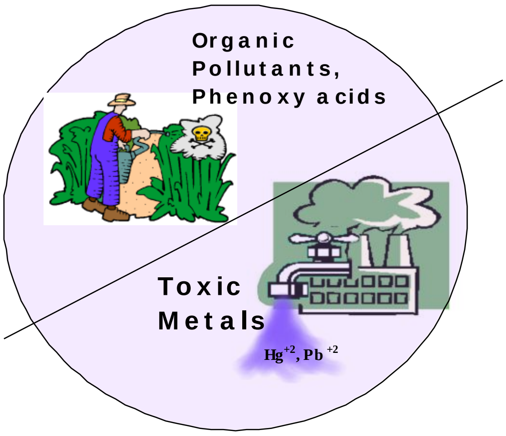

Final Activity Report

Project Number INCO-CT-2004-509159

Project Acronym: MEDINDUS

Project Title: Advanced Technologies for the Treatment of Industrial and Coastal Waters of the Mediterranean Region

Instrument: STREP

Thematic Priority:

Title of Report: Activities of MEDINDUS Months 25-30

Period Covered: 1/10/04 – 30/3/08

Date of Preparation: February 2009.

Start Date of Project: 1/10/04

Duration: 42 Months

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http://www.surrey.ac.uk/Chemistry/staff/medindus/wp1.shtml

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- **Universitat de Barcelona, Departamento de Fisiologia Vegetal, Barcelona, Spain (Partner 3).**

- **University of Cadi Ayyad, Faculty of Sciences Semlalia, Semlalia, Marrakech, Morocco (Partner 4).**
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Results;

The project was divided into six work packages as detailed below. Deliverables attached to each work package are also indicated between brackets.

Workpackage 1. The Solution Chemistry of Industrial Wastewaters and water coastal zone of the Mediterranean Region. (D1-D3)

Workpackage 2. Receptors: Synthesis, Characterisation and Computer Simulation Studies. (D4-D8).

Workpackage 3 Grafting Receptor into Silicates (D9-D14)

Workpackage 4 Process Development (D15-D20)

Workpackage5 Use of Soil applied receptors for toxic metal phytoremediation processes, (D21-D23).

Workpackage 6 Public Awareness and Understanding of Regional Environmental Problems. Enhancing University-Industry links

The results obtained for each work package including the contribution of each Prtner are now described.

Workpackage 1 (D1-D3)

The aim of this work package was to acquire knowledge about the chemical speciation in wastewater in an attempt to synthesize novel receptors for their removal from water. A tannery industry and an olive mill industry were selected in Marrakech city and a phosphate industry in the coastal city, Safi situated at 140 km from Marrakech city (Morocco) (Partner 4). As far as Tunisia is concerned, the activities were geared to these industries located in the coastal zone of Sfax (phosphate , tanning and olive oil industries) (Partner 6). Tanning is the act of converting animal hides and skins into leather. These are made mainly of proteins and minor amounts of lipids. Preliminary tannery processes or beam house process (cleaning, trimming etc) prepare the hide protein so that all undesirable impurities are removed, leaving the skin in a receptive condition to absorb the chromium or other tanning agents used in subsequent operations. Thus the main pollutants in wastewater discharges are from the tanning processes. Tanneries produce highly toxic liquids and solid wastes containing fats, sulphur compounds, chromium, hair or wool and small skin pieces. Beam house flows contain high levels of suspended solids and dissolved organic matter, curing salt and grease, in addition to unused process chemicals (particularly dissolved sulphides) they will be also alkaline and will have a high oxygen demand. Tanning produces acidic effluents, which, when derived from chromium tanning will contain unused trivalent chromium salts. The leather industry is very relevant to the national economy in Tunisia and Morocco but leads to a great deal of pollution involving heavy metal cations.

Other important source of income for these countries is the olive activity but it generates a great deal of nuisances due essentially to large volumes of waste water (margins) delivered from all production units. The high concentrations of polyphenols are a matter of great concern.

Title

The ability calix[4]pyrrole (Fig. 2b) to uptake *p* and 2-nitrophenol from water was examined by Partner 2.

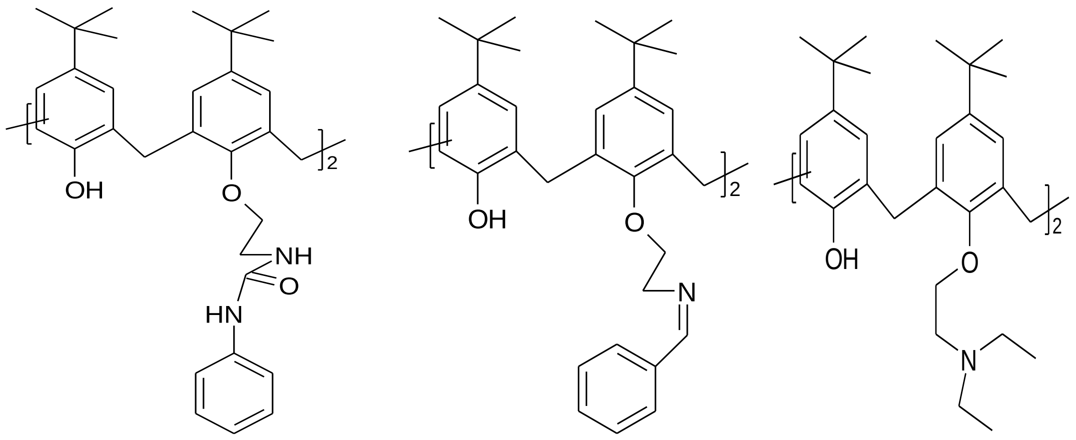
The chemical characterisation of these wastewaters showed for Morocco high concentrations of chromium and heavy metals (D2) for the tanning industry and an acidic pH while waters from the phosphate industry showed high amounts of phosphates. Heavy metals are also found in quantities much higher than those recommended by the WHO. Characterisation of water from the olive oil industry showed a very high organic load expressed as COD and BOD. Another matter of concern was the high concentrations of polyphenols found in the margin, (D1). The picture emerging from analytical measurements carried out in Tunisia showed a similar pattern. Thus the analysis of micro pollutants in collected samples from the tanning industry showed that organic pollutants could represent the main problem of these effluents as compared to the Tunisian Emission Standard for water drainage in the public sea. Indeed COD and BOD exceeded the values fixed by the Tunisian Standard. Another group of contaminants are some of the heavy metals as shown in the First Activity Report for this Contract.

Regarding the olive oil mill wastewater thus was also characterised by the very high organic load (COD, BOD and polyphenols), (4.86 ± 0.22 g/l) being 3,4-dihydroxyphenyl ethanol and *p*-hydroxy phenyl ethanol which are the most abundant monomers in olive mill wastewater. Microbiological analysis of the effluents from the phosphate, tanneries and olive oil processing industries from Morocco and Tunisia were carried out and these were discussed in the Activity Report (Year 1) (D3)

Having concluded the evaluation of Industrial wastewater of the coastal zone of the Mediterranean Coast we proceeded with the research described under WP2.

Workpackage 2 (D4-D8)

The aim of this work package was to synthesize and characterise structurally and thermodynamically selective receptors for the removal of pollutants from water. The synthetic work was aimed by computer modelling (D4), (Partner1). Thus molecular modelling on the flexible lower rim of calix[4]arene derivatives and their interaction with organic pollutants and phenoxy compounds containing carboxylic acids (herbicides which are a problem in Mediterranean countries) using the Hyperchem Computer System was carried out. Thus a series of calix[4]arene receptors showed interaction and therefore we proceeded with their synthesis and characterisation. These shown in Fig. 1 are selective receptors for organic pollutants (D5, Partner 1) and phenolic compounds (D6, Partner 1).



(a) **(b)** **(c)**

Fig. 1 Receptors based on calix[4]arenes selective for organic and phenolic compounds.

These were characterised by ^{1}H NMR and their interaction with organic pollutants was also assessed by this technique. As far as **1a**, is concerned this is a good hydrogen bond donor for carboxy anions. These hydrogen bonds are also responsible for the pre-organisation of these receptors. It is well established that self association of urea moieties takes place in aprotic media. For this reason the main goal of these studies were

i) Pollutants containing acidic group are capable of binding with these receptors.

ii) The binding process would be restricted by the strong intra and inter molecular association of host molecules.

With this purpose in mind receptor **1a**, was designed and synthesized. The main reason for adopting this strategy was to reduce inter and intra molecular association of the host molecules and to enhance their interaction with guest species. Terminal phenyl moieties were introduced in the arm groups of **1a**, to boost their mutual reception. This was successfully achieved since 1 showed moderate interaction as demonstrated by ^{1}H NMR. Details given in the Activity Report for year 1. As far as **1b** is concerned, this receptor can be regarded as a self contained receptor with strong donor groups. Thus **1b** showed strong interaction with chlorophenoxy acids in $CDCl_3$. This statement was corroborated by the downfield shifts observed for the protons in the proximity of the nitrogen and those of the phenyl group in the pendant arms. Concerning **1c** the significant chemical shift changes observed in the protons close to the amino groups strongly suggest that the interaction of this receptor with phenoxy acid takes place through the amino group of the receptor with a possible proton transfer reaction from the acid to the N atom of the receptor.

The ability of cyclodextrins to remove phenols from water was investigated by Partner 2. Thus fluorescence studies were carried out involving β-cyclodextrin (Fig 2 a) and α-naphtol and the formation of a 1 : 1 complex in water was detected. It was found that the optimum mass (0.12 g) for the uptake of naphtol (1 x 10^{-5} moldm^{-3}) by β-cyclodextrin was determined as a function of concentration of naphtol in aqueous solution. (D6) As far as selective receptors for phosphates (D7) are concerned extensive research was carried out on receptors based on calixarenes and calipyrroles.

(a)

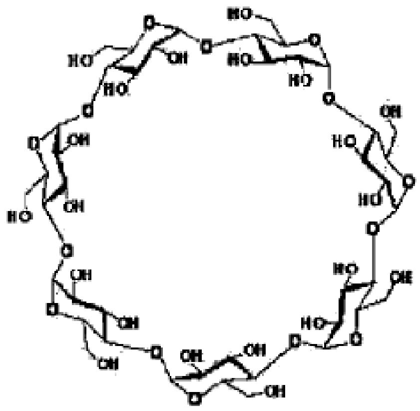
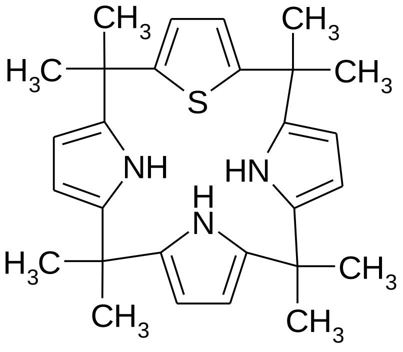
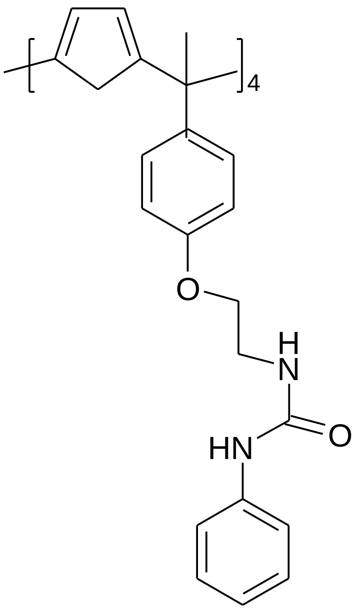


Fig. 2 Structure of β-cyclodextrin (a)

These are shown in Fig.3. These are calix[3]thienol pyrrole,**4,**and meso-tetramethyl-tetra[N-(2-phenoxy ethyl)-N-phenyl urea] calix[4] pyrrole,**5,** the ααββ isomer of meso tetra methyl tetrakis β hydroxyphenyl calix[4]pyrrole,**6** , and a calix[4]arene derivative,**7.**



4s



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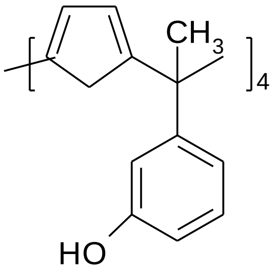

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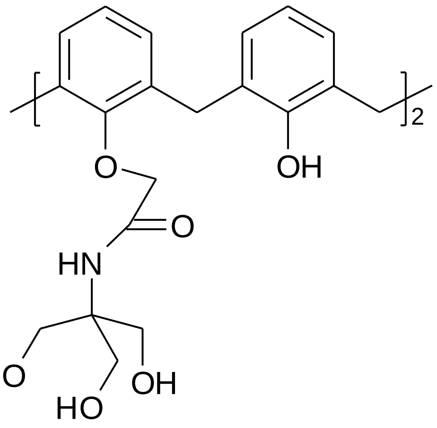

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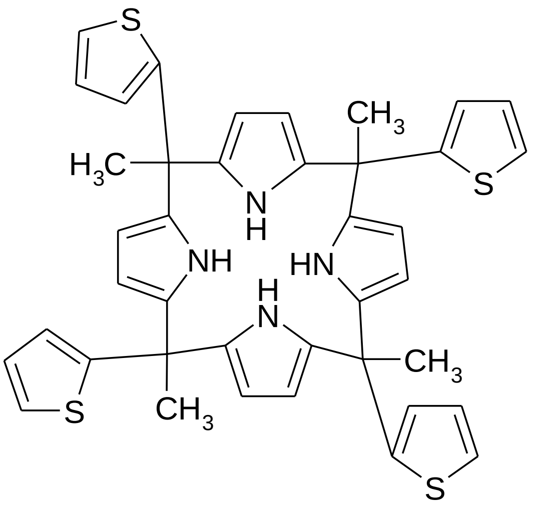
Fig.3 Receptors selective for phosphates

As far as toxic metal cations are concerned, the following calix[4]pyrrole derivatives **8** and **9** and a calix[4]resorcarene,**10** were designed and successfully used as reflected in the list of research publications cited in the final part of this report.



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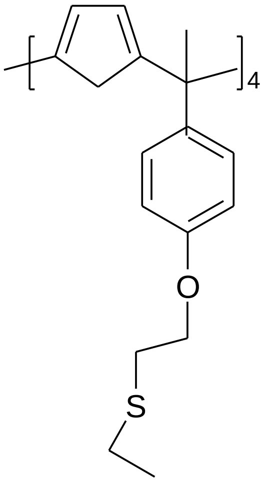

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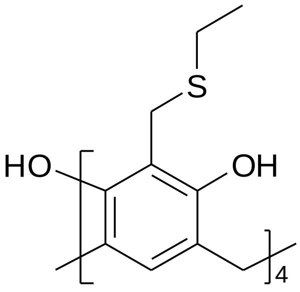

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Fig. 4. Receptors designed for toxic metal cations.

Having synthesized and characterised these receptors by ^{1}H NMR and microanalysis, we proceeded with the thermodynamics and kinetics of these systems to determine in quantitative terms the affinity of these receptors for one pollutant relative to another (D8, Partners 1 & 2) in order to select the receptors to be attached to silicates or polymerised. Regarding the thermodynamics of these systems prior to proceed with these measurements, ^{1}H NMR and conductometric techniques were explored to gain information regarding the site of interaction between the receptor and the pollutant and the composition of the complex respectively. These studies demonstrated that receptors **6-10** interact with metal cations and anions and the composition of the complexes was established. The thermodynamic for these systems are shown in Table 1 for fluorides and phosphates and in Table 2 for toxic metal cations. Thermodynamic data for the interaction of β-cyclodextrin with phosphates and chromate in water (Partner2) are listed in Table 3.

Table 1. Thermodynamic parameters for the interactions ligands (5-9) with anions in acetonitrile and N,N-dimethylformamide at 298.15 K.

Ligand	Anion (L : X)	log K_s	$\Delta_c G^o$ (kJ mol^{-1})	$\Delta_c H^o$ (kJ mol^{-1})	$\Delta_c S^o$ (J mol^{-1} K^{-1})
a) <u>Acetonitrile</u>					
	F^-				
8	1:1	3.65±0.03	-20.8±0.1	-10.6±0.2	34
9	1:1	4.81±0.06	-27.5±0.3	-16.4±0.3	37
6-ααββ	1:1	3.08±0.02	-17.6±0.1	-97.1±0.8	-267
6-ααββ	1:1	5.00±0.04	-28.5±0.2	-31.4±0.3	-10
6-αβαβ	1:2	4.72±0.01	-27.0±0.1	-61.5±0.3	-116
	Overall	9.72	-55.5	-92.9	-126
7	1:1	5.69±0.03	-32.4±0.2	-14.4±0.3	60.7
	$H_2PO_4^-$				
6-ααββ	1:1	3.60±0.02	-20.54±0.04	-24.55±0.06	-13
6-ααββ	1:2	2.50±0.03	-14.43±0.04	-22.63±0.06	-28
	Overall	6.1	-34.91	-47.2	-41
6-αβαβ	1:1	4.80±0.02	-27.4±0.3	-20.2±0.1	25
6-αβαβ	1:2	4.7±0.1	-15.2±0.5	-29.9±0.6	-50
	Overall	9.46	-42.6	-50.1	-25
7	1:1	3.84±0.06	-21.9±0.3	-46.3±0.1	-82
	$HP_2O_7^{3-}$				
6-ααββ	1:1	3.26±0.02	-18.6±0.1	-38.5±0.1	-67
6-ααββ	2:1	3.55±0.02	-20.2±0.1	-127.5±0.2	-359
	Overall	6.8	-38.8	-166	-426

6-αβαβ	1:1	3.97±0.03	-22.6±0.5	-65.4±0.1	-143
6-αβαβ	2:1	3.25±0.08	-18.6±0.7	-83.2±0.2	-217
	Overall	7.22	-41.2	-148.6	-360
7	1:1	5.10±0.08	-29.1±0.5	-59.3±0.2	-72
7	2:1	3.51±0.08	-20.1±0.5	-57.3±0.2	-125
	Overall	8.61	-49.1	-116.6	-226
b) <u>N,N-dimethylformamide</u>					
	F^-				
6-ααββ	1:1	3.4±0.1	-19.2±0.8	-13.6±0.3	19
6-ααββ	1:2	3.2±0.2	-18.2±1.1	-7.6±0.2	35
	Overall	6.6	-37.4	-21.2	54
7	1:1	4.30±0.05	-24.5±0.3	-12.1±0.7	41.6
	$H_2PO_4^-$				
6-ααββ	1:1	4.80±0.1	-27.4±0.6	-18.8±0.3	29
7	1:1	4.06±0.02	-23.15±0.09	-26.4±0.2	-10.8
	$HP_2O_7^{3-}$				
7	1:1	4.91±0.09	-28.0±0.5	-40.75±0.03	-42.7
7	2:1	3.82±0.08	-21.8±0.5	-35.72±0.06	-46.7
	Overall	8.7	-50	-76.47	-89.4

Table 2. Thermodynamic parameters for the interaction of ligands (8-10 and 7) with metal cations in acetonitrile and N,N-dimtheylformamide at 298.15 K.

8					
	($L:M^{n+}$)	Log K_s	$\Delta_c G^o$ (kJ/mol)	$\Delta_c H^o$ (kJ/mol)	$\Delta_c S^o$ (J/mol.K)
Acetonitrile					
Hg^{2+}	(1:1)	2.96±0.06	-16.9±0.3	-71.6±0.4	-184
9					
Hg^{2+}	(1:1)	3.72±0.02	-21.26±0.01	87.9±0.7	-224
Hg^{2+}	(1:2)	1.85±0.01	-10.53±0.03	-7.3±0.4	11
	Overall	5.57±0.03	-31.79±0.04	-95.3±0.3	-213
Ag^{+}	(1:1)	3.2±0.3	-18.1±0.5	-54.9±0.1	-124
10					
Pb^{2+}	(1:1)	2.83±0.01	-16.14±0.01	-35.7±0.1	-66
Ag^{+}	(1:1)	3.20±0.01	-18.25±0.01	-28.3±0.5	-34
7					
Pb^{2+}	(1:1)	3.50±0.04	-20.0±0.2	-30.8±0.1	-36.3

Table 3. Stability constants of β-cyclodextrin with pollutants (organic and chromate) at 298 K in water.

Receptor	**Pollutant**	**K_s**
β-cyclodextrin	4-nitrophenolate	5.58
β-cyclodextrin	2-nitrophenolate	5.52
β-cyclodextrin	Queicetin	6.75
β-cyclodextrin	Chromate	6.54

Conclusion

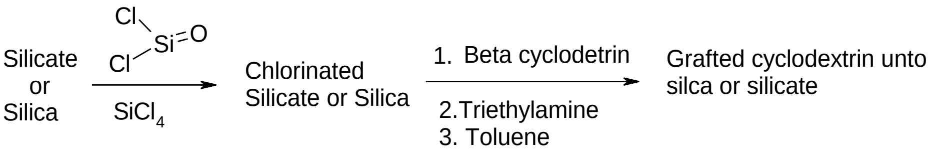
From the above discussion it follows that ten new receptors have been designed and their interaction with pollutants was demonstrated following the thermodynamic characterisation shown in Tables 1, 2 & 3. The next workpackage describes the research carried out with the aim of grafting receptors to silicates or via polymerisation.

Work package 3 (D9-D14)

The aim of this work package was to graft the receptors into solid supports in order to obtain novel and easily recyclable materials forwater decontamination. Receptors within the context of this work are decontaminating agents defined as these chemical entities designed to target a variety of pollutants known to pose environmental and human threats. For practical applications of these receptors for the removal of pollutants from contaminated sources avoiding the use of organic solvents (polluting agents) it is necessary to graft these receptors into solid supports. In this way these receptors adopt the appropriate physical state to be used in column or batch experiments for eliminating pollutants from water and soil. These should be easily recyclable; this property is of fundamental importance for commercial purposes. Partners involved in this work package were Partner 2 (Beirut Arab University, Lebanon), Dr Hassan Hammud, Partner 4 (Universite Cadi Ayyad, Morocco), Dr Naaila Quazzani and Partner 1 (University of Surrey, UK), Prof Angela F. Danil de Namor. Achievements are now described.

Immobilisation of β-cyclodextrin on Silica, talc (magnesium silicate hydroxide) and kaolin (aluminium silicate hydroxide) D9. Dr Hassan Hammud, Partner 2, BAU.

β-cyclodextrin was successfully immobilised onto silica gel, kaolin and talc according to Scheme 1 using either thionyl chloride ($SOCl_2$) on silicon tetrachloride, $SiCl_4$ as the chlorinating agents for silica and silicates.



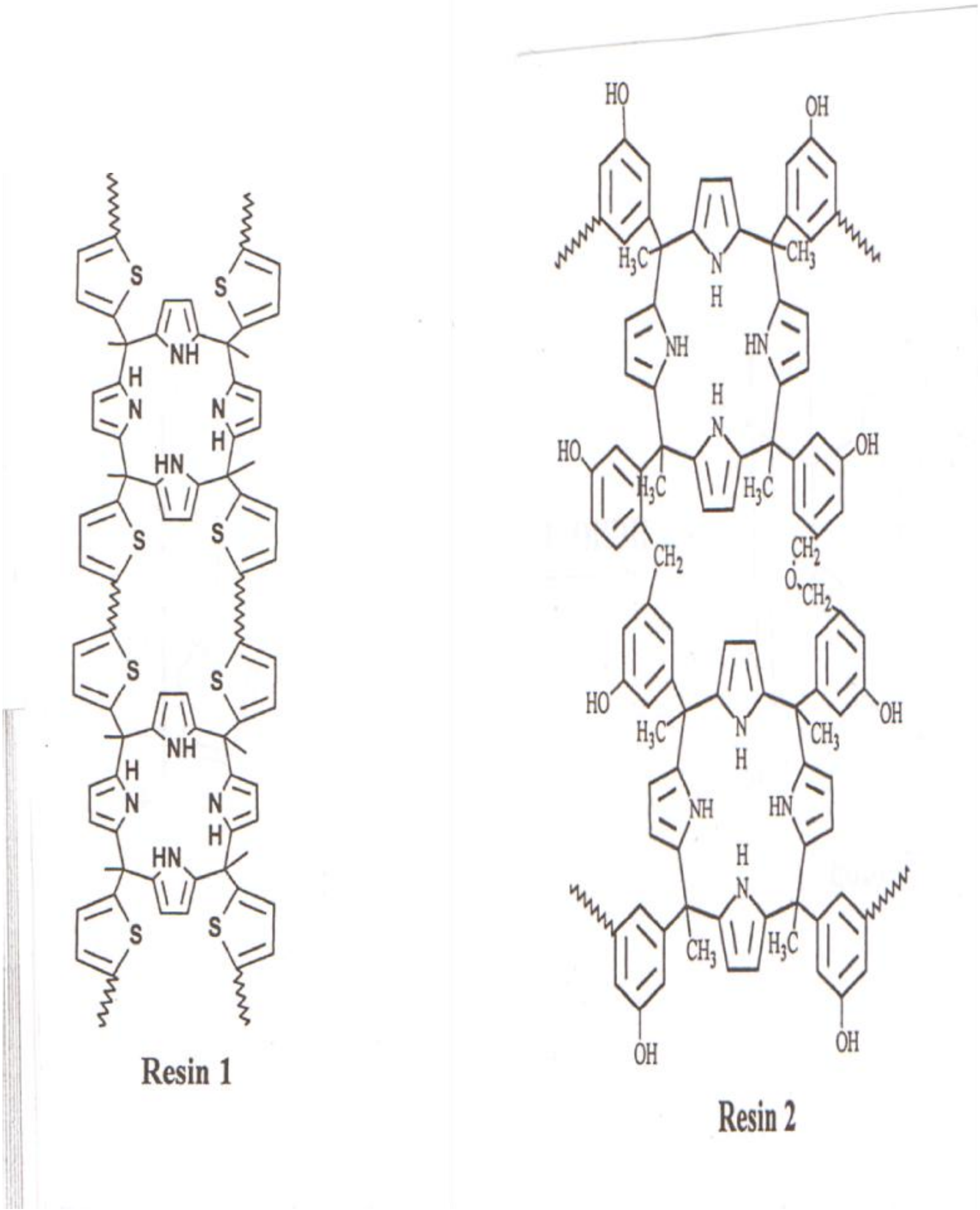
Scheme 1. Grafting cyclodextrin unto Silicates or Silica

Amounts of cyclodextrin introduced into silica was ~4.21% calculated by elemental analysis. Further characteristics of the material were established through thermal analysis, FT-IR and UV-Vis spectroscopy as detailed in Report for year 2

Availability of receptors with resorcarene and calixpyrroles as building blocks (D 11)

On the basis of the thermodynamic data and the possibility of grafting the receptors into solid supports two methods were used

1, Direct polymerisation with formaldehyde (HCHO) in sulphuric acid (H_2SO_4) or
2.Their attachment to silica.
1. Direct Polymerisation
For direct polymerisation the receptors selected were 8 (Resin 1) and 6-ααββ (Resin 2) The resins synthesised are shown in Figure 5 and its isomer with the OH group in position 4 instead of 3 (Resin 3).



Resin 1

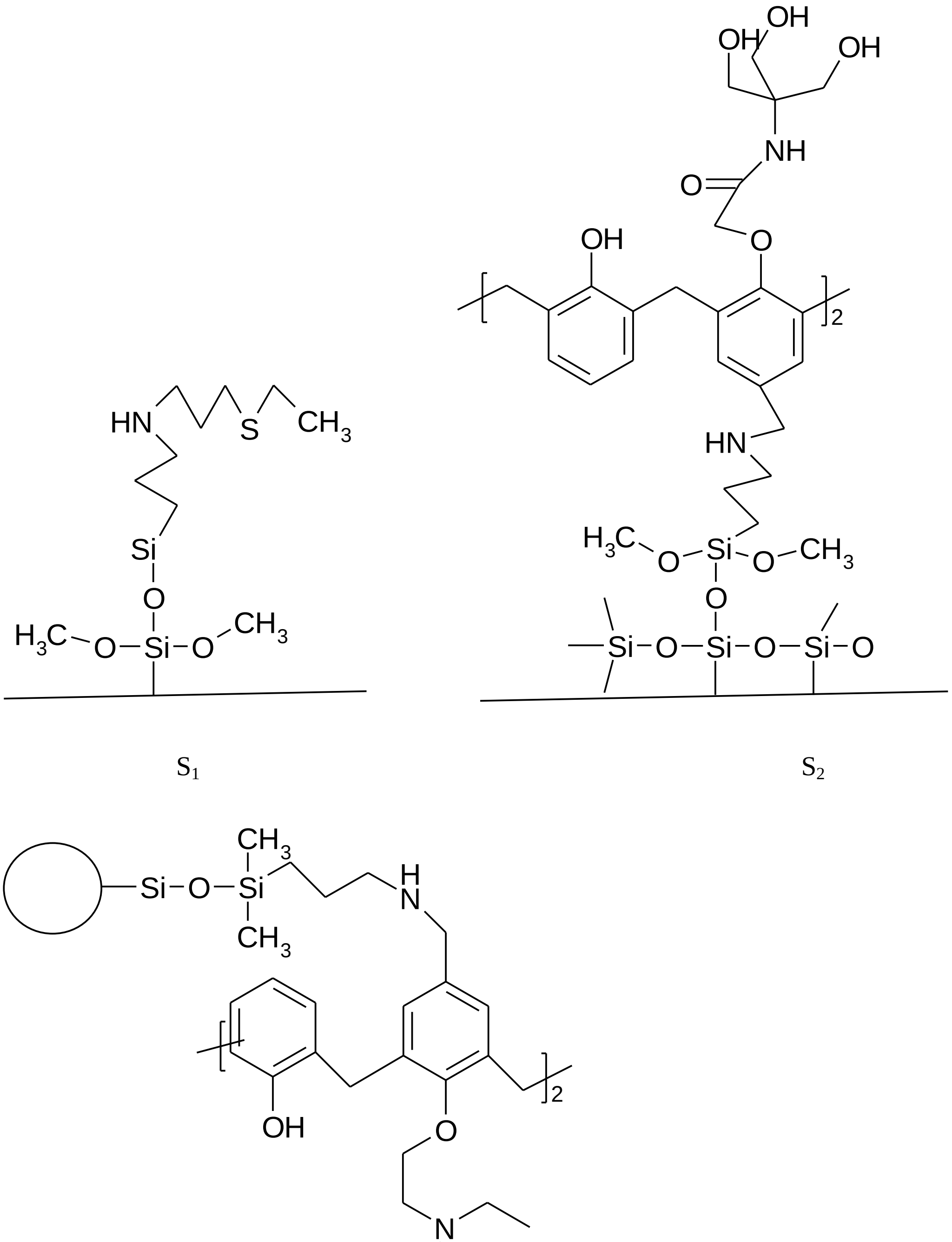
Resin 2

Fig. 5. Structures of resins 1 (containing receptors 8) and resin 2 (containing receptor 6-ααββ).

<u>Availability of silica based materials</u>, S_1, S_2, S_3 (D11)

ii) Attachment to Silica

Silica based materials containing an acrylic functional group with sulphuric donor atoms (soft donor atoms), S, receptor T, and receptor 3, S_3 were synthesised in order to make available materials with selective properties for the target pollutants. These are shown in Figure 6.



S_1

S_2

S_3

Fig.6. Silica based materials, S_1, S_2 (containing receptor 7) and S_3 (containing receptor 3).

Information about the structure of the modified silicates. (D12)

As far as the attachment of β-cyclodextrin to silica gel, talc and kaolin is concerned, thermal analysis data showed that the percentage of β-cyclodextrin attached to their silicates were 14.8, 15.7 and 16.23 for silica gel, talc and kaolin respectively, when the corresponding temperatures were 325, 280 and 210°C. Elemental analysis gave for β-cyclodextrin attached to silica gel; C: 4.19%, H: 0.77% in agreement with the calculated values (C: 4.21%, H: 0.7%). Attachment of this ligand to talc gave C: 4.11%, H: 0.78%, which are in agreement with the calculated values (C: 4.21%, H: 0.7%). Again good agreement was found for the β-cyclodextrin attached to kaolin (% found C: 4.21, H: 0.7; % calculated C: 4.21, H: 4.17). Comparison of these data with those of the silicate alone (silica gel, C: 0.62%, H: 0.61%; talc, C: 2.87%, H: 0.008%; kaolin, C: 0.08%, H: 1.05%) clearly reflect that indeed receptors were attached to the silicates.

Regarding calix[4]pyrrole polymers (fig.5), mass spectrometry was used to gain information about the number of monomers contained in each oligomer. Thus the residual peak observed at 1411.3 for Resin 1 indicated the formation of a dimer as shown in Figure 5. On the other hand the residual peaks found between 1600-1800 for Resins 2 and 3 indicated the formation of a dimer while the peaks observed between 2600-2800 reflected the formation of a molecule which is at least three times the molecular weight of the monomer. Elemental analysis on silica, silica silane and modified silicas (S_1, S_2 & S_3) was carried out to gain information regarding the percentage of C, H and N found.

Having characterised these materials experimental work was carried out to establish the capacity of these new materials to uptake the pollutants from water and this is now discussed.

Quantitative information regarding the capacity of silicates to uptake pollutants and distribution data (D13)

Spectrophotometric studies were performed to determine the capacity of immobilised cyclodextrin to uptake pollutants from water taking the β-cyclodextrin-kaolin material as representative. It was found that after an equilibration period of 24 hours, the maximum capacity of these materials to uptake 4-nitrophenolate, 2-nitrophenolate, chromate and phosphate from water was 11.99, 12.70, 14.78 and 3.96 mg/g of material respectively.

Column experiments were also carried out.

Methodology for recovering silicates . Recycling (D 14)

Several tests were carried out to recycle the materials.The most efficient one consisted in a treatment with citric acid 0.1 M. Efluents were analized and the washing of the column containing the material was carried out until no trace of pollutant was detected. Given the low cost of this organic acid, the easy recycling of these materials enhances the possibility of their commercialisation.

Conclusions:

From the above discussion it follows that nine new materials were synthesised and characterised and their capacity for the removal of pollutants was determined. The selective behaviour of these solid materials was demonstrated. In addition these materials can be easily recycled. Therefore the aims of work package 3 were successfully achieved.

Work package 4 (D15-D20)

The main aim of this work package was to proceed with process integration and development using the new materials synthesised by Surrey to target pollutants found in the tannery, phosphate industry and olive mills in the Mediterranean Region.

Computer Calculations, design of the process and experimental plants (D 15) and Optimised Hydrodynamic parameters (D 16)

Following an overview of the problems facing the environment as a result of industrial activities, the first step following the computer calculations involved hydrodynamic investigations with the material based on calix[4]arene sent by Partner 1. It was found that the material provided was very hydrophobic. Due to the low particle size of the material as shown through microscopic analysis, it was found that the pressure loss was too high for a fixed bed or a fluidisised bed application. Therefore a re-engineering of the suggested process was carried out (Partner 5). Therefore following further characterisation of the materials sent by Surrey, S_1, S_2 & R_1 (density, S_m BET and particle size) a number of processes were investigated. These were; i) fixed bed continuous flow reactor, ii) suspension batch reactor with subsequent sedimentation, iii) suspension continuous flow reactor with cross flow membrane filtration. The parameters for the design of these systems were calculated at laboratory and Pilot Plant scale. The fixed bed continuous flow reactor assumed small particle size distribution. Therefore it was required that the material needed to be sieved before application which means that the amount of unsieved material was twice higher for each material than the calculated value. The continuous flow reactor with microfiltration membranes has no particle use limitation. All three materials tested were found suitable for this process variant. The disadvantage with respect to the fixed bed continuous flow reactor and the suspension batch reactor with subsequent sedimentation was the higher energy consumption due to the cross flow velocity and abrasion of materials due to high shear forces.

Process Data from Synthetic Wastewater. (D !7)

Partner 5 decided to continue with synthetic wastewater and to focus on the methodological investigation and modelling of the process. Partner 6 continued the experiments in Tunisia with real effluents. The main results are summarized in the following Section

Phosphate uptake

The silica based materials (properties and characteristics were described previously) which were both suited for phosphate uptake were further investigated for their sorption capacities. The experiments were performed with different initial PO_4^{3-} concentrations and solid to liquid ratios. The experiments were performed for a minimum of 20 hours to achieve equilibrium conditions.

The results in Fig. 7 clearly demonstrate that no phosphate uptake can be observed at low concentrations in the range of 1 mg L^{-1}. In contrast, granular ferric iron adsorbs about 13 mg P per g. Reasons for these results might have been the small amount of material applied and the low phosphate concentration. Therefore, it was decided to investigate the solid to liquid ratio at higher initial phosphate concentrations which are typical for phosphate industry effluents.

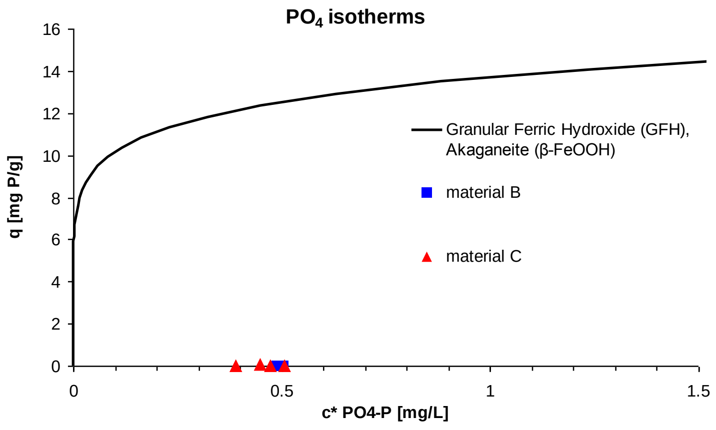
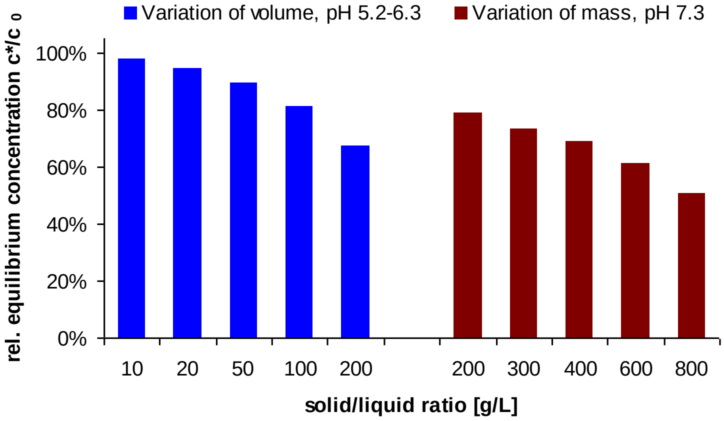
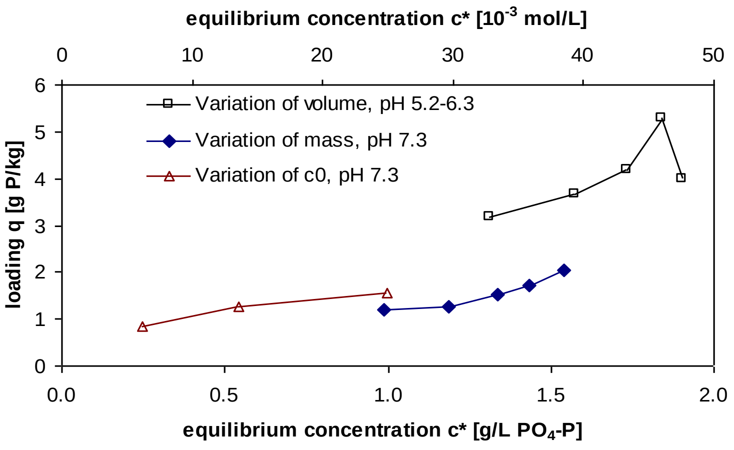
Fig. 7	Phosphate uptake for low concentrations and in comparison to other material
Material	Silicate Based material and Granular Ferric Hydroxide (GFH), a = 280 m^2 g^{-1},
PO_4^{3-} uptake Temp. = 28° C	

Fig. 8 shows the reduction in phosphate concentration as a function of the solid to liquid ratio. The experiments were started at an initial concentration of 2,000 mg L^{-1}. Adsorption of phosphate is detectable at solid/liquid ratios higher than 20 g/L. Due to edge conditions it is not possible to increase the solid/liquid ratio above 800 g/L. Nevertheless, 50 % of the phosphate was taken up by material C at 800 g L^{-1}.

Fig. 8 Phosphate uptake as a function of the solid to liquid ratio	
Material	Silicate Based Material
PO_4^{3-} uptake initial concentration: 2000 mg P L^{-1} solid/liquid ratio: 10–800 g L^{-1} Temp. = 28° C	

The experimental results can be plotted as an isotherm which is shown in Fig. 9 It is obvious that maximum loadings of more than 5 g P per kg can be achieved. The pH is influencing the capacity by more than 50 %; at an equilibrium concentration of 1.3 g PO_4^{3-}-P L^{-1} the loading can be increased from 1.7 to 3.3 g P g^{-1} by decreasing the pH from 7.3 to 5.2-6.3. At neutral pH the PO_4-phosphorus capacity of the material is 1–2 g P kg^{-1}.

Fig.9 Phosphate isotherm	
Material	Silicate Based Material
PO_4^{3-} isotherm Temp. = 28° C	

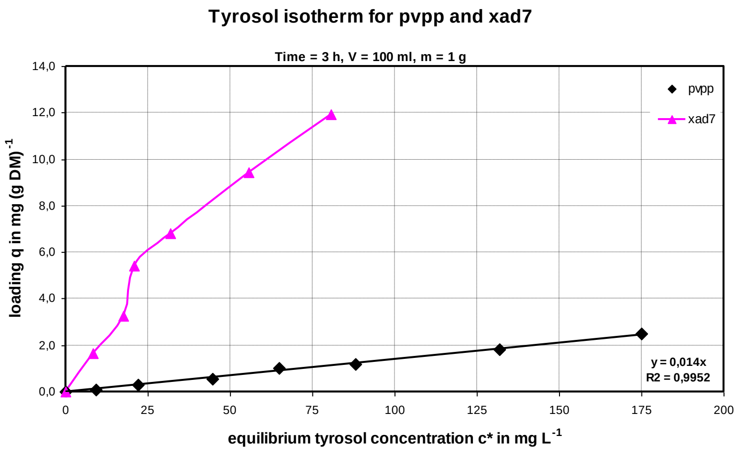
Polyphenol uptake

Olive mill wastewater contains a large fraction (up to 80 g L^{-1}) of polyphenols which can be divided into 12 classes starting with the simple C_6-phenols up to the complex condensed tannins $(C_6\text{-}C_3\text{-}C_6)_n$. More than 100 substances were identified. The composition and the absolute concentrations vary remarkably depending on the type of olives, the climatic conditions, the type of processing and the storage time etc. (see Scientific Report 1).

Hydroxytyrosol is amongst the substances with the highest concentrations (1 g L^{-1} in fresh and up to 3.5 g L^{-1} in stored OMW) and a high market potential due to the price of approximately 50 € per gram. Therefore it was chosen as a standard substance for the experiments.

Fig 10 shows the results of experiments with PVPP and XAD7 as sorption materials. PVPP (approx. 170 Euro kg^{-1}, small amounts) is an insoluble, high molecular weight, cross-linked form of polyvinylpyrrolidone. It was chosen because it complexes with phenolics and alkaloids. XAD7 (approx. 100 Euro kg^{-1}, small amounts) is a nonionic macroreticular resin that adsorbs and releases ionic species through hydrophobic and polar interactions; usually used under isocratic conditions. It is a weakly polar **adsorbent resin for** compounds up to 60,000 MW which in general is applied for: insulin, fulvic and humic compounds, dry waste, organic removal and recovery, and antibiotic recovery.

XAD7 showed the highest performance with loadings of 12 mg $(gDM)^{-1}$ at a concentration of 80 mg tyrosol per litre. It can be expected that the loading will increase with higher concentrations. Nevertheless, for continuous operation the higher range of concentrations is not as much of relevance as the lower range. The reason is the low effluent concentration of less than 10 mg L^{-1} which influence the performance of the process tremendously. Assuming a low XAD7 loading of 2 mg $(gDM)^{-1}$ the value of the separated hydroxytyrosol is 100 € per kg of XAD7. Therefore, the return of investment will be achieved after the first cycle of loading and recovery (XAD7: 100 € kg^{-1}).

Fig.10 Tyrosol isotherm	
Material	PVPP and XAD7
Target substance: tyrosol Time: 3h Temp.: 28° C	

2.1.3 Reactor

The results summarised in deliverable 15 recommended to apply a fixed bed continuous flow reactor. The flow rate as well as the influent and the effluent concentrations are given. Hydrodynamic calculations were completed and are documented in deliverable 16. Additionally, it was necessary to determine the breakthrough curve which is shown in Fig. 11.The model and the operational parameters can be summarized by the following equations which reduce the number of parameters from 10 to 4

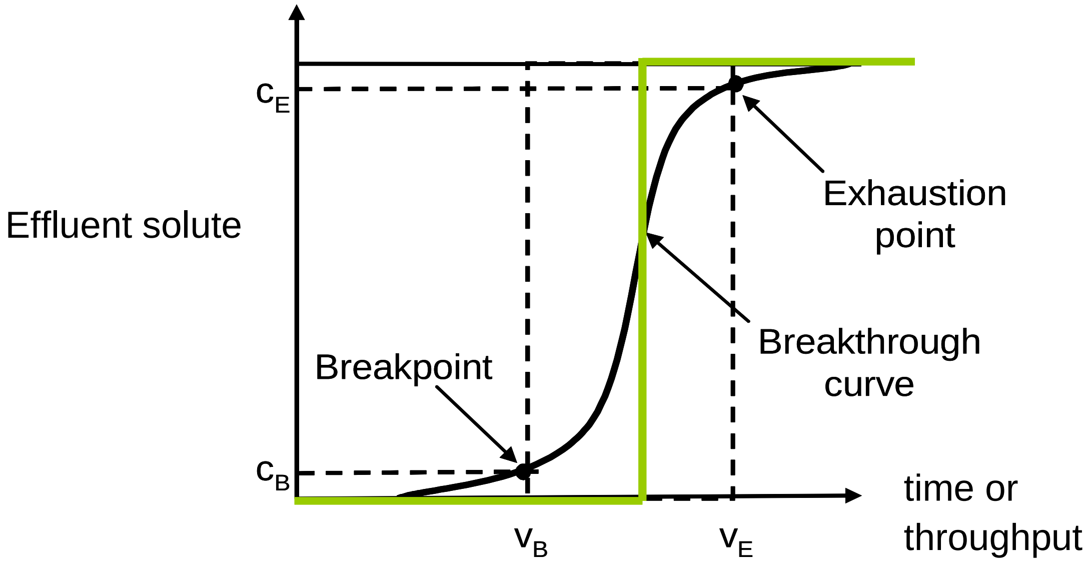
$$D_g = \frac{\rho_P \cdot q_0 \cdot (1-\varepsilon_B)}{\varepsilon_B \cdot c_0}$$

$$Biot = \frac{k_F \cdot r_P \cdot c_0}{D_S \cdot \rho_P \cdot q_0}$$

$$\text{Stanton} = \frac{k_F \cdot m_{Ads}}{r_P \cdot \rho_P \cdot \dot{V}}$$

and n

with K_F: Freundlich constant; n: Freundlich exponent; k_F: film diffusion coefficient; D_s: surface diffusion coefficient; m_{Ads}: mass of adsorbent; ρ_B: bed density; ε_B: bed porosity; d_p: particle diameter; c_0: influent concentration;



$\dot{V}$: flow rate.

Fig. 11. Breakthrough curve of continuous flow fixed bed reactor

The sorption can be divided into three categories depending on the mass transfer limitations. Fig. 12 shows the results for Biot numbers smaller 0.5, between 0.5 and 30 and above 30 which were calculated by applying the Linear Driving Force model which is a numerical solution of one ordinary differential equation.

1st category: **Biot ≤ 0.5**	**2nd category:** **0.5 < Biot ≤ 30**	**3rd category:** **Biot > 30**
liquid-phase mass transfer controlled	liquid-phase and solid-phase mass transfer controlled	solid-phase mass transfer controlled

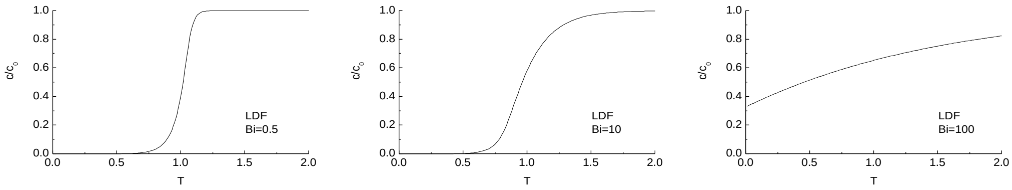
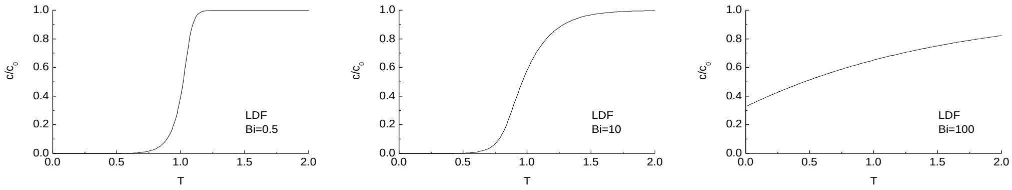


Fig 12 : Mass transfer limitations categorized by the Biot number

1st category: Biot ≤ 0.5	2nd category: 0.5 < Biot ≤ 30	3rd category: Biot > 30
liquid-phase mass transfer controlled	liquid-phase and solid-phase mass transfer controlled	solid-phase mass transfer controlled



D 18. Process Performance with Real Effluents

Fluoride and phosphate removals from Tunisian fertilizer plant effluent has been emphazied. Since the considered wastewater contains a high load in fluoride (~700 to 1300 ppm) and phosphate (~ 3500 to 5000 ppm) and the volume to treat is enormous (~ 5 800 000 m^3 per year), the detoxication procedure should be technically and economically viable. This implies the recuperation of the contaninating targets as useful (marketable) products and not as waste sludge. For this purpose, the retained technique was precipitation and the precipitation reagent chosen was lime. In order to obtain solid phases which can be recycled in the same industry or used in other sectors, the concomitant precipitation of PO_4^{3-} and F^- ions should be avoided.

Before precipitation tests, the speciation and analysis of the different species present in the considered effluent was realized (2004-2005). The obtained results showed essentially that phosphorus exist only as orthophosphate ions whereas fluoride is present under two forms: hydrofluoric acid (HF) and hexafluorosilicic acid (H_2SiF_6).

Since the behaviour of fluorosilicate ions (SiF_6^{2-}) against lime is not well known and at the other hand the fluoride and phosphate ions can co-precipitate as calcium compounds, synthetic aqueous solutions of HF, H_2SiF_6, H_3PO_4 and their mixtures were firstly used to conduct precipitation tests (2005-2006). Subsequently, the treatment of industrial effluent samples having different contents and ratios of fluoride and phosphate were undertaken (2006-2007).

Using synthetic solutions, it appeared essentially that the quantitative removal of fluoride with lime from a HF + H_3PO_4 mixture starts from pH 2.5 to 3 whereas that of PO_4^{3-} ions occurs only from pH higher than 4.2. Consequently, concomitant precipitation of PO_4^{3-} and F^- may be avoided by modulating the pH of the treated medium.

For the industrial effluent samples, the treatment with lime showed that:

Fluoride ions present a similar behaviour to that observed with the synthetic HF + H_3PO_4 mixture, wheras phosphate behave differently. Thus, pronounced precipitation of PO_4^{3-} from the effluent rather occurs at pH arround 6.6 and not at pH 4.2 as previously found. This difference may be attributed to the presence ithe effluent of a high content of sulfate ions (~ 1500 to 2500 ppm) which are lime consumers;

Best fluoride and phosphate precipitates separation is reached at pH arroud 2.5 and at this pH the treatment efficiency can reach 95% for F^- ions. After F^- removal, PO_4^{3-} ions can be quantitatively precipitated at pH > 6.6;

Residual fluoride concentration in the treated wastewaters was about 10-20 ppm whereas that of PO_4^{3-} ranges between 1.4 and 20 ppm depending on the precipitation pH considered.

It is to note that the solid phases (calcium precipitates) obtained from both synthetic solutions and real effluent were characterized by Infrared spectroscopy and X-ray diffraction.

After the pre-treatment of industrial effluent with lime precipitation, residual phosphates (up to 20 ppm) could be removed by adsorption on the solid media developed in the MEDINDUS project.

D 19 Treatment and Re-use Possibilities for the de-sorption Solutions

For reuse of the target substances it is essential to recover them from the sorption material. The general equation for the rate of desorption is

$$R = r\, c^x,$$

r: rate constant for desorption, c: concentration of the adsorbed material, x: kinetic order of desorption. The rate constant can be expressed in the form

$$r = A \cdot \exp(-\frac{E}{k \cdot T})$$

In this equation the notations used are :A: attempt frequency, E: activation energy of desorption, k: Boltzmann’s constant, T: temperature. In general desorption can be divided into chemical and physical processes. The fundamental uptake processes of the investigated material can not be clearly divided into physical or chemical sorption. Temperature increase was selected as the main desorption process. The experiments showed a release of the substances in water which was depending on the temperature, the pH and the time. The kinetics and the exact amount of released substances could

not be quantified exactly enough as the amount of available material was not sufficient for these investigations.

Conclusions: The re-use of the recovered solution is strongly dependent on the achievable concentration. One re-use option is the recycling into the phosphate factory which in general has the advantage of phosphate and water re-use.

Another option is the addition of nitrogen and ammonia which is economic , if phosphate is highly concentrated and the amount of impurities is low.

D 20. Business Management Report

For reuse of the target substances it is essential to recover them from the sorption material. The general equation for the rate of desorption is

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$$r = A \cdot \exp\left(-\frac{E}{k \cdot T}\right)$$

In this equation, A: attempt frequency, E: activation energy of desorption, k: Boltzmann’s constant, T: temperature. In general, desorption can be divided into chemical and physical processes. The fundamental uptake processes of the investigated material can not be clearly divided into physical or chemical sorption. Temperature increase was selected as the main desorption process. The experiments showed a release of the substances in water which was depending on the temperature, the pH and the time. The kinetics and the exact amount of released substances could not be quantified exactly enough as the amount of available material was not sufficient for these investigations.

The reuse of the recovered solution is strongly depending on the achievable concentration. One reuse option is the recycling into the phosphate factory which in general has the advantage of phosphate and water reuse. Another option is the addition of nitrogen and ammonia (PO_4-P:Mg:NH_4-N = 1:1:1) which is economic, if phosphate is highly enough concentrated and the amount of impurities is low.

World production of phosphate rock in 2006 was 142 Mio. t (equivalent to 44 Mio t P_2O_5 = 31%), a 6% decrease compared with that of 2005 owing mainly to lower output from Israel, Jordan, and the United States (see US Geological Survey: http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/). China (30.7 Mio t), the United States (30.1 Mio t), Morocco (27.0 Mio t), Russia (11 Mio t), Tunisia (8 Mio t), Jordan (5.9 Mio t) were the leading producing countries. World phosphate fertilizer consumption was projected to grow at an average annual rate of 2.9% during the next 5 years, according to the International Fertilizer Industry Association (2007).

The price per metric ton of phosphate rock increased constantly to 31.80 US$ in 2006 (23.40 US$ in 1996) which is equivalent to 102.6 US$ per metric ton of P_2O_5. In 2007 the price of phosphate rock increased tremendously from 50 to 200 US$ and up to 350-400 US$ in the second quarter 2008. The rise in prices is driven by global demand for fertilisers for agriculture and biofuel production. Therefore, the actual price in P_2O_5 equivalents for phosphate rock is 1,290 US$ per t which is 2,950 US$ per t of phosphate. One of the four phosphate factories in Tunisia, located in Sfax, discharges yearly 5.8 Mio m^3 wastewater containing 4,000 mg PO_4^{3-} per litre which is 23,200 t PO_4^{3-} or 7,600 t P. This is an actual market value of 22.4 Mio US$ per year which is discharged into the Mediterranean Sea assuming that the processing costs of the phosphate rock are identical to the preparation of the recovered phosphate by the investigated processes. Assuming balanced production capacities in all four Tunisian plants the specific loss via the wastewater pathway is 10 % of the phosphorus processing (273,000 t P a^{-1}).

Calculated with phosphate rock production in Maghreb and Mashrak countries (Morocco 27.0 Mio t, Tunisia 8 Mio t, Jordan 5.9 Mio t, Syria 3.9 Mio t, Israel 3 Mio t, Egypt 2.2 Mio t, Algeria 0.9 Mio t, overall 50.9 Mio t = 36% of world production) and assuming that the production processes (phosphoric acid: thermal/wet processes; phosphate fertilizer) discharge similar specific phosphate mass flows the overall loss in phosphate is 5.1 Mio t a^{-1} which is equivalent to a market price of 15 billion US$.$a^{-1}$. These calculations demonstrate clearly that the combination of economic considerations and environmental protection as investigated in this project offers unexpected and impressive opportunities.

Treatment costs for a factory in Tunisia

5.8 Mio m³ per year wastewater of phosphate factory in Sfax (influent 4 g L^{-1} phosphate, pH 1.6)

After treatment with lime (CaO) and precipitation → ~18 mg P/L, pH ~6

Effluent concentration: 1 mg P L^{-1}

Concentration difference: 17 mg P L^{-1}

Flow rate: 15,900 m^3 d^{-1} = 660 m^3 h^{-1}

Removed mass flow: 270 kg P d^{-1}

Sorption with Material C material from UK

Loading: ~1 g P/kg, increase by factor 4 feasible within 3 to 4 years

→ 68 t of material C for daily regeneration

Material price approx. 18 € kg^{-1} (estimated industrial production costs)

1,220,000 €

Bed density: 716 kg m^{-3}

Bed volume: 380 m^3

Bed length: 12 m

Diameter: 6.4 m

Area: 32 m^2

Superficial velocity: 5 m h^{-1}

Adsorber costs incl. piping, pumps etc.: 300,000 €

Total investment incl. material, engineering etc.: 1,520,000 €

Measured permeability (see D16): $k = \frac{\varepsilon_B{}^3 \; d_p{}^2}{180(1-\varepsilon_B)^2} = 6.6\,10^{-10}\; m^2$

Pressure drop

$$\Delta p = \frac{\eta L}{k A}\dot{V} = \frac{0.001 \cdot 12}{6.6 \cdot 10^{-10} \cdot 32} \cdot 0.183 = 1.04\, bar$$

Energy consumption of pumps

$$\dot{E} = \Delta p \cdot \dot{V} = 1.04 \cdot 10^5 \cdot 0.183 = 19\, kW$$

Energy costs for pumping (+ 10 % transport): 0.2 € kWh^{-1} → 100 € d^{-1}

Regeneration, recovery and cleaning costs: 100 € d^{-1}

Sales of 270 kg P d^{-1}: 2,950 € per t P → 800 € d^{-1}

Conventional phosphate elimination by flocculation with $FeClSO_4$ and sedimentation or filtration; no regeneration possible!

Practical molar ratio Fe:P = 1.5 → removal: 2.7 kg Fe/kg P → 730 kg Fe d^{-1}

Price: 1.1 €/kg Fe ($FeCl_3$, 40%) → 800 € per day = 300,000 € per year

Profits including abandonment of phosphate precipitation, without investment: 1,400 € d^{-1}

Return of investment: 3 years (excluding interest)

Conclusions

All the objectives of WP were achieved and these calculations demonstrate that the investigated sorption material has the potential for industrial application. The major assumptions are the further increase of sorption capacity by a factor of 4 within the next 3 to 4 years and the industrial production costs of 18 € per kg. In comparison to the conventional techniques the supramolecular sorption material offers the opportunity of phosphate recycling. Nevertheless, the sorption material has to be optimized to enhance its capacity and to transfer the production into technical scale. Due to the latest increase of phosphate rock prices by a factor of 10 within the last 2 years, the worldwide increasing demand, the limited phosphate rock deposits as well as the dramatically increasing pollution and eutrophication of the Mediterranean Sea, the investigated process is extremely attractive and offers a large potential for further optimization and application.

Workpackage 5 (D 21-D23)

The aim of this workpackage was to evaluate the ability of plants for phytoextraction of heavy metal cations in the presence and absence of soil applied receptors (D 21), to quantify the underlying mechanisms by which plants accumulate heavy metals (D 22) and to establish a comparison with existing technologies (D 23)

Partners involved were Dr Anna Febrero (University of Barcelona), Dr Naaila Ouazzani, University Cadi Ayyad, Morocco and Partner 1 providing the receptors tested in this workpackage.

Evaluation of the ability of plants for phytoextraction of heavy metals. (D 21)

The selection of the best analytical method for the determination of heavy metals was carried out. With this purpose in mind, ICP/MS (Inductively Coupled Plasma? Mass Spectrometry and X Ray Fluorescence were compared and the former technique was selected. Several assays were performed. Among them are i) *Iris Pseudocorus L* for the accumulation and tolerance for Cr(III) and Zn(II) and its ecophysiological evaluation and ultrastructural studies ii) *Arando Donax* and its resistance to Chromium. In addition comparative studies were carried out between *Arando Donax,*

Phragmites\Australis and Typha Latifolia in their physiological response to heavy metal cations. Electron Transmision Microscopy images of *Iris Pseudocorus L* show ultrastructure of the base portion of the leaves. The highly electrodense spots found in the treated samples , but absent in the control samples are related to the rough endoplasmic reticulum and probably to vacuoles and may be associated to the accumulation of proteins and may be related to metal tolerance strategies. This work carried out by the University of Barcelona was complemented by the research performed by Dr Ouazzani , Partner 4. This Partner assessed the bioaccumulation of chromium by *Typha Latifolia* and *Phragmites australis* demonstrating that both leaves and roots of *Typha Latifolia* accumulate chromium but the quantities found were two to five times much higher in the plant roots that in the leaves .Experimental work carried out with *Phragmites australis* showed that it is possible to treat the tannery effluent (diluted at 50 %) by this plant .This type of treatment led to pH neutralization , elimination of 33 % of the organic load and very efficient removal of chromium (100 %). The elimination of chromium by this procedure occurs through a combination of different processes in the soil such as adsorption, precipitation ,sedimentation as well as biological ones. It was concluded that plants play a major role in the improvement of the hydraulic functioning of the system. The speciation of chromium in the plant-soil system is under the organic fraction in the first 20 cm of the upper layers of the soil. The chromium retention is enhanced in the root zone of the planted system.

Quantification of the Underlying Mechanisms by which plants accumulate /tolerate heavy metals in the presence and absence of soil-applied receptors. (D 22).

The presence of different ions on the degree of separation of phosphates from synthetic wastewater by using different coagulants was assessed Thus Figs 13,14 and 15 show the effect of sodium chloride, sodium hydrogen carbonate and magnesium sulphate respectively on the removal of phosphates by lime. It is concluded that the composition of the synthetic water plays an important role in the removal of phosphates. The results presented in these Fig demonstrate that the presence of these salts decrease the phosphate's removal by about 3 %. However with an increase in the calcium/phosphate ratio , the percentage of phosphate removed is enhanced by 3 %.

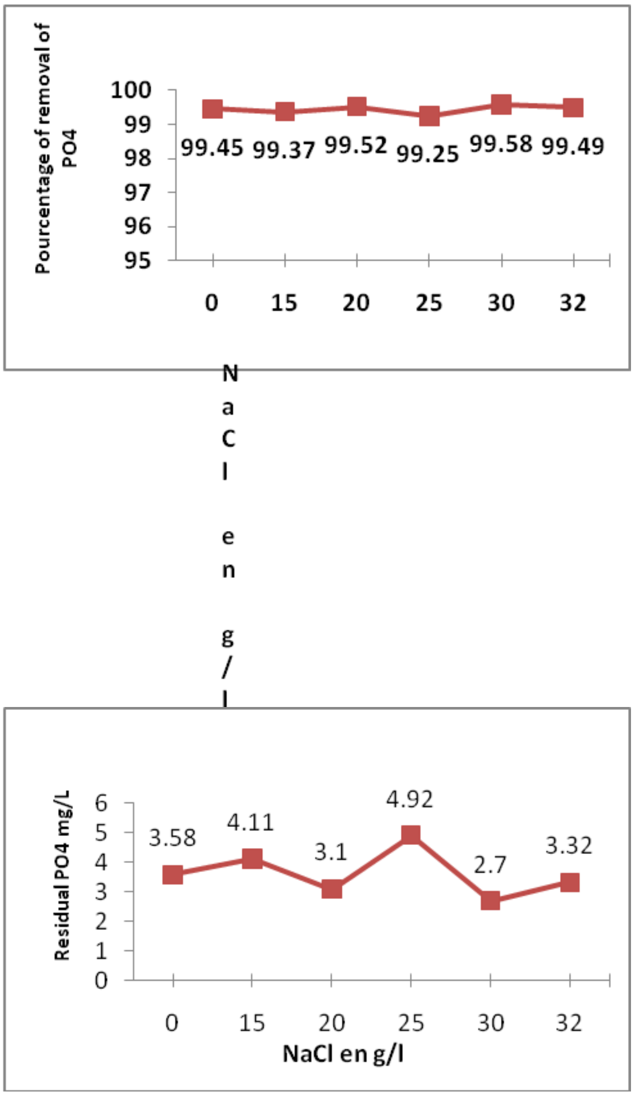

Figure 13. The dependence of percentage removal of $PO_4^{3-}$and residual PO_4^{3-} on different dose of NaCl, at pH4

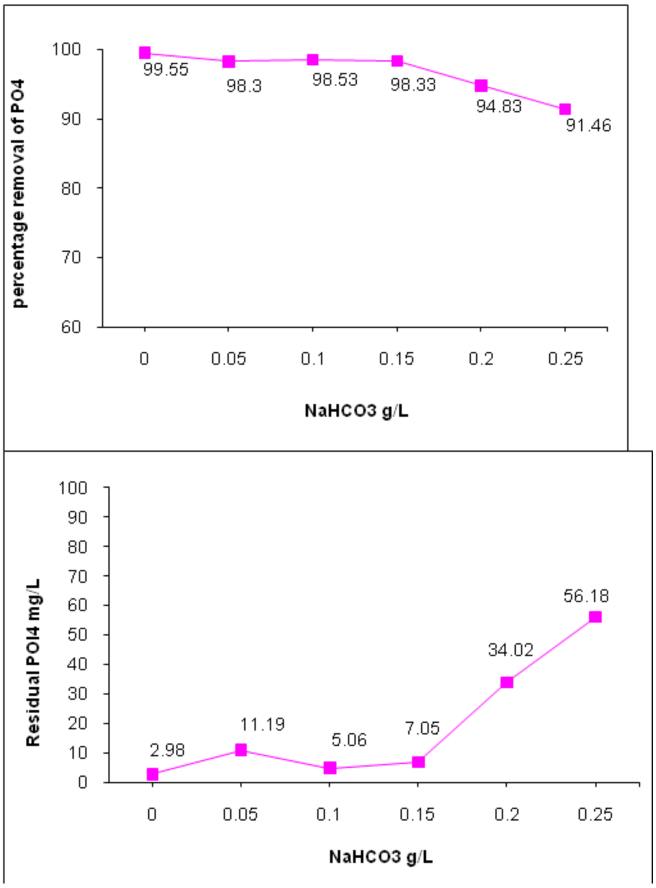

Fig.14. The dependence of percentage removal of PO_4^{3-} on different dose of $NaHCO_3$, at pH = 4

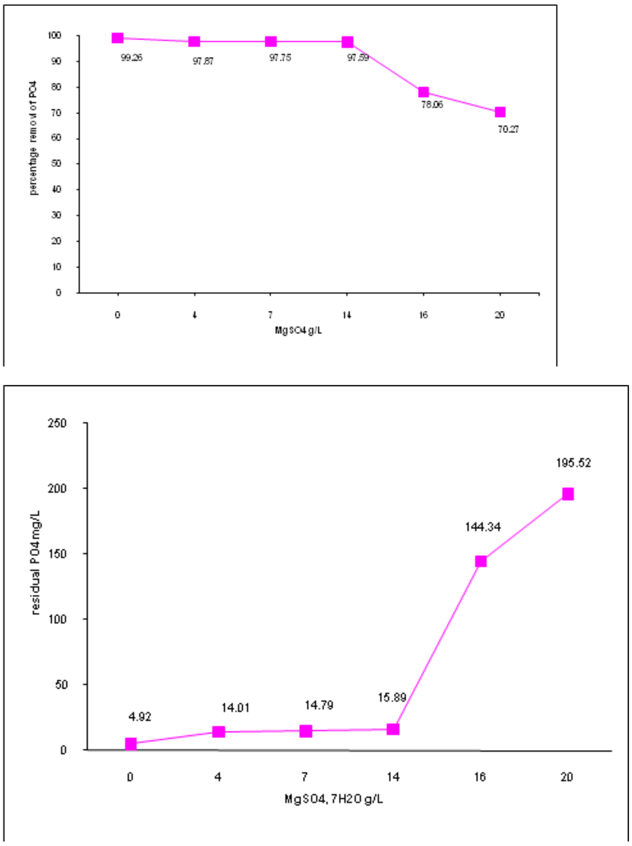

Fig.15. The dependence of PO_4^{3-} percentage removal on different dose of MgSO4, $7H_2O$ at pH4

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Comparison with existing technologies (D 23)

It was not always possible to establish comparisons with existing technologies due to the different experimental conditions in which the work was carried out. However as far as the materials are concerned, ion exchangers are commonly used for the purification of water but these materials unlike the ones produced in this work lack selectivity. Therefore ion exchangers not only remove polluting ions but also biologically essential ions.

Conclusions. From the above discussion it follows that the objectives of this workpackage were successfully accomplished. Thus a series of plants have the

property of accumulating polluting ions and these were identified. The mechanism involved was assessed under different experimental conditions.

Workpackage 6 Public Awareness and Understanding of Regional Environmental Problems. Enhancing University-IndustryLinks. (D 24 and D25)

Educational Programme on the Environment (D 24)

As discussed in previous reports all Partners participated in this workpackages in several ways either by the organisation of an International Conference (which took place in Tunisia in May 2007. Full details were given in the previous report) or by taking part in taught courses. Thus during this Period, Prof. Naaila Ouazzani and her colleague, Prof. Laila Mandi have taught to postgraduate students on the results obtained in the Medindus Contract as part of the Master on 'Sanitation Engineering and Environmental Management' run by Cadi Ayyad University , Morocco. Visits were also organised to the Tannery and Olive Mill Industries with students in Marrakech to make them aware of the environmental problems associated with industrial process.

In February 2008 , Prof. Ouazzani was allocated 15 minutes in the radio to discuss the outcome of the Medindus Contract.

. Another industrial links were established by Partner 3, Thus several regional industries, associations, high schools, technical Universities, and Companies interested in the topic of this Contract have been contacted. These are **AIICA** (Asociacion de la Investigacion de las Industrias del Cuero y Anexas) . This was visited in April 2007 to establish an University- Industry Link. Dr Adzet , Research Director and Mr Marginet, Managing Director expressed their interest in proceeding with an agreement of Cooperation . Another contact with the aim of exchanging ideas and research interests was established with the **Technical University, School of Industrial Engineering of Igualada (Tannery School) in Catalunya,** Spain through Dr R. Puig .**Phragmites S.A** has also been contacted as a SME . The main interest of this Company is on phytoremediation. This contact facilitates further exchangeof people and ideas with the purpose of assessing the potential market of phytoremediation in the Mediterranean Region.. Another Company approached was **Stachys** with the purpose of exploring landscape uses of phytoremediation through characterised vegetal materials (Hyper-accumulator species). It should be emphasised that most of the pioneering work on phytoremediation took place in academic laboratories. The 2005 law has given a new context for industrial-academic links on phytoremediation in Spain and The Consortium is strongly of the view that The Medindus Contract enhances and facilitates University-Industry links which are not much developed in Spain..

The training of students was an important contribution to the educational programme in this Contract.. Students trained were

1. Ismail Abbas (partially financed) gained a PhD degree from the University of Surrey,
2. Tomas Matsufuji (fully financed by this Contract) graduated with a Surrey PhD in December 2008.
3. Abdelaziz El Gammouz (partially financed by this Contract) completed his PhD in 2009
4. Rasha .Khalifeh (partially funded), Surrey PhD 2008.
5. V.Withams (fully financed by this Contract , MRes. Surrey 2005
6. Jinane Chaaban (partially financed by this Contract), Surrey PhD 2005
7. Nadim Hourani (partially financed by this Contract) Surrey MRes, 2008
8. Rachida Soualhi (partially financed by this Contract, Doctor Degree Cadi Ayyad University, 2007
9. C.Calderas, (fully financed), Dr University of Barcelona
10. Naoufal Diebli, Dr Cadi Ayyad University
11. L. Oucham (funded by this Contract) PG student Cadi aAyyad University.
12. M.Gourdar, doctoral student ENICS, Tunisia

Another industrial links were established by Partner 3, Thus several regional industries, associations, high schools, technical Universities, and Companies interested in the topic of this Contract have been contacted. These are **AIICA** (Asociacion de la Investigacion de las Industrias del Cuero y Anexas) . This was visited in April 2007 to establish an University- Industry Link. Dr Adzet , Research Director and Mr Marginet, Managing Director expressed their interest in proceeding with an agreement of Cooperation . Another contact with the aim of exchanging ideas and research interestswas established with the **Technical University, School of Industrial Engineering of Igualada (Tannery School) in Catalunya,** Spain through Dr R. Puig .**Phragmites S.A** has also been contacted as a SME . The main interest of this Company is on phytoremediation. This contact facilitates further exchangeof people and ideas with the purpose of assessing the potential market of phytoremediation in the Mediterranean Region.. Another Company approached was **Stachys** with the purpose of exploring landscape uses of phytoremediation through characterised vegetal materials (Hyper-accumulator species). It should be emphasised that most of the pioneering work on phytoremediation took place in academic laboratories. The 2005 law has given a new context for industrial-academic links on phytoremediation in Spain and The Consortium is strongly of the view that The Medindus Contract enhances and facilitates University-Industry links which are not much developed in Spain.

Booklet on Environmental Technologies for Water Decontamination (D 25).

A copy of the booklet was send to the Commission in the Fourth Activity Report.

EU-Mediterranean Conference (D 26)

As part of this work-package a very successful International Conference was organised in Djerba, Tunisia on the 24th-26th May 2007. The title of this Conference was '**Technologies for Industrial Wastewater Treatment and Reuse in the Mediterranean Region'**. I am pleased to report that all Partners participated and contributed with Plenary, oral and posters presentations and with advertising fully this event, This was organised by the Centre of Biotechnology and the National School of Engineering, both located at Sfax and the University of Surrey, UK. .Undoubtedly this Conference enhanced the Public Awareness (it was reported by several communication media) and Industry- University links.. Indeed several academic and industrial Representatives from EU and non EU Mediterranean Countries attended it. In addition international Companies exhibited professional equipment for water treatment. Participants (172) from nineteen Countries (**Algeria, Italy, UK, Germany, France, Greece, Belgium, Spain, The Nederland , Morocco, Japan, Morocco, Egypt, Lebanon, Morocco, Libya, Nigeria, Jordan**, **Tunisia)** from which twenty were from national (13) and international (7) companies and institutions related to the environmental field.

The socio-economic impact of the materials produced during the course of this Contract.

The large number of materials produced for decontamination purposes opens the possibility of pursuing this research activity further in order to reach the commercialisation of these materials which are of relatively low cost.In order to achieve it we need to optimise the production and to look for enterprises which are able to produce these materials in large scale. These have a great potential for socio-economic development for the following reasons. Industry is the major source of income of a country. However the sustainability of industry is greatly dependent of its environmental concern, something that is not universally considered in non-European Mediterranean Countries. Such is the case in Morocco, Tunisia and Lebanon and other Mediterranean Countries. There is no doubt that the implementation of technological approaches based on the use of these materials will greatly improve the environmental problems encountered in these countries and consequently the social welfare of their population particularly their health given that the presence of these toxic compounds poses a serious threat to human's

Final Plan for Using and Disseminating the knowledge

Following the various papers published in top journals , the number of Plenary and Keynote lectures presented at international Conferences the final plan for using and disseminating the results is currently carried out through the large number of people trained at Master and PhD level with the financial assistance provided by this Contract. Some of these people have academic posts in the Mediterranean Countries. Representative examples are Dr Ismail Abbas who after his PhD and a period of time working in the British Industry he returned to Lebanon and holds an academic position as a Lecturer at the Beirut Arab University. Also Dr Jinane Chaaban who is at present a Lecturer at the Lebanese University in Beirut.. This knowledge will also be expanded to other Mediterranean Countries through the submission of Proposals with these and Partners in other Mediterranean Countries to the European Commission under the FP7.

Publications

1- New Insights on Anion Recognition by Isomers of a Calixpyrrole Derivative, A. F. Danil de Namor; M. Shehab, I. Abbas, M. V. Withams, J. Zvietcovich-Guerra, *J. Phys. Chem.,* 2006, **110**, 12653.

2-Cation/Anion Recognition by a Partially Substituted Lower Rim Calix[4]arene Hydroxyamide, A Ditopic Receptor, A.F. Danil de Namor, J. K. Chaaban, I. Abbas, *J. Phys. Chem.*, A, 2006, **110**, 9575.

3. A New Calix(4) Pyrrole Derivative and its Anion (Fluoride) / Cation (Mercury and Silver) Recognition**.** A. F Danil de Namor, I. Abbas and H. Hammud. *J. Phys. Chem.,* 2007, *111,* 5803.

4.The Fluoride Dilemma .Thermodynamics of Anion Recognition by Calixpyrroles, A.F. Danil de Namor, *J. Thermal Analysis & Calorimetry,* 2007, *87,* 7.

5.Water Purification: From Ancient Civilization to the XXi Century , A. F Danil de Namor, *J.Water Sci and Techn.,* 2007, 7, 33

6."Water Quality Survey of the Mediterranean Sea, Coastal and Inland Regions of Lebanon", A.H. Hammoud, A.F. Danil de Namor and H.H. Hammoud, *Res. J. Chem. & Environm.,* 2007..

7. A Modified Calix[4]pyrrole Receptor ; Solution Thermodynamics of Anion Complexation and a Preliminary Account on the Phosphate Extraction Ability of its Polymer. A. F Danil de Namor, M. Shehab, R. Khalife and I. Abbas, *J. Phys. Chem.;* 2007, 111 ,12177.

8.Litany, Ibahim and Damour Rivers of Lebanon. H.Hammud and A.F. Danil de Namor; *J.Ultra. Chem.*, 2007, 3, 17.

9.A Partially Substituted Calix(4)Reesorcaene Receptor and Its Selective Recognition for Soft Metal Cations (Silver and Mercury). A. F. Danil de Namor and J. Chaaban, *J. Phys. Chem.;* 2007, in the press.

10.Detection and Quantification of Unbound Phytochelatin 2 in Plant Extracts of *Brassica Napus* Grown with Different Levels of Mercury. S, Iglesia-Turino, A. Febrero, O. Jauregui, C.Caldelas, J.L.Araus and J. Bort, *Plant Physiology,* October 2006, 142, 742.

11.Mercury Uptake and Element Composition in Water Hyacinth exposed to Mercury Chloride and Potassium Nitrate. C. Candelas, S. Iglesias-Turino, J.L. Araus, A. Febrero and J. Bort, 2007, Paper Submitted to the *International Journal of Phytoremediation.*

12. A Calix[4]pyrrole Derivative. Recognition of Fluoride a nd Mercury Ions and Extracting Properties of the Receptor Based Material. A.F.Danil de Namor and R Khalife , *J.Phys.Chem. B,* 2008, *112,* 15766..

Plenary and Keynote Lectures given at International Conferences

1.**Keynote Lecture**, Molecular Receptors: Responding for Social Demands Through Advanced Science and Innovative Technology, A. F. Danil de Namor, 27/4/ 06, H. *National Senate of Argentina*.

2. **Keynote Lecture**, The Fluoride Dilemma: Thermodynamics of anion recognition by calixpyrroles A.F Danil de Namor, CALORIMETRY AND THERMAL ANALYSIS CONFERENCE (CALCAT '06), Santiago de Compostela, Spain, 9-12, July 2006

3**.Keynote Address ,** Supramolecular Chemistry in Water Decontamination , A.F Danil de Namor, Third International Conference on Water Resources in the Mediterranean, (WATMED 3) Tripoli (Lebanon), November 2006

4.Plenary Lecture. Water Purification: From Ancient Civilization to the XXI Century. A.F.Danil de Namor,International Conference, Crete, Greece, October 2006

5.**Keynote Address**. Calix[4]pyrrole Polymeric Materials for the Extraction of Dihydrogen Phosphate from Aqueous Medium, A.F Danil de Namor, Technologies for Industrial Wastewater Treatment and Reuse in the Mediterranean Region, TIWAMED International Conference, Jerba, Tunisia, May 2007

6.**Plenary Lecture**. New Advances on the Chemistry and Applications of Calixpyrole Based Receptors. A..F. Danil de Namor , IV International Congress on Biotechnology and II International Congress in Pharmacy and Biochemistry , Arequipa Peru, June 2007.

7.**Plenary Lecture.** Supramolecular Receptors Based on Calixarenes and Calixpyrroles and Their Environmental and Clinical Applications. A.F.Danil de Namor, XV National Congress of Toxicology, Neuquen, Argentina, September 2007.

8.**Inaugural Lecture**: Advances on New Materials for Desalination and Decontamination Processes Based on Calixarenes and Calixpyrroles. Ceremony for the Award of Doctor Honoris Causa given to A, F Danil de Namor by the Alas Peruanas University, Peru, June 2007.

9**. Plenary Lecture** . The Chemistry of Calixpyrroles A.F.Danil de Namor,. National Congress of Chemistry, Tucuman, Argentina, September 2008.

10. **Plenary Lecture**. A.Latin American Congress of Chemistry, Peru, October 2008.

11.**Plenary Lecture**, 60th Anniversary of INIFTA, UNLP, Argentina, November 2008-11-11

Other Presentations at International Meetings Resulting from Activities in this Contract

1. Interaction of Calix[4]pyrrole Derivatives with Toxic Pollutants: Thermodynamic Studies and Foreseen Applications., R.Khalife, A.F. Danil de Namor , TIWAMED International Conference, Jerba, Tunisia, May 2007.

2.Adamantane and its interaction with heavy metal cations, N.Nwogu and A. F. Danil de Namor ; TIWAMED International Conference, Jerba, Tunisia, May 2007

3.Removal of phenolates by calixarene-based materials, H.H.Hammud, E.E.M.Mansour, K. Hijazi, A. F. Danil de Namor, TIWAMED International Conference, Jerba, Tunisia, May 2007

4. Elimination des ions phosphates et fluorures du rejet hydrique de l' industrie des phosphates : orientation vers une valorisation des sous produits de traitement. M.Gouider, J. Bouzid, M.Feki,O. Mouedhen and S. Sayadi; International TIWAMED Conference, Tripoli, Lebanon, November 2006.

5.Lime Treatment of an industrial effluent rich in Fluorides and Phosphates: Performances of the Process and Identification of the generated solid phases. M. Gouider, J. Bouzid, M. Feki and S.Sayadi, International TIWAMED Conference, Djerba, Tunisia, May 2007.

6.Physiological Response of *Iris Pseudacous* L to Chromium and Zinc Stress, . C.Caldelas, S. de la Iglesia- Turino , J.L.Araus, J. Bort and A. Febrero, TIWAMED International Conference, Djerba, Tunisia, May 2007.

7.'Salinity and Zinc Stress : Impact in Tomatoe Plant Development.. S. de la Iglesia-Turino, C.Caldelas, J.L.Araus, A. Febrero, J. Bort, TIWAMED International Conference, Djerba, Tunisia, 2007.

8.El Risc Ambiental del Fangs Toxic de l' embassament de flix. Accions realitzades per minimitzar-ho. C. Candelas and A. Febrero, Departament of Medi Ambient I Habitatge, Generaltat of Catalunya, Spain.

9.Treatment of Olive Mill Wastewater by a Combined System of Sand and a Mixture of Aquatic plants (Phragmites australis, Typha latifolia and Juncs subulatus), M.Achak, L.Mandi, N.Ouazzani,. TIWAMED International Conference, Djerba, Tunisia, 2007.

10.Purification of Olive Mill Wastewater by a Sand Filter: Granulometric Effect. M.Achak, L. Mandi, N. Ouazzani . TIWAMED International Conference, Djerba, Tunisia, 2007.

11.Chemical characterisation of phosphate industry effluents, L. Ouchah, L.Mandi, N. Ouazzani , TIWAMED International Conference, Djerba, Tunisia, 2007.

12.Treatment of Yannery Wastewater by Bioremediation. S. Tiglyene, A.Jaouad, L.Mandi, TIWAMED International Conference, Djerba, Tunisia, 2007.