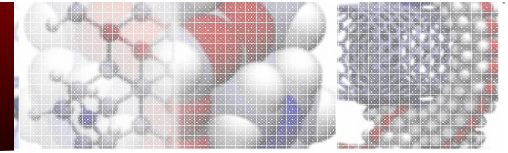


MICROPARTICLES SYNTHESIZED BY HIGH PRESSURE SPRAYING METHOD AND THEIR ADSORPTION PROPERTIES FOR PHENOL DERIVATIVES

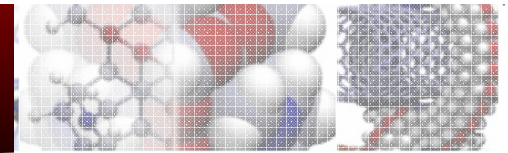
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OBJECTIVES

- **To study the interaction between cationic chitosan and an anionic surfactant sodium bis-(2-ethyl hexyl) sulfosuccinate (AOT).**
- **To synthesize chitosan based microparticles at atmospheric pressure and by high pressure method.**
- **To prove the chitosan/AOT complex formation by Fourier Transform Infrared (FTIR) Spectroscopy, and to characterize the size and shape of microparticles by optical and SEM microscopy.**
- **To investigate the behaviour of lyophilized microparticles in contact with phenol derivatives.**
- **To study the influence of medium pH and the amount of microparticles on the phenol adsorption efficiency.**
- **To monitor the time evolution of phenol derivatives sorption by microparticles.**



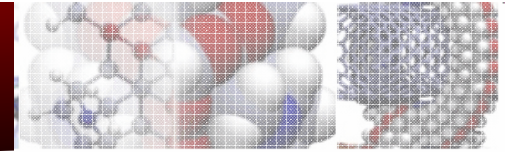
EXPERIMENTAL

Methods

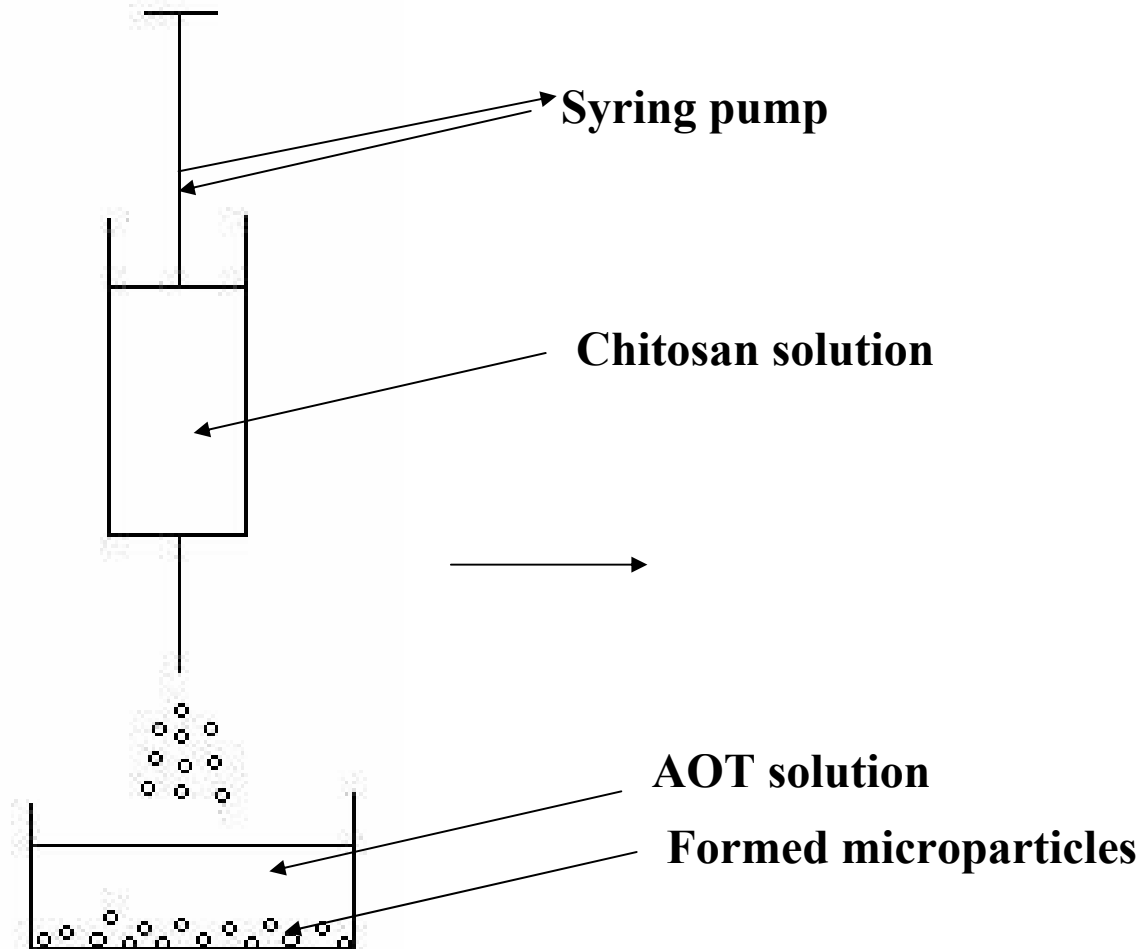
- **Fourier Transform Infrared (FTIR) Spectroscopy - Nicolet iN10 FT-IR Microscope –Thermo Scientific**
- **UV-Vis spectroscopy Cary 100 Bio - VARIAN**
- **Optical Microscopy - Magnum T Microscope**
- **Scanning Electron Microscopy (SEM) using a Zeiss EVO LS10 Apparatus**
- **Freeze drying - ALPHA 1-2 LD**

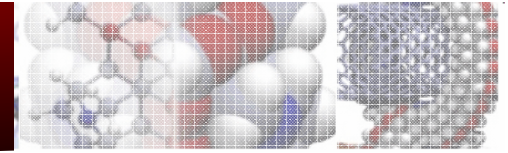
Materials

- **Chitosan - medium molecular weight ($M_w = 120 \pm 70$ kDa) - Aldrich**
- **Sodium bis (2-ethyl hexyl) sulfosuccinate (AOT) 98% - Sigma**
- **Carbon dioxide with 99.9% - Linde Gas Romania**



MICROPARTICLES PREPARARED AT ATMOSFERIC PRESSURE

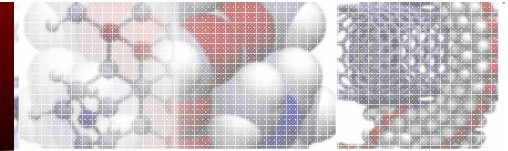




MICROPARTICLES PREPARED AT ATMOSPHERIC PRESSURE

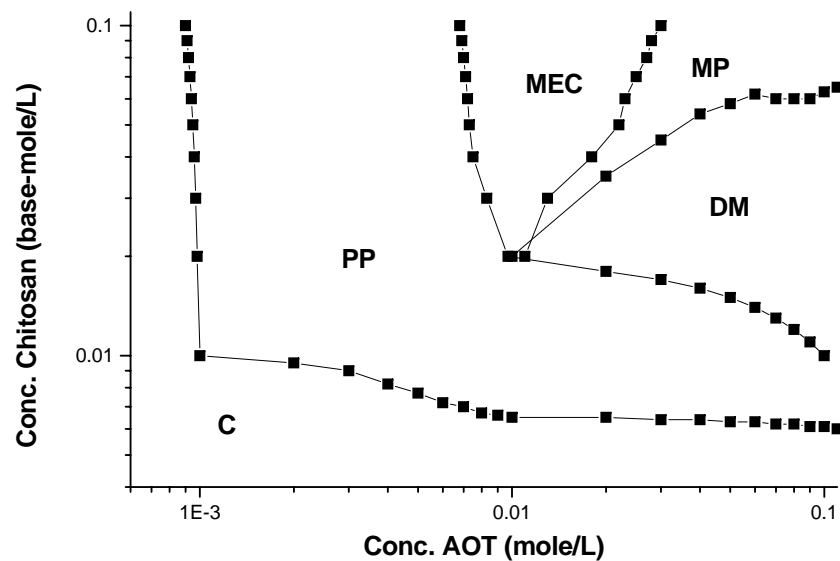
Domains of phase diagram

- 1) **HOMIGENEOUS SOLUTIONS**, monophasic and transparent within domain C;
- 2) **PRECIPITATES**, preceded by the appearance of an advanced turbidity within domain PP;
- 3) **GEL-TYPE MEMBRANES**:
 - domain MEC (microcapsule that expels its content - Fig. 2b);
 - domain MP (microparticles - Fig.2a);
 - domain DM (shrunked microcapsule - Fig.2c).

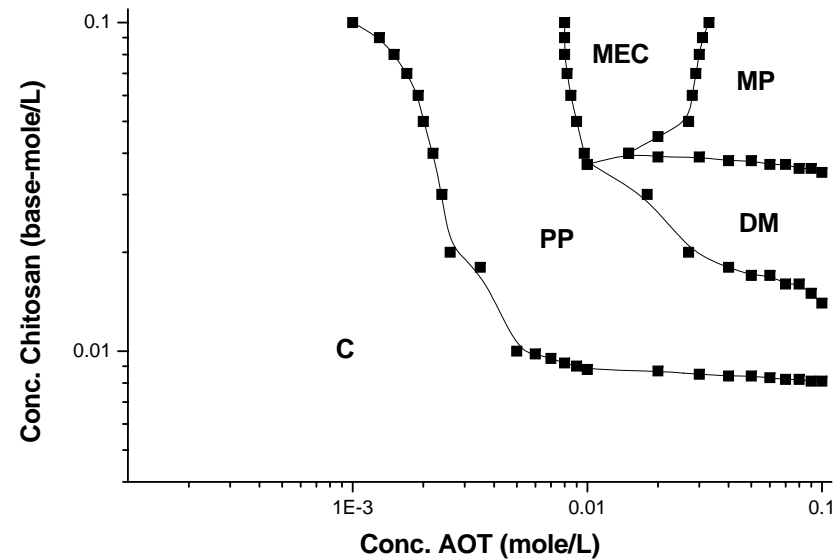


MICROPARTICLES PREPARED AT ATMOSPHERIC PRESSURE

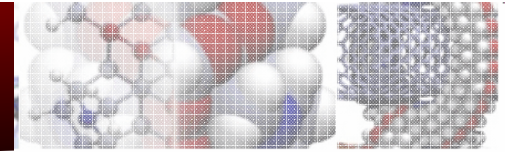
Domains of solubility for Chitosan-AOT complex-gel



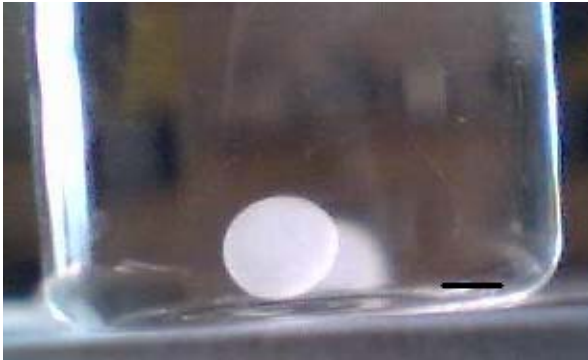
Protonated with 1% wt acetic acid



Protonated with 2.5% wt acetic acid



Microcapsule

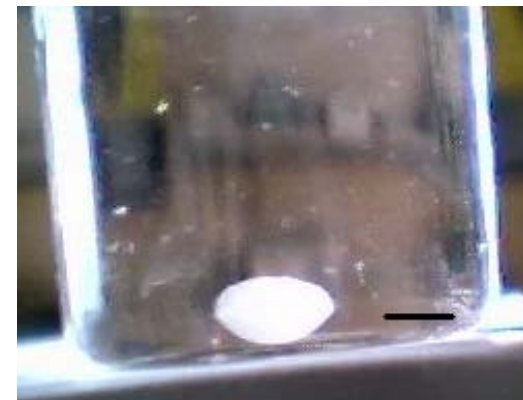


GEL-TYPE MEMBRANES

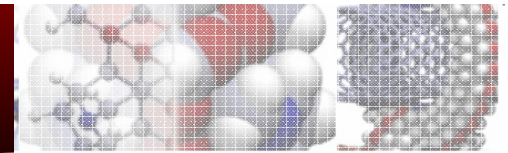
**Microcapsule that
expels its content**



Shrunked microcapsule



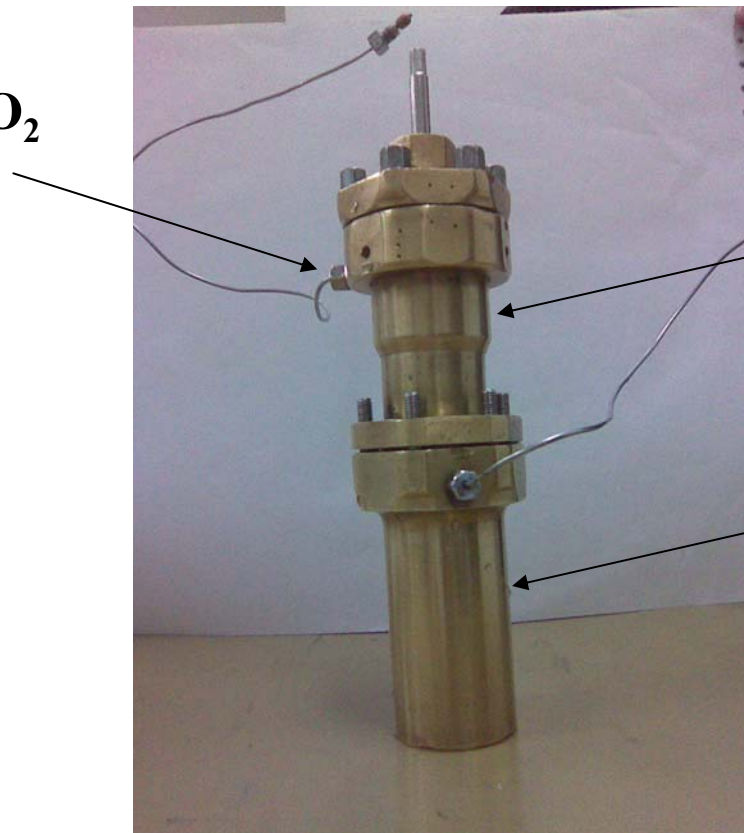
Bar = 1000 μm



MICROPARTICLES PREPARED BY HIGH PRESSURE SPRAYING METHOD

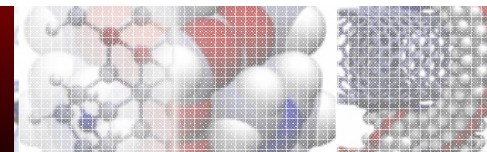
Experimental apparatus

Input pressure CO₂



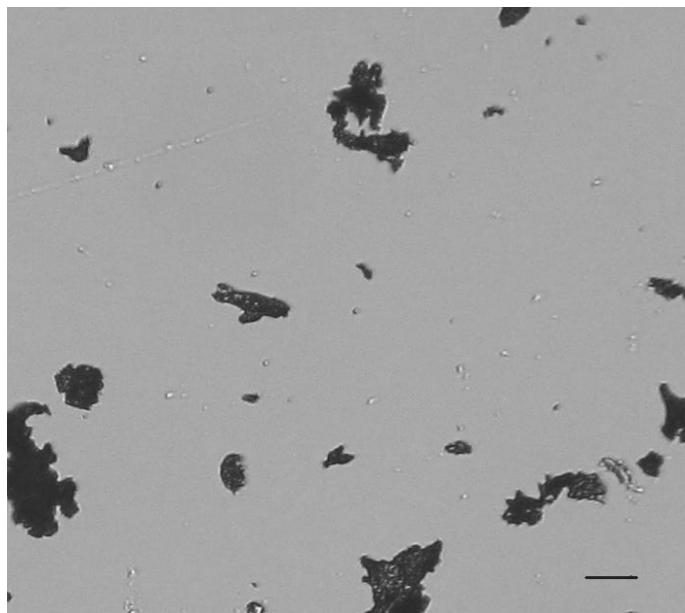
High pressure cell

Low pressure cell

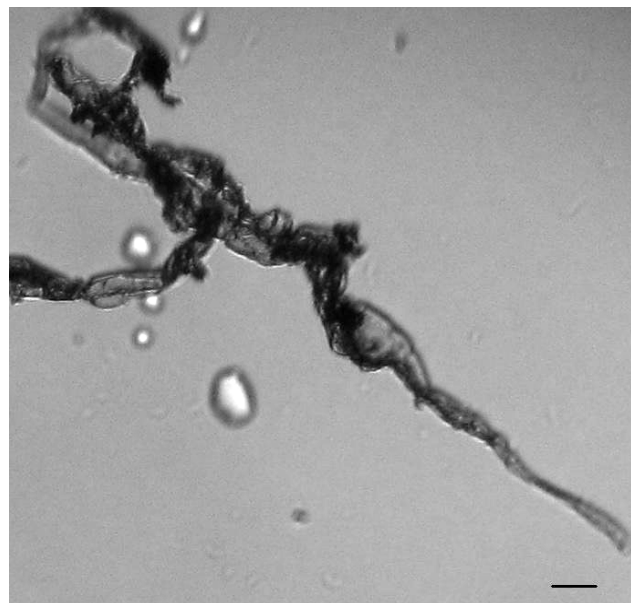


POLYMER-SURFACTANT COMPLEX PREPARED AT HIGH PRESSURE

Optical microscopy

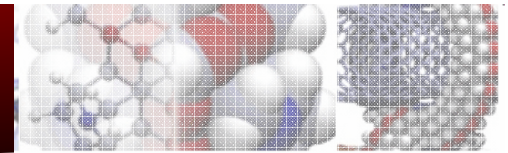


Microparticles



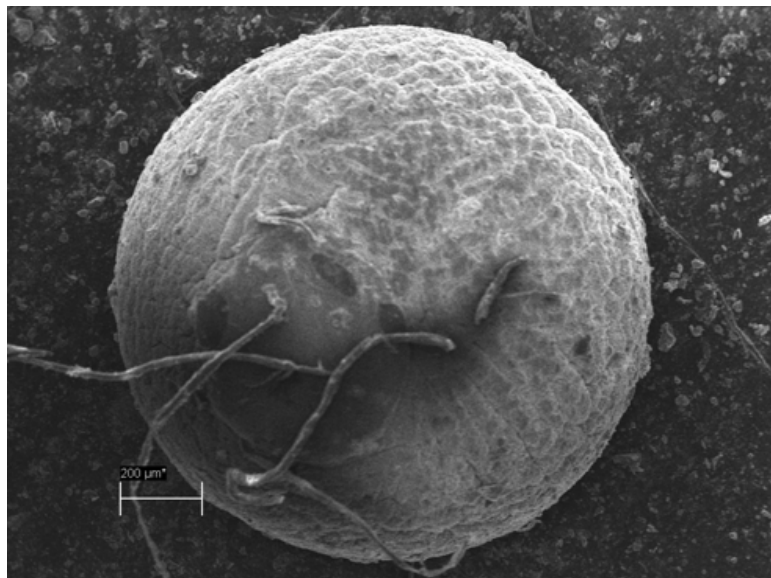
Wires

bar = 500 μm

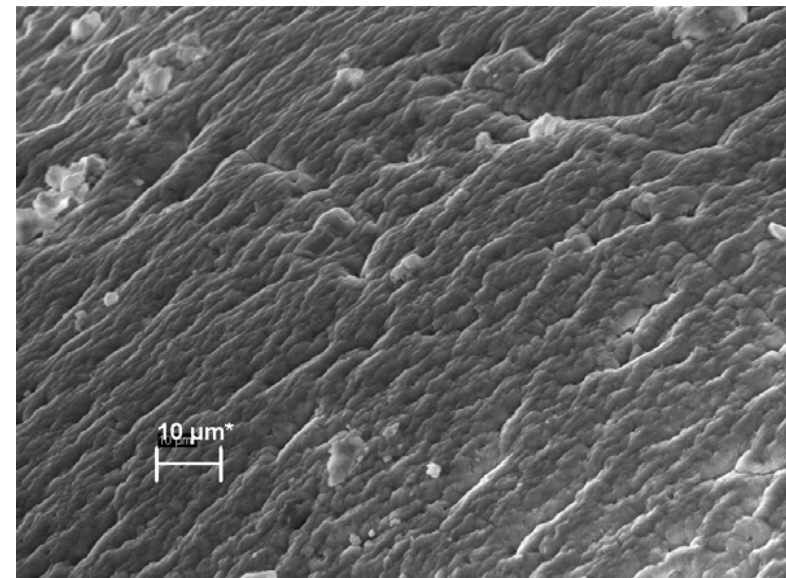


CHITOSAN-AOT WET MICROSPHERES

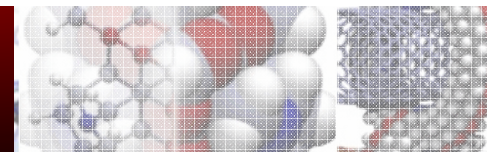
SEM micrographs



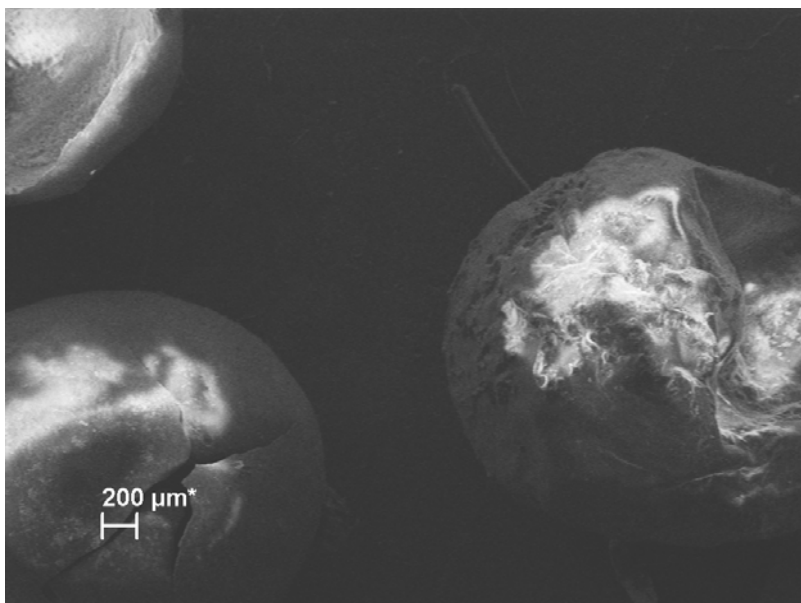
Microparticle



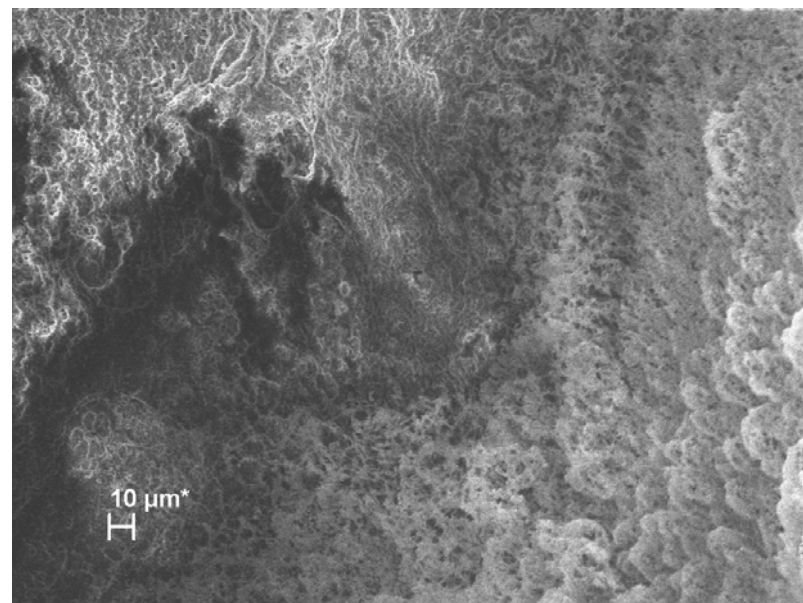
Surface of microparticle



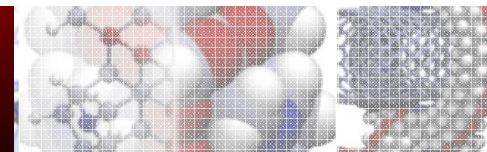
SEM micrographs



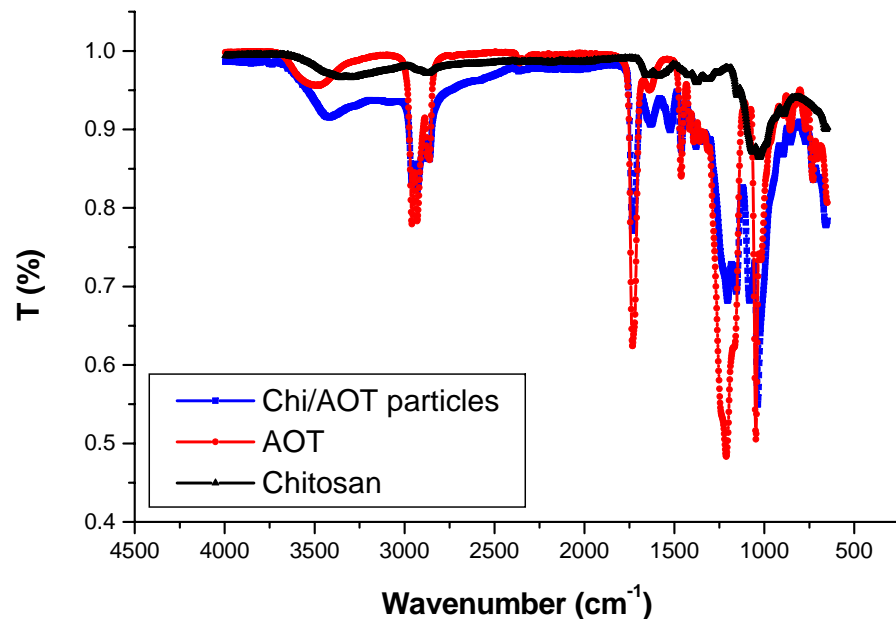
Microparticle



Surface of microparticle



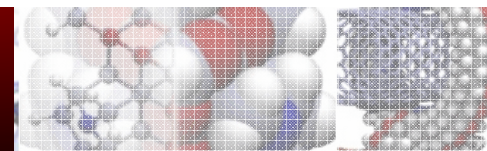
INTERACTION BETWEEN CHITOSAN-AOT



FTIR measurements

The specific values for Chi/AOT complex

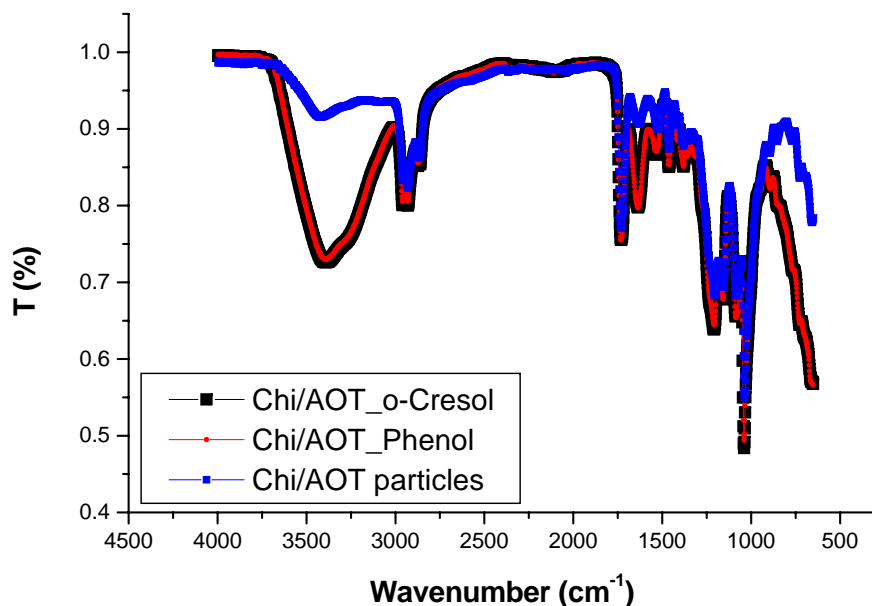
Chitosan ν (cm^{-1})	AOT ν (cm^{-1})	Microparticles Chi/AOT ν (cm^{-1})	Assignment
1642		1634	νNH , δNH_2
1586		1522	δNH_2
	1212	1204	νSO
	1093	1082	νSO



ADSORPTION OF PHENOL DERIVATIVES

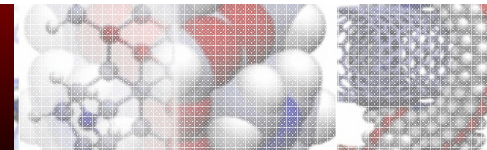
Interaction between lyophilized microparticles with phenol and o-cresol

FTIR measurements



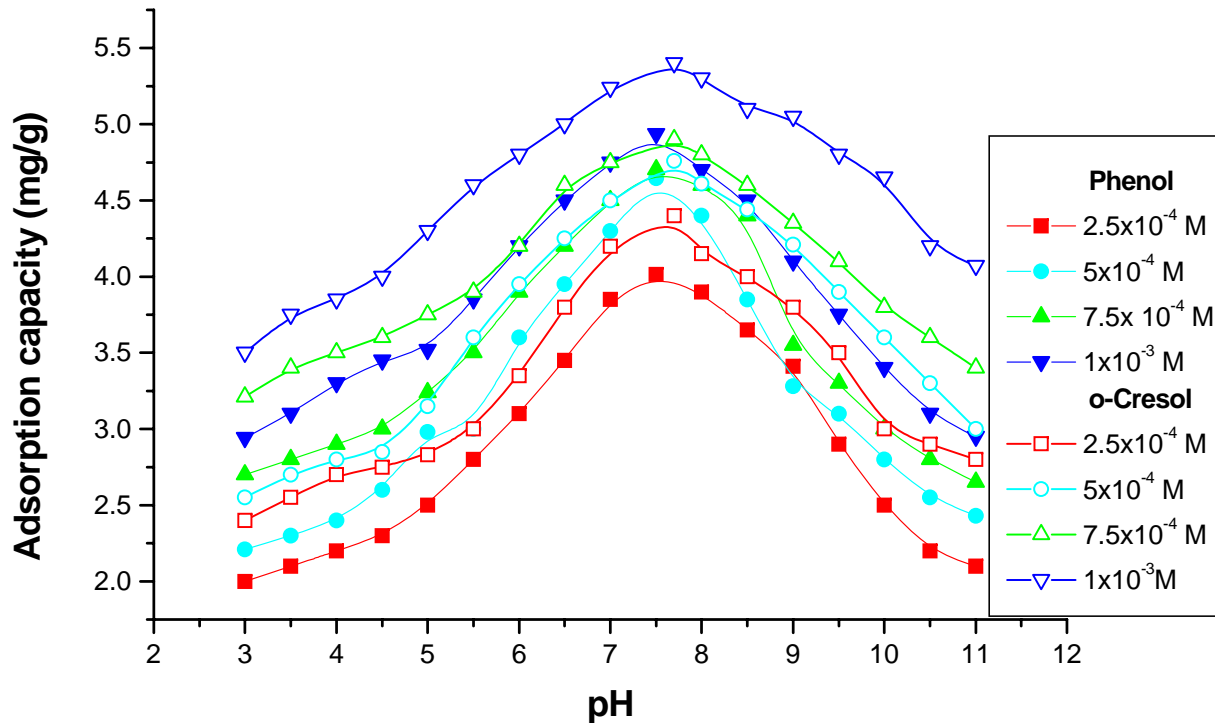
Specific values for interaction phenol, o-cresol

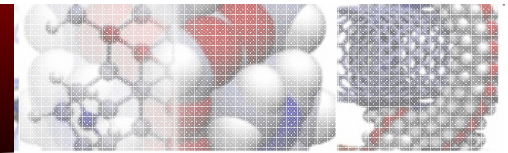
Chi/AOT-o-Cresol ν (cm ⁻¹)	Chi/AOT-Phenol ν (cm ⁻¹)	Microparticle Chi/AOT ν (cm ⁻¹)	Assignment
3395.02	3396.44	3413.92	Bonded OH; position and shape depend on degree of association; CH aromatic stretching.
2873.43	2873.52	2860.65	H bond; intramolecular with C=O; chelatic OH.
1635.96	1635.96	1634.69	C-C aromatic stretching.
1532.96	1533.48	1522.56	δ NH; CH aromatic stretching.



ADSORPTION OF PHENOL DERIVATIVES

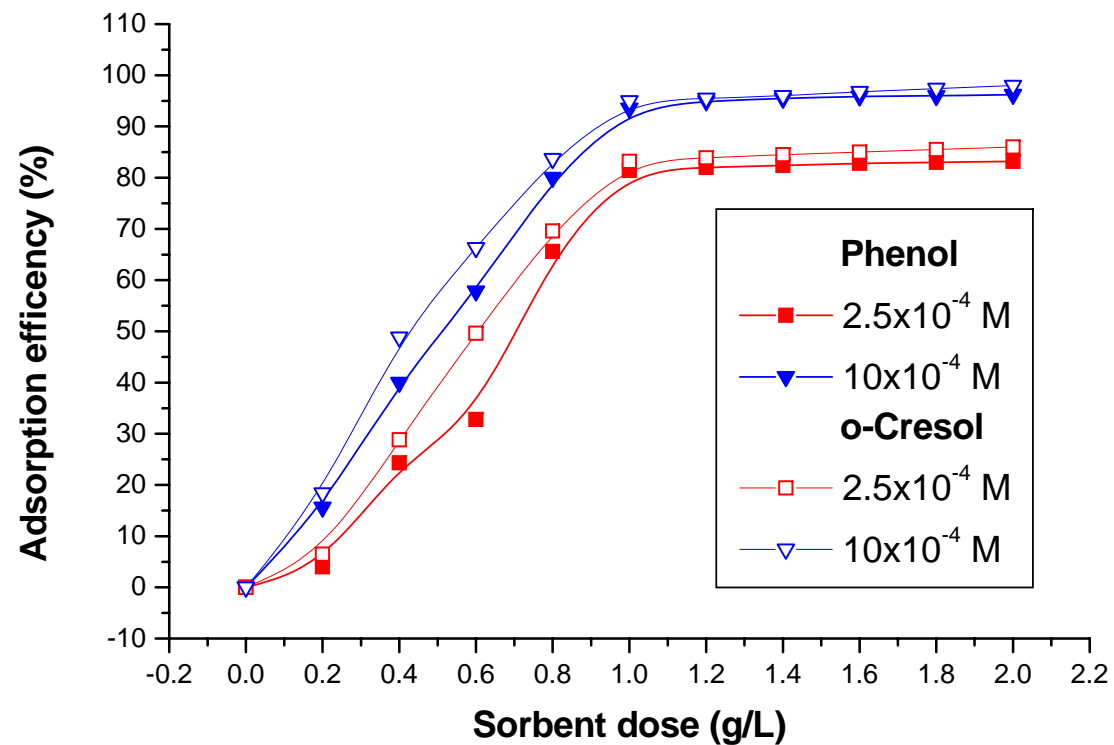
Effect of pH on contaminant removal

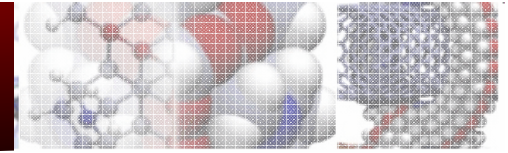




ADSORPTION OF PHENOL DERIVATIVES

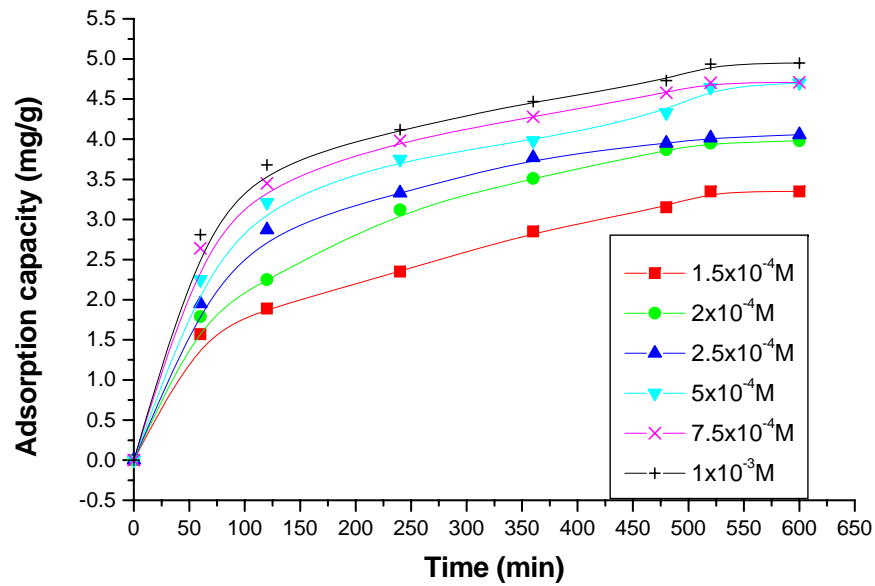
Effect of sorbent dose



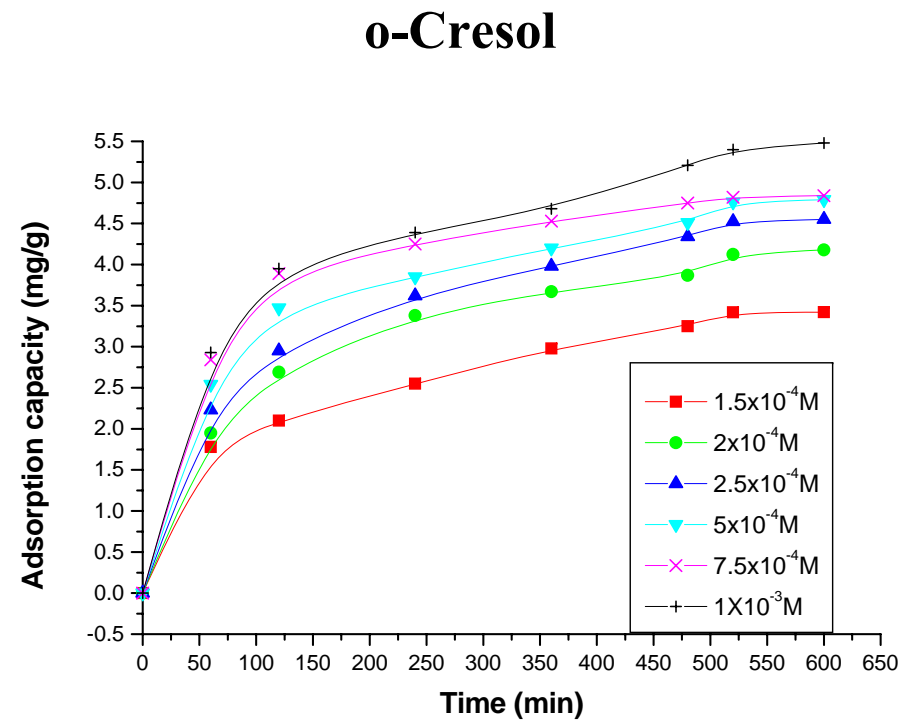


ADSORPTION OF PHENOL DERIVATIVES

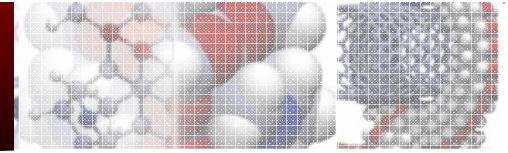
Kinetics of pollutant adsorption



Phenol

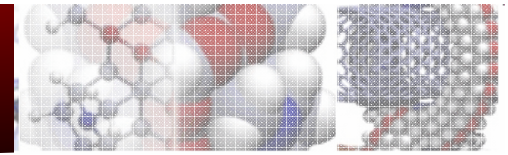


o-Cresol



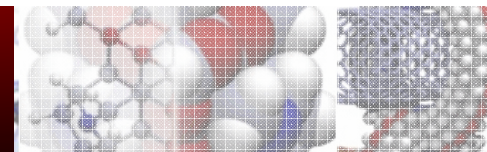
CONCLUSIONS

- **Two methods to obtain ultrafine particles by the interaction between chitosan and an anionic surfactant, sodium bis (2-ethyl hexyl) sulfosuccinate (AOT), were developed.**
- **Chitosan-surfactant complex synthesized at atmospheric pressure may take the form of stable microparticles at optimal concentrations of the reactants.**
- **An experimental apparatus equipped with a high pressure cell for spraying the polymer into the anionic surfactant solution produces either ultrafine particles or wires depending on the spraying pressure.**
- **The interaction between chitosan and AOT is proved by FTIR, whereas SEM shows that the lyophilized chitosan/AOT microparticles present a higher roughness and porosity than the wet particles.**
- **Lyophilised chitosan/AOT microparticles have been successfully used in advanced treatment of wastewaters for the retention of phenol and o-cresol.**
- **The contaminant removal for phenol and o-cresol attain a maximum in the range of pH 7-8, increases with the amount of used particles and decreases with increasing of initial pollutant concentration.**
- **The adsorption of phenol and o-cresol occurs rapidly in the first 60-120 minutes followed by a slow process that takes about 520-600 minutes.**



ACKNOWLEDGMENTS

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