Innovative materials for waste water purification systems to be installed in tourist and other small polluting objectives on the Black Sea coast- IMAWATCO

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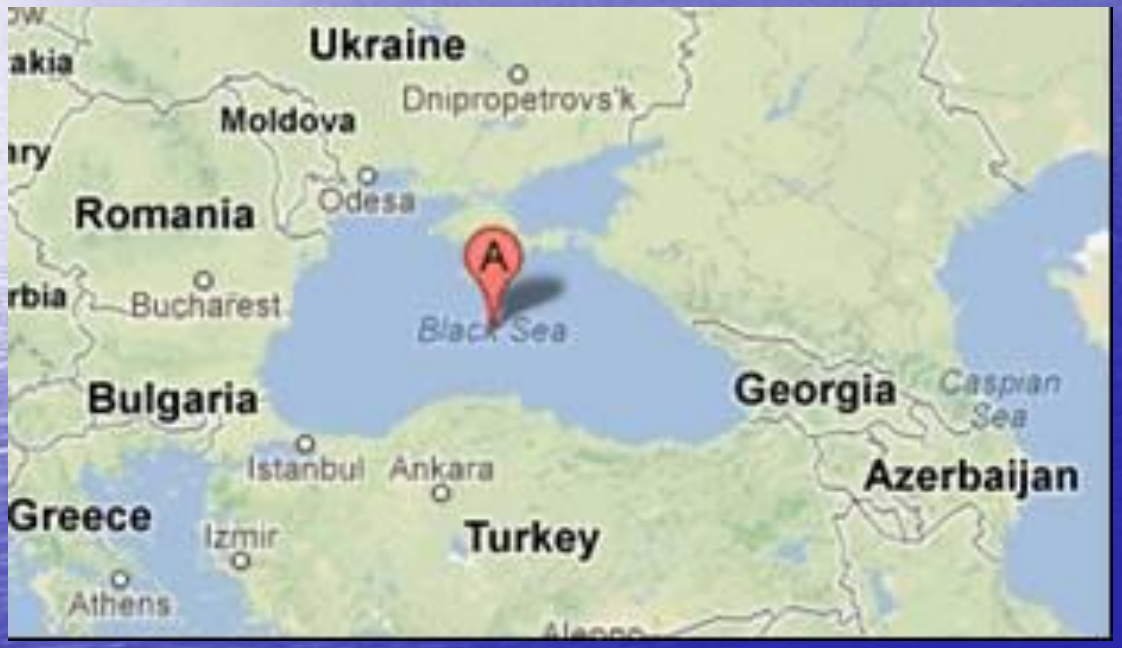
Coordinator organization: INCDCP-ICECHIM Bucharest- Romania

P1- Institute for Organic Chemistry – BAS- Bulgaria

P2- Space and Solar-Terrestrial Research Institute – BAS- Bulgaria

P3- Istanbul technical university- Turkey

PROBLEMS

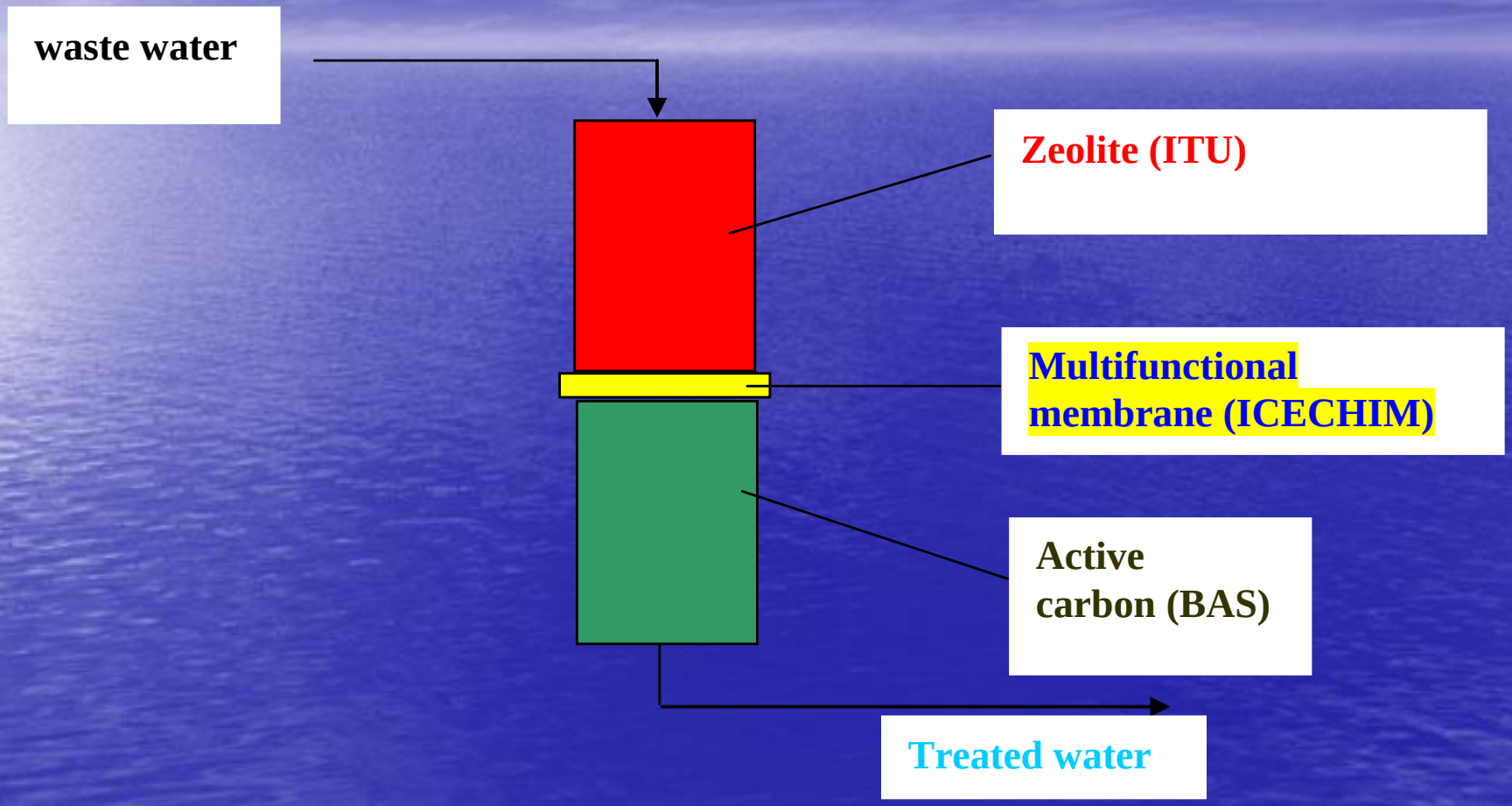


1. Practically closed sea
2. By layered: under layer contains H_2S
3. Huge pollution of the incoming rivers
4. Hotels and small industries spread all around the borders with no water treatment station
5. Imminent ecological disaster

The overall goal is to contribute to the implementation of environmental-friendly technologies in the BSEC countries with particular attention paid to the promotion of innovative, cost-effectively and resource saving technologies.
Taking into consideration the BSEC Action Plan for Cooperation in the Field of Environmental Protection this project is a practical instrument to address the environmental challenges arising in the Black Sea coast.

The main goal of IMAWATCO project is to develop and improve the purification process of the waste waters exhausted into the Black sea mainly from polluting sources as industry and tourism, agriculture and different social objects.
An effective and cost-saving model solving the small industry and tourism pollution will be developed based on the integration of innovative filtration systems within local installations for purification, attached to the objects which are sources of pollution.

Project principle



The proposed filtering-treatment unit for water purification has an integrated conception: natural zeolites as the filtrating and primary purifying layer, polymer membranes as second ultra filtration layer and selective adsorption layer and an adsorbent for complete purification of exhaust water.

To achieve main goal four main tasks were identified:

1. Appropriate selection of the raw materials and optimization of the treatment conditions in order to reach active carbon absorbents;
2. To produce ultra filtration polymer membranes, having also selective properties, as for instance ion exchanging membranes or membranes with covalently immobilized enzymes;
3. To perform investigations on adsorption properties of some natural zeolites and to establish suitable treatments for improving their adsorption efficiency
4. To find the best assembly of the three kind of material in order to obtain a high performance purification device.

The implementation of the project is carried out by researchers with necessary qualification in organic synthesis and chemistry of polymers, adsorption and desorption of organic and inorganic substances on porous materials, ecology.

The project is run by 4 research teams from 3 countries: Romania (coordinator), Bulgaria and Turkey allowing joining efforts and experience but also the equipment of the participating institutes.

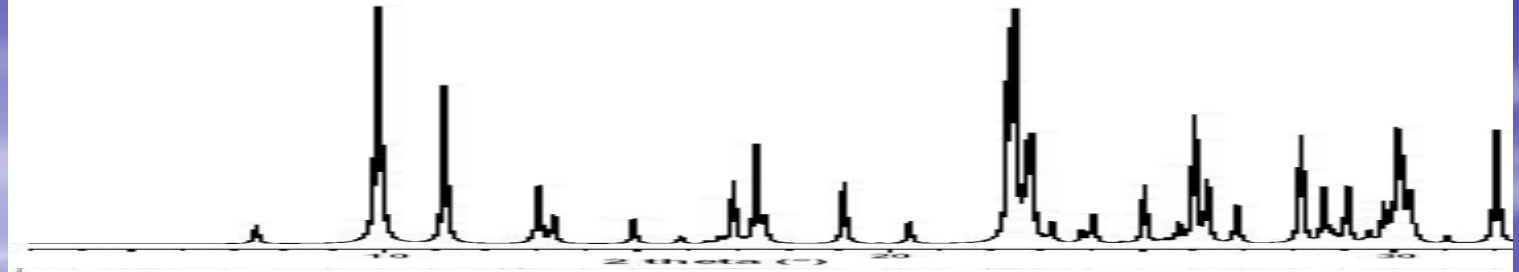
Important results from the work is expected to be:

- the reduced energy consumption for production of the adsorbents, by appropriate selection of raw materials and optimization of their treatment conditions;
- design and development innovative technology method;
- increasing the efficiency and lowering the price of the final product - purification filter.

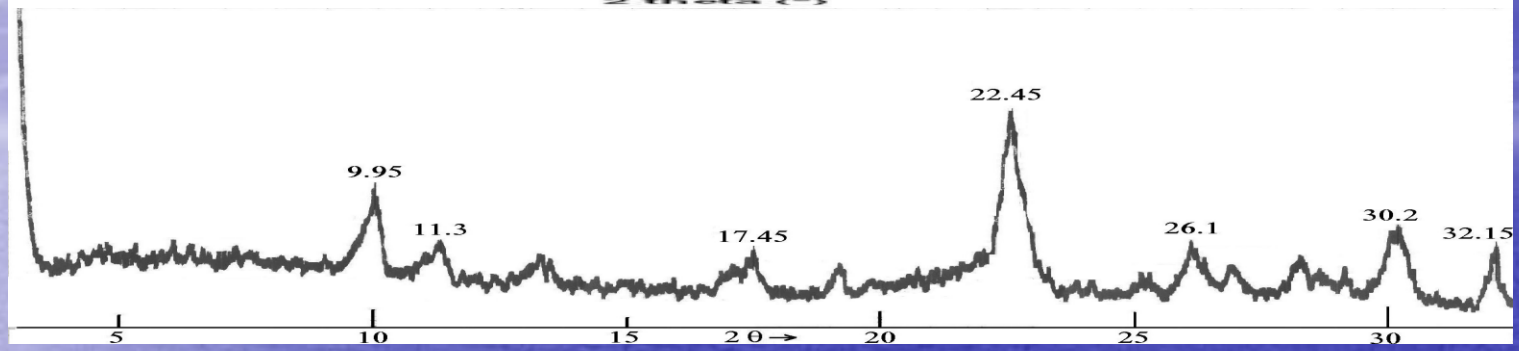
A communication strategy is set in order to disseminate the project results widely, to organize 2 targeted workshops and to prepare patent asking documents

1. Cation Exchange Properties of Clinoptilolite Samples from Bigadic, Gordes and Marsid Regions (ITU)

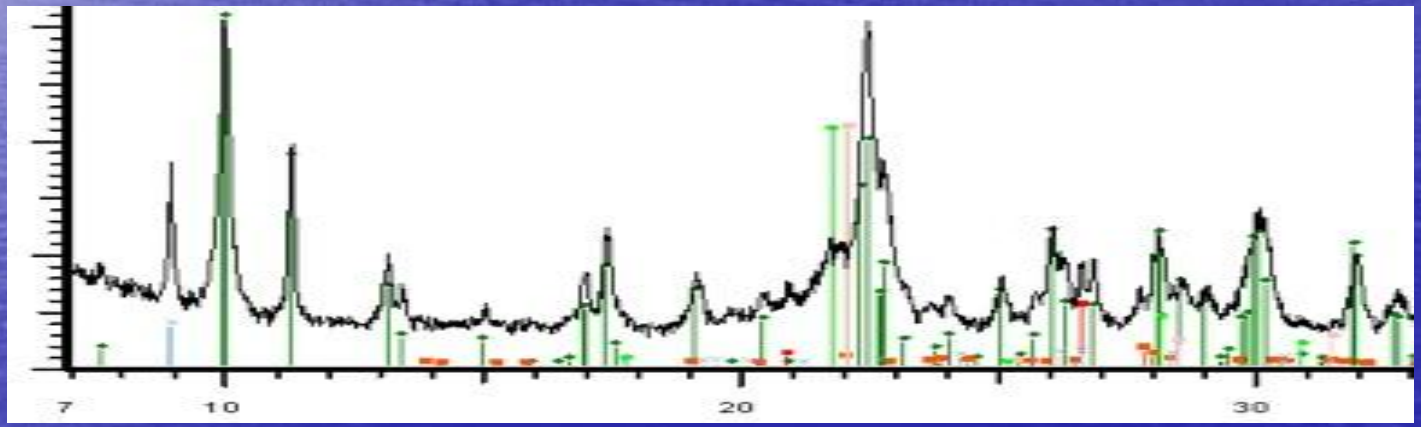
Standard



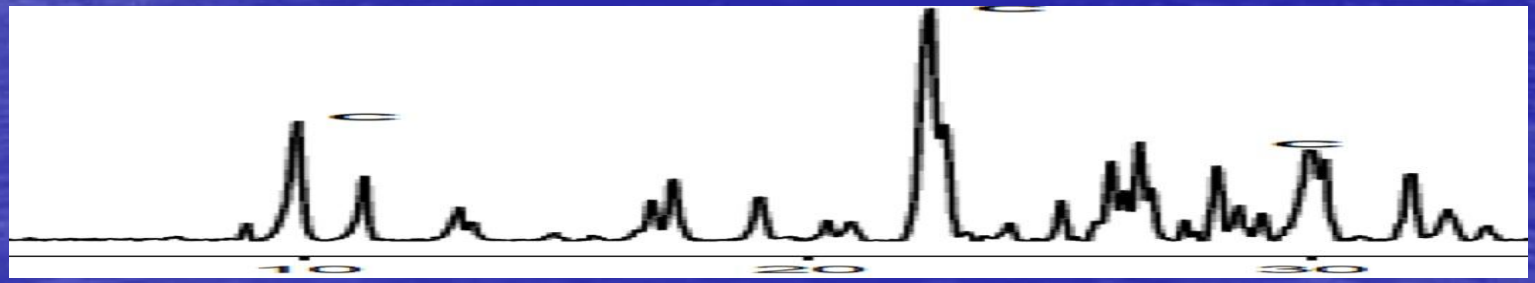
Gordes



Marsid



Bigadic



XRD of clinoptilonite from different sources

Clinoptilolite

	Bigadic	Gordes	Marsid
Clinoptilolite Content %	≈ 95	>96	75-80
Plagioclase	+		+
Cristobalite	+		+
Quartz	+	+	+
Biotatite	+	+	
Clays	+	+	

Experimental

Method
NH_4^+ exchange at 293 K
NH_4^+ exchange at 353 K
Treatment with NaCl at 353 K for 5 hours followed by NH_4^+ exchange at 353 K
Repeated treatment with NaCl at 353 K for 5 hours followed by NH_4^+ exchange at 353 K
Repeated NH_4^+ exchange at 353 K with fresh solution

Chemical Composition of the clinoptilolite samples

	Bigadiç	Gördes	Marsid
SiO_2	64.00	71.98	66.21
Al_2O_3	13.56	12.56	12.37
Na_2O	0.45	0.92	0.39
K_2O	3.61	4.28	2.43
CaO	3.61	1.99	2.44
Fe_2O_3	1.35	0.45	0.74
MgO	-	0.42	0.86
H_2O	5.67	7.40	6.82
SiO_2/Al_2O_3	4.72	6.32	5.35

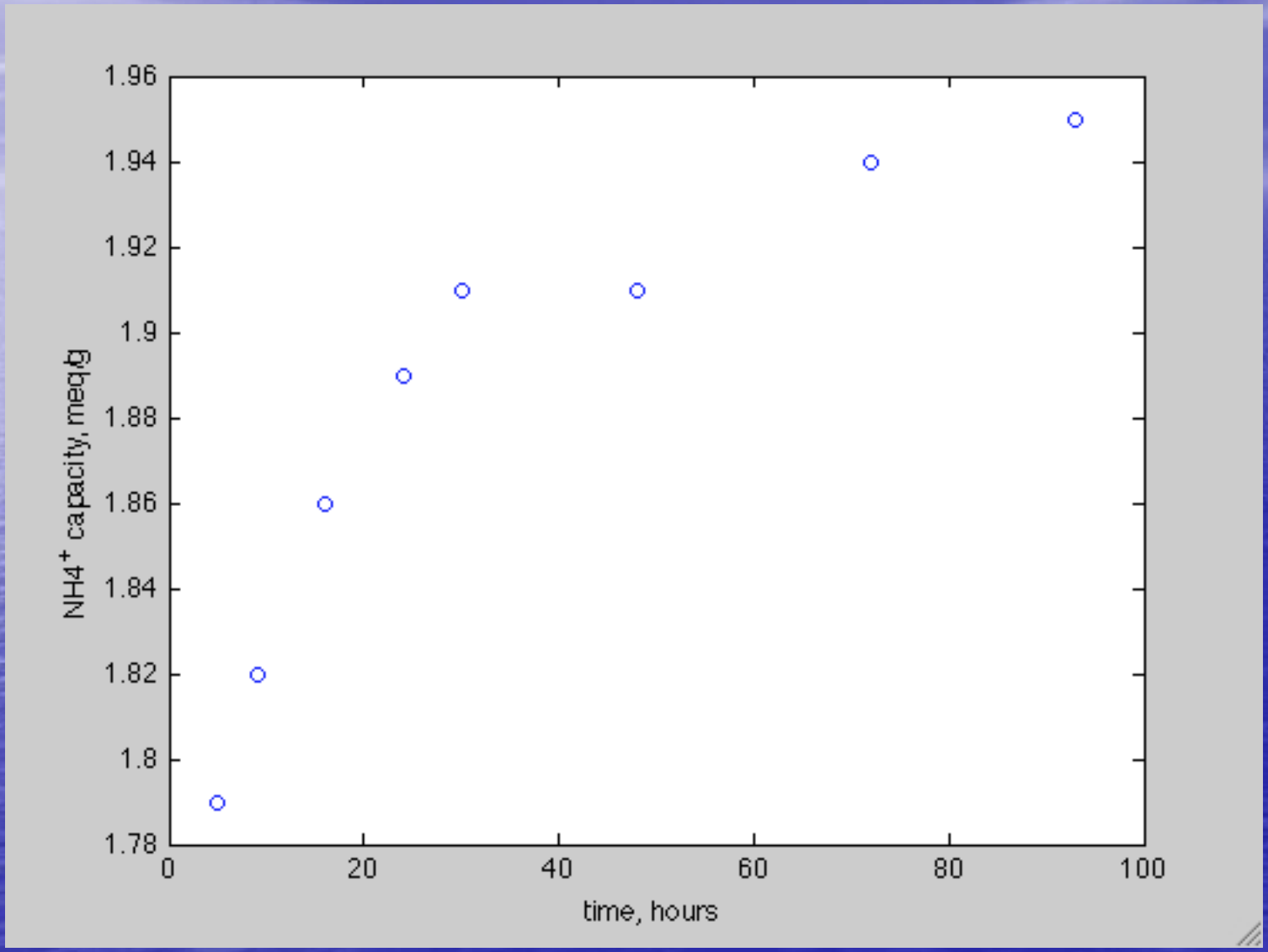
Cation exchange capacities of the clinoptilolite samples, meq/g

	NH_4^+	Cu^{+2}	Zn^{+2}	Pb^{+2}
Bigadic	1.71	1.58	1.10	0.39
Gordes	1.31	1.16	0.94	0.42
Marsid	1.72	1.18	1.56	0.38

*Cation selectivity of Marsid clinoptilolite $NH_4^+ > Cu^{+2} > Zn^{+2} > Mn^{+2}$

*B. Pode, G. Burtica, V Pode, A Iovi, E Popovici, Studies in Surface Science Series, 1999 Krisci (ed)

NH_4^+ exchange capacity of washed (with hot water) clinoptilolite samples from Bigadic



Effect of acid treatment

		Duration, h						
Acid Conc. M	Method	1	2	3	4	5	6	8
0.01	A*	1.69	1.69	1.61	1.64	1.70	1.73	1.73
	B**	1.68	1.71	1.73	1.74	1.79	1.80	1.81
0.10	A	1.68	1.55	1.69	1.50	1.47	1.45	1.44
	B	1.69	1.58	1.70	1.62	1.53	1.50	1.45
0.50	A	1.53	1.52	1.53	1.53	1.49	1.34	1.29
	B	1.67	1.59	1.55	1.54	1.51	1.38	1.35

A: only treated with acid

B: acid treatment followed by NaCl treatment

Effect of base treatment

Base	Conc.	Method	Duration, h							
			1	2	3	4	5	6	7	8
NaOH	0.5 M	A	1.51	1.57	1.59	1.66	1.59	1.52	1.51	-
		B	1.68	1.61	1.59	1.67	1.60	1.62	1.55	-
	1.0 M	A	1.60	1.48	1.48	1.47	1.37	1.44	1.15	-
		B	1.61	1.58	1.61	1.66	1.70	1.81	1.73	-
KOH	0.5 M	A	1.72	1.56	1.64	1.68	1.68	1.60	1.60	1.57
		B	1.71	1.59	1.69	1.81	1.74	1.59	1.60	1.56
	1.0 M	A	1.60	1.57	1.59	1.69	1.59	1.49	1.52	1.49
		B	1.67	1.63	1.64	1.84	1.71	1.61	1.54	1.50

A: only treated with base

B: base treatment followed by NaCl treatment

2. Active carbon and zeolites (BAS)

Sample	Synthesis method	Specific surface area m^2/g
Activated carbon from peach stones - 1	Carbonization/activation	850
Activated carbon from peach stones - 2	Carbonization/activation	500
Activated carbon from olive stones	Steam carbonization	600
Synthetic carbon from furfural/coal tar pitch	Carbonization/activation	700

Adsorption capacities of the activated carbons towards sulphonate and phenolate compounds

Sample	Adsorption capacities , g/g	
	Sulphonate compounds	Phenolic compounds
AC from peach stones (800 mg/g I_2)	0.54	0.52
AC from peach stones (500 mg/g I_2)	0.26	0.22
AC from olive stones	0.56	0.50
AC from furfural/coal tar pitch	0.57	0.50
AC from asphaltites	0.50	0.48

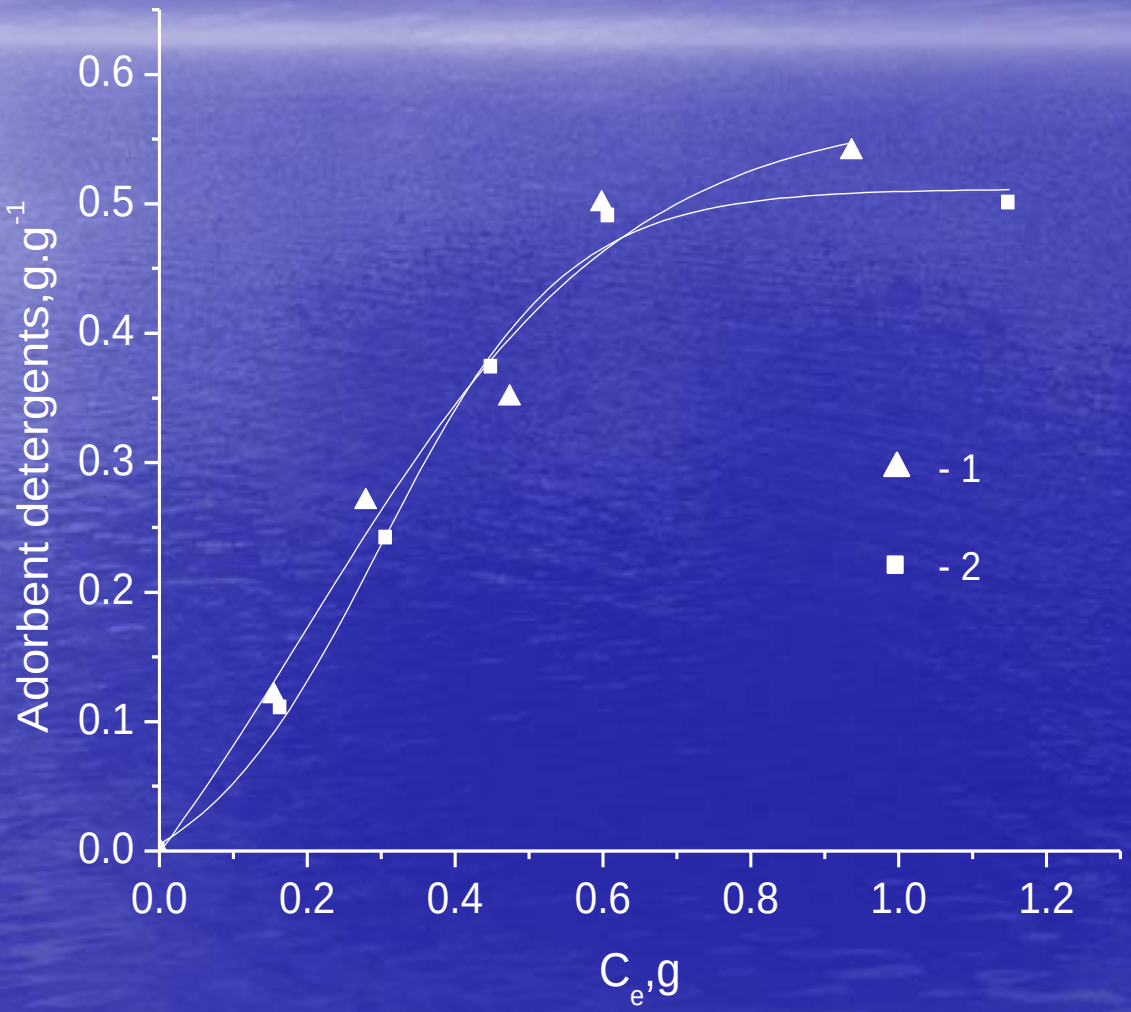
Adsorption capacities of the zeolites

Sample	Adsorption capacities, g/g	
	Sulphonate compounds	Phenolic compounds
Zeolite Gordes G	0.16	0.13
Zeolite Bioodic B	0.14	0.12
Zeolite PZ	0.39	0.38
Zeolite F5	0.34	0.29

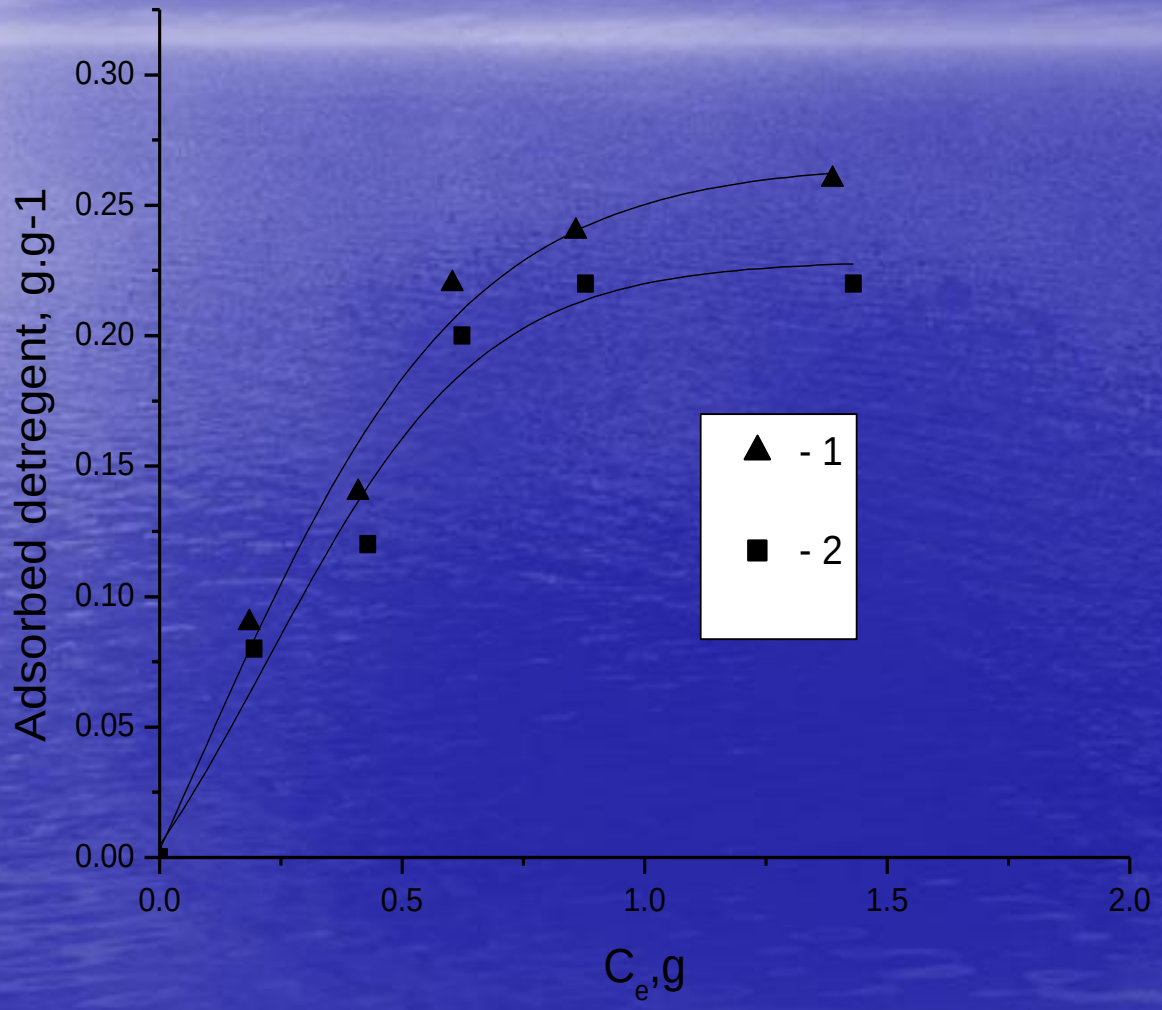
Influence of the amount of activated carbon (800 mg/g I_2, from peach stones) on the removal of detergents

Amount of the sample (g)	0.05	0.10	0.20	0.40	0.60
Removal of sulphonate detergent	0.375	0.520	0.540	0.540	0.540

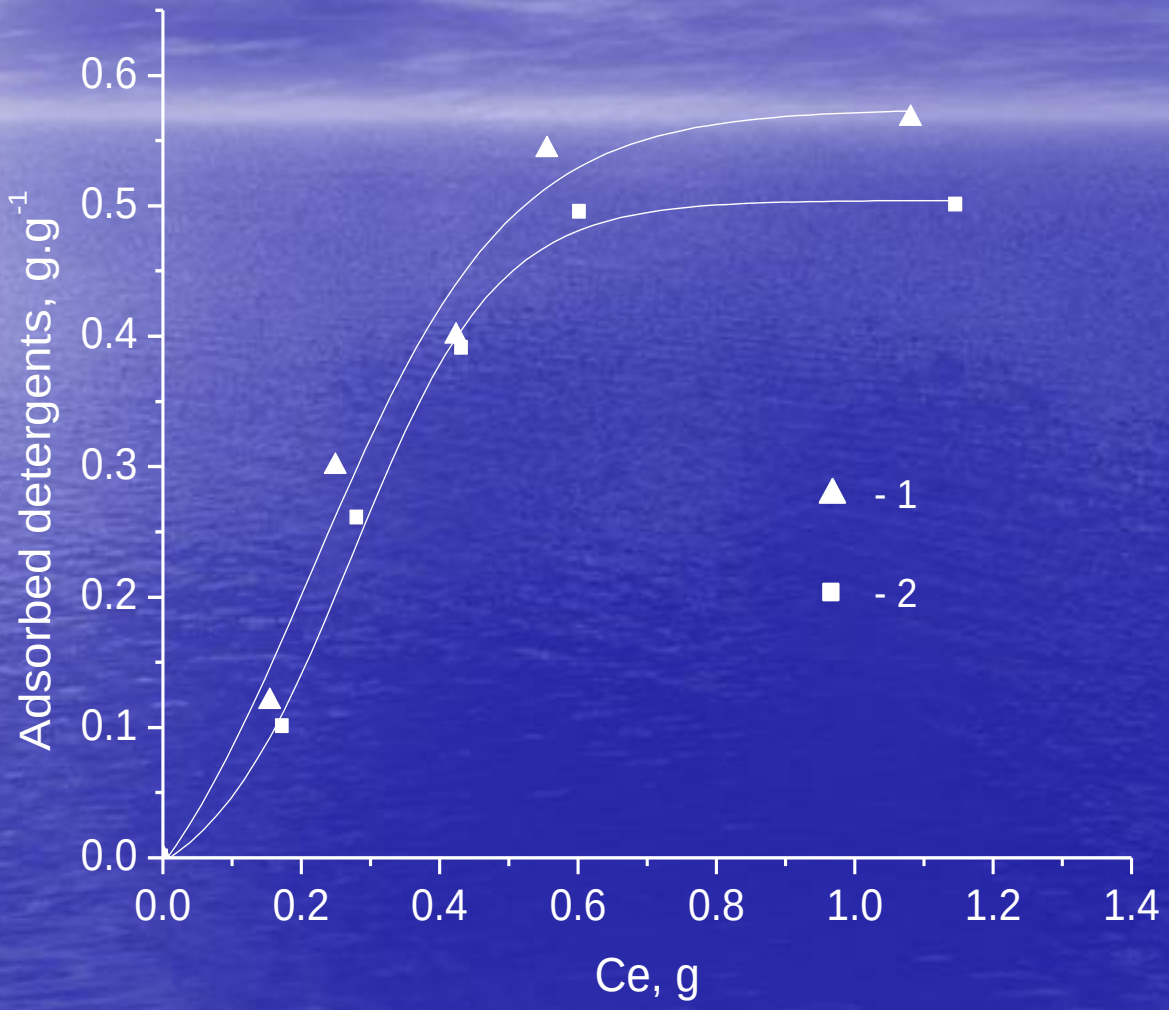
Adsorption isotherm of AC from peach stones (800 mg/g I_2):
1 – sulphonate compounds; 2 – phenolic compounds



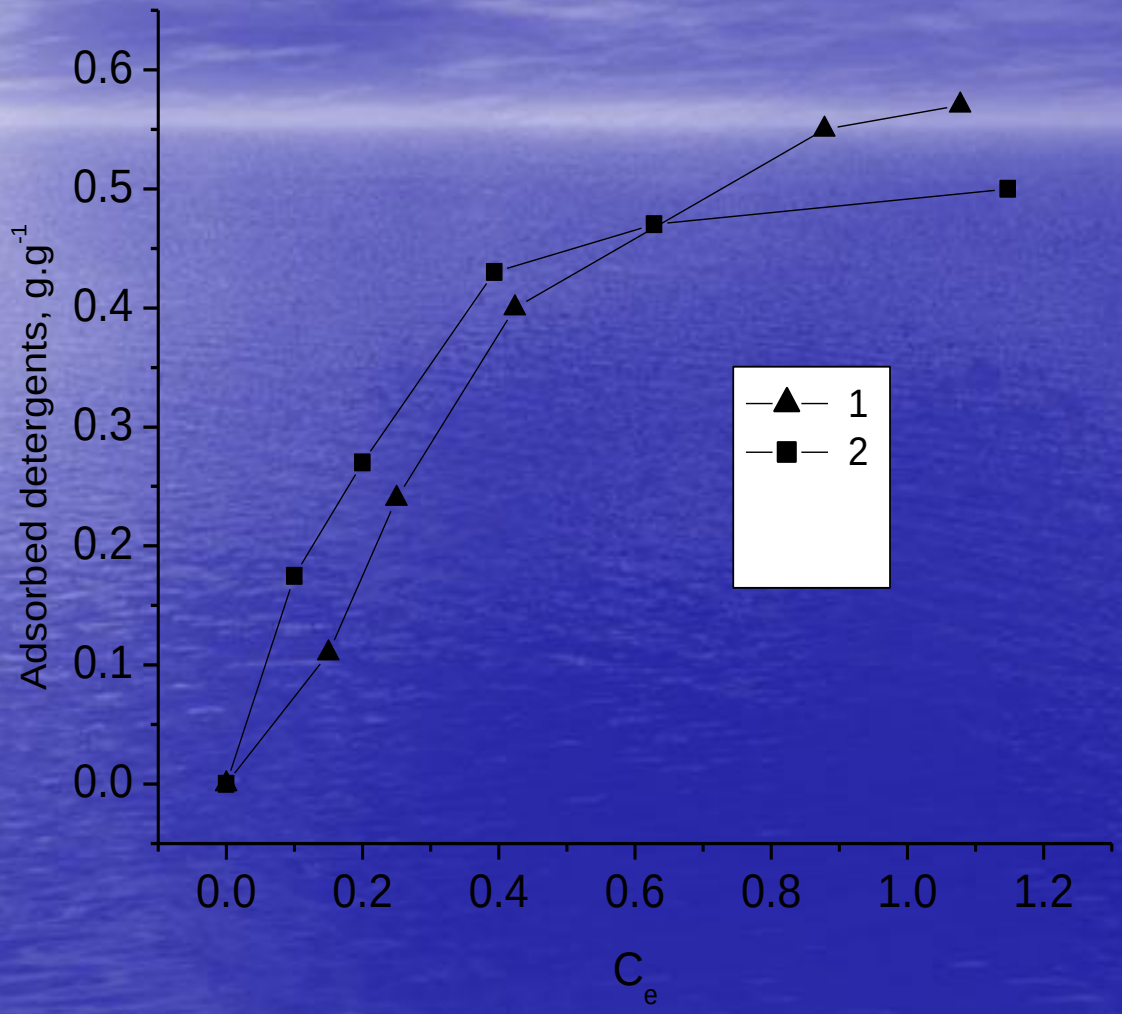
Adsorption isotherm of AC from peach stones (500 mg/g I_2):
1 – sulphonate compounds; 2 – phenolic compounds



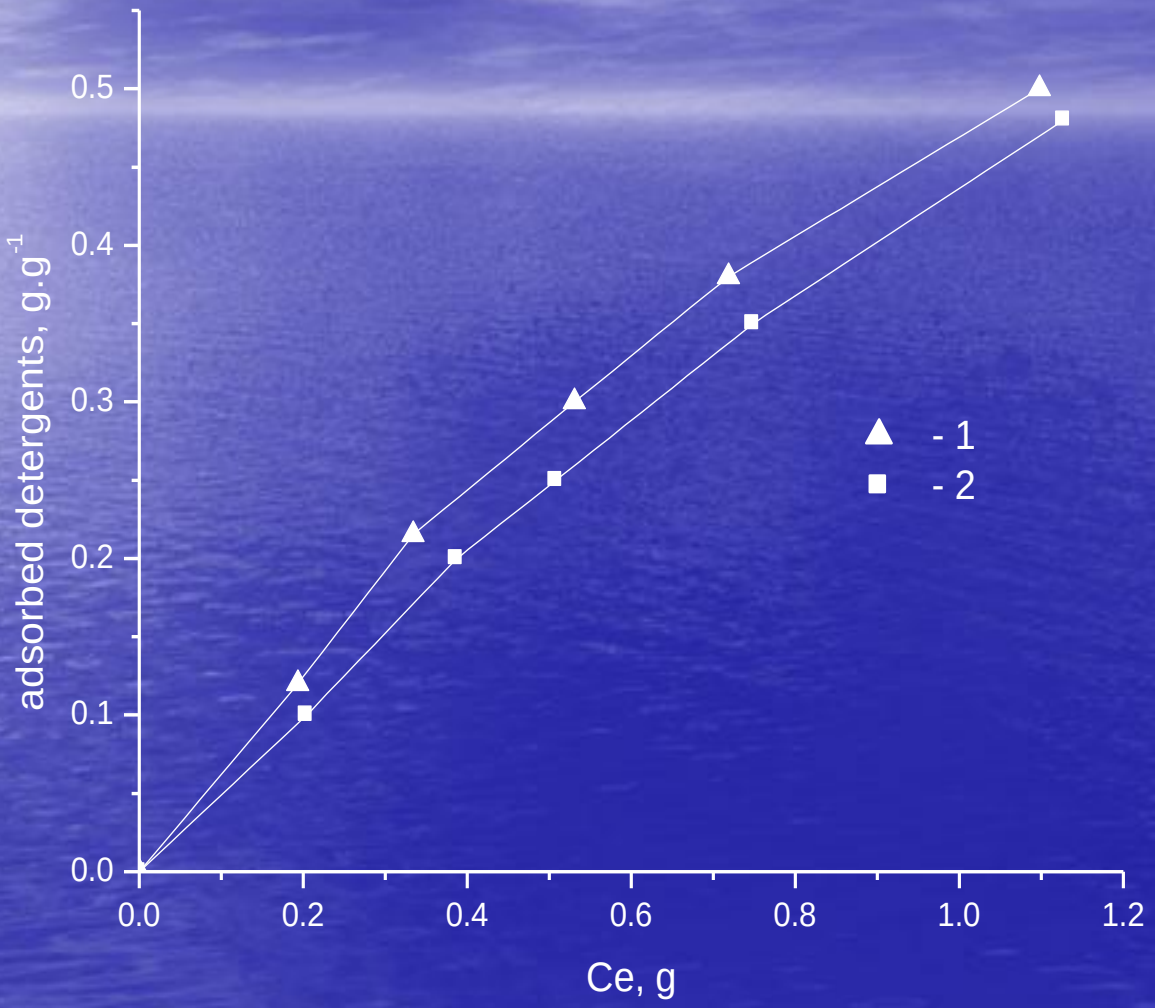
Adsorption isotherm of AC from olive stones:
1 – sulphonate compounds; 2 – phenolic compounds



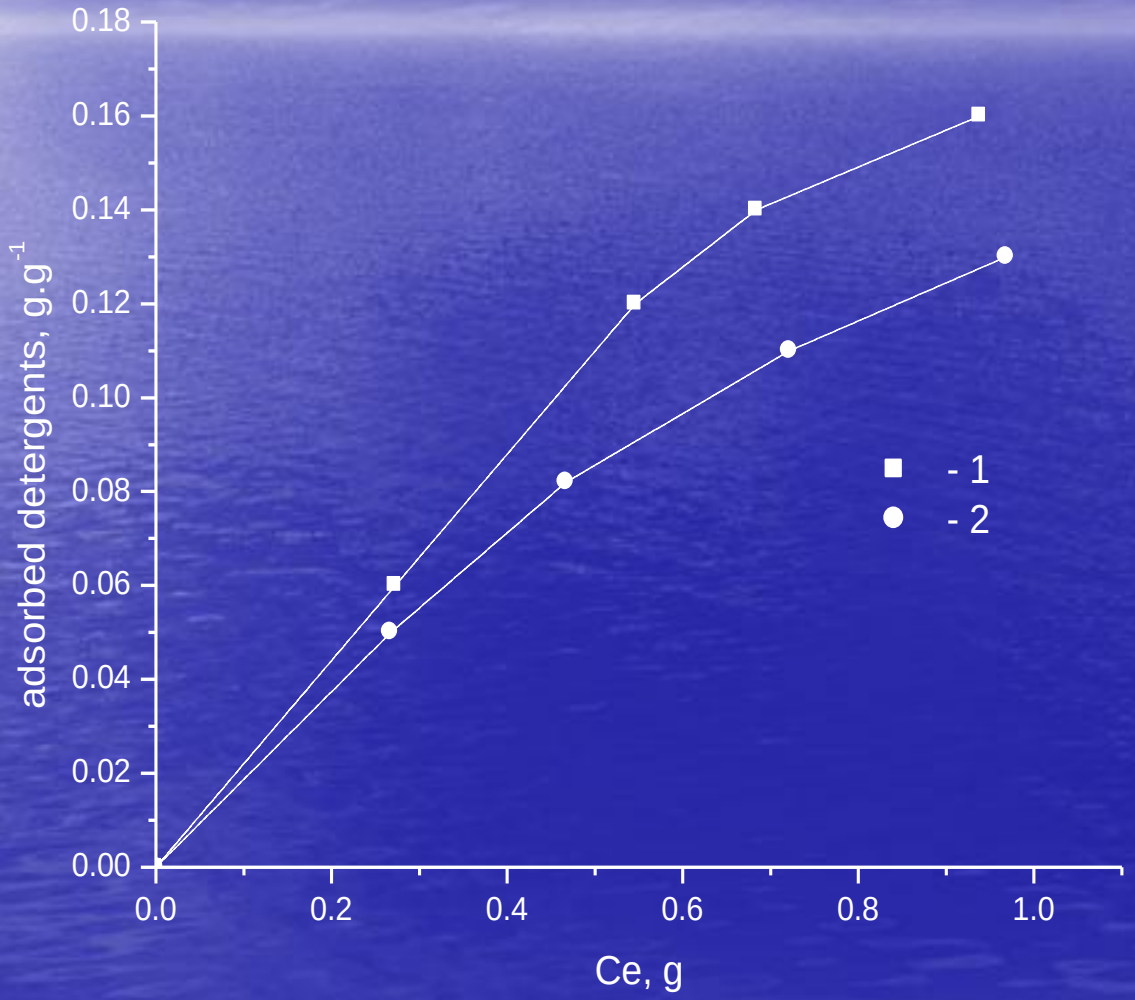
Adsorption isotherm of AC from furfural and coal tar pitch:
1 – sulphonate compounds; 2 – phenolic compounds



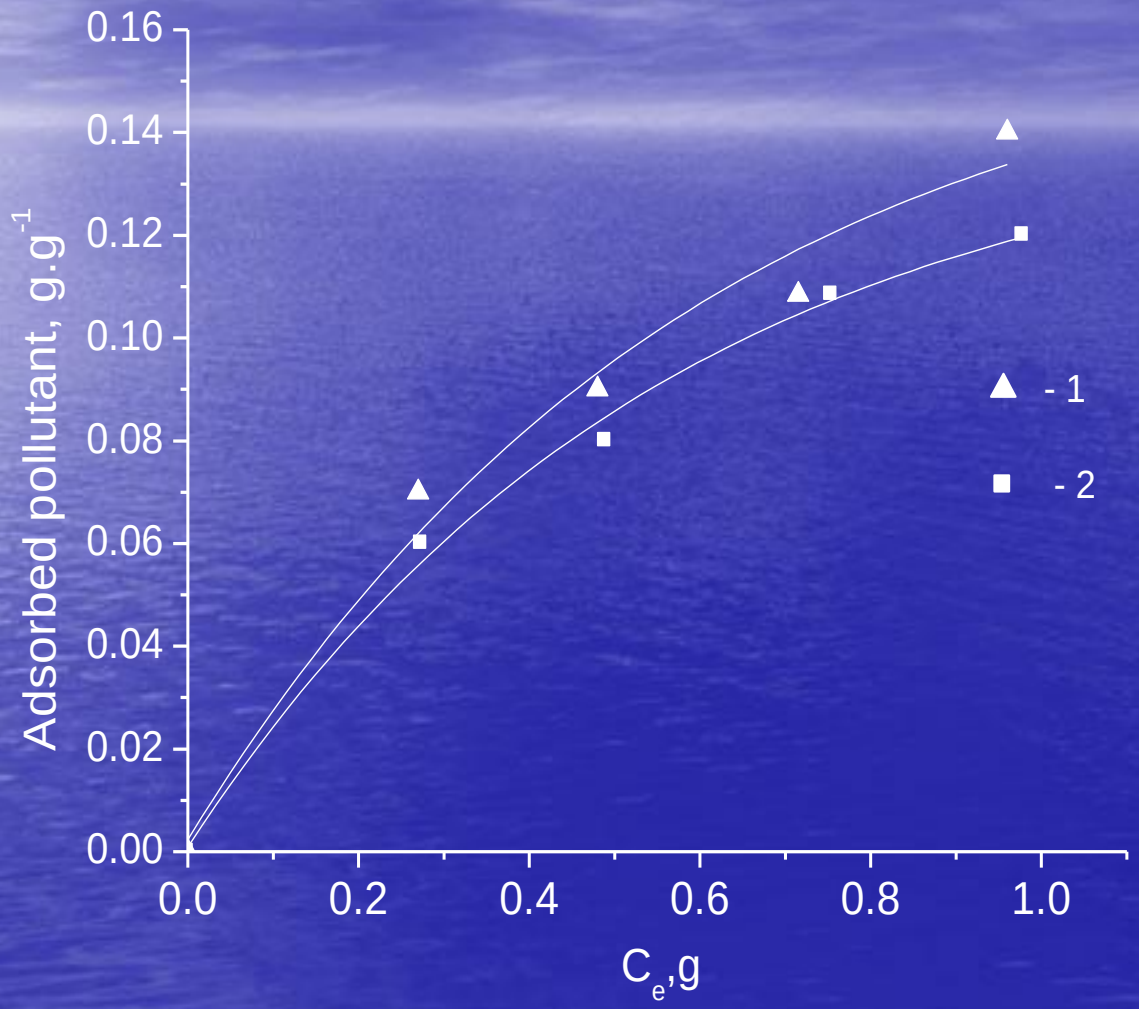
Adsorption isotherm of AC from asphaltites:
1 – sulphonate compounds; 2 – phenolic compounds



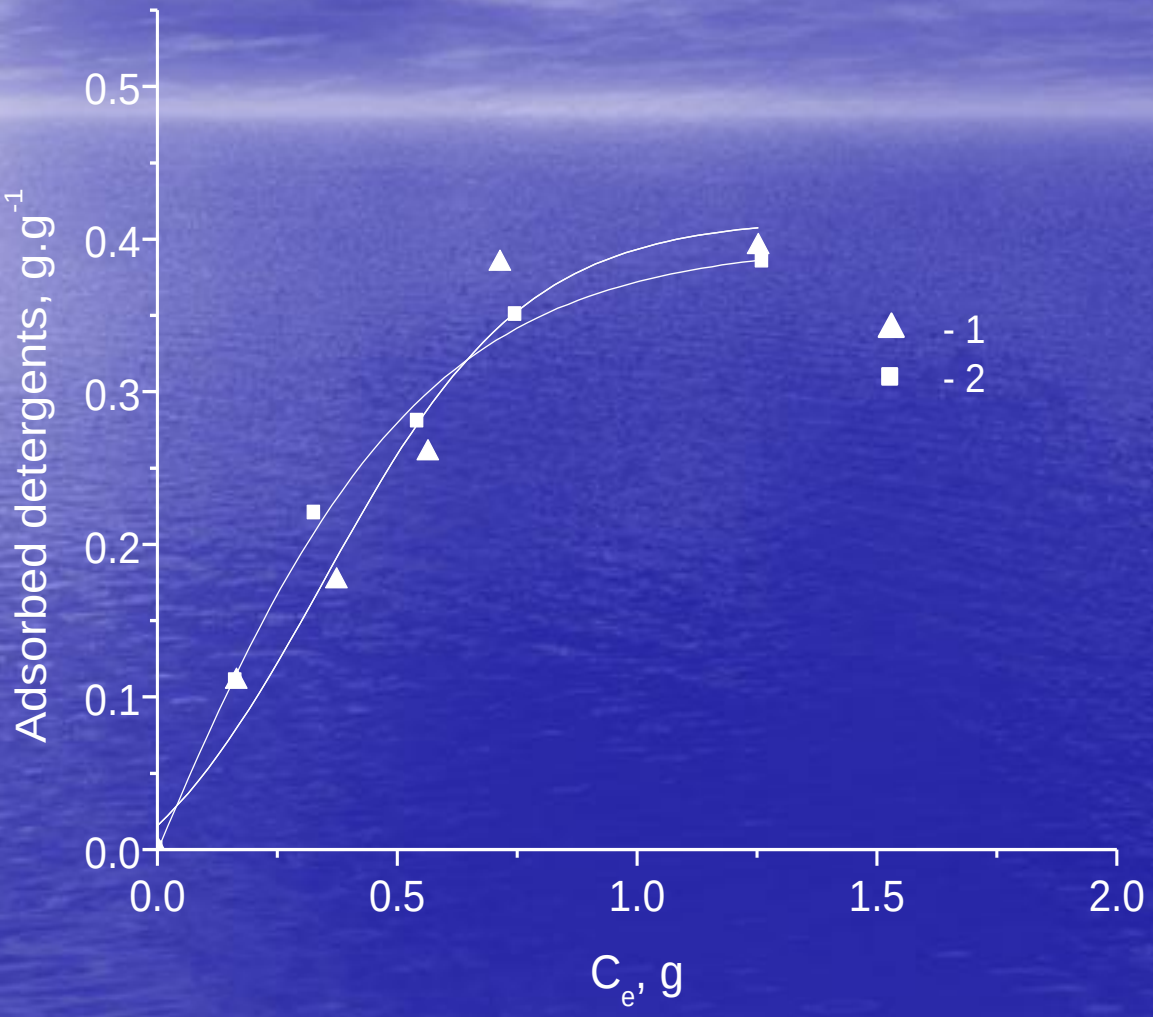
Adsorption isotherm of Zeolite Gordes G:
1 – sulphonate compounds; 2 – phenolic compounds



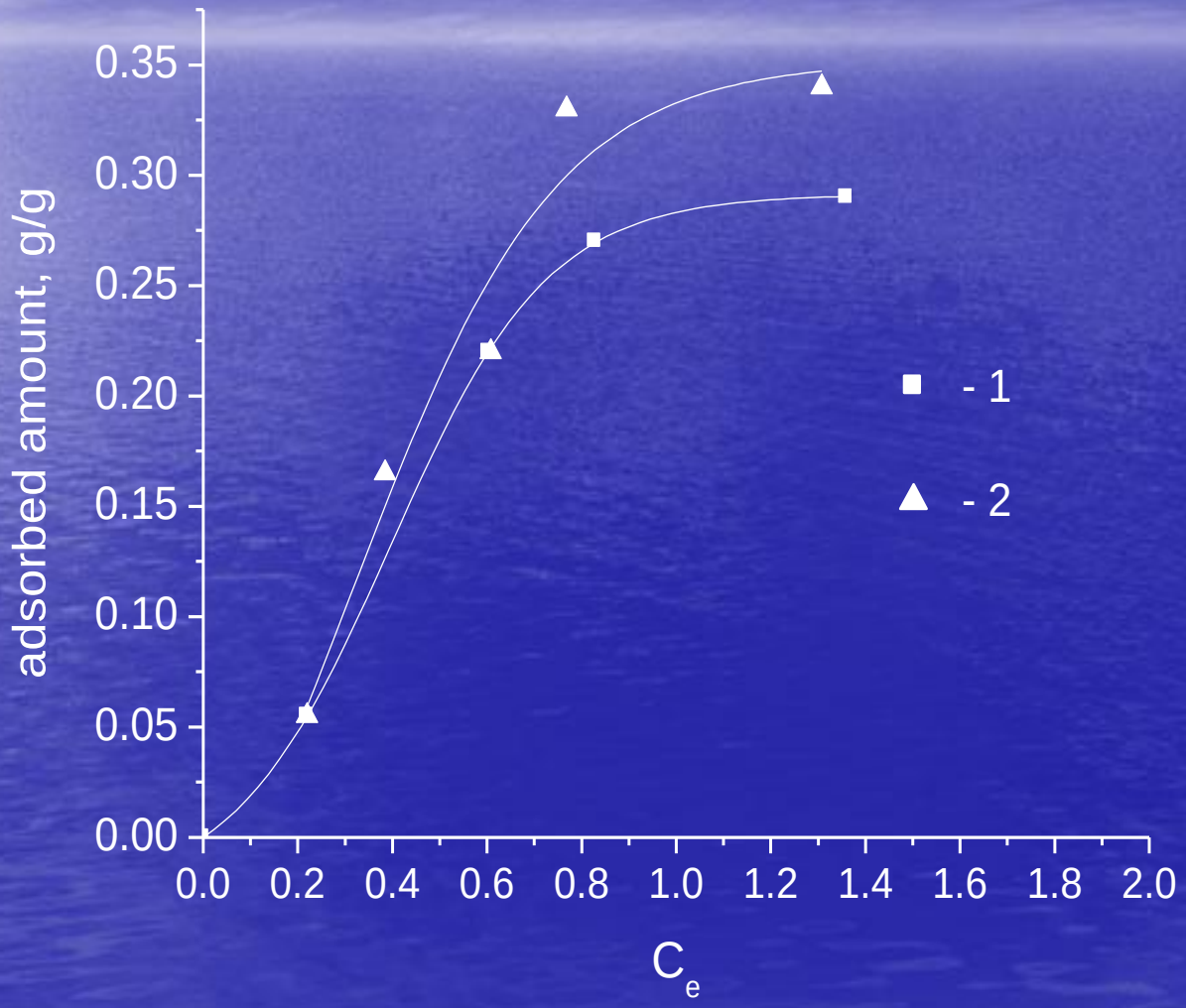
Adsorption isotherm of Zeolite Bioodic B:
1 – sulphonate compounds; 2 – phenolic compounds



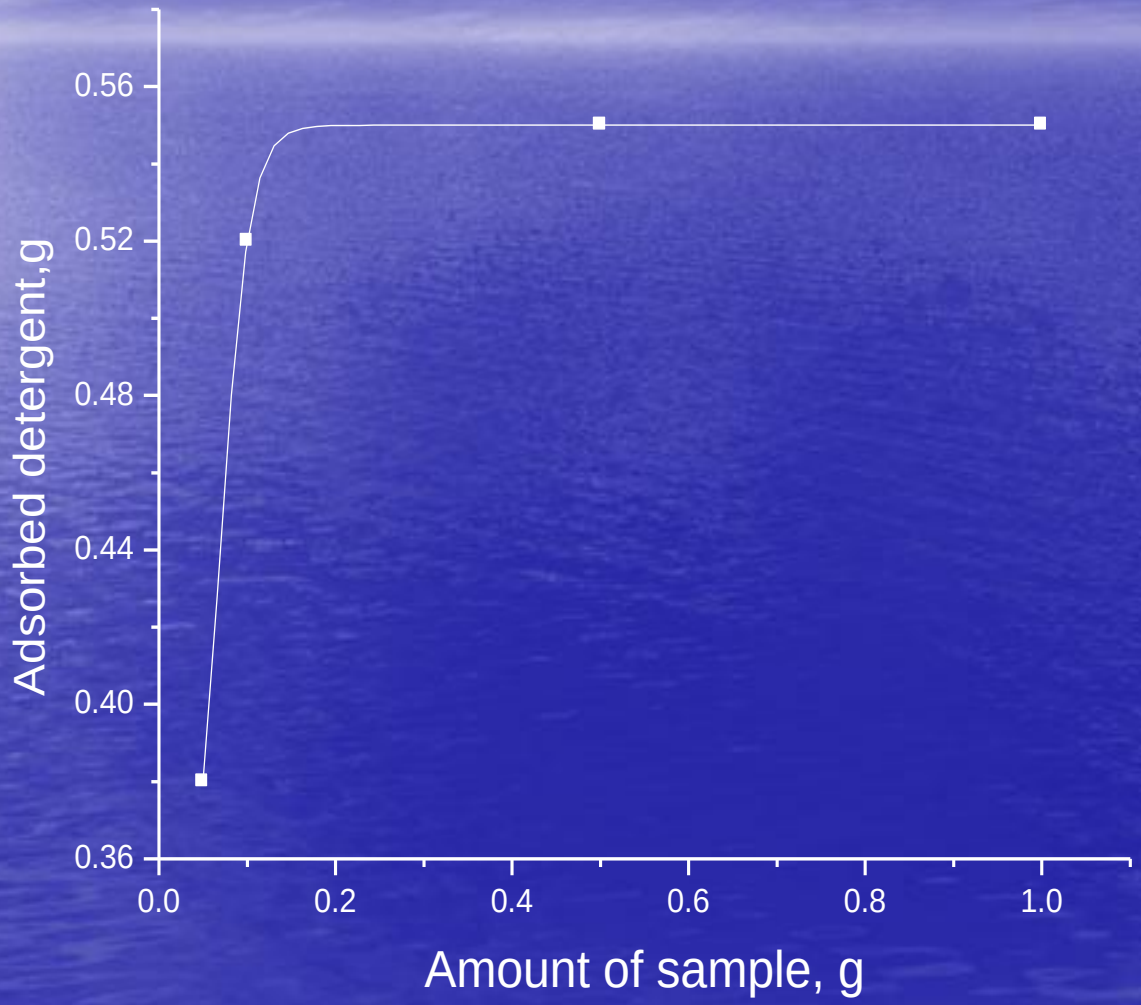
Adsorption isotherm of PZ zeolite:
1 – sulphonate compounds; 2 – phenolic compounds



Adsorption isotherm of F5 zeolite:
1 – sulphonate compounds; 2 – phenolic compounds



Influence of the amount of the sample on the adsorption of sulphonates by AC from peach stones (800 mg/g I_2):



3. Studies about composite multifunctional ultra filtration membranes (ICECHIM)

I. Copolymerization

Table 1: The relative viscosities of the synthesized copolymers

Copolymer	η relative
AN-AV (90-10)	1.58
AN-AV (80-20)	2.59
AN-AV (70-30)	1.48

Table 2: Elemental composition of the 3 copolymers, weight %

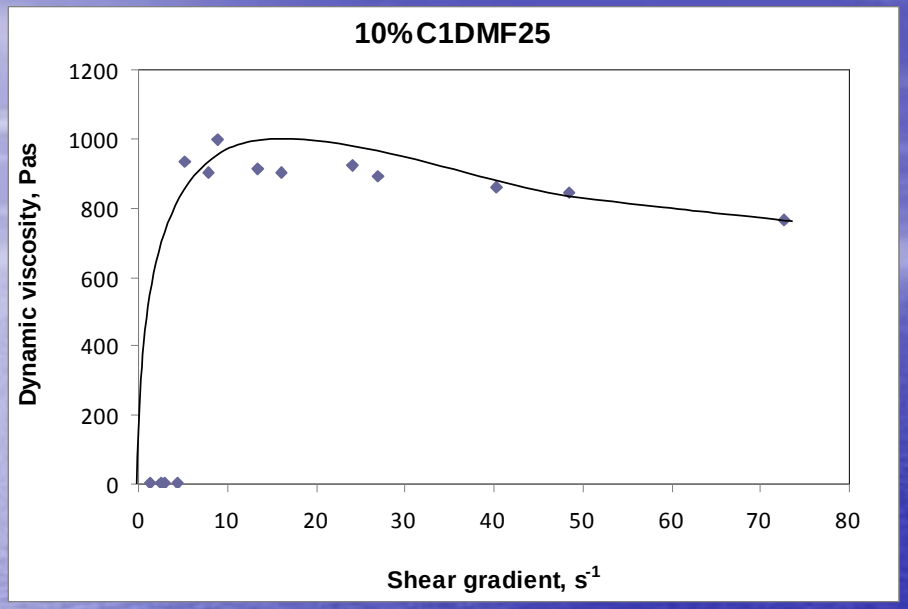
Copolymer	C, %	H, %	N, %	S, %	O, %
AN-AV (90-10)	65.79	6.10	24.27	0.85	2.99
AN-AV (80-20)	65.00	6.22	22.53	0.78	5.47
AN-AV (70-30)	64.14	6.48	20.57	0.90	7.91

I. Copolymerization

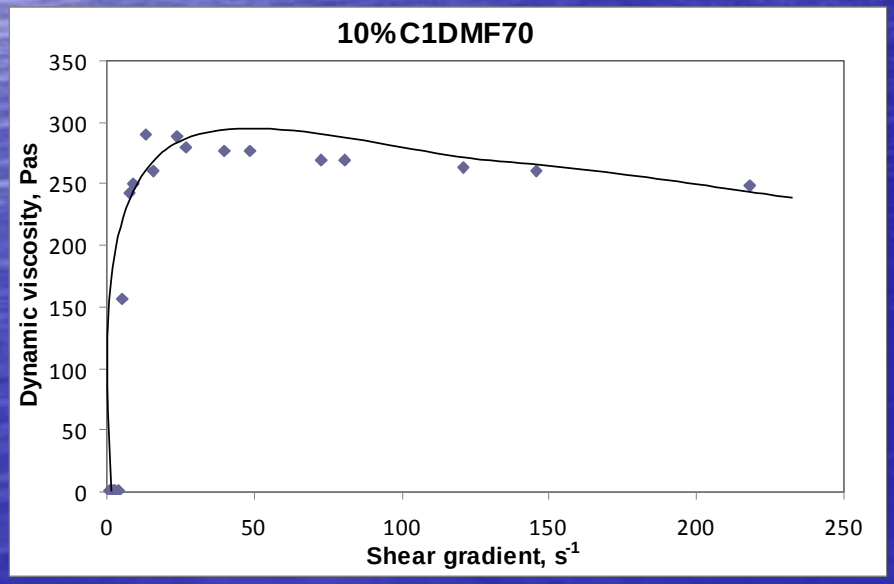
Table 3: The monomer content in the feed monomer mixture and in copolymers, weight %

Copolymer	Monomer mixture		Copolymer content	
	AN, %*	AV, %*	AN, %*	AV, %*
C1	90	10	90,68	9.78
C2	80	20	82,47	17.53
C3	70	30	74,82	25,18

II. Rheology in DMF



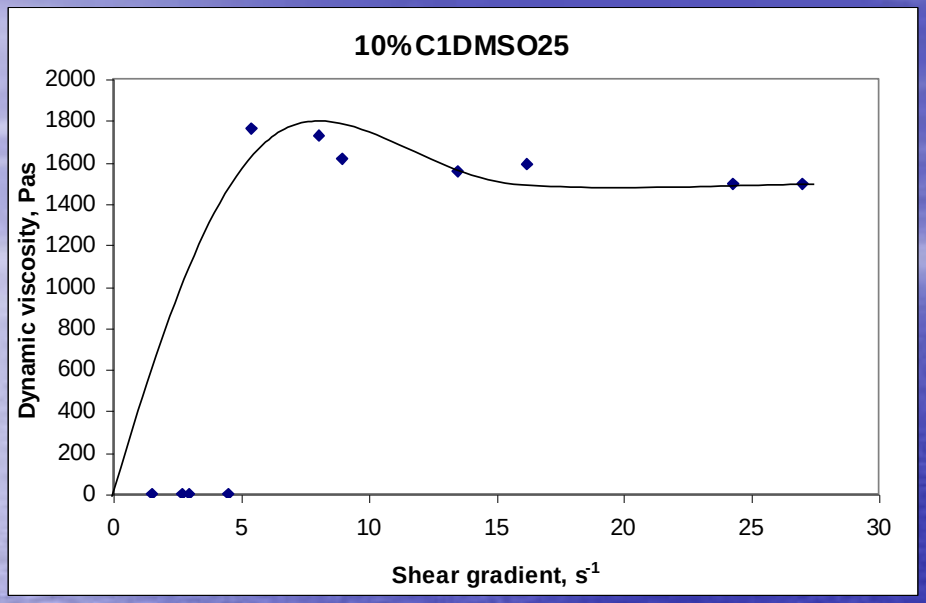
a



b

Figure 1: Dependence of dynamic viscosity of shear gradient for the solution of copolymer 1 (90 AN:10 AV) in DMF having the polymer concentration 10%
a- at 25 °C
b- at 70 °C

III. Rheology in DMSO



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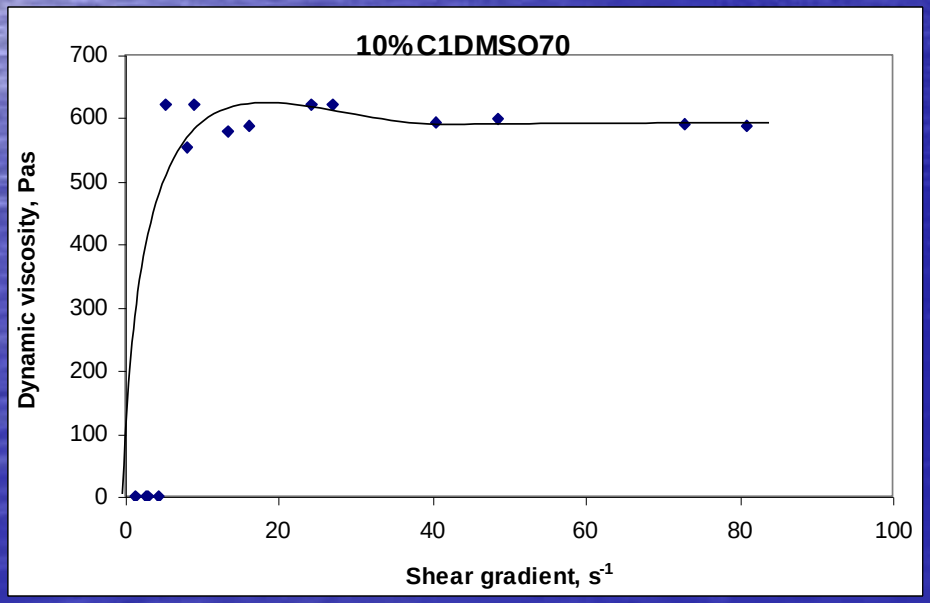
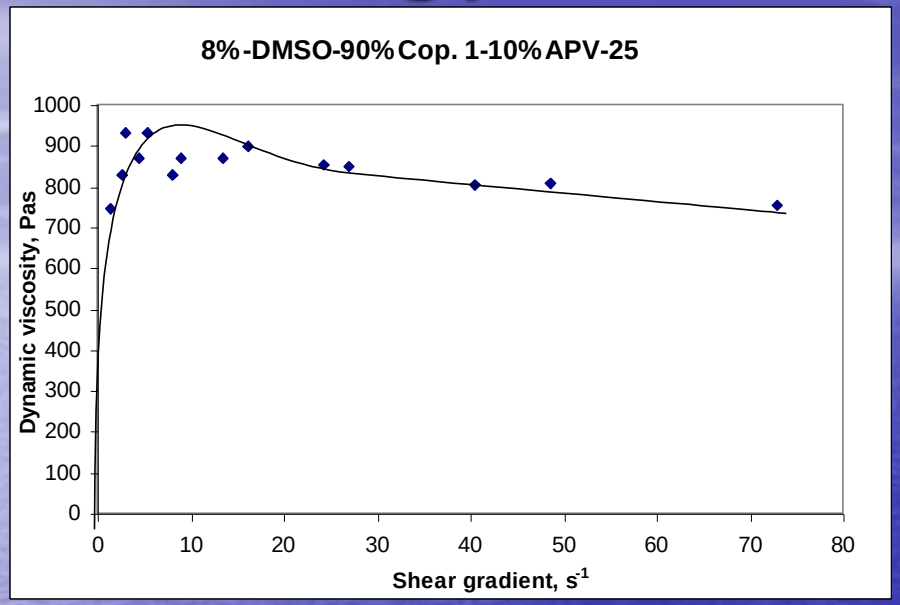


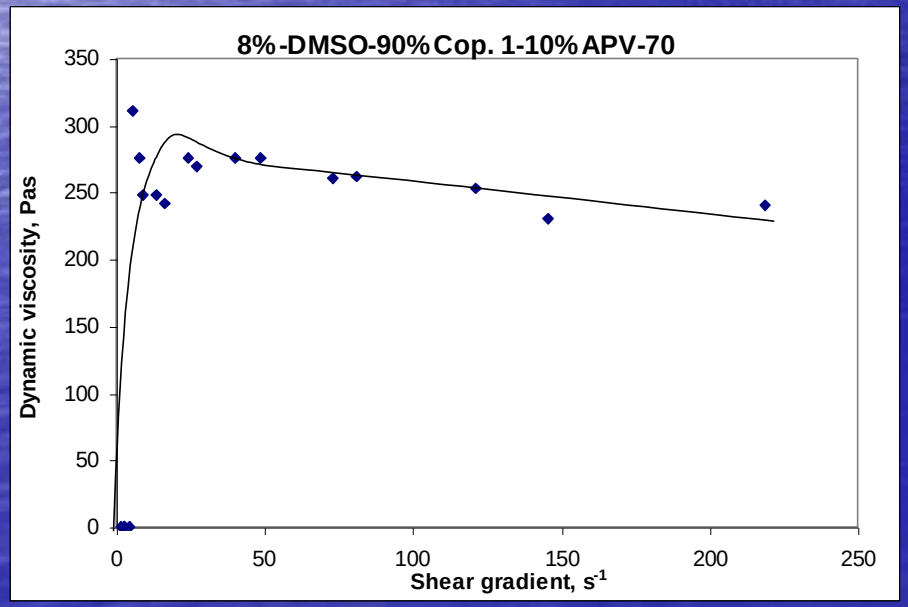
b

Figure 2: Dependence of dynamic viscosity of shear gradient for the solution of copolymer 1 (90 AN:10 AV) in DMSO having the polymer concentration 10%
a- at 25 ^{o}C
b- at 70 ^{o}C

IV. Rheology of blends in DMSO



a



b

Figure 3: Dependence of dynamic viscosity of shear gradient for the solution of blends of copolymer 1 (90 %) with PAV (10 %) in DMSO, having the polymer concentration 8%
a- at 25 °C
b- at 70 °C

VI. COAGULATION BATH

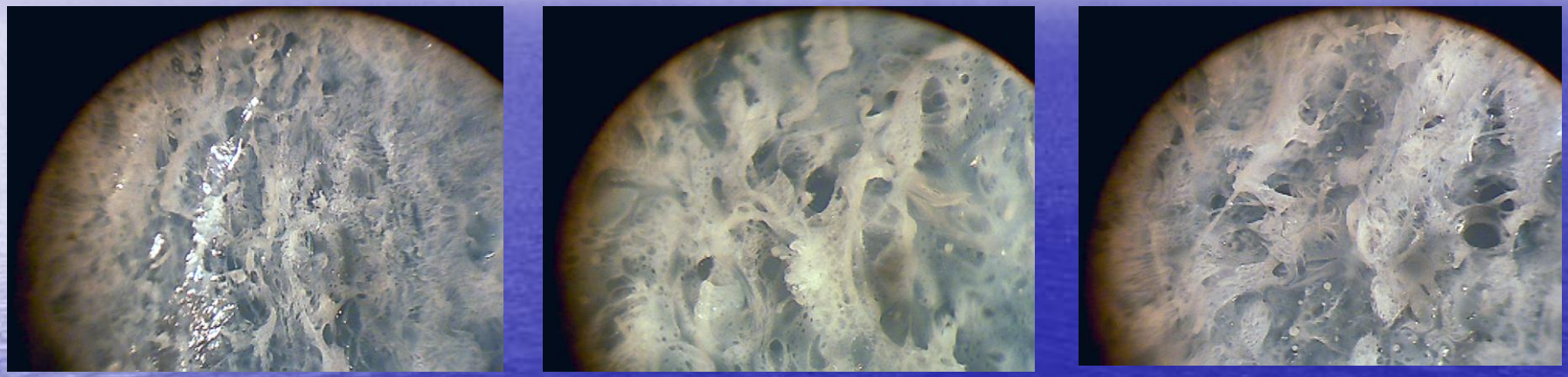


Figure 4: Coagulation in water of membrane obtained from 90% copolymer C1 + 10 % PVA

VI. COAGULATION BATH

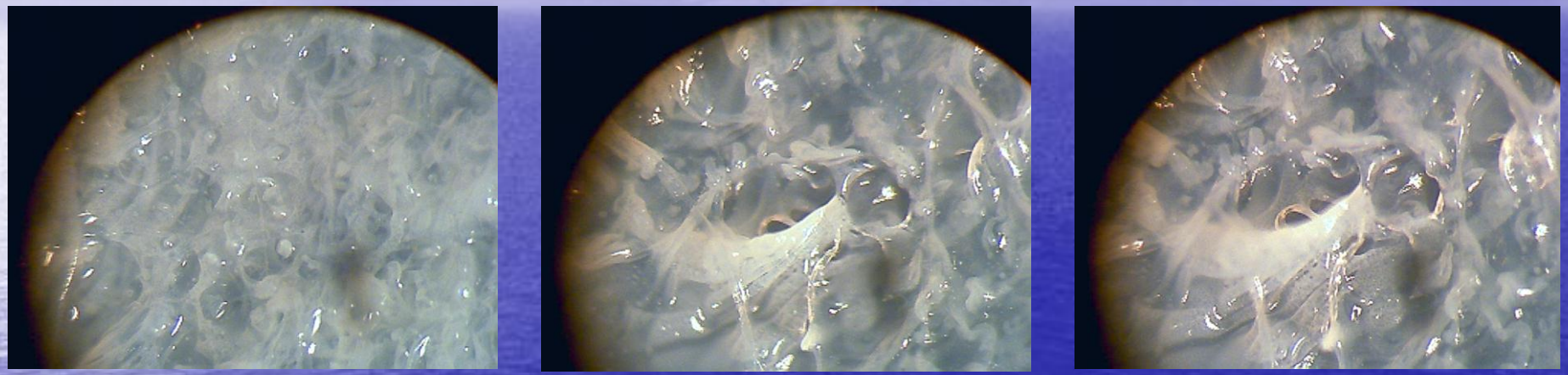


Figure 5: Coagulation in CH_3OH of membrane obtained from 90% copolymer C1 + 10 % PVA

VI. COAGULATION BATH

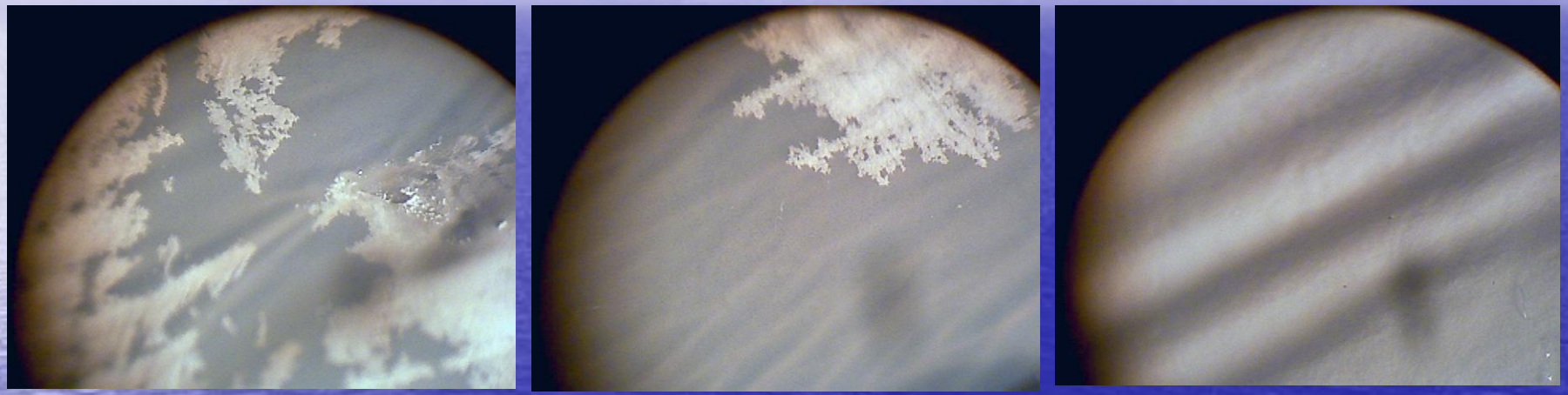


Figure 6: Coagulation in iso propanol of membrane obtained from 90% copolymer C1 + 10 % PVA

VI. COAGULATION BATH

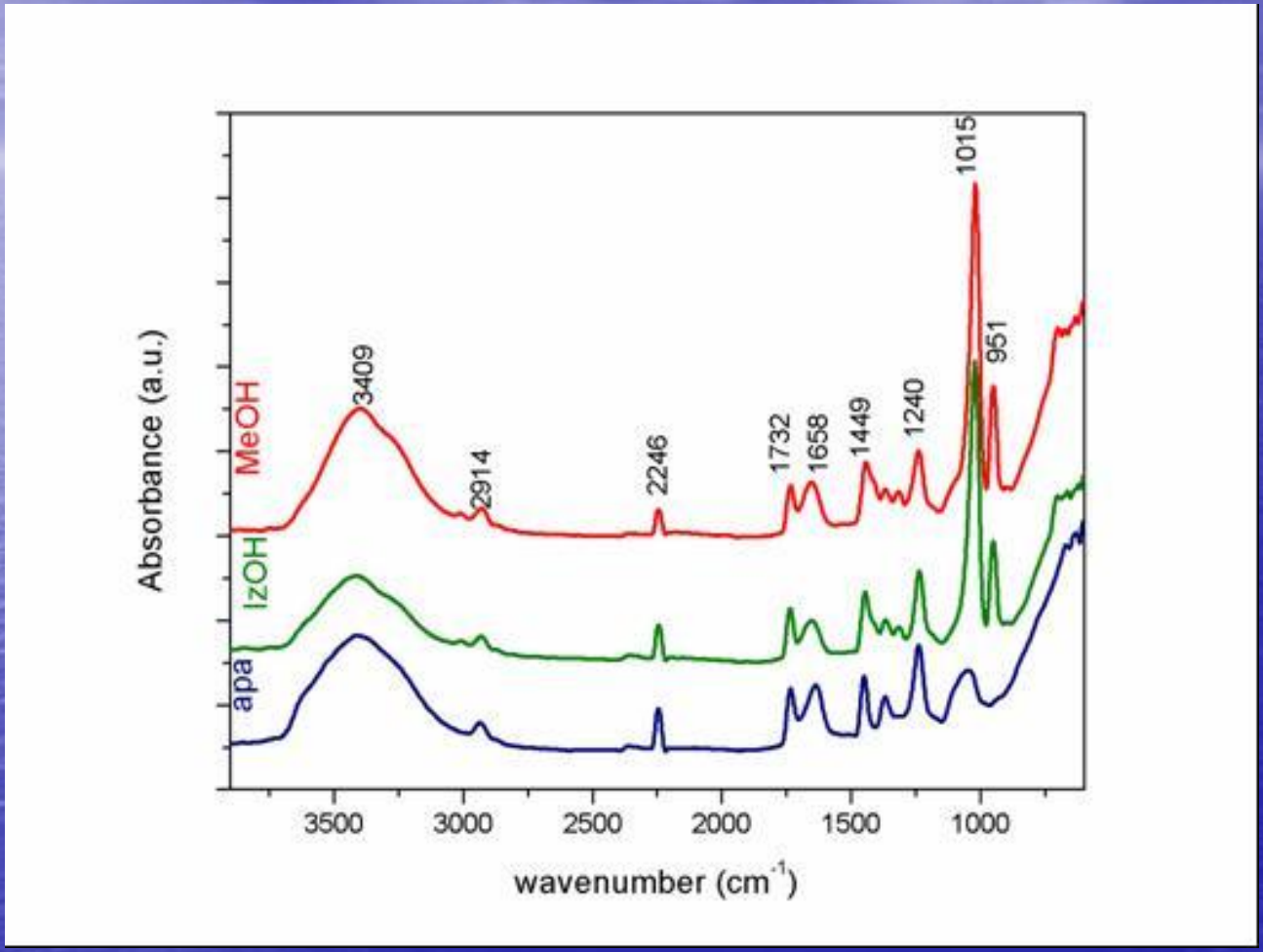
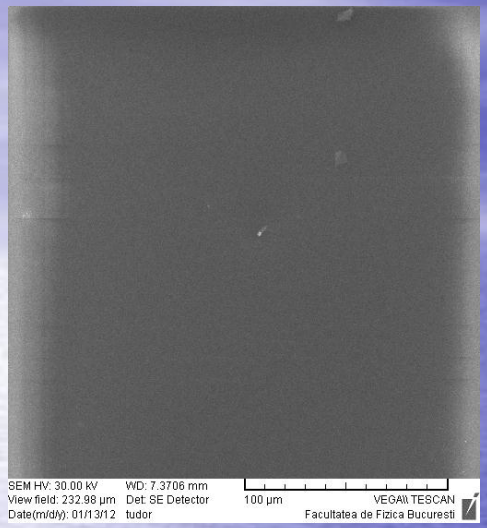
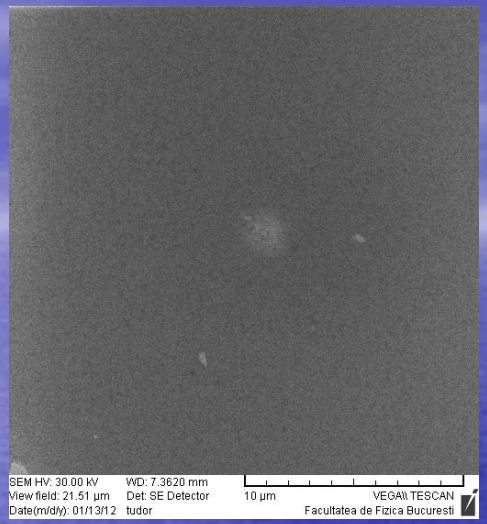


Figure 7 FTIR spectra of membranes prepared from 90 % copolymer C1 + 10% PVA, coagulated in different bath: Water, Methanol and Izo propanol

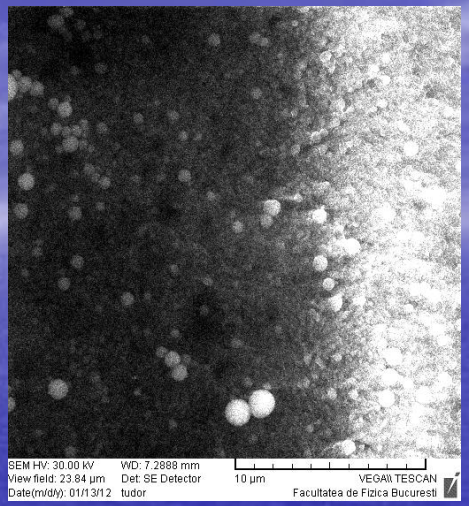
VI. COAGULATION BATH



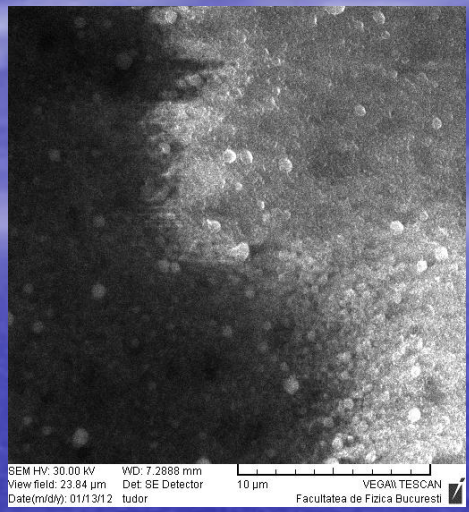
DMSO 8% Cop 1 (100%) at 100 µm



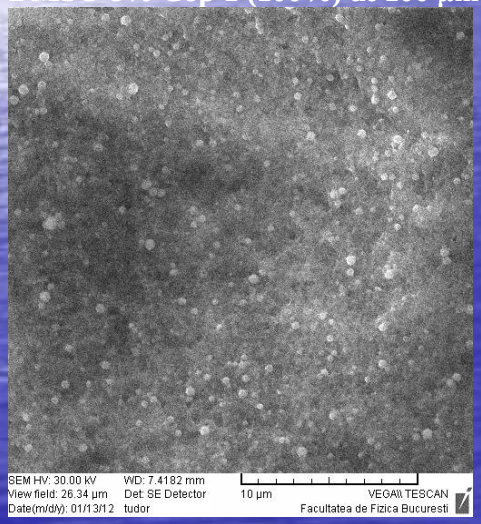
DMSO 8% Cop 1 (100%) at 10 µm



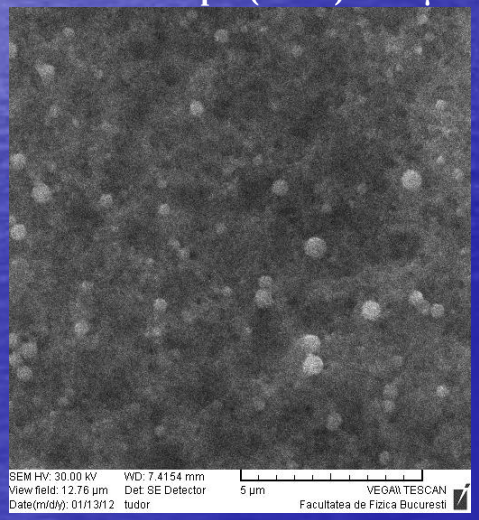
DMSO 8% (85% Cop 1-15% PVA) at 10 µm



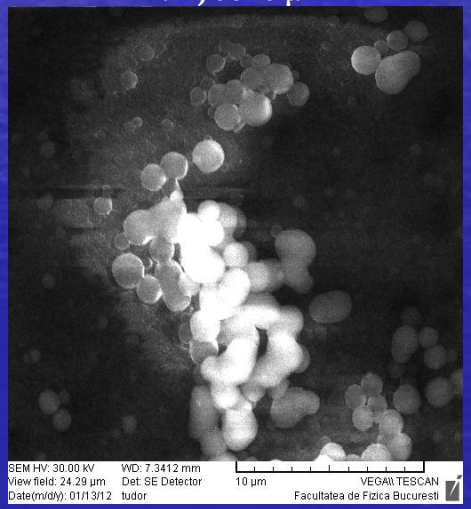
DMSO 8% (85% Cop 1-15% PVA) at 10 µm



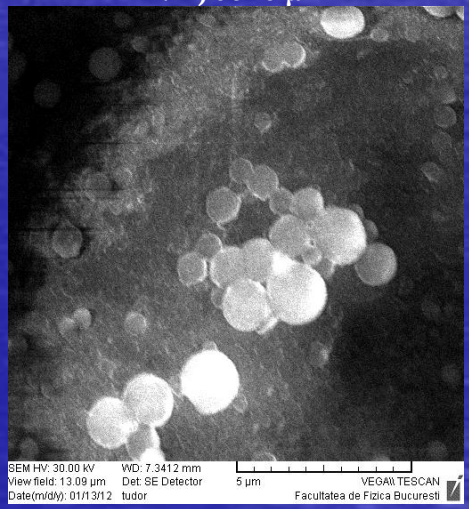
DMSO 8% (90% Cop 1-10% PVA) at 10 µm



DMSO 8% (90% Cop 1-10% PVA) at 5 µm



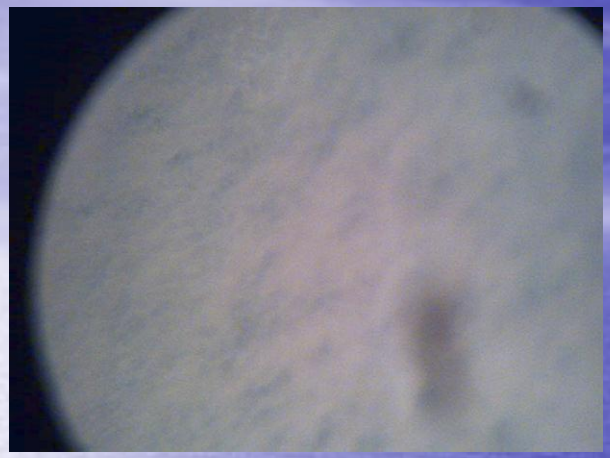
DMSO 8% (80% Cop 1-20%PVA) at10 µm



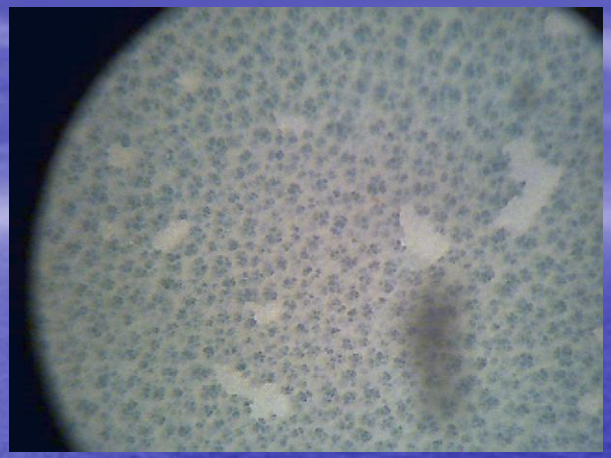
DMSO 8% (80% Cop 1-20% PVA) at 5 µm

Figure 8: SEM photos: Influence of PVA content of membranes obtained from solutions of copolymer 1 by phase inversion in iso propanol

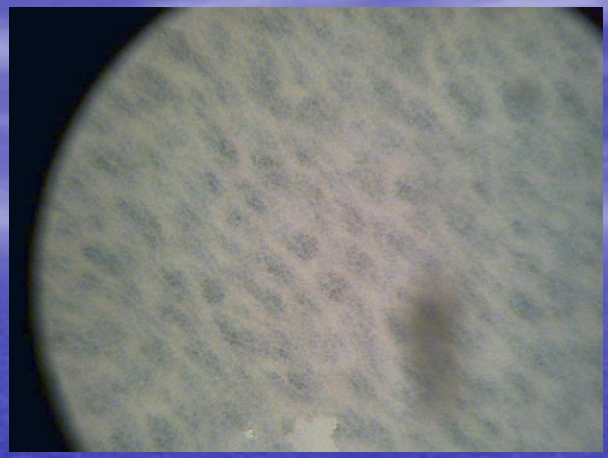
VII. Membranes Morphology



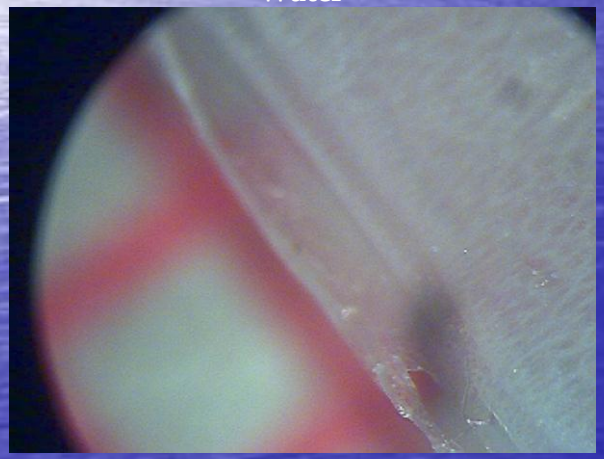
90 % C3+10 % PVA; 50 % IzOH+50 % Water



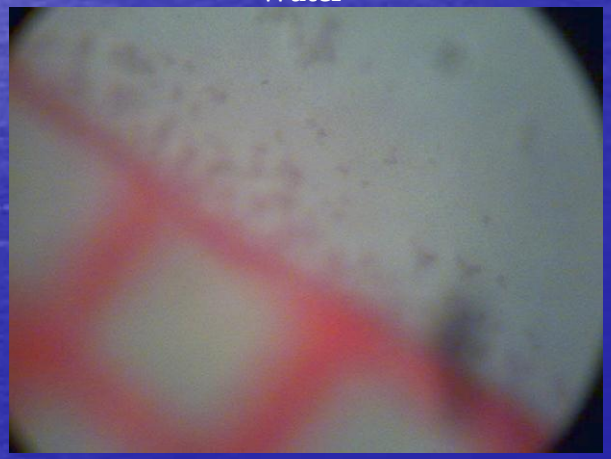
90 % C3+10 % PVA; 60 % IzOH+40 % Water



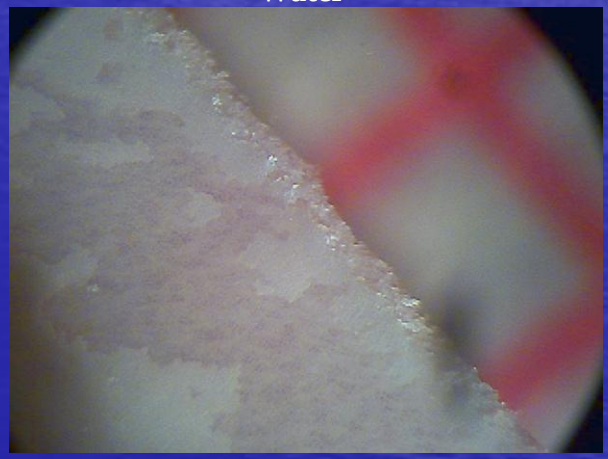
90 % C3+10 % PVA; 70 % IzOH+30 % Water



90 % C3+10 % PVA; 50 % IzOH+50 % Water



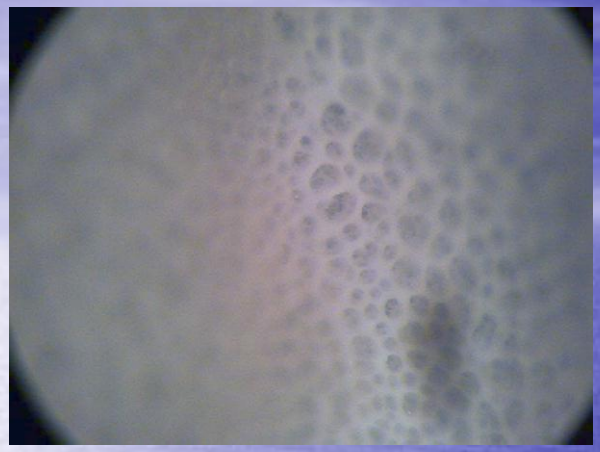
90 % C3+10 % PVA; 60 % IzOH+40 % Water



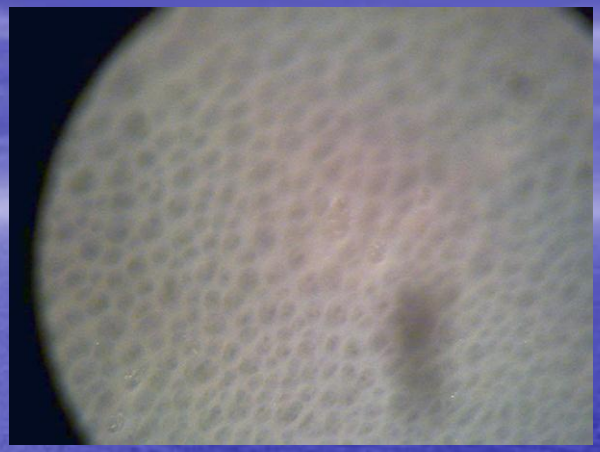
90 % C3+10 % PVA; 70 % IzOH+30 % Water

Figure 9 Influence of the inversion phase mixture on the structure of the membranes prepared from blends of 90% copolymer 3 with 10% PVA. Optical microscopy

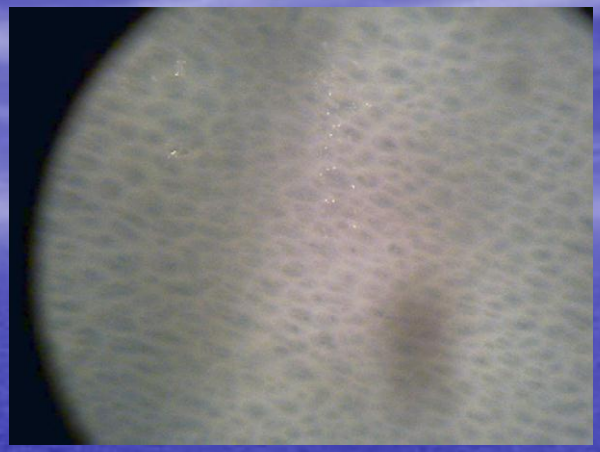
VII. Membranes Morphology



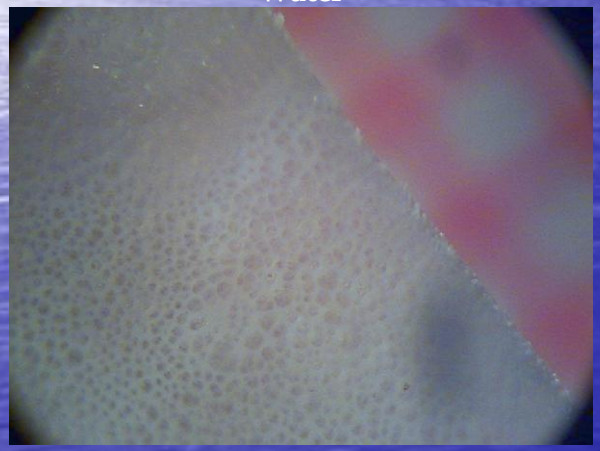
75 % C3+25 % PVA ; 50 % IzOH+50 % Water



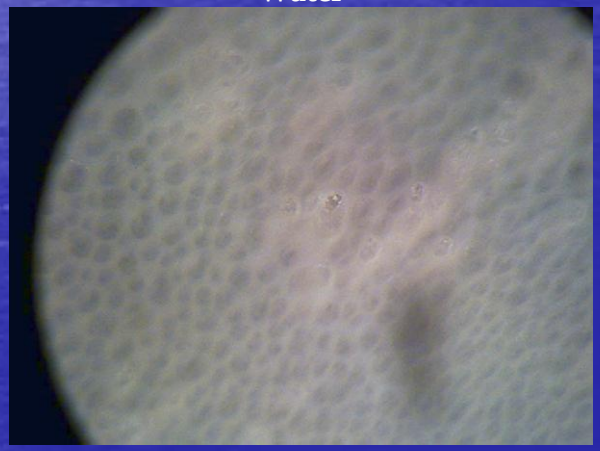
75 % C3+25 % PVA ; 60 % IzOH+40 % Water



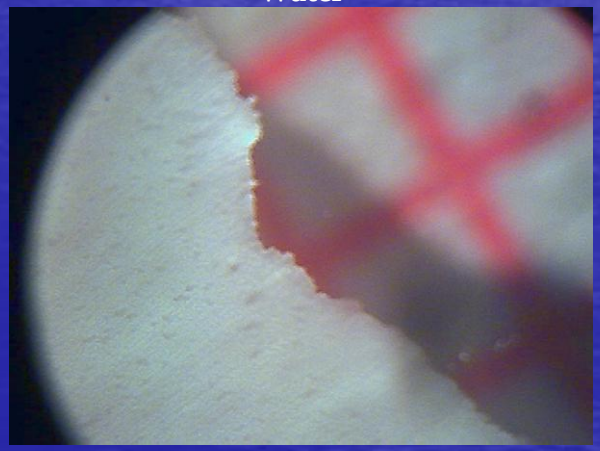
75 % C3+25 % PVA ; 70 % IzOH+30 % Water



75 % C3+25 % PVA ; 50 % IzOH+50 % Water



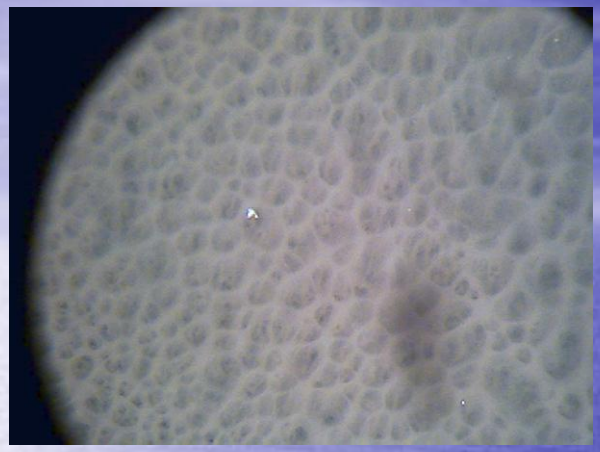
75 % C3+25 % PVA ; 60 % IzOH+40 % Water



75 % C3+25 % PVA ; 70 % IzOH+30 % Water

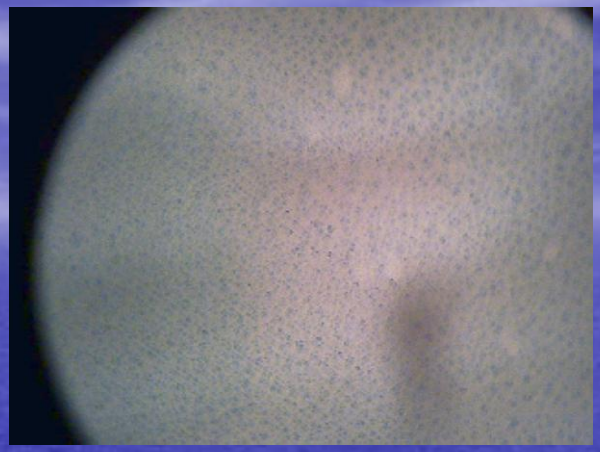
Figure 10 Influence of the inversion phase mixture on the structure of the membranes prepared from blends of 75 % copolymer 3 with 25 % PVA. Optical microscopy

VII. Membranes Morphology

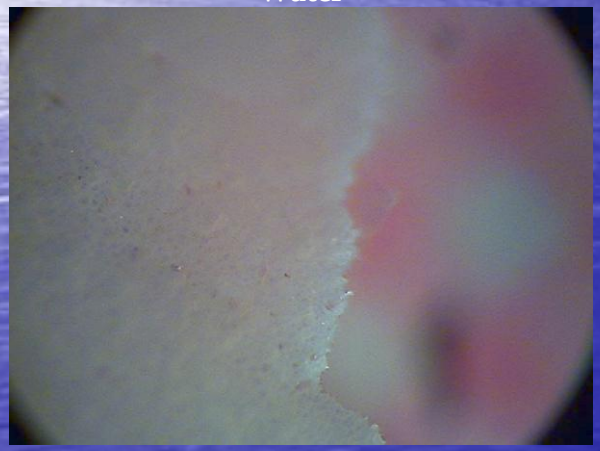


80 % C3+20 % PVA ; 50 % IzOH+50 % Water

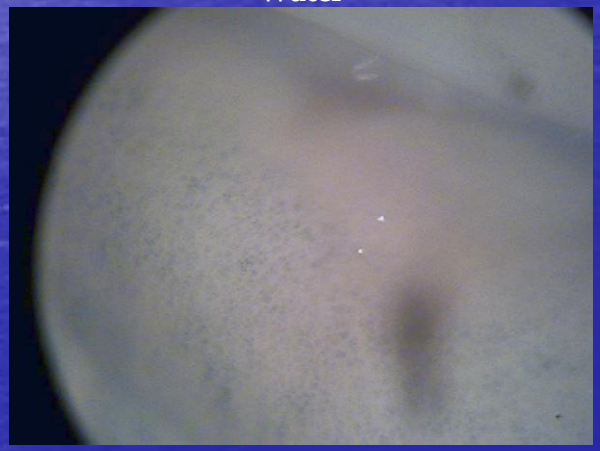
80 % C3+20 % PVA ; 60 % IzOH+40 % Water



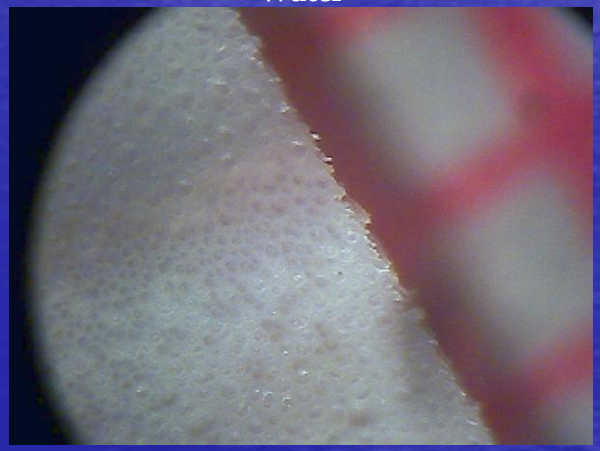
80 % C3+20 % PVA ; 70 % IzOH+30 % Water



80 % C3+20 % PVA ; 50 % IzOH+50 % Water



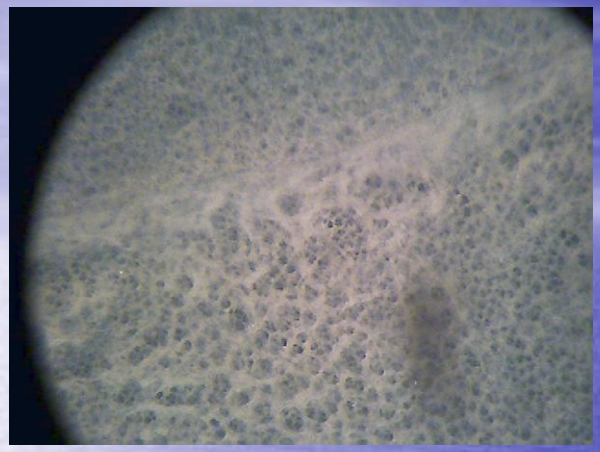
80 % C3+20 % PVA ; 60 % IzOH+40 % Water



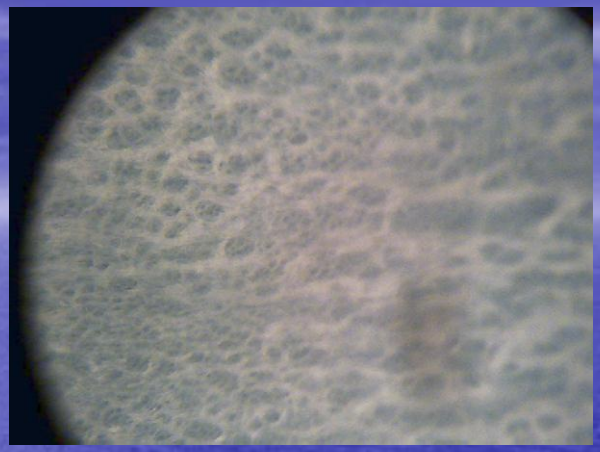
80 % C3+20 % PVA ; 70 % IzOH+30 % Water

Figure 11 Influence of the inversion phase mixture on the structure of the membranes prepared from blends of 80 % copolymer 3 with 20 % PVA. Optical microscopy

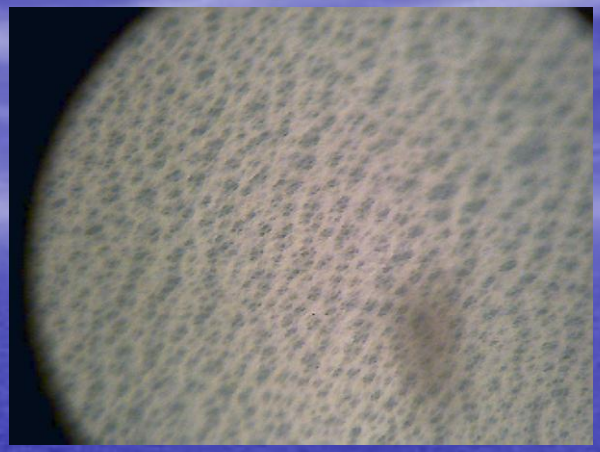
VII. Membranes Morphology



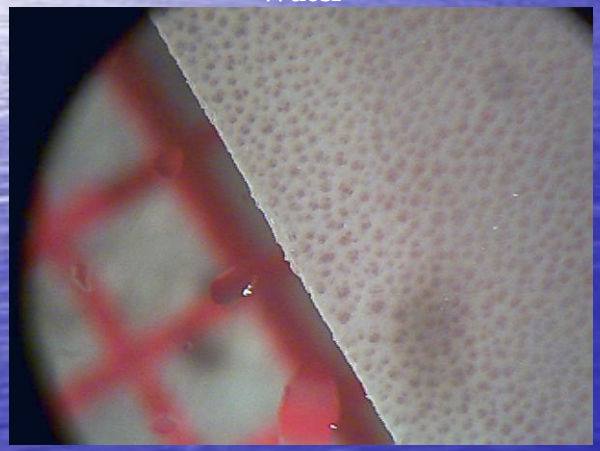
80 % C2+20 % PVA ; 50 % IzOH+50 % Water



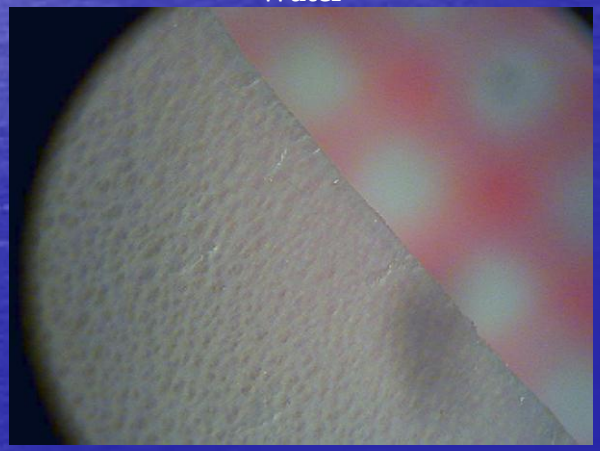
80 % C2+20 % PVA ; 60 % IzOH+40 % Water



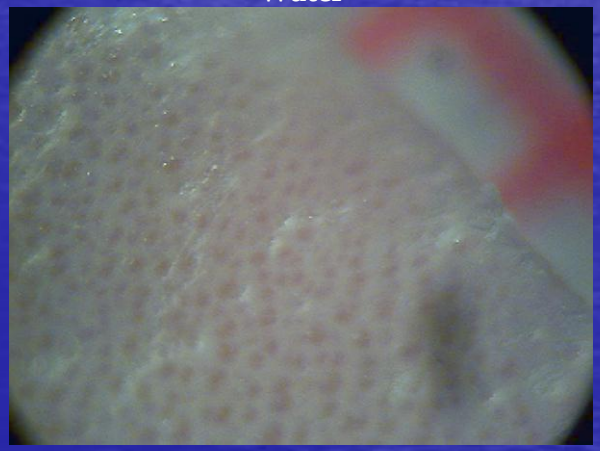
80 % C2+20 % PVA ; 70 % IzOH+30 % Water



80 % C2+20 % PVA ; 50 % IzOH+50 % Water



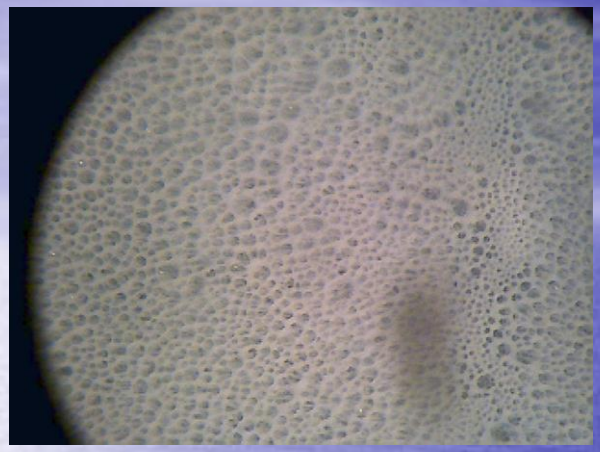
80 % C2+20 % PVA ; 60 % IzOH+40 % Water



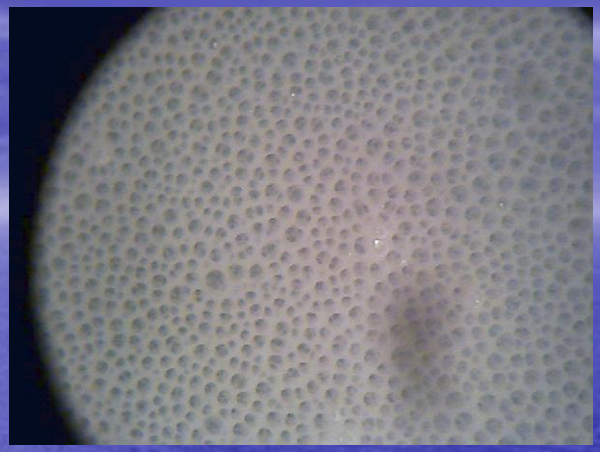
80 % C2+20 % PVA ; 70 % IzOH+30 % Water

Figure 12 Influence of the inversion phase mixture on the structure of the membranes prepared from blends of 80 % copolymer 2 with 20 % PVA. Optical microscopy

VII. Membranes morphology

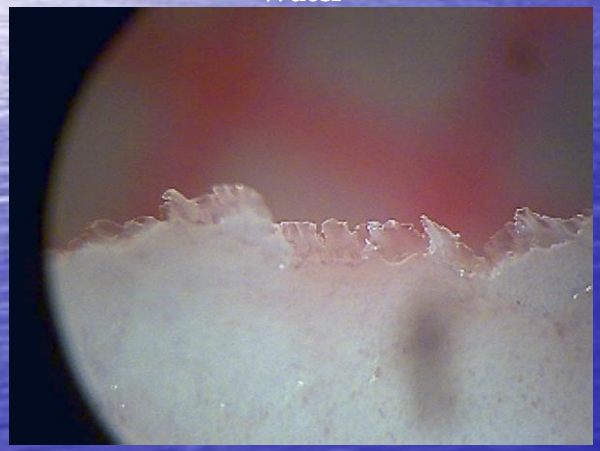


80% C1+20 %PVA ; 50 %IzOH+50 % Water

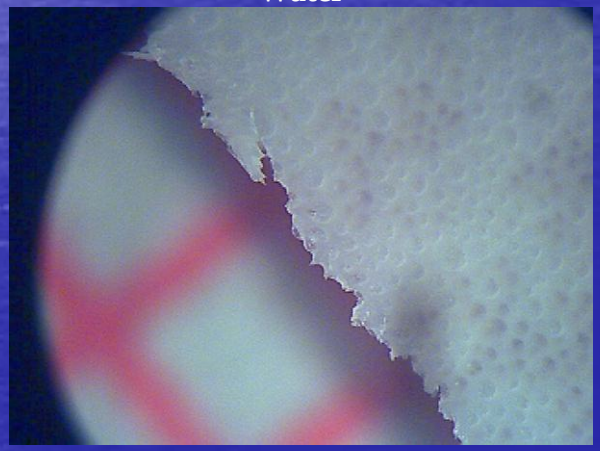


80% C1+20 %PVA ; 60 %IzOH+40 % Water

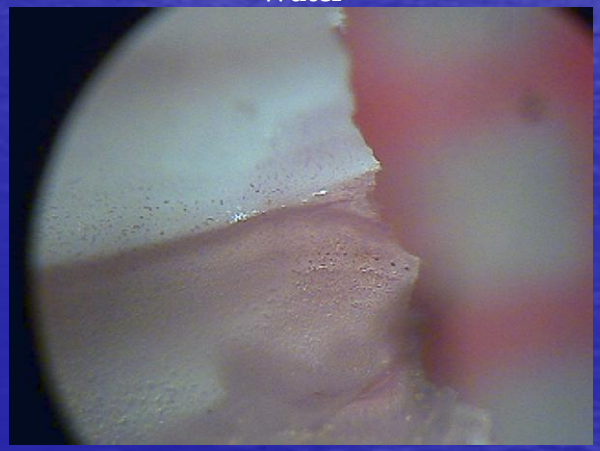
80 % C1+20 % PVA ; 70 % IzOH+30 % Water



80% C1+20 %PVA ; 50 %IzOH+50 % Water



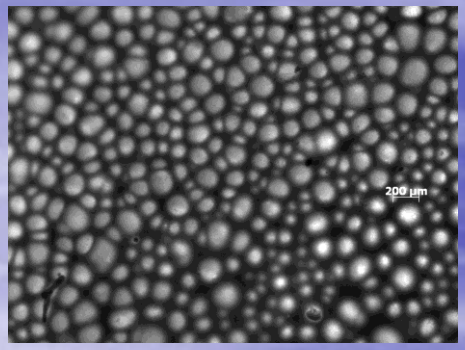
80% C1+20 %PVA ; 60 %IzOH+40 % Water



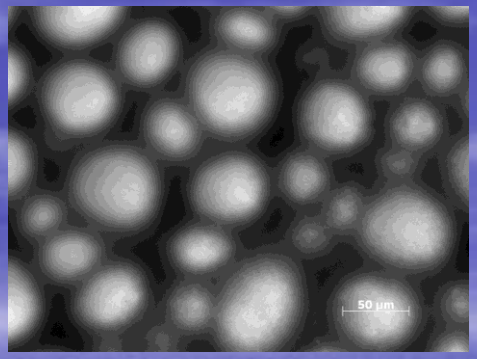
80 % C1+20 % PVA ; 70 % IzOH+30 % Water

Figure 13 Influence of the inversion phase mixture on the structure of the membranes prepared from blends of 80 % copolymer 1 with 20 % PVA. Optical microscopy

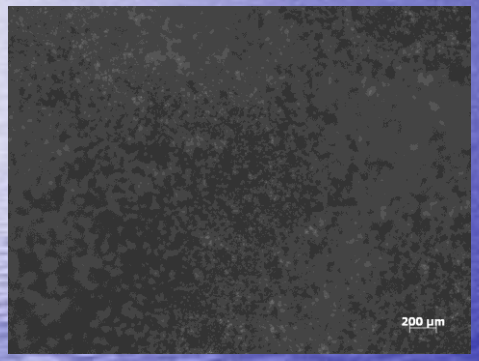
Membranes Morphology



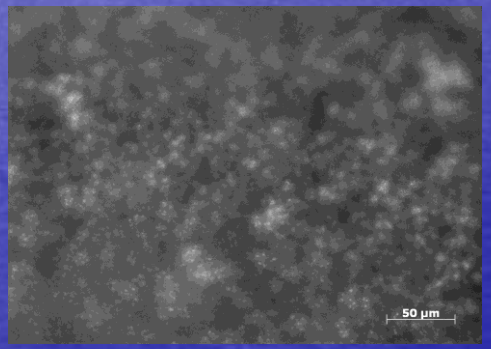
M1



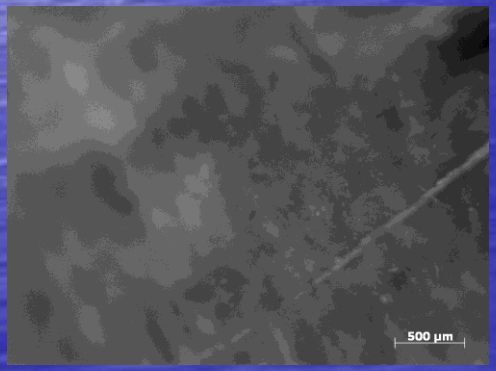
M1



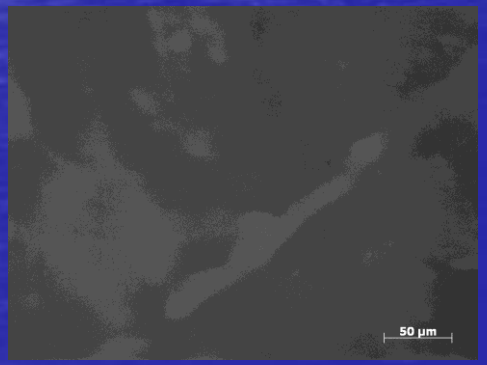
M2



M2



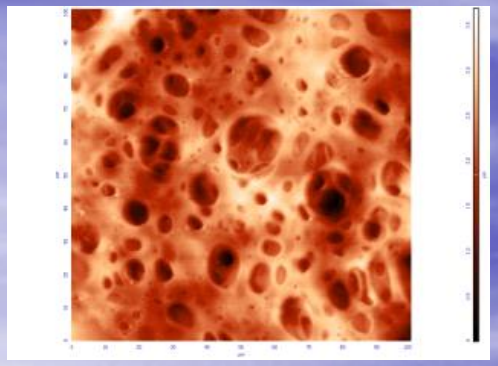
M3



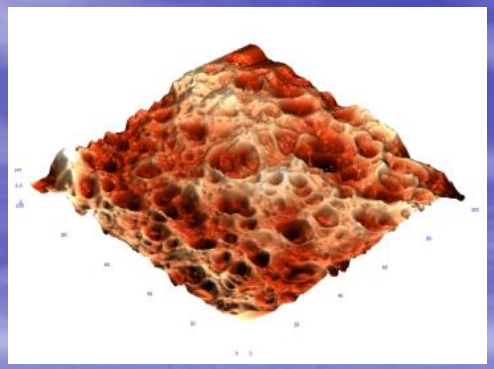
M3

Figura 14. Imaginile membranelor M1, M2 şi M3 la diferite rezoluţii

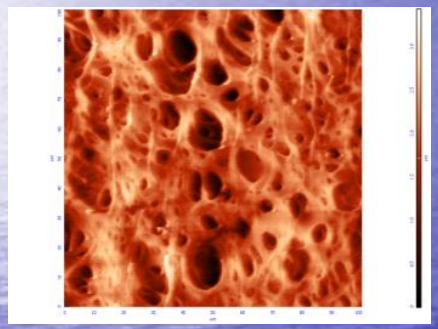
Membranes Morphology



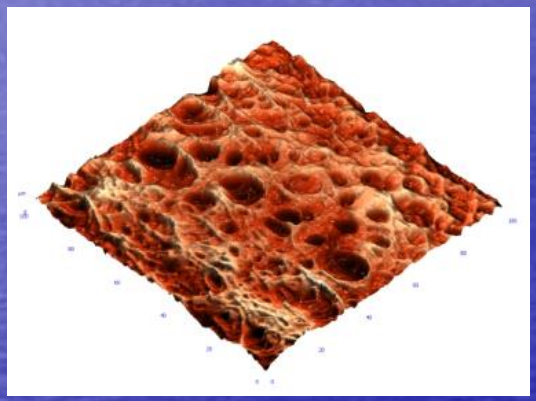
M4-100 µm



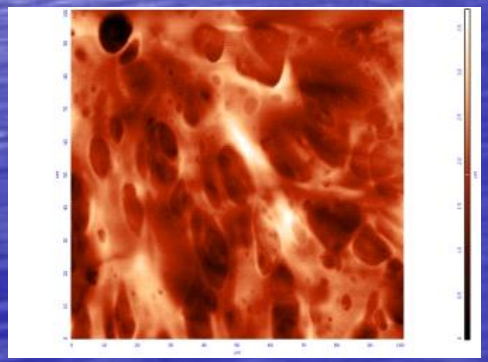
M4-100 µm



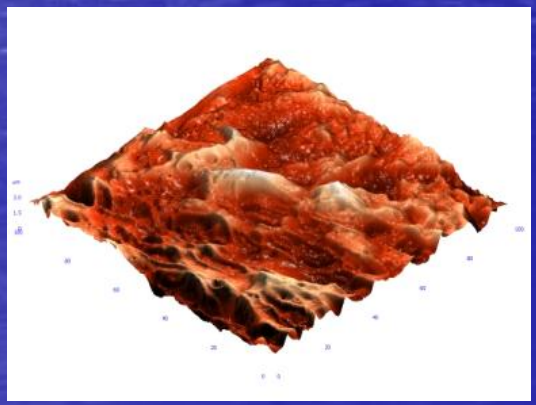
M 5-100 µm



M 5-100 µm



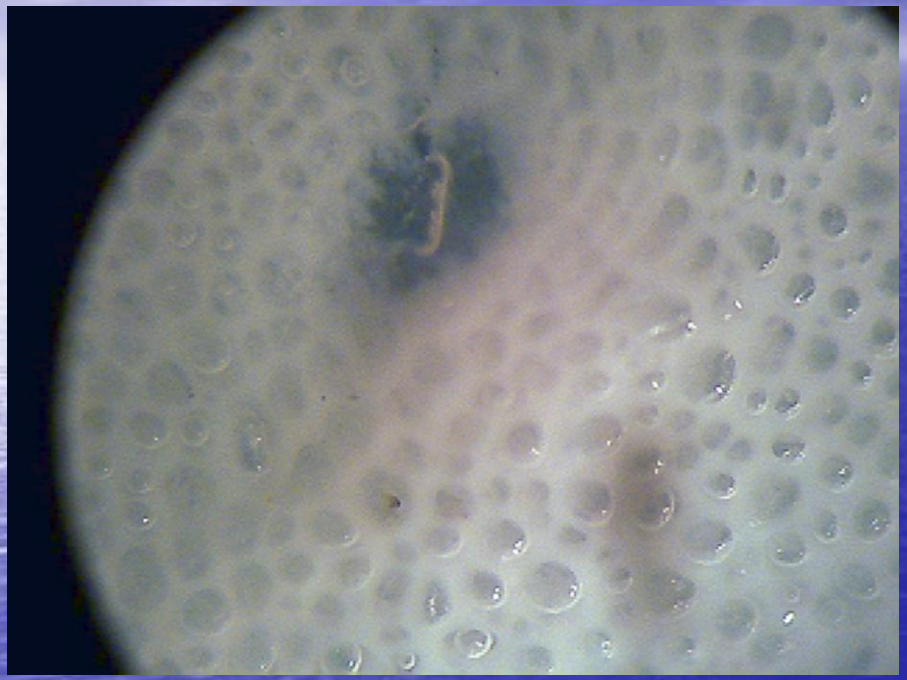
M 6-100 µm



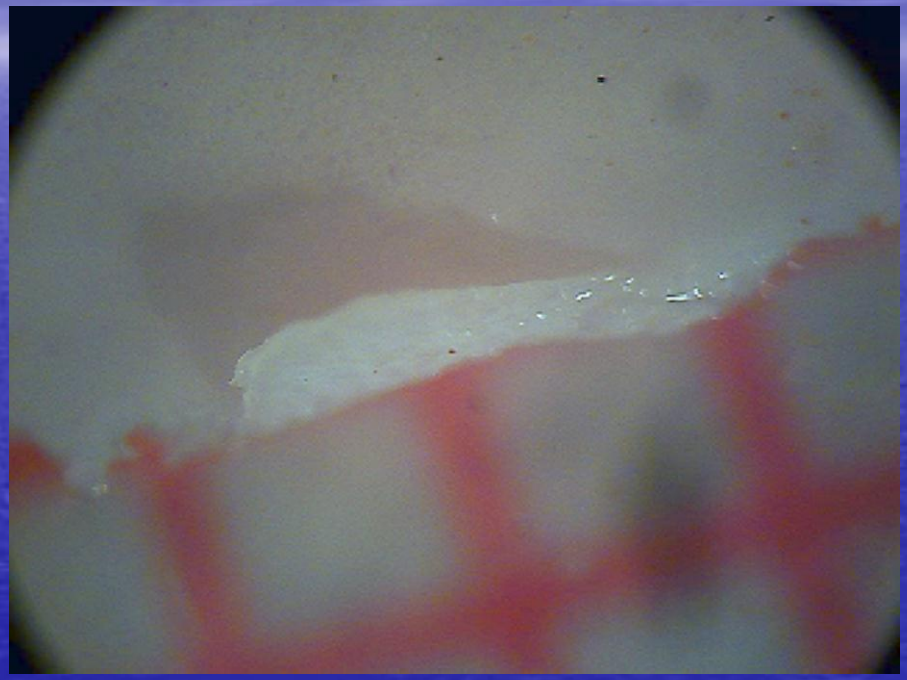
M 6-100 µm

Figura 15. Imaginile AFM ale membranelor M4, M5, M6

VII. Enzyme binding



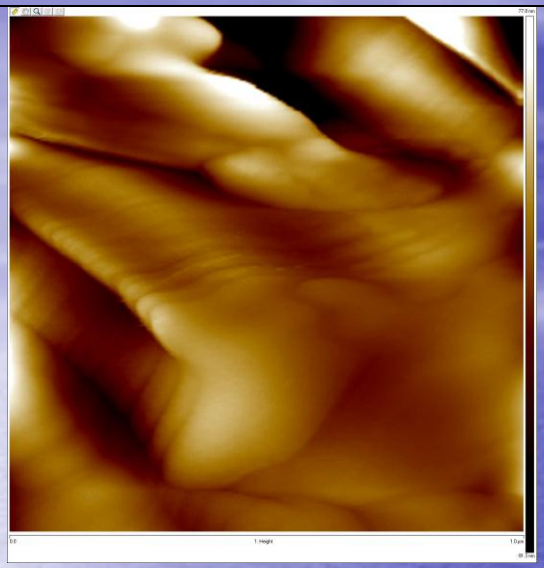
80% C1+20 %PVA ; 60 %IzOH+40 % Water + Tyrosinase



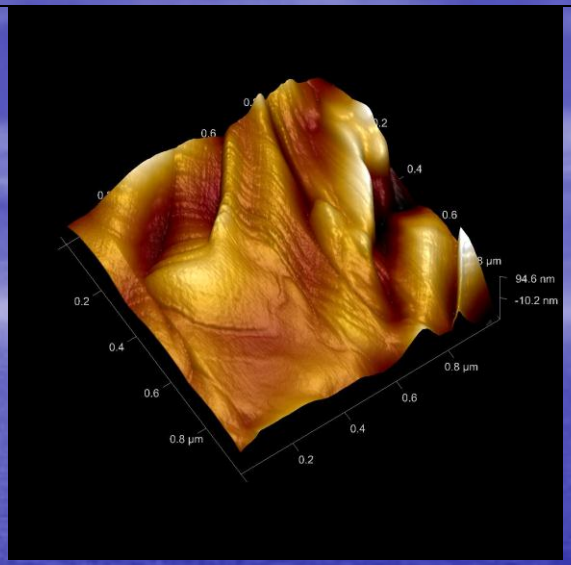
80% C1+20 %PVA ; 60 %IzOH+40 % Water + Tyrosinase

Figure 16 Immobilization of Tyrosinase onto membranes prepared from blends of 80 % copolymer 1 with 20 % PVA coagulated in 60% IzOH+ 40% Water. Optical microscopy

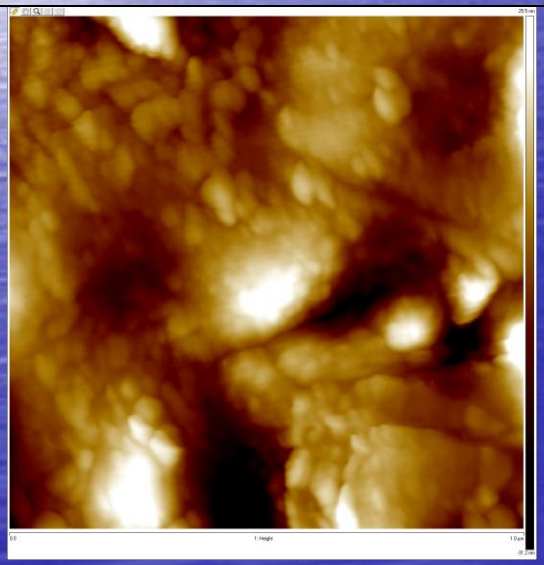
VII. Enzyme binding



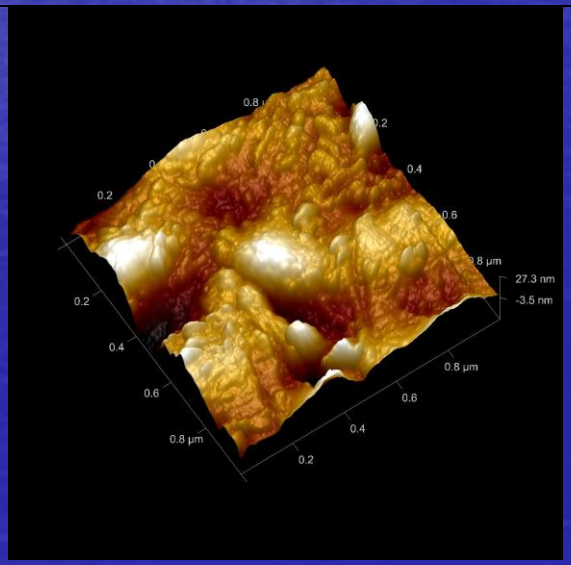
(a)



(b)



(c)



(d)

Figura 17. Imaginile AFM ale probelor M13-GA (a si b) si M13-GA-Tyr (c si d)

VIII. FTIR analysis

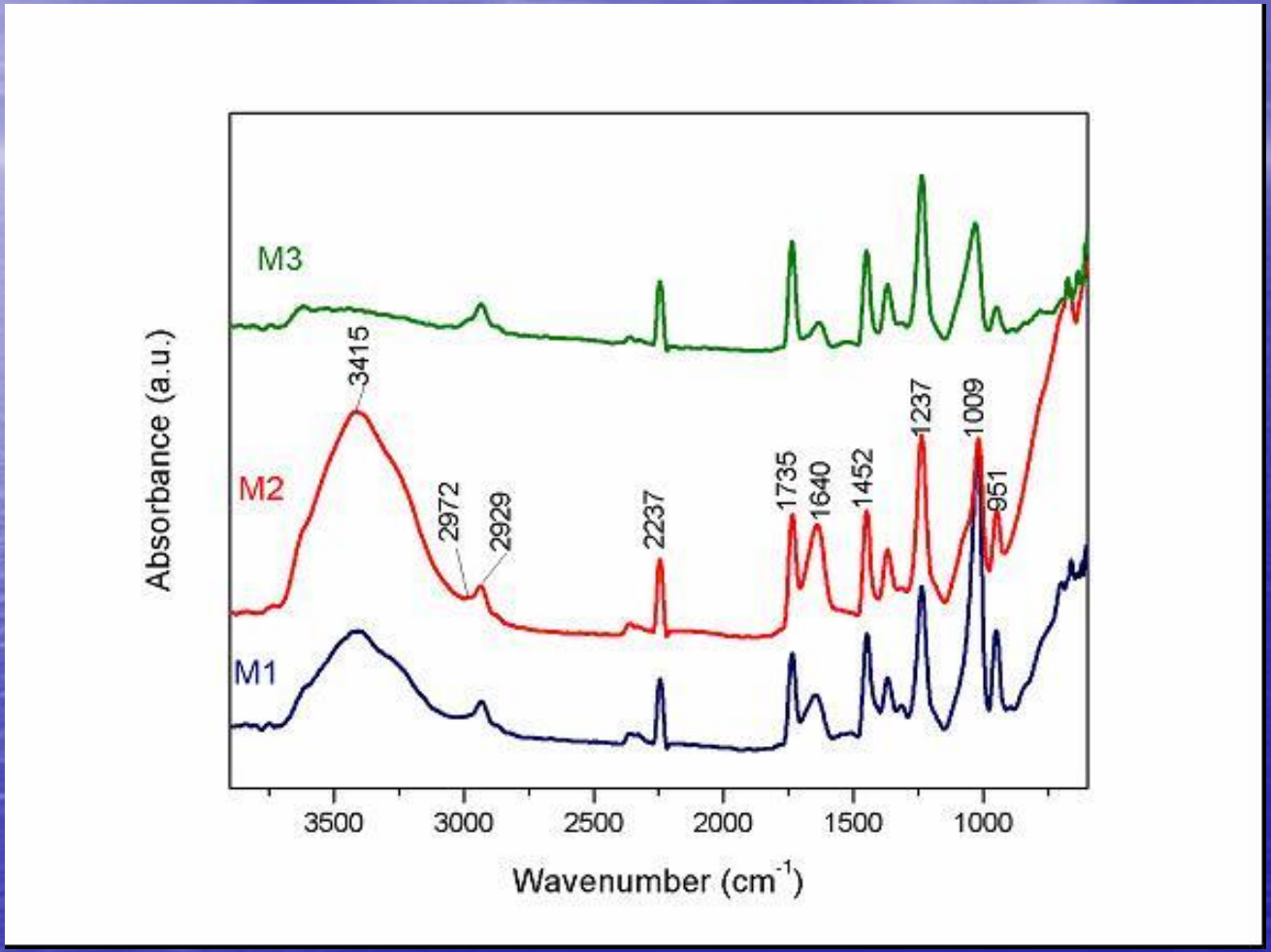


Figure 18 FTIR spectra of membranes prepared from 80% copolymer C1 + 20% PVA, coagulated in mixtures of izo propanol with various content of water: M1: 50%, M2: 40%, M3: 30%

VIII. FTIR analysis

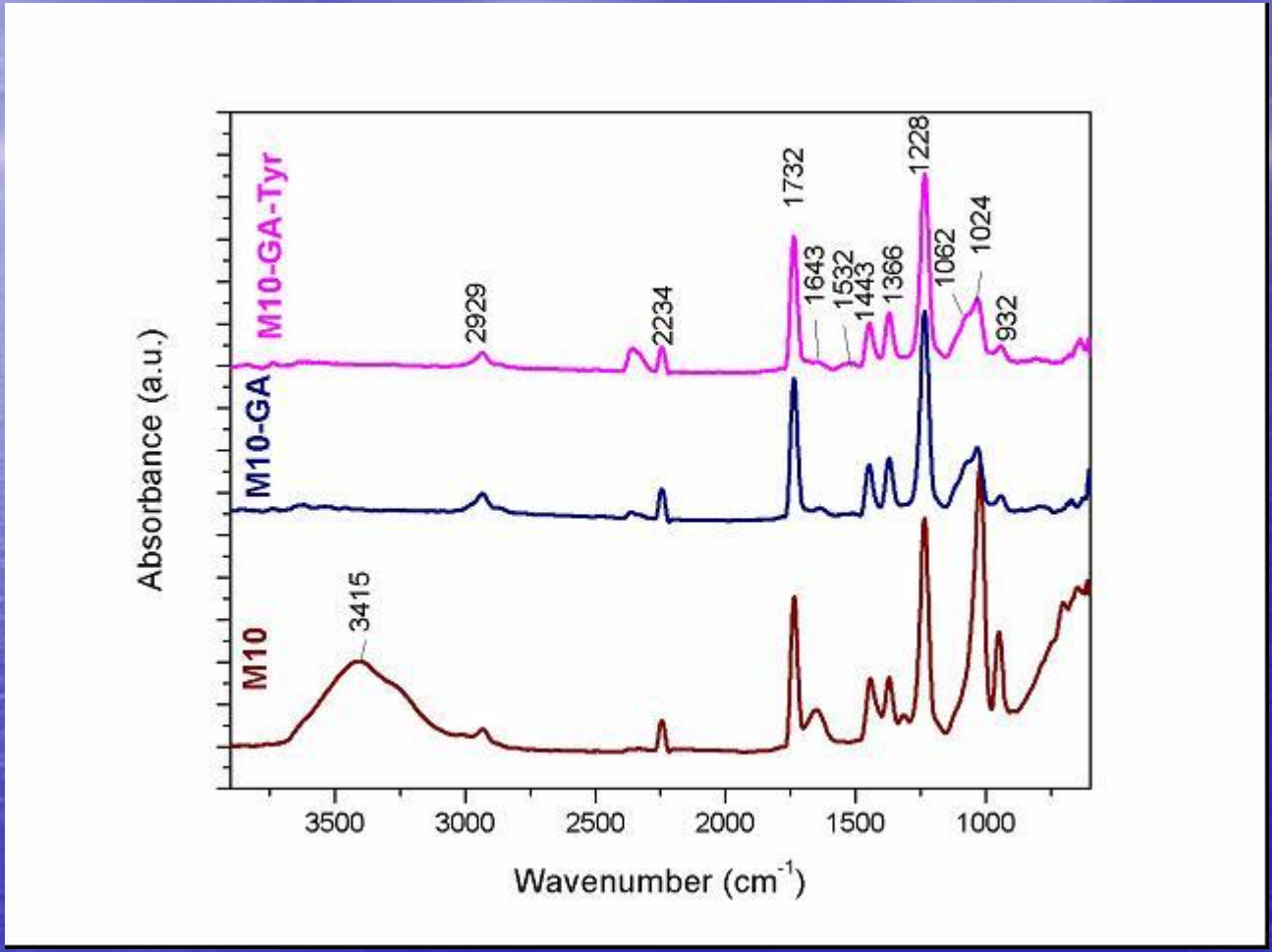


Figure 19 FTIR spectra of membranes prepared from 80 % copolymer C1 + 20% PVA, coagulated in mixtures of izo propanol with: 40% water before (M2) and after (Me-Tyr) tyrosinase immobilization

CONCLUSIONS

- Zeolites from Marsid Romania, are the most appropriate for intended use, because of high retention capacity of NH_4^+ and heavy metals cations and easy recovery
- The active carbon from peach stones, olive stones and asphaltite are very useful in the retention of various type of detergents
- The bicomponent multifunctional acrylic membranes may be tailored at various pore dimensions and contains covalently immobilized enzymes
- The experimental program of the first 2 stages is accomplished.

Perspectives

- Studies will be performed with zeolites and active carbon on samples of waste waters
- The membranes will be thoroughly characterized, determining the cut off and enzyme activity
- A laboratory module will be realized with the bulgarian colleagues
- Patents will be asked
- The dissemination will be extended

Dissemination

- **Articles:**
- **"Removal of detergents from waste waters by activated carbons"** and with authors B. Tsyntsarski, B. Petrova, T. Budinova, N. Petrov, A. Sarbu, T. Sandu, M. Ferhat Yardim, A. Sirkecioglu was submitted to the journal Hazardous Materials.
- **"Application of zeolites and membranes for detergent removal"** and with authors B. Tsyntsarski, B. Petrova, T. Budinova, N. Petrov, A. Sarbu, T. Sandu, M. Ferhat Yardim, A. Sirkecioglu was submitted to the journal Bulgarian Chemical Communications

- **Communications:**
- **International Conference on Applied Sciences. Chemistry and applied chemistry**, 24-27 April 2012, Bacau, **Polymer ultrafiltration membranes prepared from blends of acrylonitrile copolymer-polyvinyl alcohol,** *Teodor Sandu, Andrei Sarbu, Silviu Vulpe, Neculae Antohe, Horia Iovu*
- **Annual World Conference on Carbon 2012,** 17th- 22nd June, 2012, Krakow, Poland, **Carbon Materials on the Base of Inorganic-Organic Polymer Nanocomposite Precursors**, *MF. Yardim, A. Radu, BG. Tsyntsarski, AM. Lungu, TK. Budinova, NV. Petrov, A. Sarbu, BN. Petrova*
- **Le 7-eme colloque Franco- Roumain de Chimie appliquée**, Bacau, 27- 29 Juin 2012, **La caractérisation des membranes obtenues en utilisant des mélanges de copolymères d'acrylonitrile avec APV** *Teodor Sandu, Andrei Sarbu, Silviu Vulpe, Raluca Somoghi, Horia Iovu*
- . **International conference on advanced materials – ROCAM,** Brasov, 28-31 august 2012**, Researches about the covalent immobilization of enzymes on polymers, for various applications.** *Andrei Sarbu*
- **Chemsitry priorities for a sustaina,mble development PRIOCHEM- a VIII-the edition**, 25-26 octombrie 2012**,** Bucuresti**,** Enzymatic composites synthesized by covalent immobilization on polymer membranes *T. Sandu1, 2, A. Sârbu2, C. M. Damian1, H. Iovu1*

- THANK YOU FOR ATTENTION!