

2015

# MODELING OF POLLUTANT ADSORPTION ON NOVEL MODIFIED BIOMASS AS A MEANS OF SEAWATER DECONTAMINATION

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## Recommended Citation

Dimitrios Sidiras, F. Batzias, C. Siontorou, I. Konstantinou, I. Salapa, and S. Zervopoulou, "MODELING OF POLLUTANT ADSORPTION ON NOVEL MODIFIED BIOMASS AS A MEANS OF SEAWATER DECONTAMINATION" in "Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes", Nicolas Abatzoglou, Université de Sherbrooke, Canada Sascha Kersten, University of Twente, The Netherlands Dietrich Meier, Thünen Institute of Wood Research, Germany Eds, ECI Symposium Series, (2015). [http://dc.engconfintl.org/biorefinery\\_I/15](http://dc.engconfintl.org/biorefinery_I/15)

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Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass  
Conversion and Related Processes. September 27-October 2, 2015  
Chania (Crete), Greece

**MODELING OF POLLUTANT  
ADSORPTION ON NOVEL MODIFIED  
BIOMASS AS A MEANS OF SEAWATER  
DECONTAMINATION**

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# Introduction

- Adsorbents collect liquid hydrocarbons on the solid phase, thus they can remove oil spills from the sea surface water.
- The thermochemical treatment of lignocellulosic waste biomass can provide a fraction that can be used as a low-cost adsorbent with increased sorption capacity and biodegradability for cleaning by adsorption the oil spills.
- The modification of lignocellulosic wastes can provide adsorbents with relatively high sorption capacity, biodegradability, and cost-effectiveness for the adsorption of dyes, heavy metals and oil products.

- Acid hydrolysis can fractionate the three basic components of lignocellulosic: hemicelluloses, cellulose and lignin.
- Dilute sulfuric acid has been used to commercially manufacture furfural from cellulosic materials.
- The hydrolysis of cellulose is a significant entry point into the **biorefinery scheme** based on carbohydrates for the production of biofuels and biochemicals.
- The long-term success of the **biorefinery concept** depends on the development of energetically efficient processes to convert cellulose directly or indirectly into biofuels and chemicals.

- This work focuses primarily on modeling the process of adsorption of diesel and crude oil on modified biomass fraction.
- The experimental measurements were performed using mainly seawater, and simulated/substitute seawater.
- The modeling of adsorption of mixtures of fluids and colloids, containing water, hydrocarbons, salts, dispersants and predetermined contaminants was .
- Agitation simulated the sea waves' movement in the case of shoreline flows.

# Experimental

- The wheat straw was obtained from the Kapareli village, close to the city of Thiva (Thebes) city at the Kopaida area (former lake Kopaida) in central Greece.
- The moisture content of the material was 9% w/w.
- After screening, the particle sizes isolated were 14-24 cm.



Untreated (left) and pretreated (right) wheat straw; particle size 14-24 cm; pretreatment conditions: 100 °C, sulfuric acid 0.45 M, 4 h, and liquid-to-solid ratio = 20:1.

The wheat straw was pretreated by sulfuric acid hydrolysis; the acid hydrolysis process was performed in a 20 L CHEMGLASS reactor for scaling up.







Field-water sampling locations (two ports for seawater, one lake and one stream):

ΛΠ = Piraeus Port,

ΛΣ = Skaramaga Port,

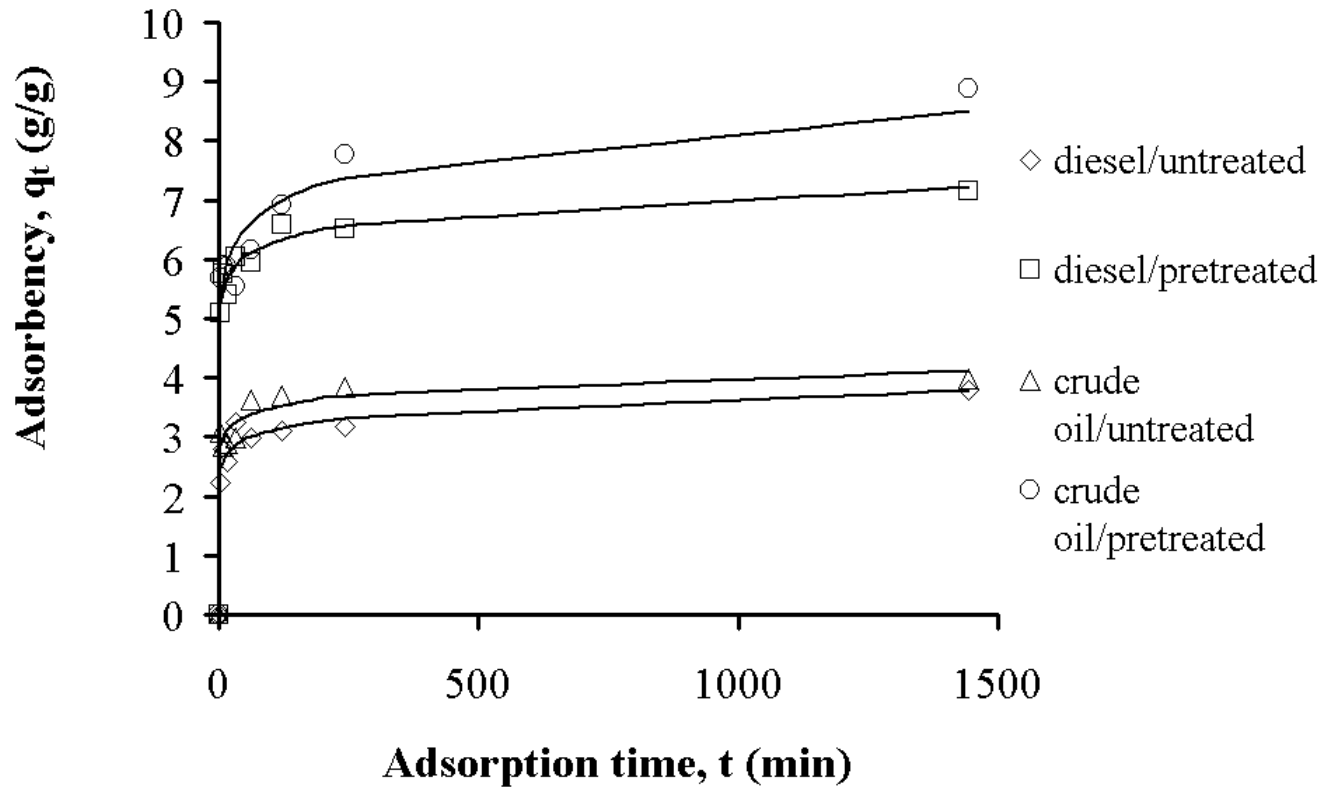
ΛΚ = Koumoundourou Lake, and

P6 = Pikrodafnis Stream.

Sampling period: 2013-2015.

# Kinetic models

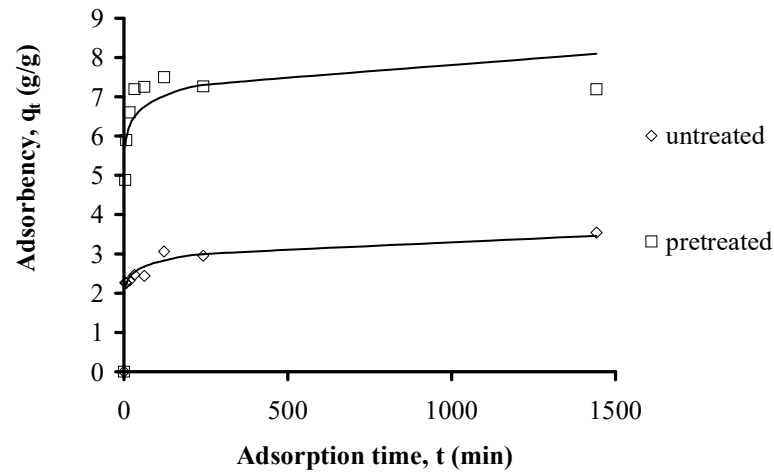
| Model                          | Equation                               | Parameters   | Ref. |
|--------------------------------|--|--|------|
| Lagergren                      | $q - q_t = q \cdot e^{-k \cdot t}$     | $q$ , $q_t$ are the amounts of oil adsorbed quantity (in g) per g of straw after equilibrium time and adsorption time $t$ , respectively; $k$ is the pseudo-first order rate constant (in $\text{min}^{-1}$ )    | (28) |
| Second order                   | $q_t = q - [q^{-1} + k_2 t]^{-1}$      | $k_2$ is the pseudo-first order rate constant  | (29) |
| Intra-particle diffusion model | $q_t = c + k_p \cdot \sqrt{t}$         | $q_t$ is the amount of MB adsorbed at time $t$ , $c$ is a constant ( $\text{mg g}^{-1}$ ), $k_p$ is the intra-particle diffusion rate constant in ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )                       | (30) |
| Elovich                        | $\frac{dq_t}{dt} = a \exp(-\beta q_t)$ | $q_t$ is the amount of oil adsorbed quantity after adsorption time $t$ , $\alpha$ is the initial oil sorption rate ( $\text{g g}^{-1} \text{min}^{-1}$ ) and $\beta$ is the desorption constant ( $\text{g/g}$ ) | (31) |
| Fractional                     | $q_t = at^b$                           | $q_t$ is the amount of the adsorbate sorbed by the adsorbent at a time $t$ , while $a$ and $b$ are constants with $b < 1$  | (32) |



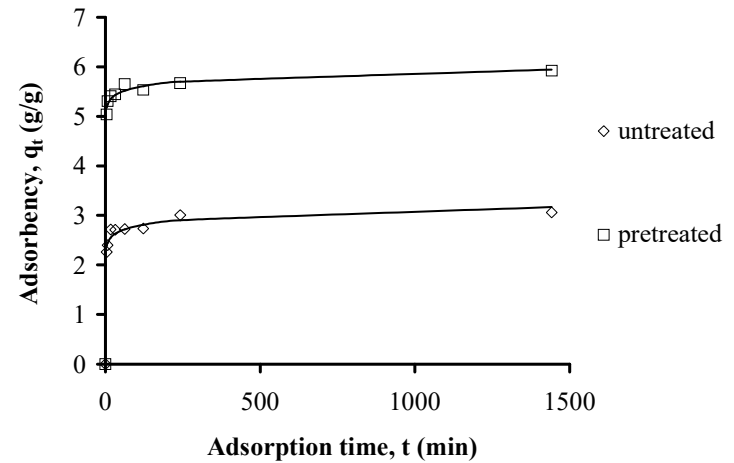
Oil adsorbency (diesel and crude oil) for untreated and pretreated wheat straw vs. adsorption time; oil spill on seawater (Piraeus Port); the fractional kinetic model was applied.

Diesel and crude oil amount adsorbed on untreated (UWS) and modified wheat straw (MWS) for spills formed on five types of water;  $q$  estimated according to the second-order kinetic model.

| $q$ (g/g)        | Diesel/UWS | Diesel/MWS | Crude oil/ UWS | Crude oil/ MWS |
|------------------|------------|------------|----------------|----------------|
| Fresh Water      | 2.970      | 7.257      | 3.532          | 8.027          |
| Sea Water        | 3.301      | 6.488      | 3.624          | 7.177          |
| Substitute Water | 3.225      | 6.554      | 4.151          | 7.533          |
| Stream Water     | 3.402      | 6.908      | 3.923          | 8.918          |
| Lake Water       | 3.314      | 5.407      | 3.905          | 5.720          |

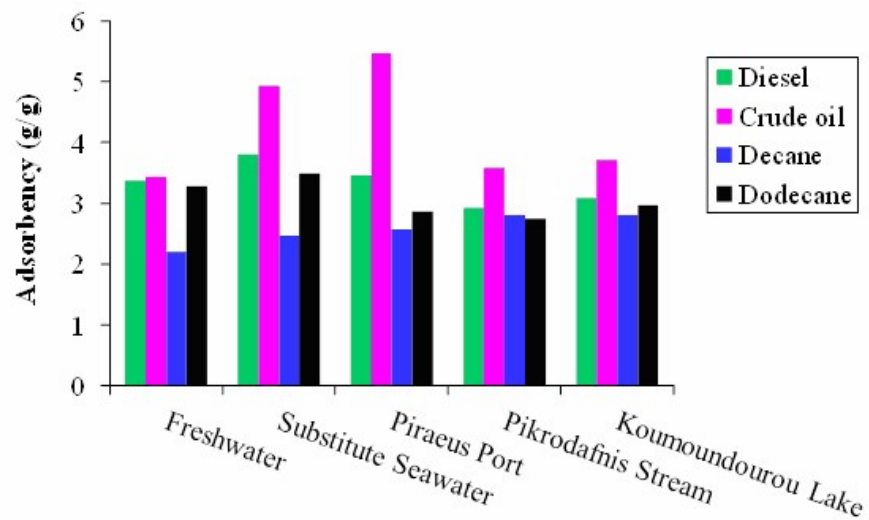


**(a)**

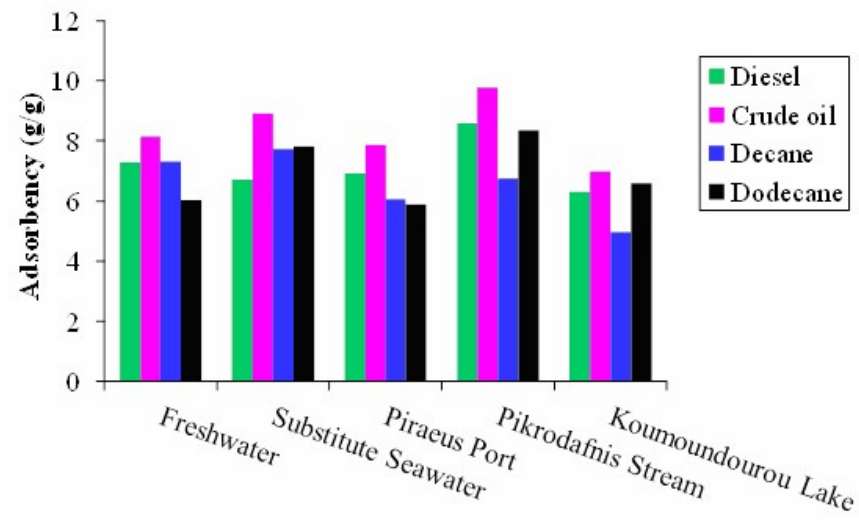


**(b)**

Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: for (a) decane and (b) n-dodecane; hydrocarbon spill on fresh water; the fractional kinetic model was applied.

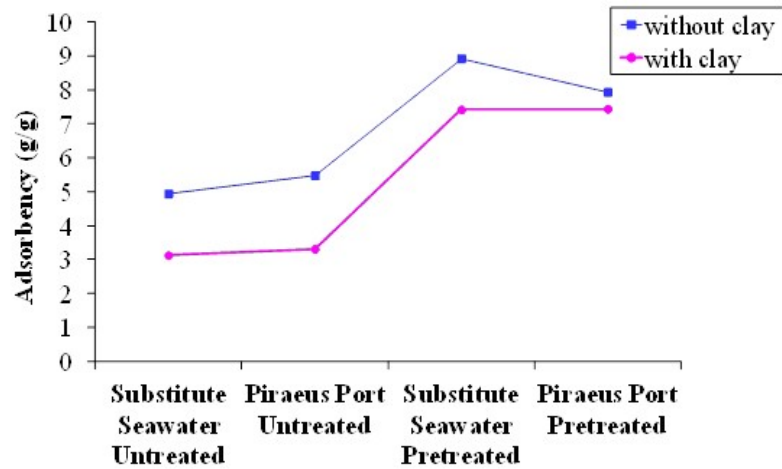


(a)

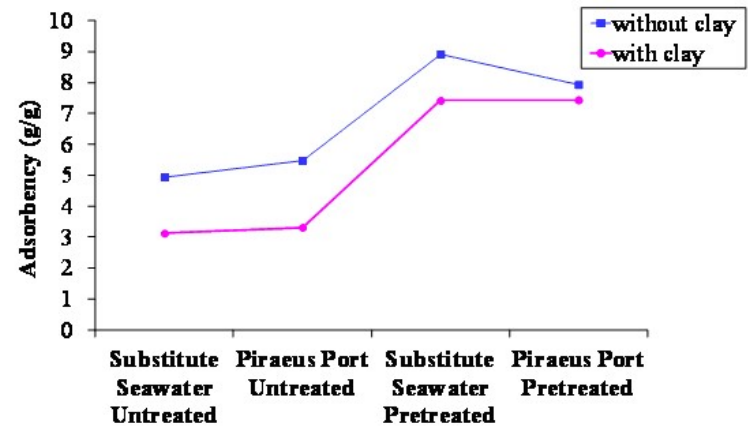


(b)

Adsorbencies of diesel, crude oil, decane and n-dodecane (a) on untreated and (b) on modified wheat straw; hydrocarbon spill on freshwater, substitute seawater, seawater, stream water and lake water

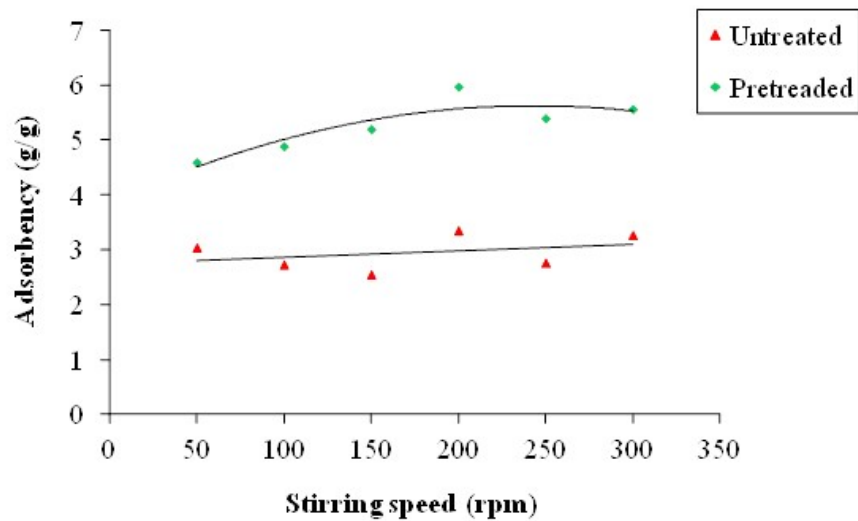


(a)

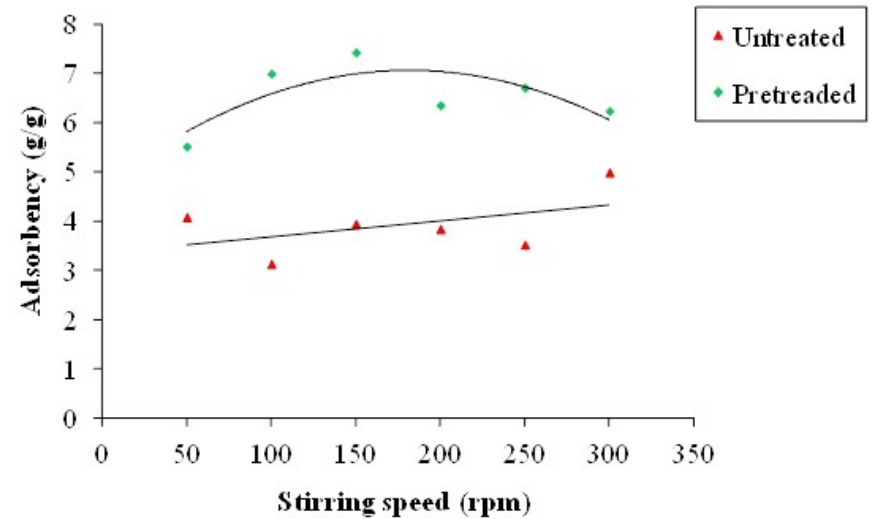


(b)

Oil adsorbencies on untreated and modified wheat straw for (a) diesel and (b) crude oil spills with or without **clay** (simulating suspended solids in shoreline water) on substitute seawater and seawater.



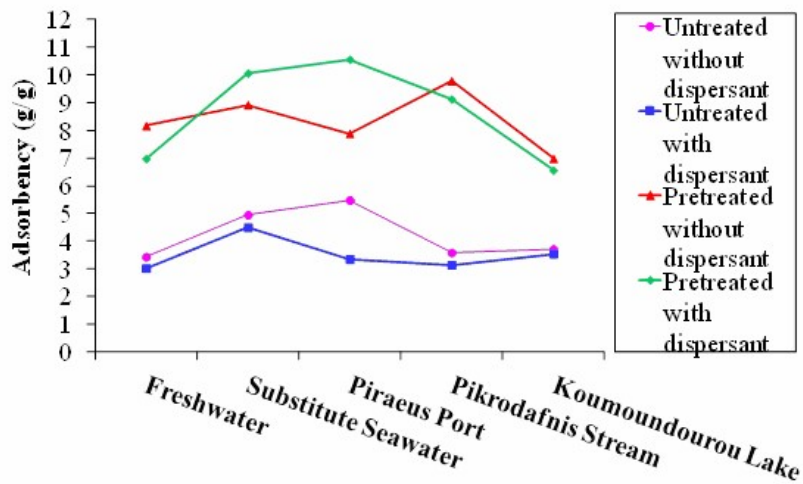
(a)



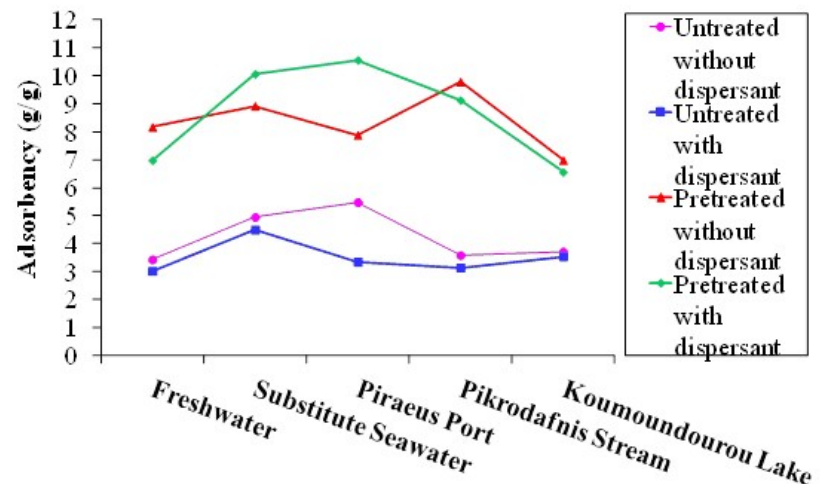
(b)

Oil adsorbencies on untreated and pretreated wheat straw for (a) diesel and (b) crude oil spills on seawater under the effect of **stirring** (simulating sea waves).





(a)



(b)

Oil adsorbencies on untreated and modified wheat straw of (a) diesel and (b) crude oil spills with or without **dispersant** on freshwater, substitute seawater, seawater, stream water and lake water.

# Conclusions

- The fractional power kinetic model presented the best fitting on the experimental data of the adsorption process for diesel, crude oil, decane and n-dodecane spills on untreated and modified lignocellulosic biomass.
- Crude oil adsorption on original and modified wheat straw showed significantly the highest adsorbency on all types of water.
- The oils' adsorbencies were higher on modified wheat straw comparing to the untreated one in all oil kinds and water types.

- The presence of clay (simulating suspended solids in shoreline water) had negative impact in all cases of oil adsorbency on wheat straw and especially in the case of crude oil spill on seawater and substitute seawater
- The effect of stirring (simulating sea waves) was positive as regards oil spill adsorbency, especially in the case of diesel and crude oil on modified wheat straw.
- The effect of chemical dispersant had negative impact on diesel and crude oil spills adsorbency regarding all types of water.

# ***Acknowledgment***

- This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS. Investing in knowledge society through the European Social Fund. - Project: THALIS – University Of Piraeus – Development of New Material from Waste Biomass for Hydrocarbons Adsorption in Aquatic Environments.



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**Co-financed by Greece and the European Union**

