

Publishable Executive Summary

Shortage of water is one of the most serious problems affecting the South and Western Mediterranean Countries, characterised by arid and semi-arid regions. The extent of the problem is such that this is now a matter of priority concern. As such, urgent actions are required. The increase in population together with socio-economic developments and the climatic changes undergoing in this area are leading to temperature increase and rainfall decrease and consequently the situation is further deteriorated. In general, water resources in the Mediterranean Region are seriously affected by internal and external factors. Indeed the situation calls upon innovative approaches aiming to overcome some of the existing problems. The use of non-conventional water resources through desalination of seawater and irrigation flow water offers an excellent alternative to help the situation. In addition, salination and alkalization of soils are among the main problems for crop production, which often leads to land abandonment. However, available desalination technologies need to be significantly improved to gain efficiency. Based on the above statements, the main objectives of this Proposal are:

- (i)* The development of highly selective, and recyclable calixchitosan polymers (cheap to produce) for the desalination of seawater, irrigation flow waters and soil with a view of improving substantially current methodology.
- (ii)* Use of biotechnological modes and means for promoting efficient and nutrient use of water by plants improving their immunity and resistance towards diseases and droughts.
- (iii)* Combination of (i) and (ii) to improve soil and water quality and add nutrient value to irrigation.

In order to fulfill these objectives the research programme was divided into seven workpackages.

Thus following the selection of two Pilot Sites in Morocco and Palestine, selected crops, salted water resources and soil were characterized leading to libraries of nutrients (cations and anions) and organic compounds (pesticides) as well as gaining knowledge regarding

the chemical compositions of salted water sources and soil projected for desalination (WP1). This information was very valuable for the design and synthesis of calix based receptors as extracting agents for desalinating purposes. A wide variety of receptors were designed and synthesized based on calixarenes and crown ethers. These were characterized using various analytical techniques such as ^1H NMR, mass spectroscopy and microanalysis. Their selective behaviour for alkali and alkaline earth metal cations was assessed through the thermodynamic characterization of these receptors in their complexation with these cations. Based on these data, which provided a quantitative evaluation of the affinity of the receptor for a given ion, the most selective receptor were selected for their attachment to solid supports. These new materials were tested for their capacity to remove the species of interest from water and several recycling processes were considered. Results obtained on the removal capacity of these receptors for salts were compared to commercially available ion exchangers. Among these materials two of them have a capacity to remove sodium from water which was found to be four times higher than the capacity of commercially available desalinating agents. Furthermore after recycling the material eighty one times its capacity was still comparable to that found in the market (Workpackage 2). The optimal conditions for salt removal such as the kinetics of the process, temperature, pH of the aqueous solution were determined. Experiments were carried out at Laboratory and Pilot Plant Scale. The results obtained in this workpackage were combined to design a mobile system for soil desalination (Workpackage 6). A desalination unit was designed and constructed. In doing so not only the optimal conditions for the highest efficiency of the material was considered but also the technological details for the industrial construction of a viable and low cost commercial unit as well as a practical, easy to use unit in the social agricultural environment of its final destination were taken into account. Thus the following factors and conditions have been considered.

- The breaking tendency or hardness of the free particles of the selected material, (estimated to be of an intermediate hardness equivalent to point 4 ± 1 on the Mohs scale, (*Perry's Chem Engineers Handbook 7th Ed.*), as observed below.
- The need to retain the fine particles on a closed and reduced compartment which allows the fluid passage avoiding the particle to escape.

- The need of establishing a balance between the potential swelling of the particle during the salt removal process and the movement or displacement as well as collisions between particles leading to their breakage. This balance was achieved by the provision of an extra space in the close compartment which was large enough to allow for the swelling process, but not as large as to allow the movements and collision between particles.
- Easy regeneration of the selected material and control 'in situ' with a minimum volume of solution without wastage.
- The selection of commonly used organic acids in the food industry and the rural environment to lower significantly the cost of the recycling process.

The desalination unit is being incorporated in the mobile vehicle purchased and adapted for this purpose (Workpackage 7).

In addition, organic and inorganic silicon oligomers were used to synthesize a set of novel silicon-containing lignocellulosic derivatives for the application of the composition of plant nutrients to be added to the desalinated irrigation water or as a growth activator/fertilizer/protector of plants (Workpackage 5). Thus the use of main mineral fertilizers, their anti-stress action in terms of plant resistance against drought conditions and their adaptation to water deficiency in soils were demonstrated. This was explained in terms of the ability of plants to form a powerful root system in the presence of lignosilicon compounds that provide the plant with a better water supply and nutrition. Experimental work carried out with cereals as well as with forage plants and soil showed that low doses of lignocellulosic derivatives have a positive effect on the development of the crop. It was also demonstrated that those compounds can be produced from waste of phytomass chemical (technical lignins) and wood mechanical processing after treatment with selected microbes.

The effect of silicon-containing lignocellulosic materials on the resistance of vegetables towards unfavourable growth conditions was investigated using *cucumber salivas* (brand 'Pioneer') as a representative sample. Relative to the control, the effect of silicon-containing lignocellulosic materials on the development of the cucumber plant was as follows; the third leaf formed earlier, an increase in the chlorophyll content; earlier

flowering; crop mass was 30 % higher due to the increase of the number of unit per plant (an average of 12 units against 8 for the control); the fruitage period was longer and the yellowing of leaves and drying off of stems began later.

Following the development of the desalination system and the use of nutrients and taking into account the selected plants an investigation (workpackage 4) was carried out to assess the ability of selected plant species to respond to desalinated or post-irrigation water and treated soil under Mediterranean conditions. Thus the effect of receptors and chelating agents (some of them synthesized in the course of this Contract) in tomato growing with salinity. A few chelating agents did not affect the accumulation of sodium in the control experiment but a slightly **XXXXXX** was found under salinity conditions. It was found that the content of nitrogen in the plants was reduced by salinity as an adaptive response to the stress. The salinity treatment also affected the content of carbon in the tissues. It was concluded that although changes of $\delta^{13}\text{C}$ values. These results were indicative that plants growing under salinity conditions did not close stomata when supplied with the chelating agent thus allowing them to maintain higher photosynthetic sites. Studies carried out on the use of soil-applied receptors for sodium accumulation processes in Rape (*Brassica napus*) showed that the root growth was not affected by salinity while shoot growth was clearly impaired. The effect of receptors on growth was clearly root and shoot biomass accumulation. Although sodium accumulation was reduced in aerial parts of the plants, the sodium content in the roots fraction was not altered. Accumulation of iron and magnesium was reduced by the salinity treatment while an increase of potassium in roots and shoots was observed. Salinity tolerance in Barley as well as the response of *Eucalyptus globus* to salinity were also investigated.

Studies on the effects of salinity on plants physiology of *okra*, *Lucerne* and *gombo* demonstrated a depressive effect on the plants growth which was observed at different stages in the plant culture even in seeds at germination level. It is therefore concluded that the objectives of the project were fully accomplished. A number of people were trained under this Contract at postgraduate level. The work involved in this Contract was the subject of plenary and keynote lectures, several presentations at national and international Conferences. Other dissemination activities involved radio interviews, interaction with industries, addresses to the public sector.

Following the various papers published in international journals (list of publications attached) as well as the presentations at national and international Conferences (list attached) involving the various Partners. The final plan for using and disseminating the knowledge involves an application for a patent, the content of which is described as follows,

During the course of these investigation, a new material containing selective functional groups has been designed, synthesized and characterized by the use of several analytical techniques. This new material is easily recyclable. The material has a capacity to remove sodium from water which is four times greater than that of commercially available materials. Thus experimental work demonstrated that after eighty one recycling processes the material still has a capacity for sodium removal equivalent to that of commercially available materials. The optimum conditions for sodium removal (kinetics of the process, temperature, pH of the aqueous solution) have been determined. We are now in the process of collecting all information available in the literature on desalinating materials to provide convincing evidence of the potential that this new desalinating agent offers as compared with existing ones. Following this literature review we will proceed with the registration of this invention to protect the knowledge and hen we will publish all information regarding the physico-chemical characteristics of the new material, which can form the basis for a new technological approach for water desalination. The success of this invention will open the way to proceed to its commercialization through production in large scale.

Within the financial plan, knowledge will be disseminated through a number of phenoxy lectures and vial presentations at national and international Conferences by members of the Consortium. A further task will be the submission of research proposals by the Consortium under the different Calls of Proposals in FP7 under the programmes on 'Nanoscience and Nanotechnology', 'Environment' and 'Food, Agriculture and Fisheries'.

Papers Published and to be Published under this Contract.

1. A. F. Danil de Namor, *Water Purification : from Ancient Civilization to the XXI Century*, *J. Water Sci. and Techn*, 2007, **7** 33.
2. A.F. Danil de Namor and K. Zegarra-Fernandez, Thermodynamics of ethyl-*p-tert*-butyl calix[5]arene Pentanoate and its Cation Complexes in Non-aqueous Media. *J. Phys. Chem.*, 2007, **111**, 7321.
3. G. Telysheva, T. Dizhbite, G. Lebedeva, N. Zaimenko, S. Popovs, Regulation of lignocellulose materials sorption properties by modification for environmental application. - J.M. Loureiro, M. Kartel (Eds.), *Combined and Hybrid Adsorbents. Fundamentals and Applications*, Springer, Netherlands, 2006, p.p. 271-276.
4. T. Bikova, G. Rossinska, T. Dizhbite, G. Telysheva. Multiwave UV/Vis detection at SEC analysis. Evaluation of reactive sites and polyconjugated substructures over MW distribution of lignins. *La Chimica e l'Industria*, 2006, No 2, 72-76.
5. G. Telysheva , G. Dobeles, D.Meier, T. Dizhbite, G. Rossinska, V. Jurkjane, Characterization of transformations of lignocellulosic structures upon degradation in planted soil, *J. Analyt. Appl. Pyr.*, 2007, **79**, N1, 52-60.
6. G. Telysheva, N. Mironova-Ulmane, T. Dizhbite, L. Jashina, A. Andersone. Synthesis of lignin-based hybrid materials using α -Keggin's type polyoxometalates as inorganic building blocks. *Latvian Journal of Physic and Technical Sciences*, 2006, no 2, 13-22.
7. T. Dizhbite, G. Telysheva, A. Skujina, A. F. Danil de Namor. Lignocellulosic-based products for enhancing mineralization of pesticide 2,4-D by soil-indigenous microflora. - In: *Biomass for Energy, Industry and Climate Protection*, Eds. D.O Hall, G. Grassi, H. Scheer. Ponte Press, Brussell-Luxemberg, 2004, pp. 2033-2036.
8. G. Telysheva, T. Dizhbite, A. Andersone, A. Volperts. Adsorption behavior of lignosulphonates on the interfaces water-inorganic/organic solids, used for paper production. J.P. Mota and S. Lyubchik (Eds.), *Recent Advances in Adsorption Processes for Environmental Protection and Security*, 2007, Springer, p.p. 55-64.
9. T. Dizhbite, N. Mironova-Ulmane, A. Volperts, A. Andersone, L. Jashina, T. Kärner and G. Telysheva, Elaboration and characterization of organic/inorganic hybrid nanoporous material incorporating Keggin-type Mo-Si polyanions. *J. of Physic, Conf. Ser.*, 2007, **93**, 012011, 1-6.

Plenary and Keynotes Addressed at International Conferences

1. Keynote Address: Supramolecular Chemistry in Water Decontamination. A.F. Danil de Namor. Third International Conference on Water Resources in the Mediterranean (WATMED), Tripoli, Lebanon, November 2006.
2. Plenary Lecture. The Lizardo Lecture. A.F. Danil de Namor, Calorimetry and Thermal Analysis Conference, CAICAT, Santiago de Compostela. Spain, July 2006.

Presentations to National and International Conferences.

1. G. Telysheva, T. Dizhbite, G. Lebedeva, V. Nikolaeva, A. de Namor. Adsorption – Chemical modification of wood processing waste for decontamination of ecosystem. – Intern. Conf.”” Monitoring Systems and Novel Technologies for Detection/Removal of Pollutants in/from Ecosystems, Buenos Aires, Argentina, April 18-22, 2004, p. 24.
2. G. Telysheva, G. Lebedeva, T. Dizhbite. Promoting roots development of plant, used for remediation of ecosystem. – Intern. Conf.”” Monitoring Systems and Novel Technologies for Detection/Removal of Pollutants in/from Ecosystems, Buenos Aires, Argentina, April 18-22, 2004, p.62.
3. G. Telysheva, T. Dishbite, V. Nikolaeva, A. Abacherli. Lignin products for decontamination of environment objects from pathogenic microflora. – 7th Inter. Forum” Bringing Lignin Back to the Headlines: Priority, Research and New Approach”, Barselona, Spain, April 27-28, 2005, p.p. 71-74.
4. G. Telysheva, G. Lebedeva, T. Dizhbite Regulation of sorption properties of commercial lignins by their modification Proc. International Conference «Physicochemistry of lignin», Arkhangelsk, 3 – 6 July 2005, p.p. 213-216.
5. G. Telysheva, T. Dizhbite, G. Lebedeva, G. Rossinskaja, G. Dobele, V. Nikolaeva. Si- and n-modified lignocellulosics: biodegradation in phytocenotic conditions and effects on soil microorganisms. Abstracts IBBS (International Biodegradation and Biodeterioration Symposium), Madrid, Spain, September 4-9, 2005, p.163.
6. G. Telysheva, T. Dizhbite, G. Lebedeva, V. Nikolaeva, A.F. Danil de Namor, S. Grigiskis. Influence of lignin products on efficiency of bioremediation of contaminated ecosystem objects. Abstracts IBBS (International Biodegradation and Biodeterioration Symposium), Madrid, Spain, September 4-9, 2005, p. 294.
7. G. Telysheva, T. Dizhbite, G. Lebedeva, V. Nikolaeva, N. Zaimenko. Regulation of lignocellulose materials sorption properties by modification for environmental application. Abstr. NATO Workshop Combined and Hybrid Sorbents. Fundamentals and Applications, Kiev, Ukraine, September 15-17, 2005, p.14.

8. V. Nikolaeva, N. Arhipova, G. Telysheva, T. Dizhbite, G. Lebedeva. Application of lignocellulosics for long-term stimulation of autochthonous microorganisms and remediation of soil. – Abstr. Int. Conf. EcoBalt'2005, May 2005, Riga, p. 154.
9. T. Bikova, G. Rossinska, T. Dizhbite, G. Telysheva. Multiwave UV/VIS detection at SEC analysis for the evaluation of reactive sites and polyconjugated substructures over MW distribution of lignins. Proc. Int. Conf. ITALIC'3 „Wood Derivatives and Agroindustry Waste Valorisation”, L'Aquila, Italy, June 23-24, 2005, p.p. 112-114.
10. T. Dizhbite, G. Telysheva, V. Jurkjane. Evaluation of antioxidant properties of lignin products from pulping processes. In: Advances of Chemistry and Processing of Lignocellulosics”, Proc. 9th EWLP, August 27-30, 2006, Vienna, p.p. 227-230.
11. G. Telysheva, T. Dizhbite, G. Lebedeva, J. Ponomarenko. Intercalation of Cu-cations into lignin products for alteration their ability for contaminated water cleaning. In Proc. Inter. Conf. EcoBalt'2006, May 11-12, 2006, Riga, p.p. 53-54.
12. G. Telysheva, T. Dizhbite, G. Lebedeva, J. Ponomarenko, U. Viesturs. Sorption active lignocellulosics modified for environmental application. In: Book of Abstracts, ISEB'2006, July 9-13, 2006, Leipzig, p. 407.
13. O. Bikovens, V. Jurkjane, T. Dizhbite, G. Telysheva, Wood wastes as raw material for biologically active polyphenols. Proceedings of 15th European Biomass Conference “From Research to Market Deployment”, Eds.: K. Maniatis, H.-P. Grimm, P. Helm, A. Grassi, ETA-Renewable Energies, Florence, Munich, 2007, p.p. 2118-2120.
14. G. Lebedeva, G. Telysheva, S. Rancane, L. Tiltina. Application of lignosilicon in growing of red clover (*Trifolium Pratense L.*). Proc. 6 Inter. Conf. Environment. Technology. Resources. Rezekne, Latvia, June 20-22, 2007, 141-149.
15. G. Lebedeva, I. Alsina, G. Telysheva. The influence of lignin containing products on cereals drought tolerance. Proc. 6 Inter. Conf. Environment. Technology. Resources. Rezekne, Latvia, June 20-22, 2007, 132-140.
16. G. Telysheva, T. Dizhbite, L. Jashina, A. Andersone, A. Volperts, N. Mironova-Ulmane, Synthesis of lignin-based inorganic/organic hybrid materials favorable for detoxification of ecosystem objects. Proc. Book, Italic 4 Intern. Conference: Science & Technology of Biomasses: Advances and Challenges. Materials, Chemicals & Processes from Agricultural and Forest Biomass. May 8-10, 2007, Roma, p.p. 304-307.
17. Dr. Tamimi (PHG) participated at the Conference organized by the European Desalination Society in November 2006 in Trieste (Italy).

18. Dr. Tamimi (PHG) has submitted the paper entitled ‘Socio-economic based water pricing of desalinated water’ (Case Study-Palestine). This will be presented at the UNESCO Conference in Amman in September 2007.
19. N. Manaf, N. Tahlil, L.Mandi and N.Ouazzani ; 2008, Tolerance of Lucerne and okra to water irrigation salinity: eco-physiological and biochemical criteria. WATMED IV, March, 2008, Algeria.
20. S. de la Iglesia-Turiño, C. Caldelas, J.L. Araus, A. Febrero, J Bort. “Salinity and zinc stress: impact in tomato to plant development”. TIWAMED International Conference on “Technologies for Industrial Wastewater treatment and reuse in the Mediterranean Region” Djerba, Tunes 2007, 24-26 May. Proceedings, 283

Public Talks, Teaching and Demonstrations.

- Lectures given by the Coordinator at the National Academy of Sciences, University of Lujan and University of Nordeste (Argentina), Dec 2006.
- Training of high school students in water desalination at the thermodynamic laboratory.
- Inaugural lecture at the National Congress of Toxicology , Neuquen, Argentina, September 2007.
- Lecture in Tunes, Tunisia at the infestation of the British Council, Tunisia in January 2009.
- Demonstration on the use of the materials by the Coordinator at the University of Cadi Ayyad, Morocco, December 2007.
- Desalination of brackish water solution for the future to the water scarcity in Morocco. In fourth edition of national week of sciences organized by the University of Cadi Ayyad, Marrakech. 17-24, April 2006.
- Presentation of the progress of Irriseasoil project in the ‘Journnéé d’étude sur la reserve de biosphere des oasis du sud Marocain. Organised by the Office de Mise en Valeur Agricole De Ouarzazate (ORMVAO) in Ouarzazate, 30 October 2006.
- Participation on Latvian national and regional public meetings and exhibitions with lectures and demonstration materials revealed efficiency of siliceous products synthesized on the basis of wood processing waste, in order to organize the public acceptance. (June 2007 - two public lectures on the Conference “Environment. Technology. Resources”, Rezekne; May 2007 – presentation on the Conference Eco-Balt’2007, Riga). G. Telysheva and co-workers.
- Training of students of the University of Latvia: involvement of students of Chemical and Biological department into the work for the IRRISEASOIL Project on study of sorption and complexing properties of Si-containing lignin products and assessment of their biological activity. G. Telysheva and co-workers.
- Consulting and training of professional agronomists, amateurs and farmers for usage of Si-containing lignin products at cultivation of agricultural plants, vegetables, flowers and ornamental plants *via* lectures all over the Latvia, leaflets and little test samples preparing for end-users. The team have arranged good contacts with the Centre of agricultural consulting and

education (Jekabpils district) working for dissemination of biological agriculture in Latvia. G. Telysheva and co-workers.

-Preparing the articles for public press and broadcast talks (2005 – 2007 years– three articles in the Latvian newspapers and magazine in Latvian language and one in Russian language). G. Telysheva and co-workers.

-Development of the contacts with end-users working in the area of biological agriculture of the designed Si-products. G. Telysheva and co-workers.

-Questionnaires regarding Irriseasoil aims in Palestine (1st Activity Report), Dr. Tamimi and Co-workers.