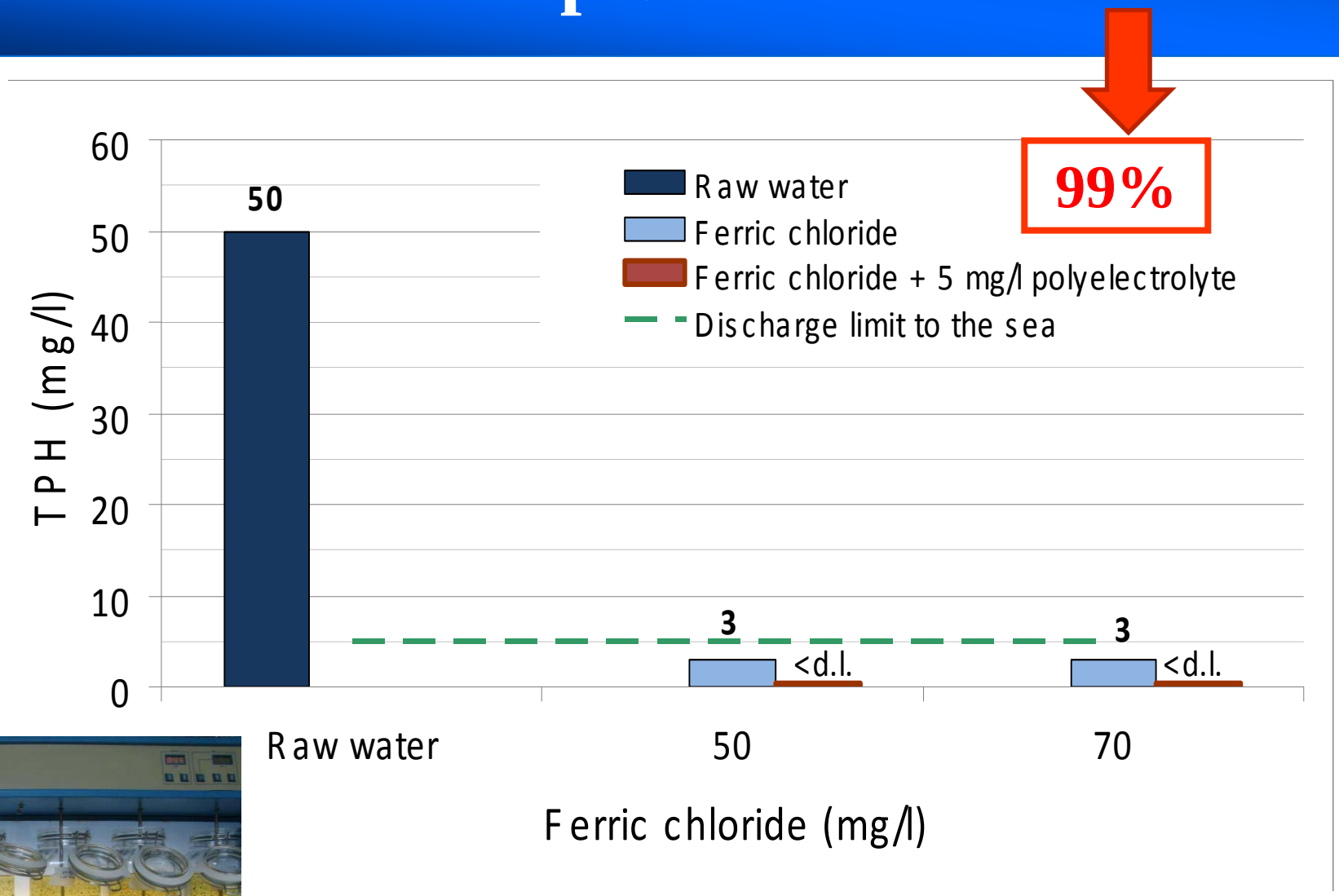
Diesel Slops Pre-Treatment- De-Oiling- Coagulation



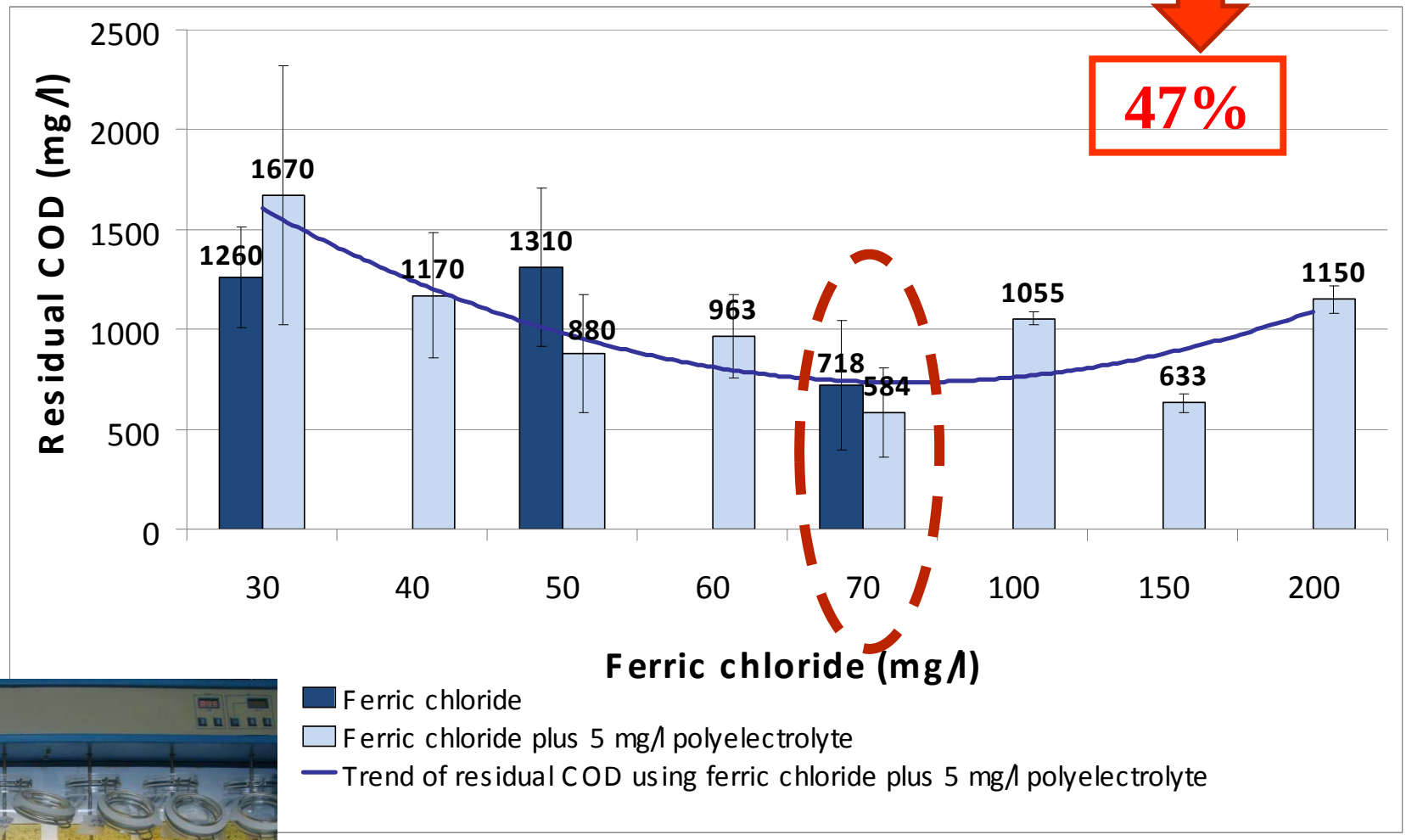
Ferric chloride ($FeCl_3$)
Aluminum sulfate ($Al_2(SO_4)_3$)
Polyaluminum chloride ($Al_2(OH_3)Cl_3$)
Organic flocculant



Jar test on slops: TPH removal



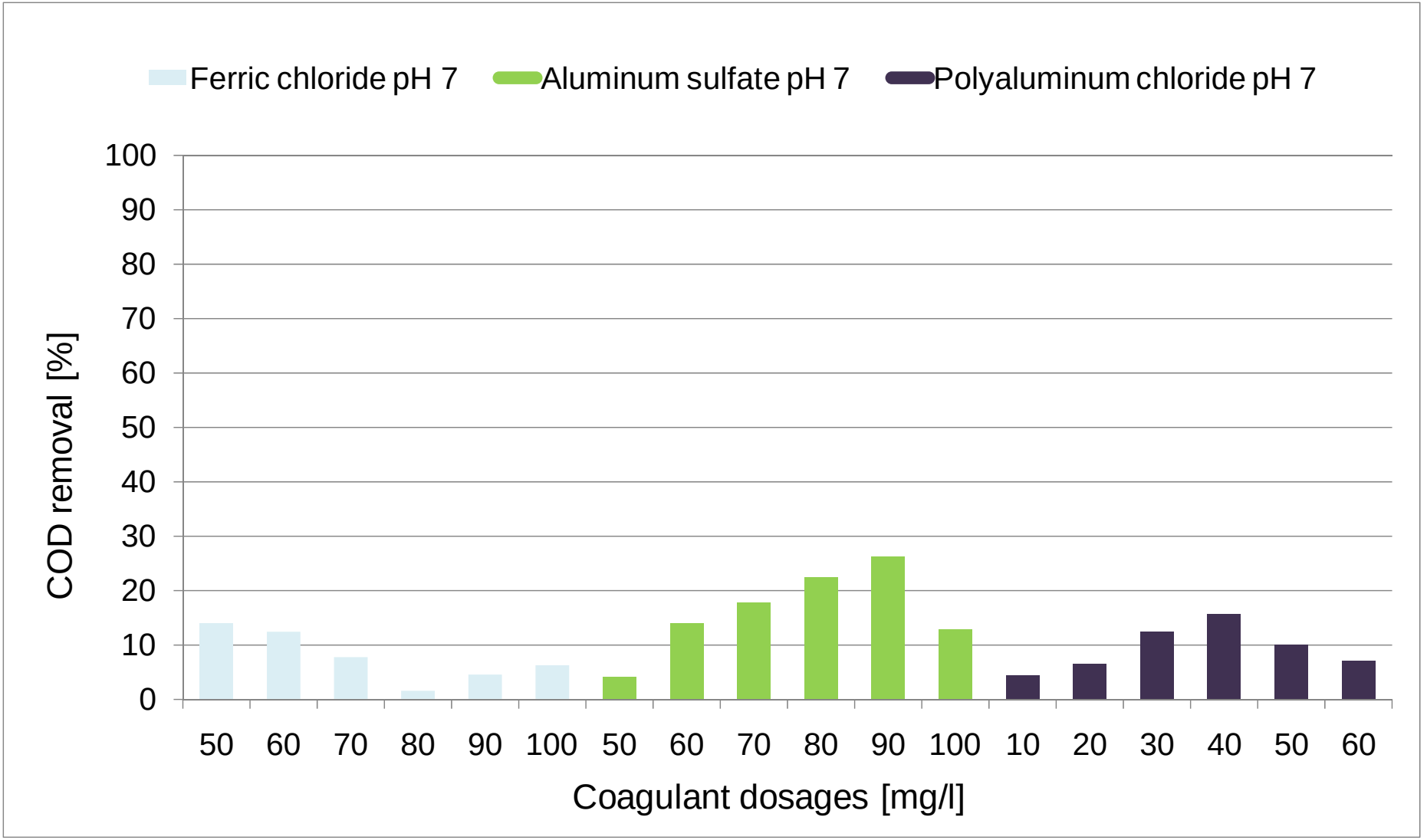
Jar test on slops: COD removal



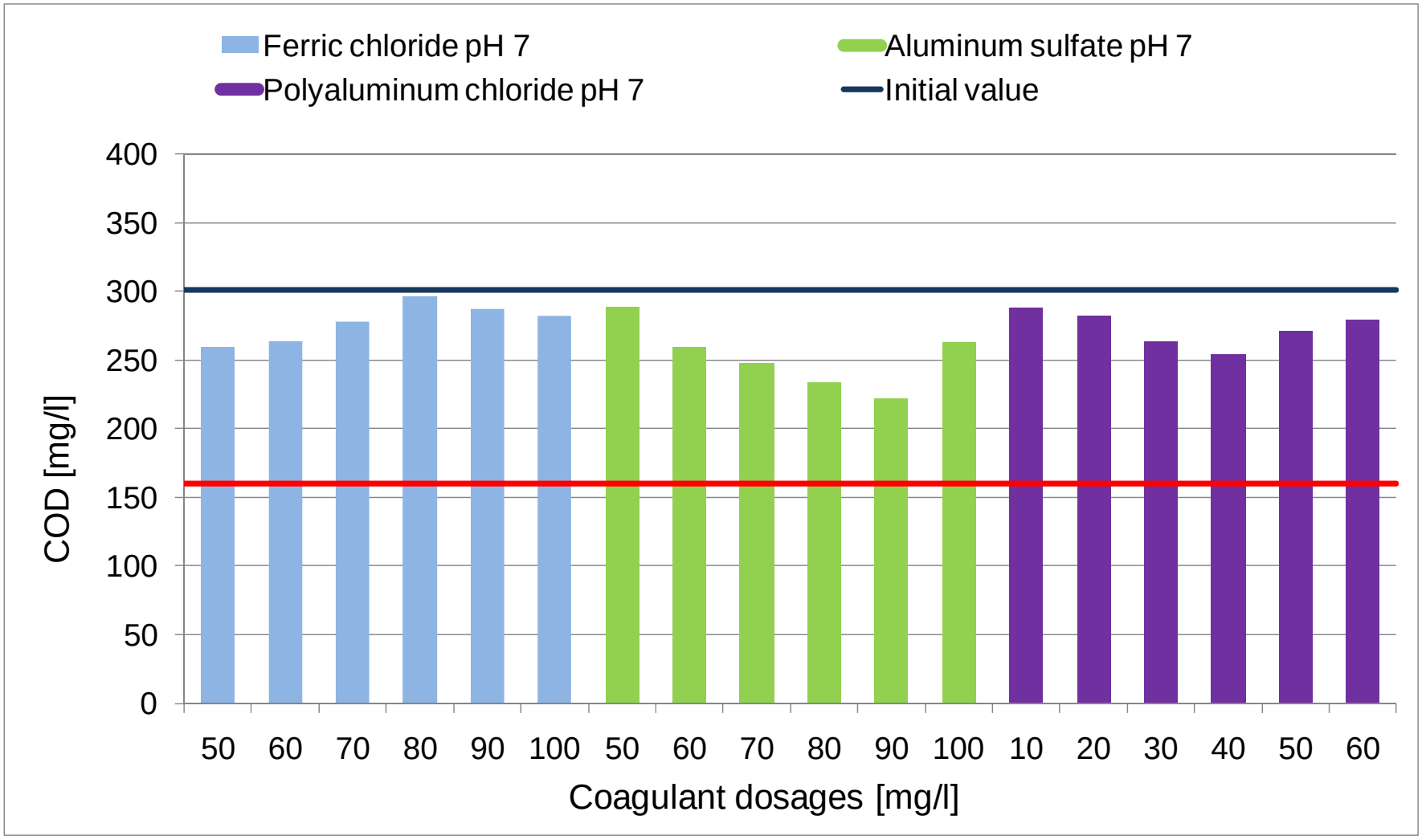
RESULTS
Slops and Dockyard characterization

Parameters	Units	ex diesel slops	dockyard waters
pH		7.0	7.4
Light hydrocarbons from C6 to C10	(mg/l)	< 0.01	0.80
Heavy hydrocarbons from C > 10 to C20	(mg/l)	6.66	143.99
Heavy hydrocarbons from C > 20 to C30	(mg/l)	2.72	72.00
Heavy hydrocarbons from C > 30 to C40	(mg/l)	0.49	74.57
Heavy hydrocarbons from C > 40 to C50	(mg/l)	< 0.006	3.52
Sum of heavy hydrocarbons from C > 10 to C50	(mg/l)	9.88	294.09
TPH from C6 to C50	(mg/l)	9.88	294.89
TOC	(mg/l)	114.8	478.5
COD	(mg/l)	301.0	930.0
Chlorides Cl^-	(mg/l)	20320.0	809.0

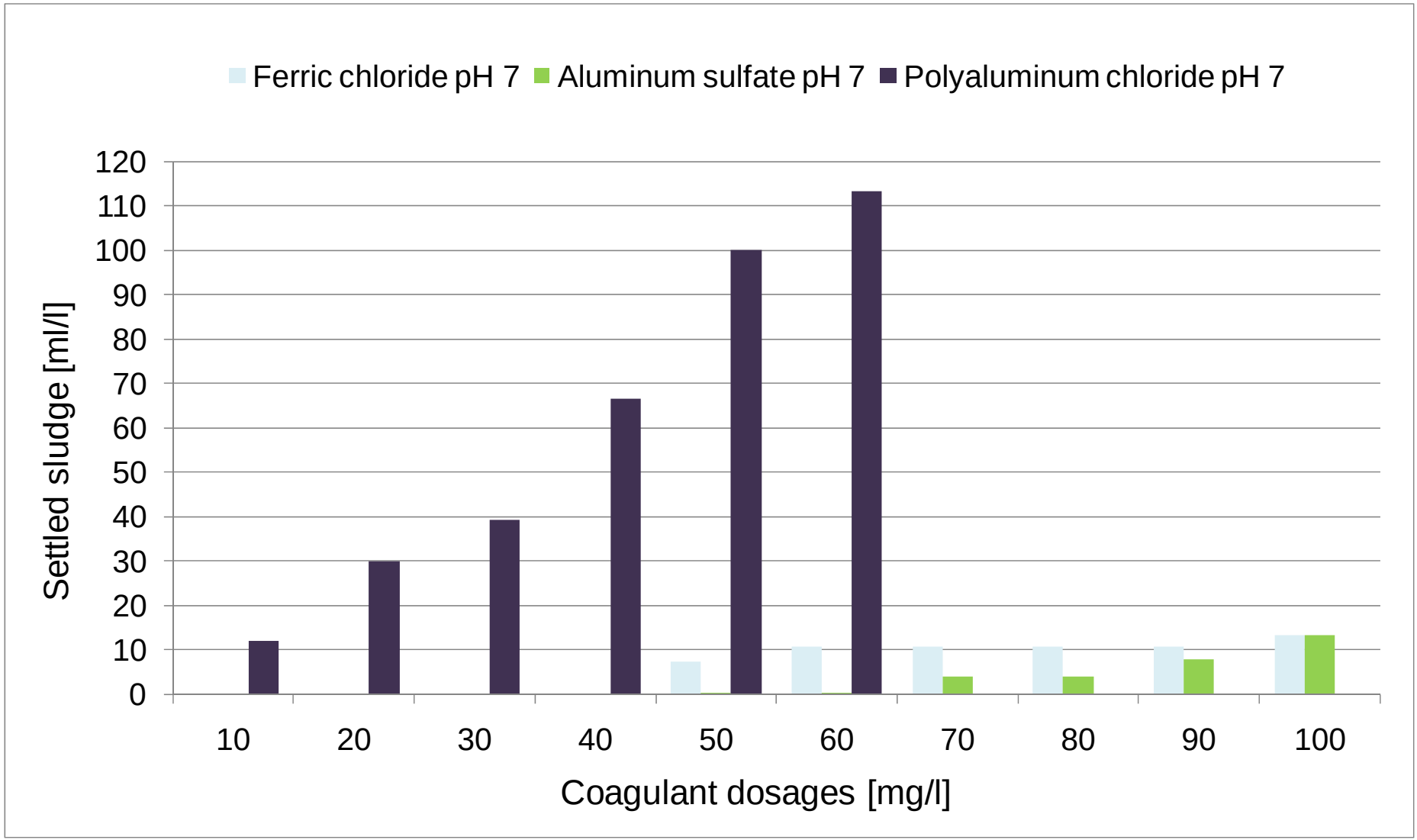
Jar test on slops: COD removal



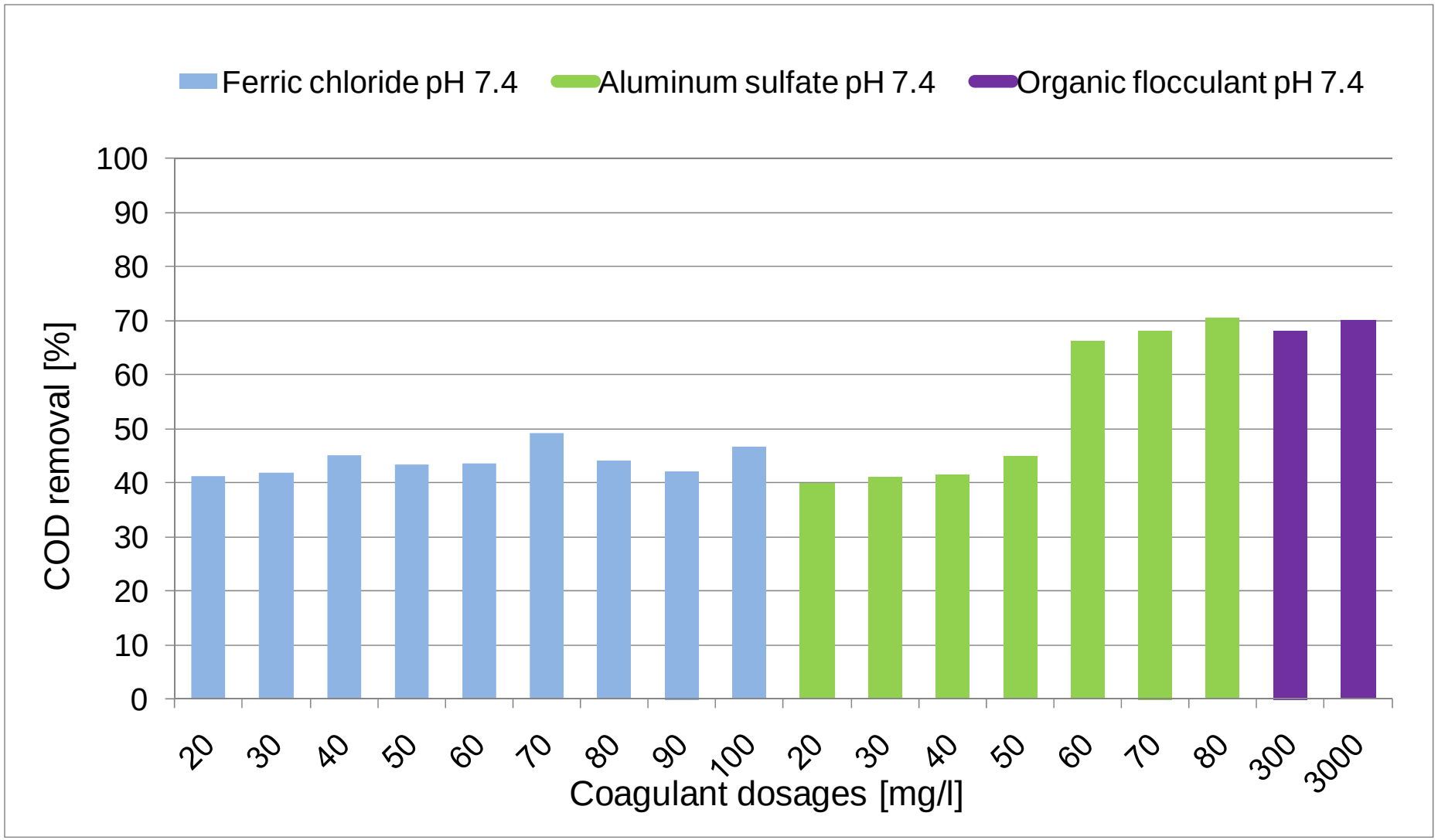
Jar test on slops: COD removal



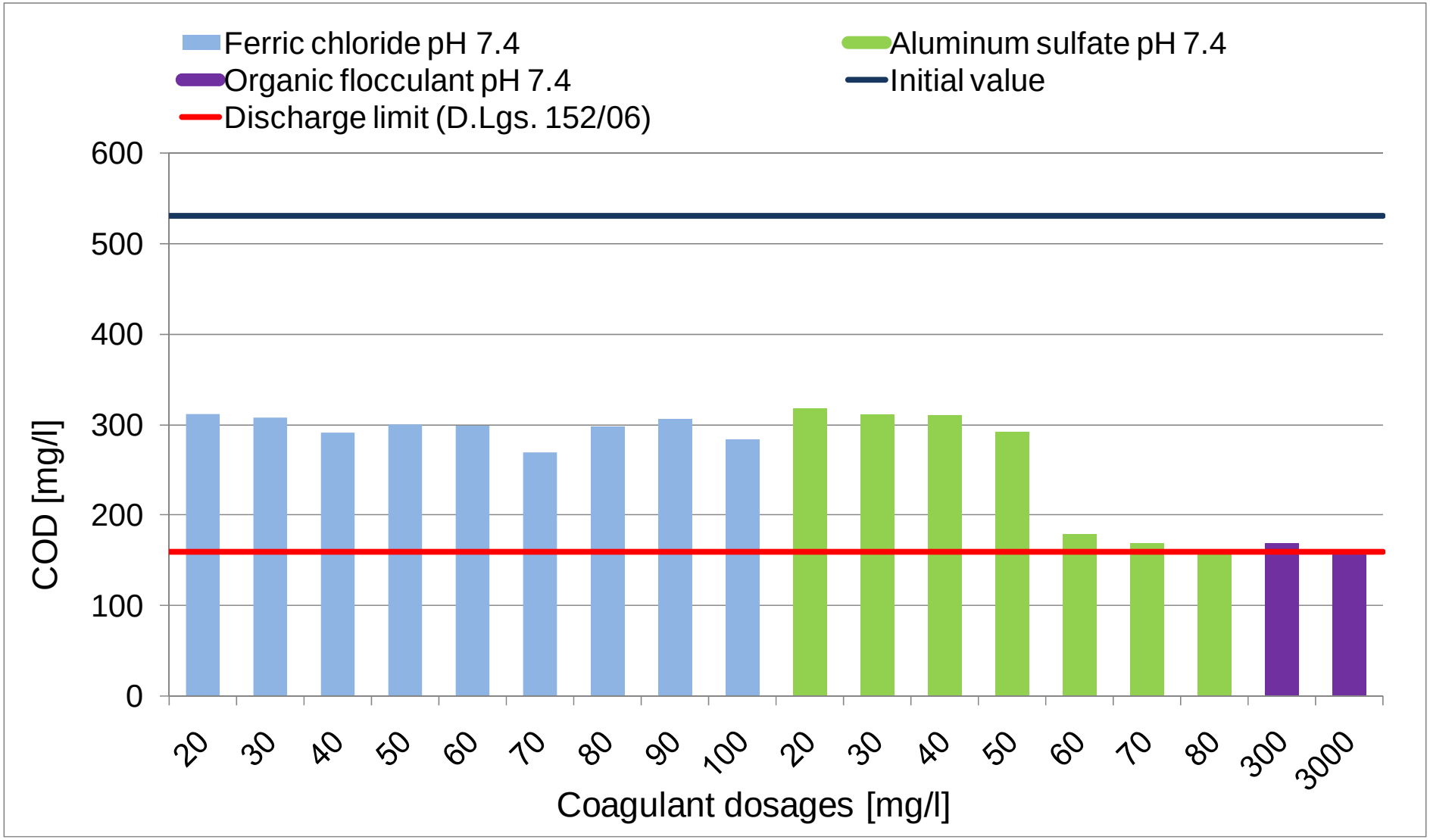
Jar test on slops: sludge production



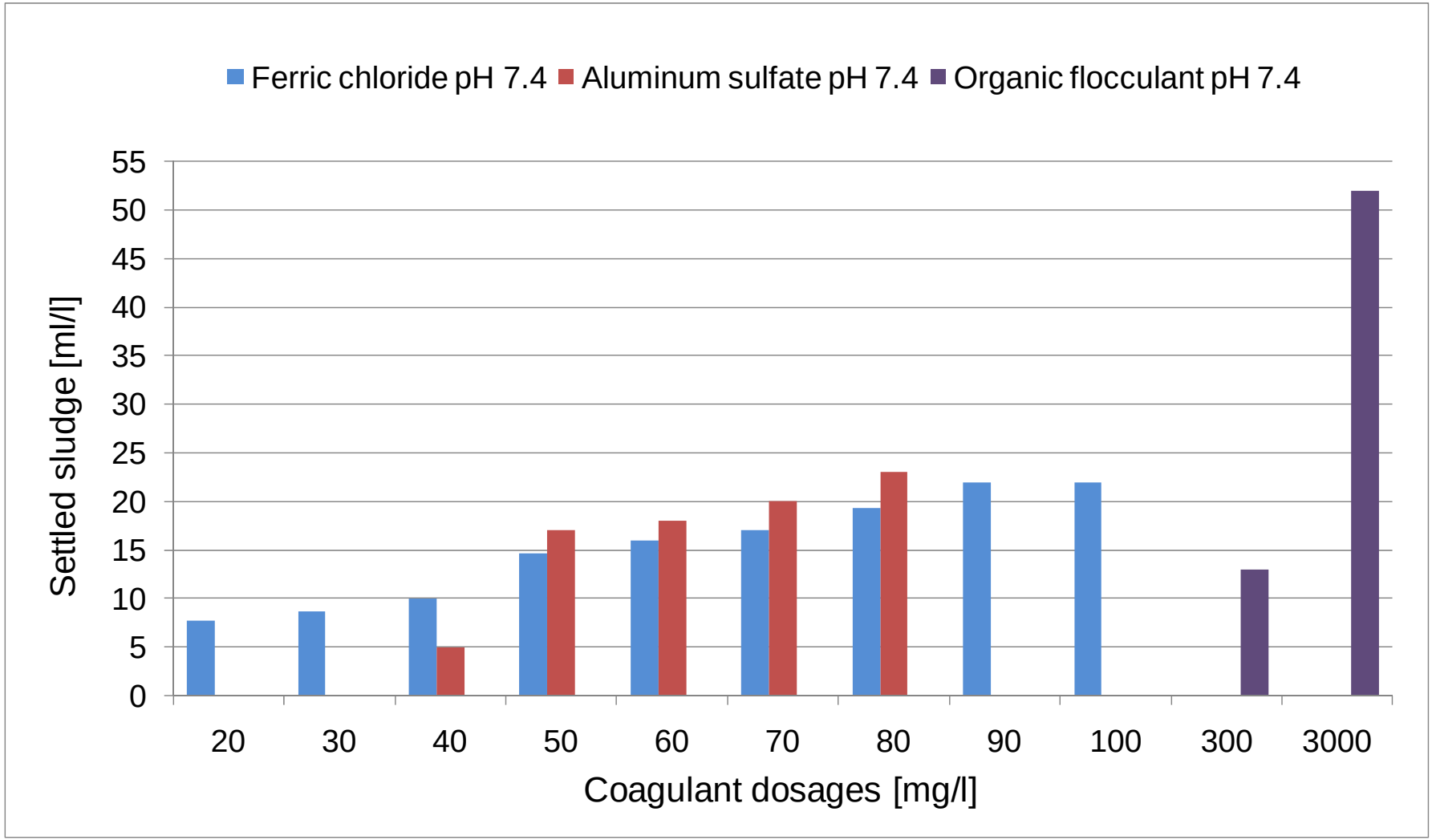
Jar test on dockyard waters: COD remov.



Jar test on dockyard waters: COD remov.



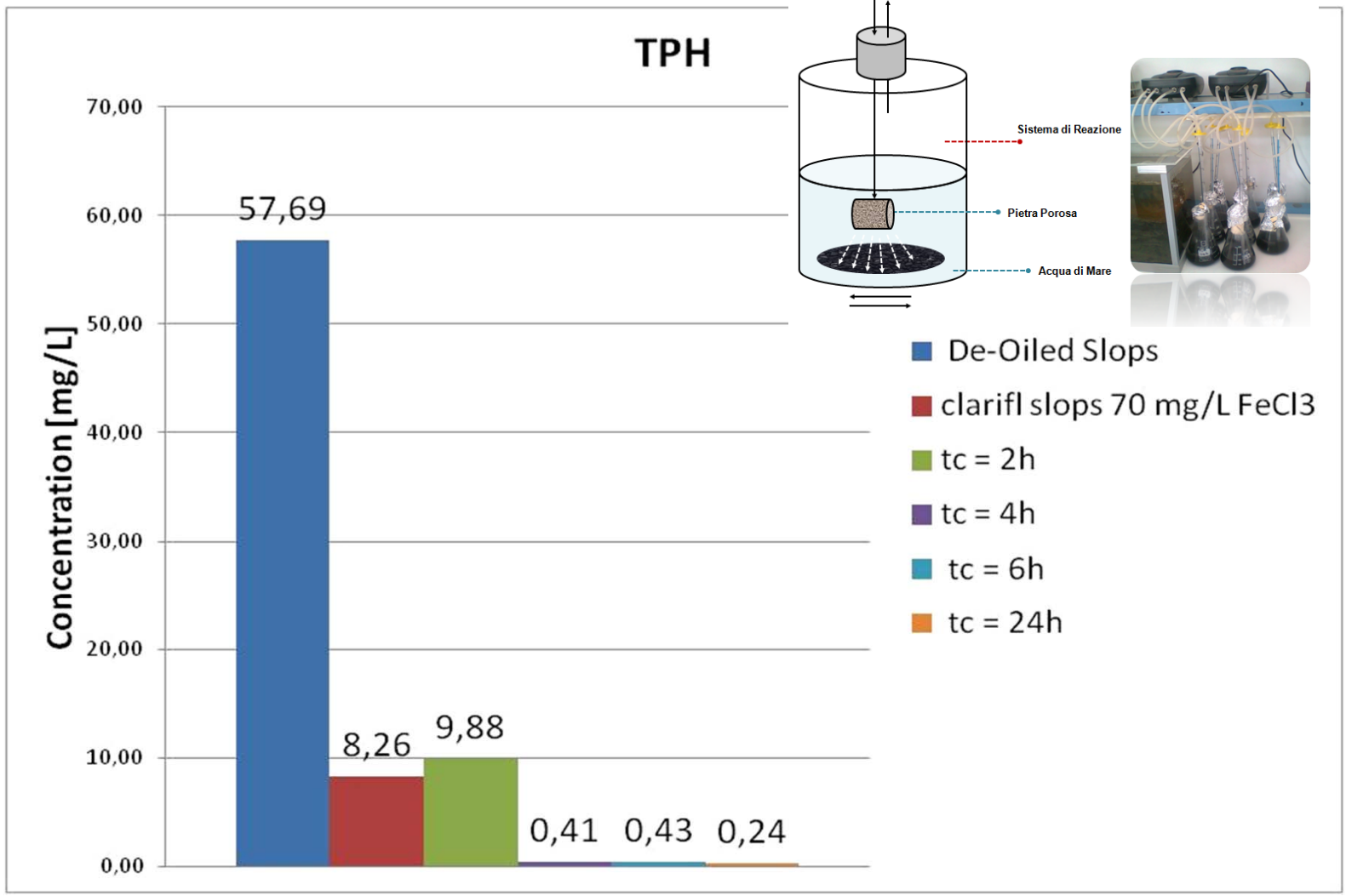
Jar test on dockyard waters: sludge prod.



Experimental Activities

Diesel Slops Adsorption & Kinetic Studies

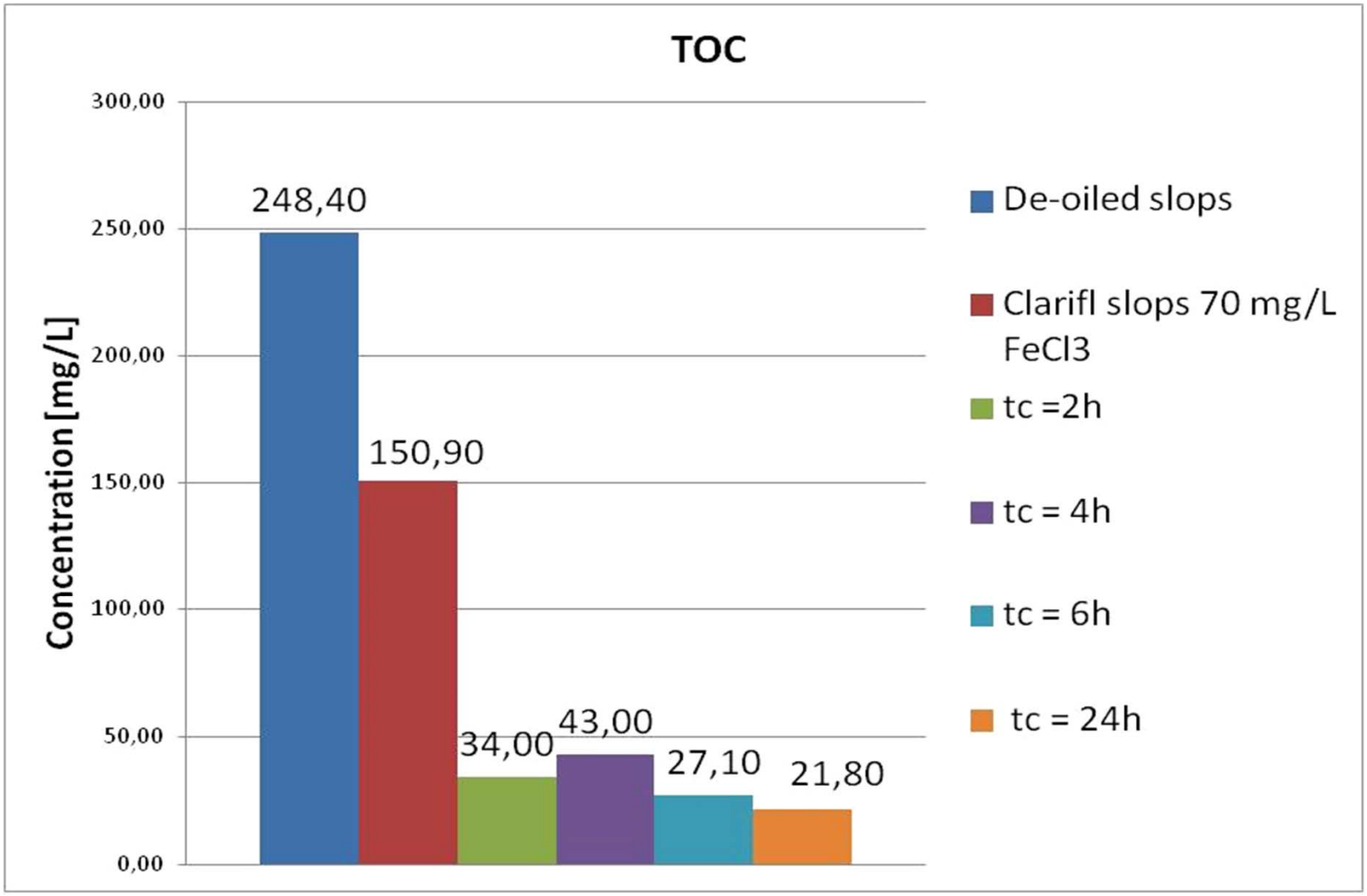
- Coagulant: $FeCl_3$ 70mg/L
- GAC: Filtrasorb 400
- Parameter: TPH



Experimental Activities

Diesel Slops Adsorption & Kinetic Studies

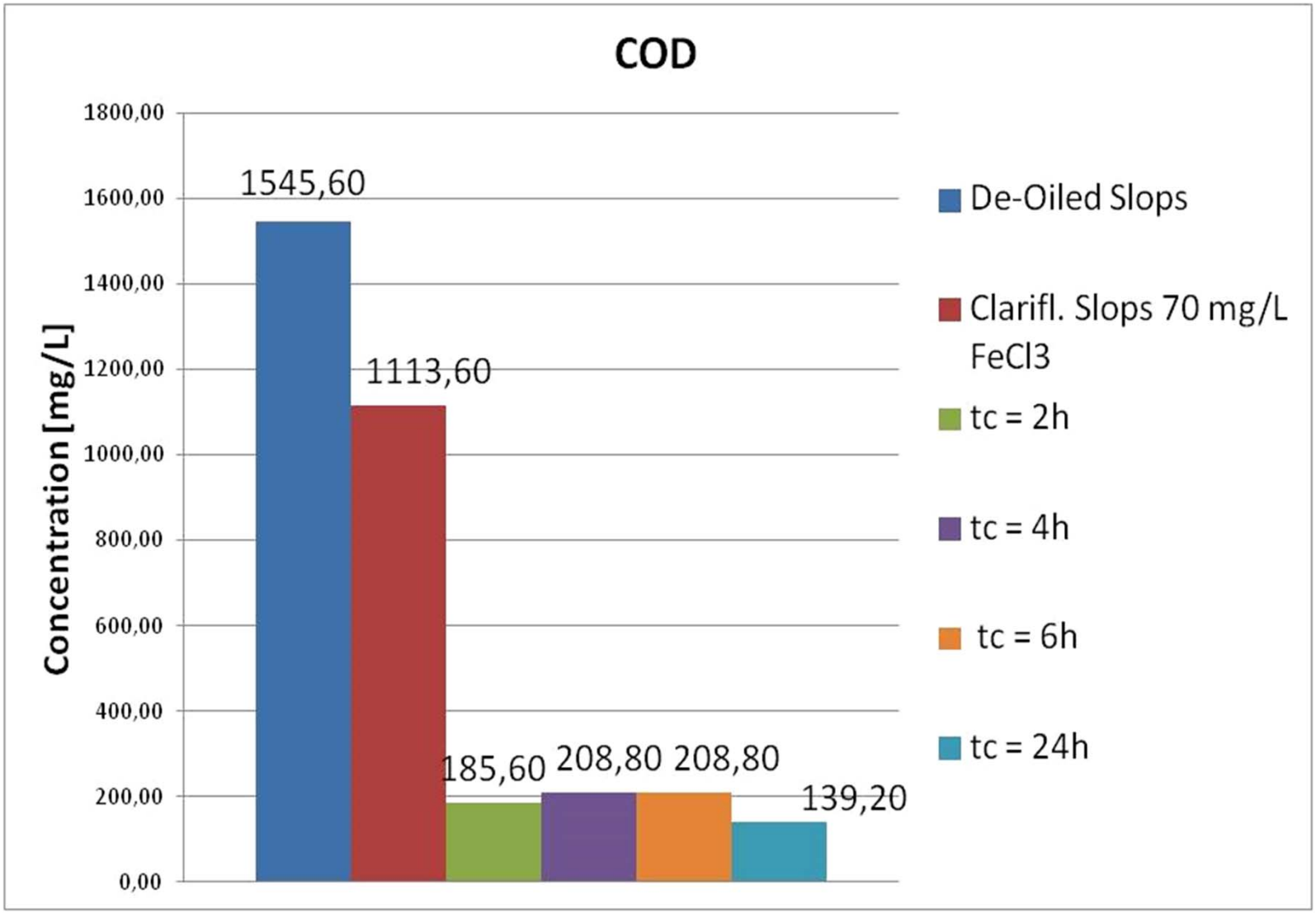
- Parameter: TOC
- Coagulant: $FeCl_3$ 70mg/L
- GAC: Filtrasorb 400



Experimental Activities

Diesel Slops Adsorption & Kinetic Studies

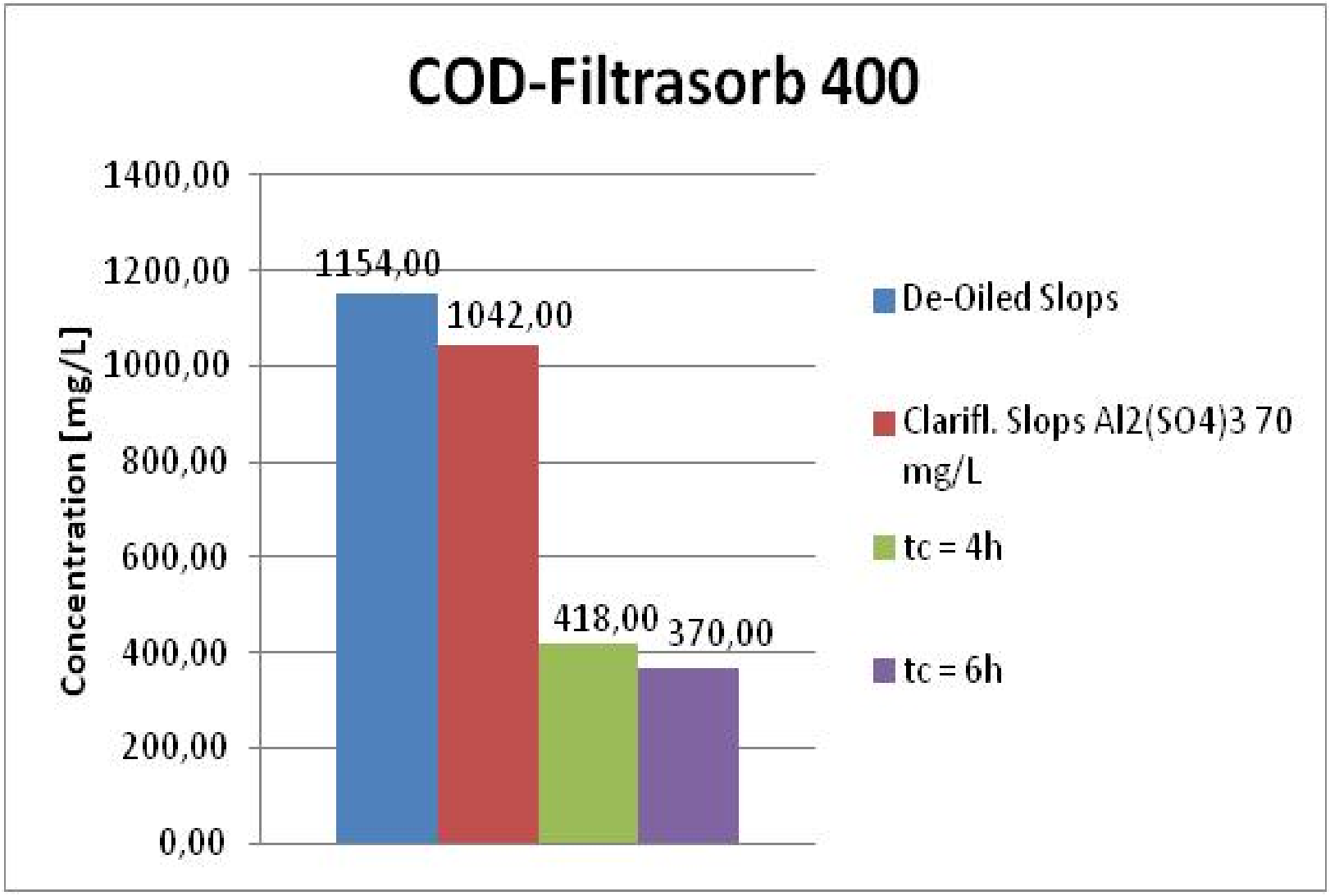
- Parameter: COD
- Coagulant: $FeCl_3$ 70mg/L
- GAC: Filtrasorb 400



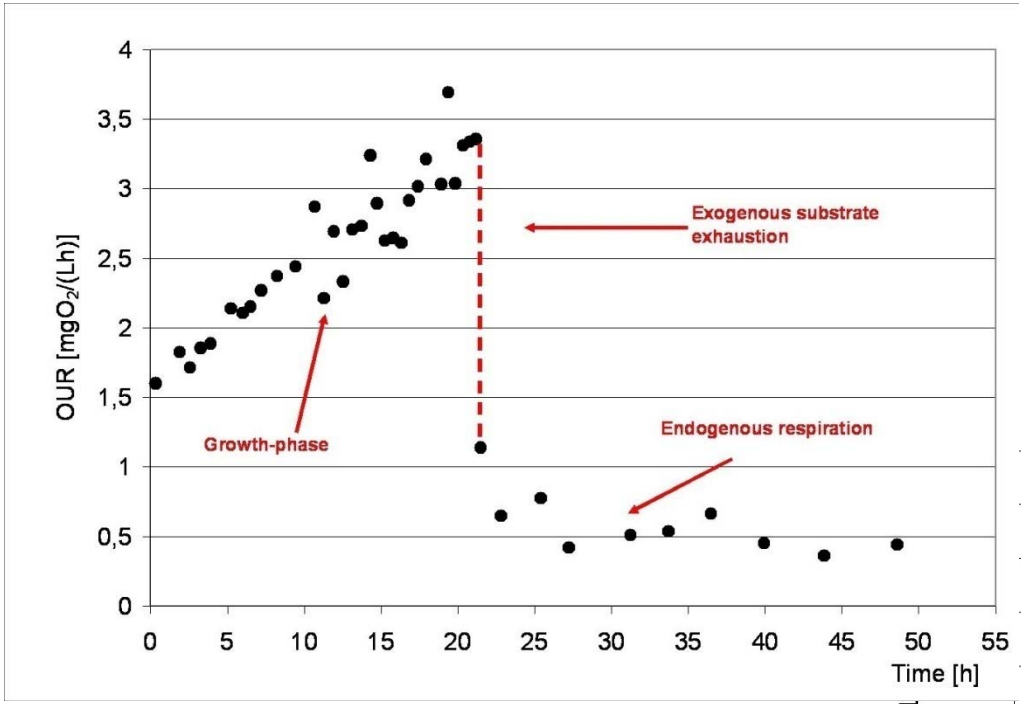
Experimental Activities

avio Jet A-1 Slops Adsorption & Kinetic Studies

- Coagulant: $Al_2(SO_4)_3$ 70mg/L
- GAC: Filtrasorb 400
- Parameter: COD

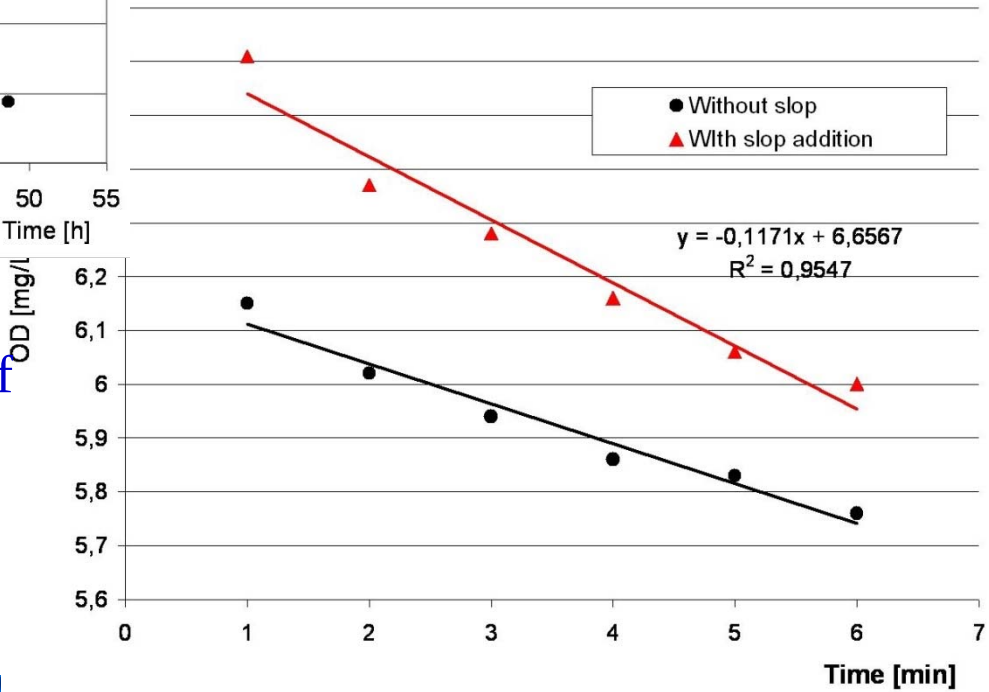


First respirometric tests results

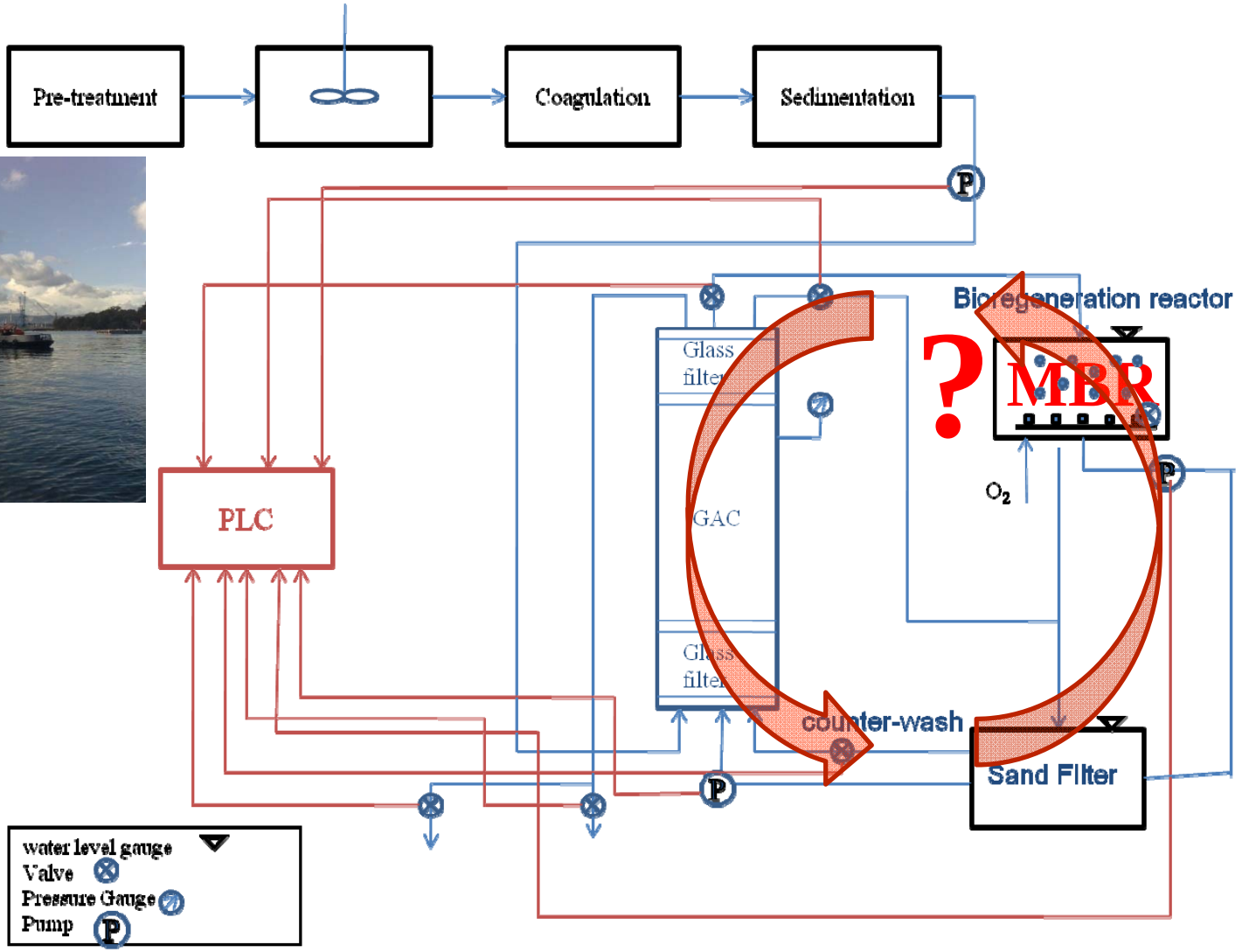


Respirogram of acclimatized biomass from a CAS process with the addition of sodium acetate

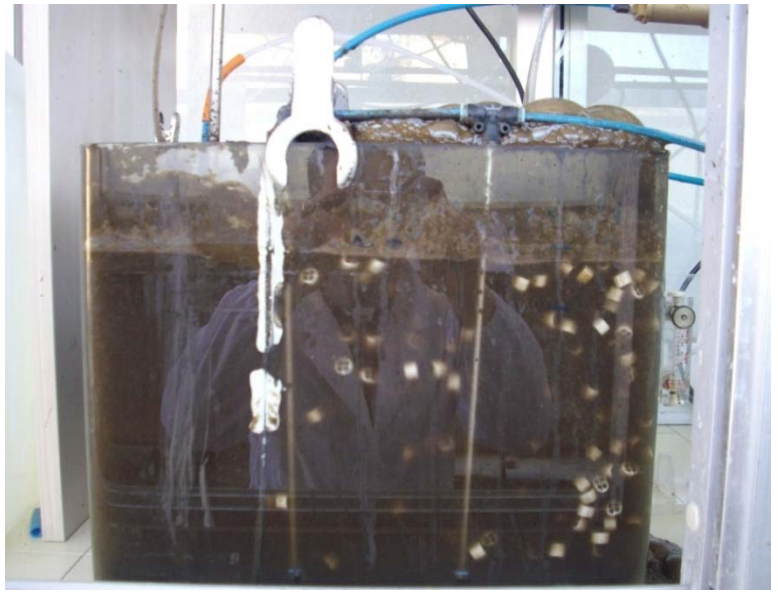
Respirometric batch test of CAS bacteria fed with slop



Main goal of the research activities (GAC on-line Bioregeneration)

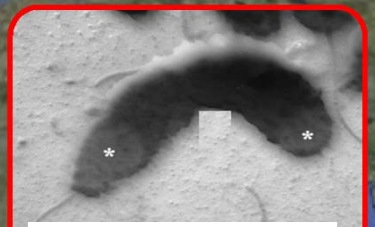


Hybrid Moving Bed Biofilm Reactor (HMBBR) - University of Palermo)



Halophilic bacteria from oil spills

Alcanivorax borkumensis
(1998 Borkum Island, Germany)



Thalassolituus oleivorans
(2004 –Milazzo Harbour, Italy)

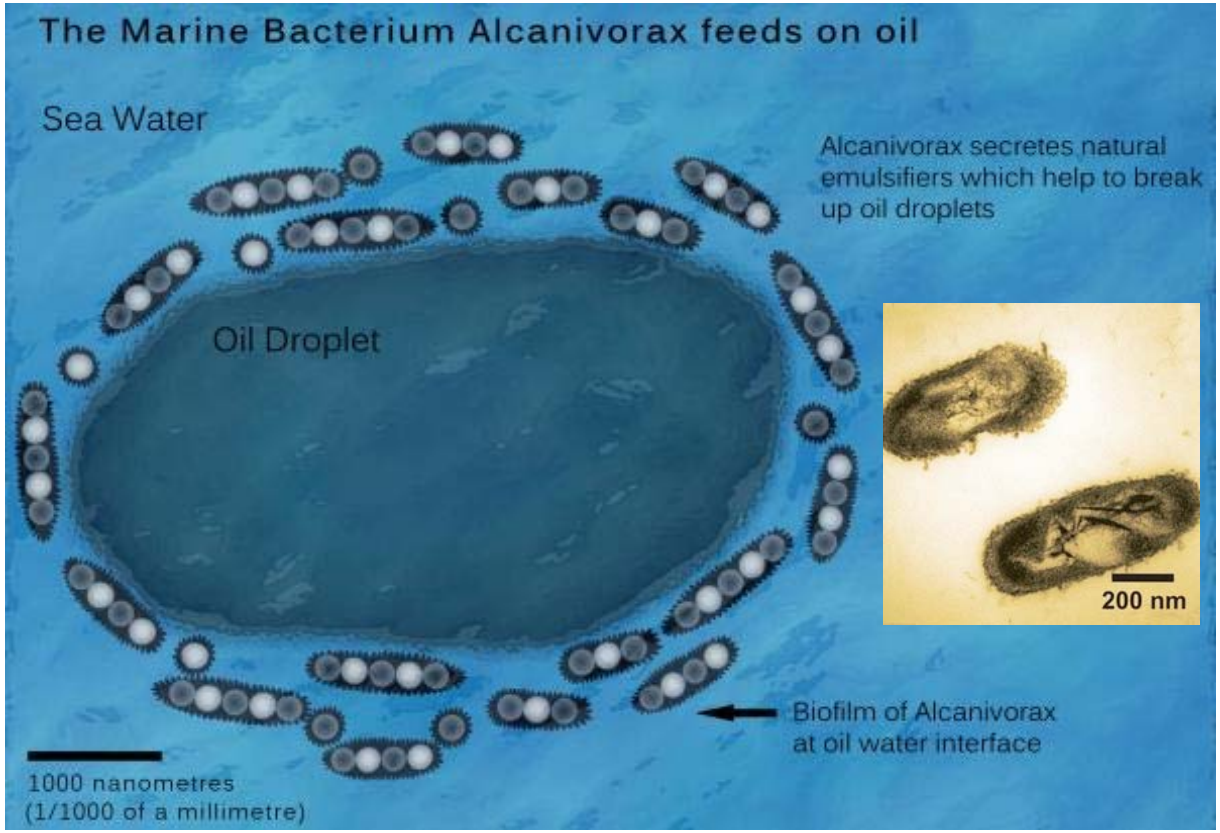
Oleispira antartica
(2003 – Ross Sea, Antartica)

Oleiphilus messinensis
(2002 – Messina Harbour, Italy)

IAMC
Istituto per l'Ambiente Marino Costiero
Consiglio Nazionale delle Ricerche

Halophilic bacteria from marine oil-polluted sites (CNR-IAMC)

A strain of Alcanivorax borkumensis strain SK2T (Genebank accession number Y12579; =DSM 11573T) was used in the experiments. This bacterium grows at 28°C, in aerobic conditions and it is able to grow on many saturated petroleum fraction constituents



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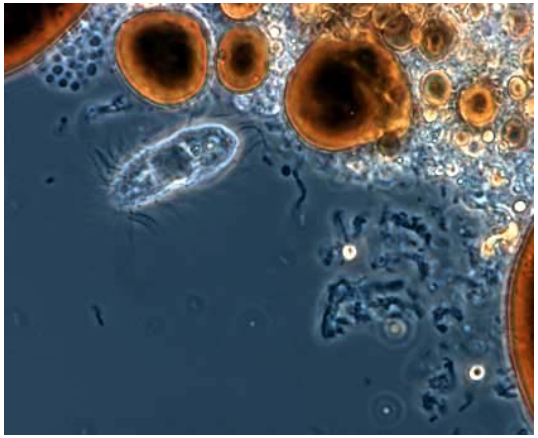
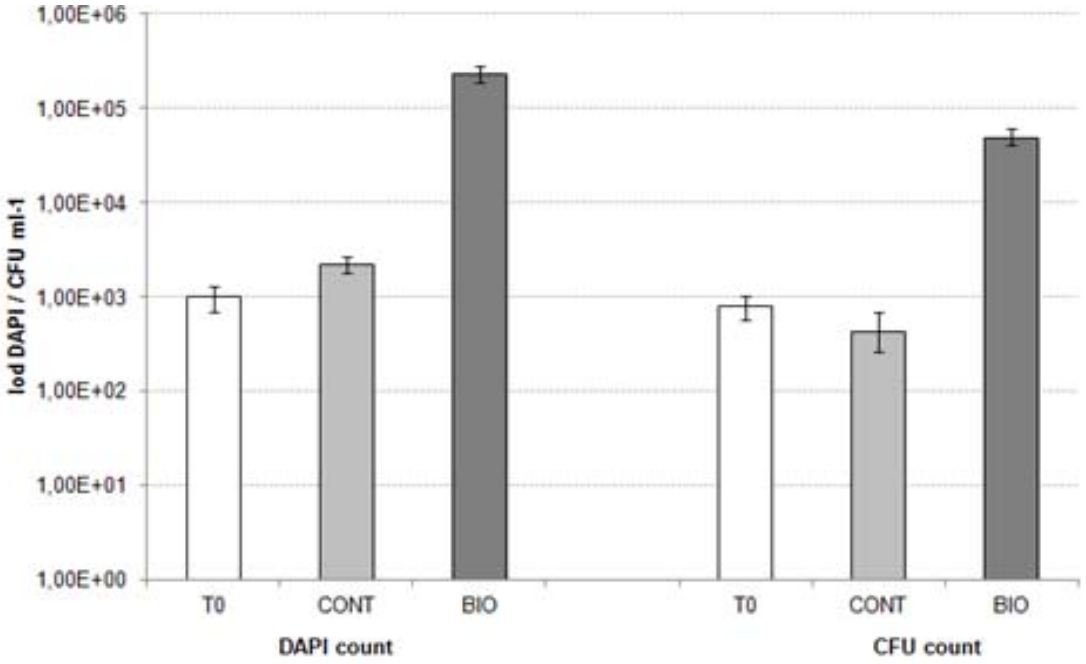
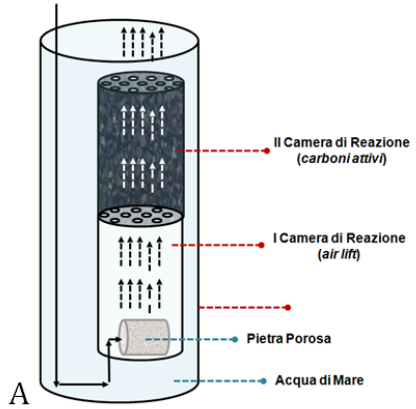
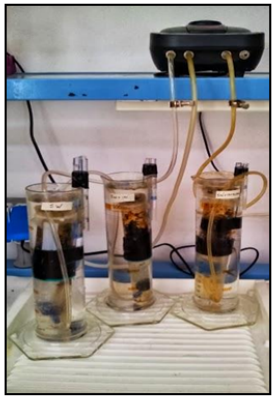


Bacterial densities determined by DAPI staining and measure of cultivable bacteria (CFU)



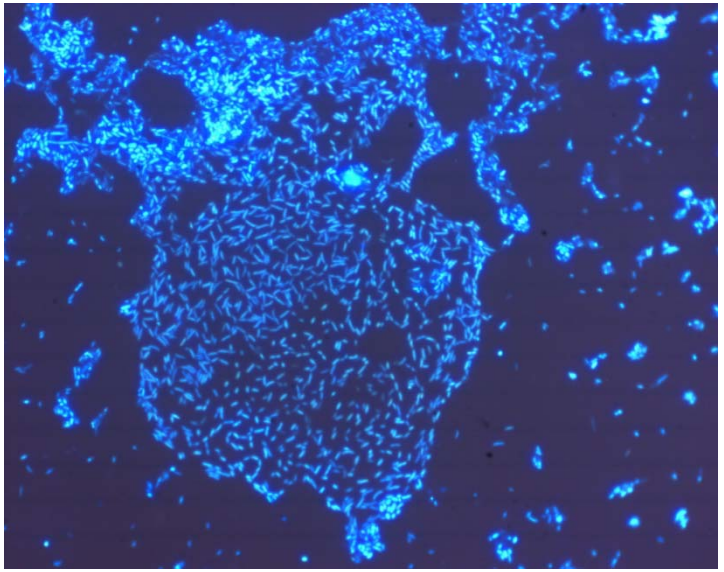


A

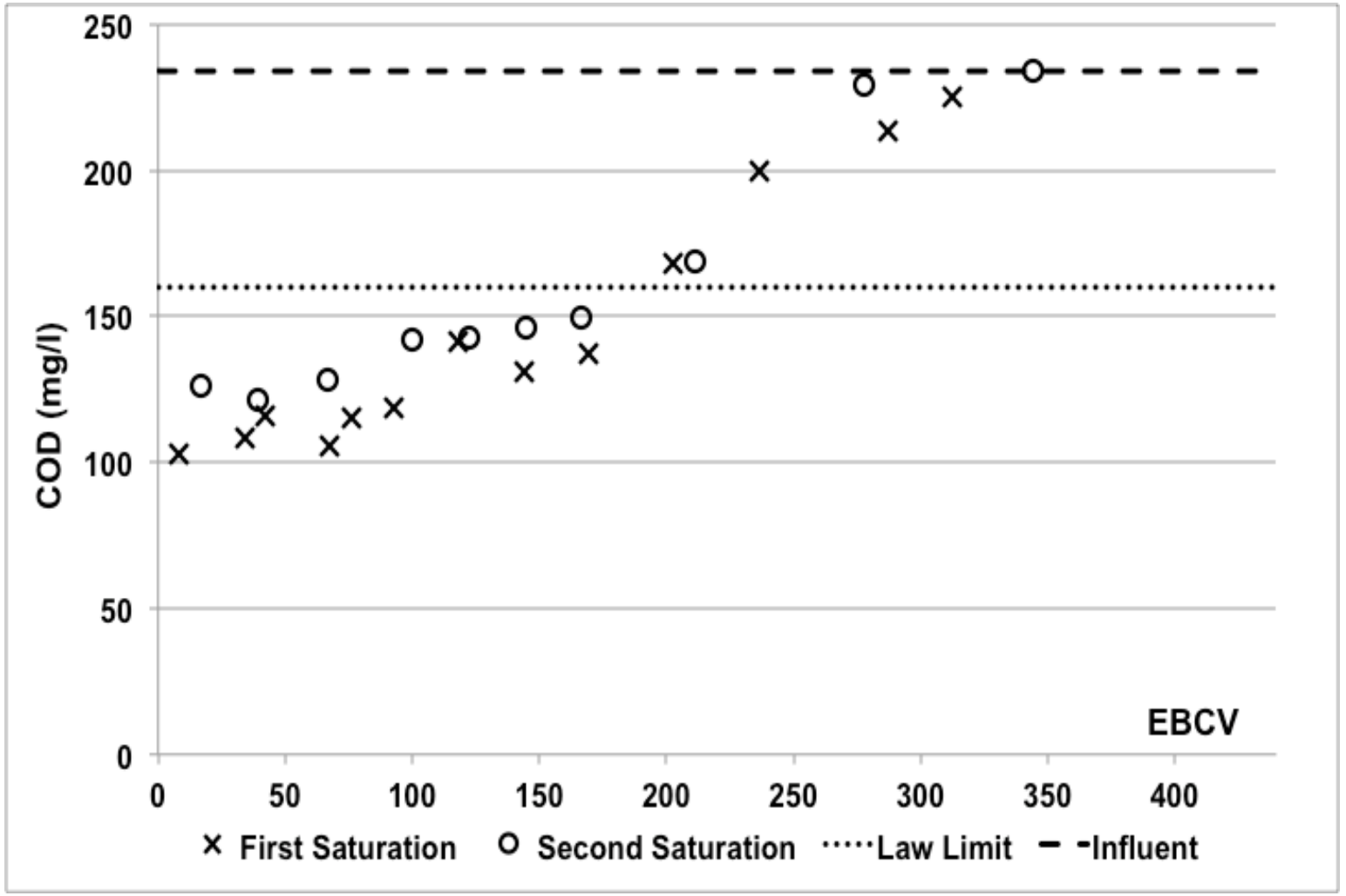


B

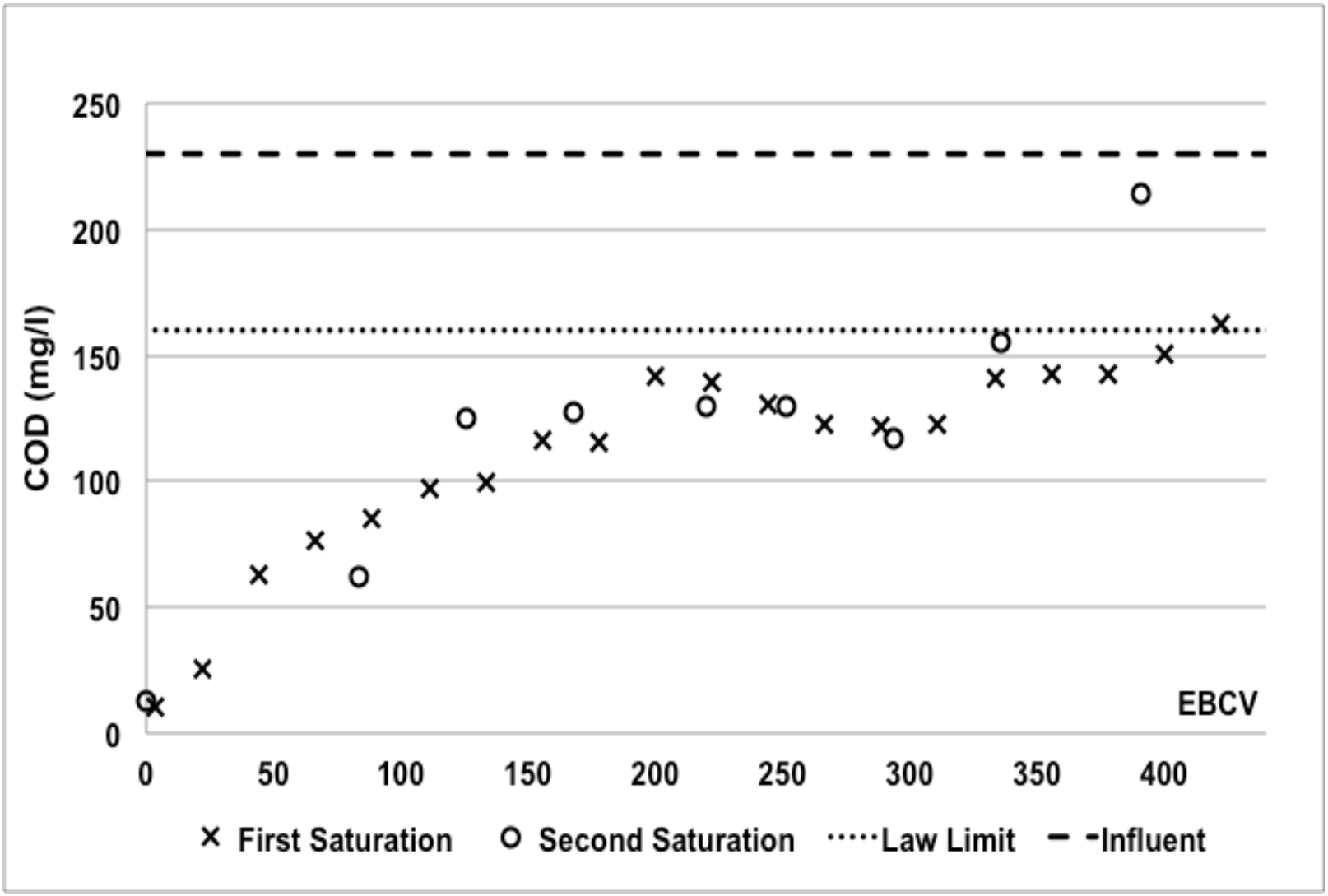
Photography in fluorescence microscopy (DAPI staining) of A. borkumensis SK2 during the growth in crude oil



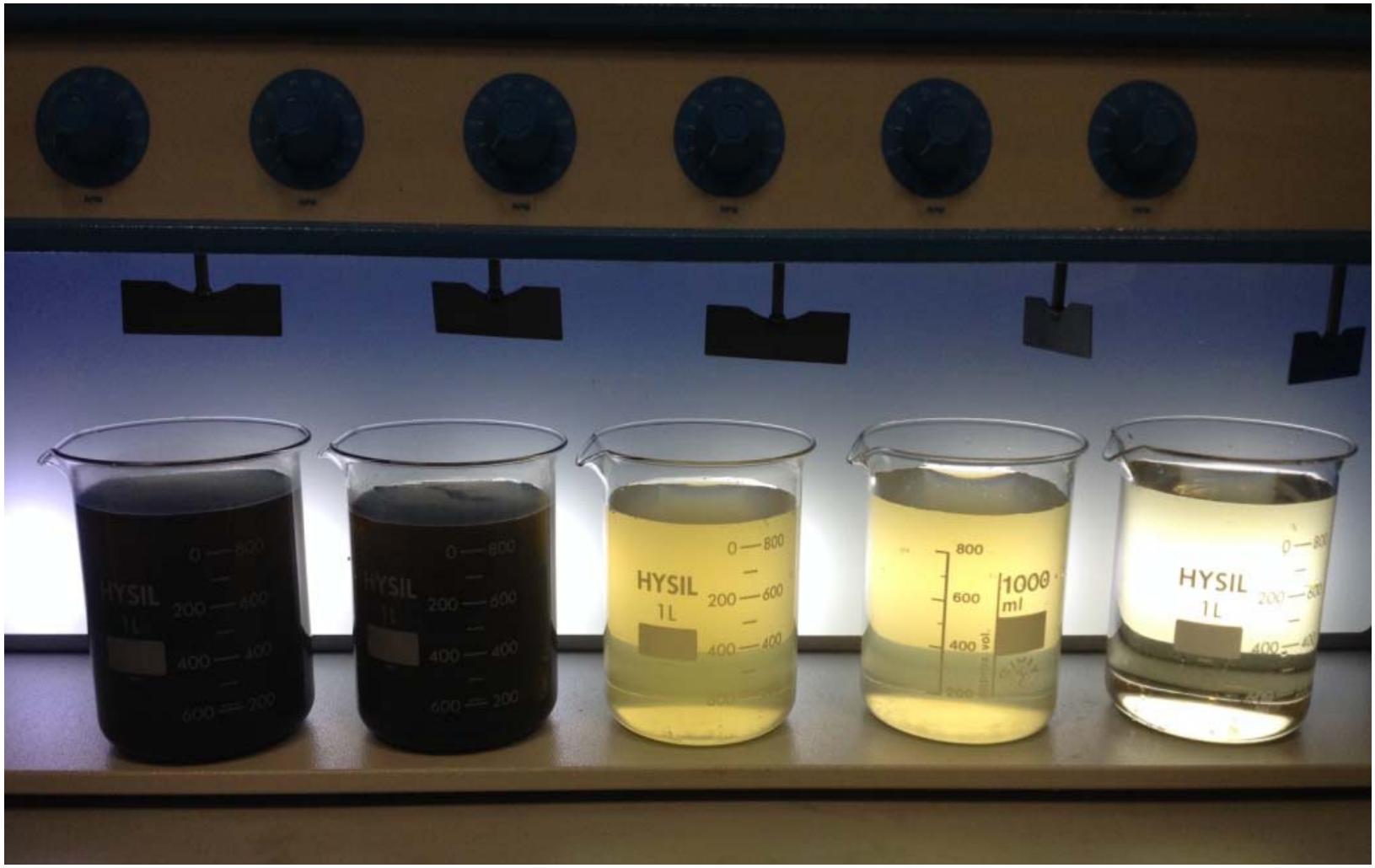
GAC bioregeneration (Slops): comparison of the virgin and bio-regenerated GACs



GAC bioregeneration (dockyard wastewaters): comparison of the virgin and bio-regenerated GACs



Qualitative improvement of the dockyard waste(water)s over the full process



Conclusions

- Pre-treatment of wastewater must be optimized for the specific treated waste(water)s. Generally Aluminum sulfate ($Al_2(SO_4)_3$) perform better on slops while interesting results were also obtained for the dockyard waters through the use of the organic flocculant
- Tests on bioregeneration of exhaust GAC, gave encouraging results in recovery a relevant part of exhausted carbon absorption capacity.
- Although biological treatment is usually inhibited by high salt concentrations, results from the present research proved the feasibility of using salt-adapted micro-organisms consortia capable of degrading the main pollutants contained in these oily and salty contaminated waters.
- Bioregeneration of GAC loaded by TPH from slops of dockyard waste(water)s can thus increases the service-life of the GAC and, not requiring the GAC to be removed from the filter, it can allow a further reduction in GAC management costs

…even from a disaster you can get something good!!!

THANK YOU FOR YOUR KIND ATTENTION

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