WASTEWATER TREATMENT USING CHITOSAN: ADSORPTION AND COAGULATION-FLOCCULATION PROCESSES

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EBA 2018, Gramado
(Brazil)

April 24, 2018

CONTENTS

Treatment of industrial or city effluents depends on:

- Nature of contaminants (metal ions, dyes, pharmaceuticals….)
- Interest in recycling
- Toxicity

Processes

- Precipitation

- Membranes
- Liquid/liquid extraction
- Electrochemical processes
- Adsorption ➔ BIOADSORPTION

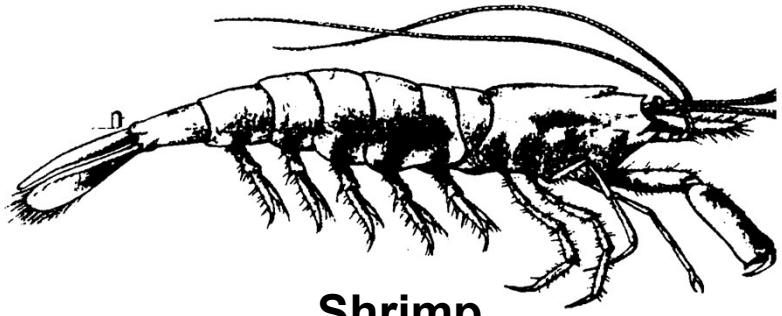
INTEREST on the EXPLOITATION of BIOMASS RESOURCES

For the development of new materials

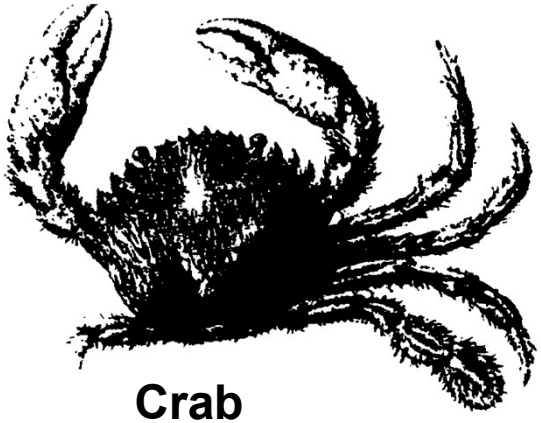
Polysaccharides (*cellulose, chitin, chitosan, starch*) are of increasing interest as new functional polymeric renewable materials because of their abundance and specific properties.

CHITIN : Sources

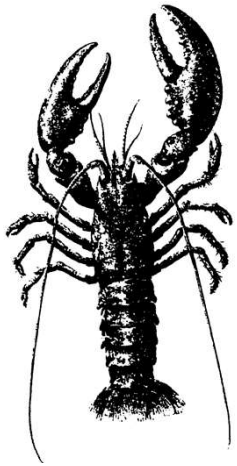
Sources : exoskeleton or cuticles of invertebrates or cell walls of fungi or algae



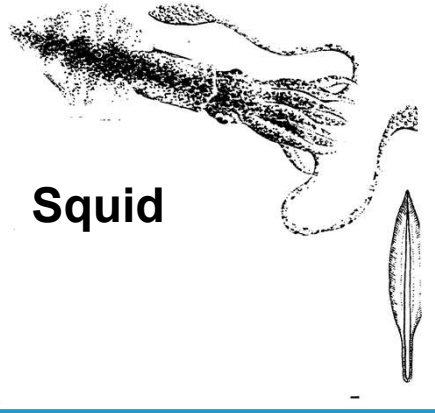
Shrimp



Crab



Lobster

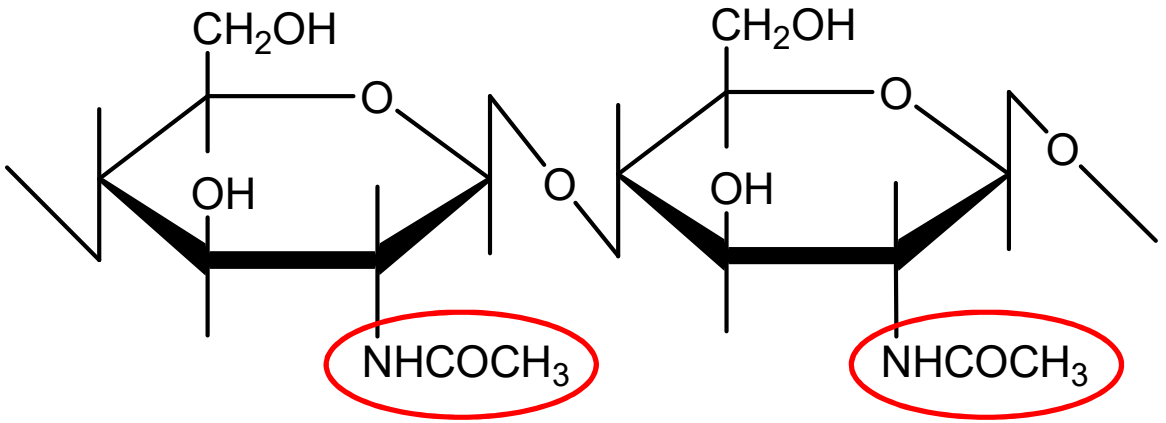


Squid

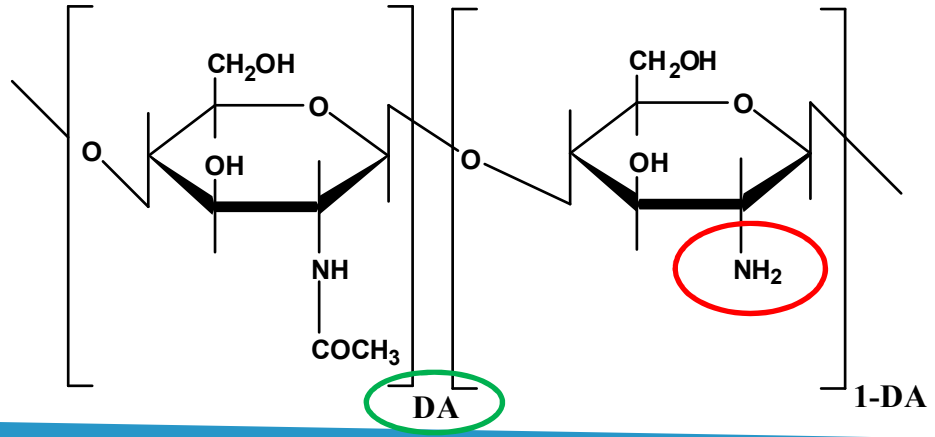
CHITIN and CHITOSAN

One of most abundant natural polymers with a similar structure to cellulose

Chitin



Chitosan



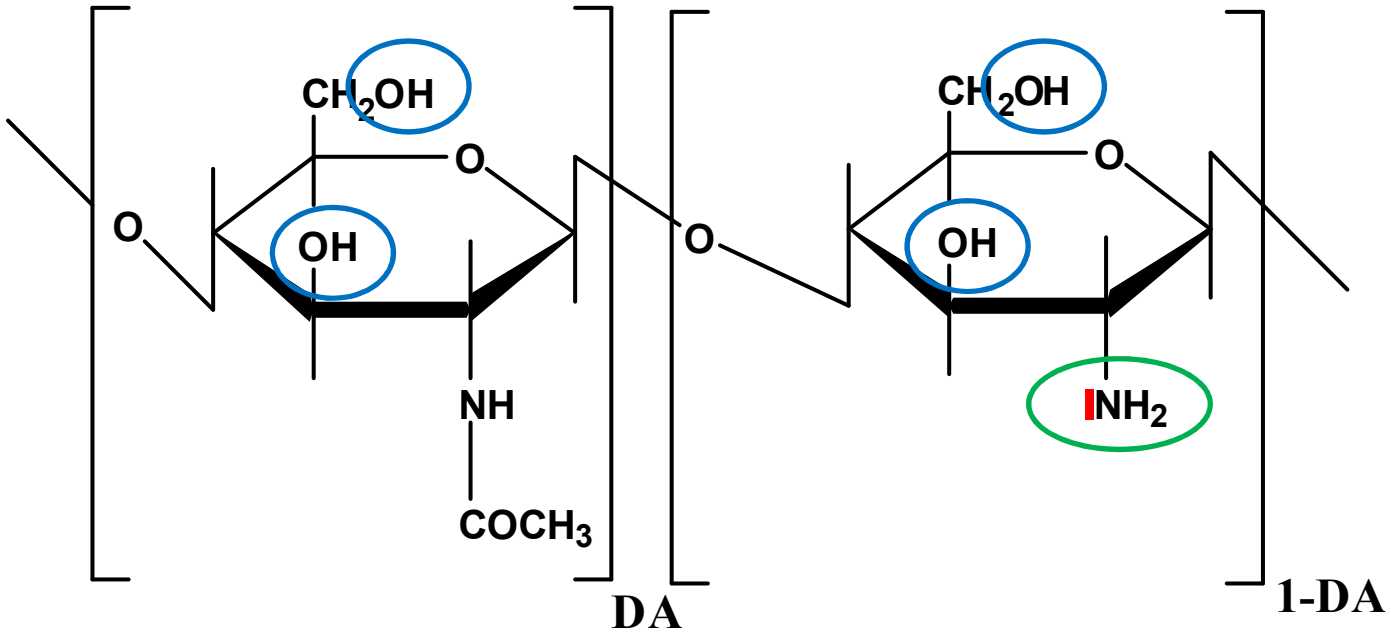
CHITOSAN PROPERTIES

- Non-toxic
- Biodegradable
- Biocompatible

Chitosan can be used:

- Under solid form in ADSORPTION
  Presence of hydroxyl and amino groups
- Under liquid form for charge neutralization and COAGULATION-FLOCCULATION of anionic compounds
  - Hydration
  - pKa ~ 6
  - Degree of Acetylation (DA)
  - Molar mass
  - Cristallinity

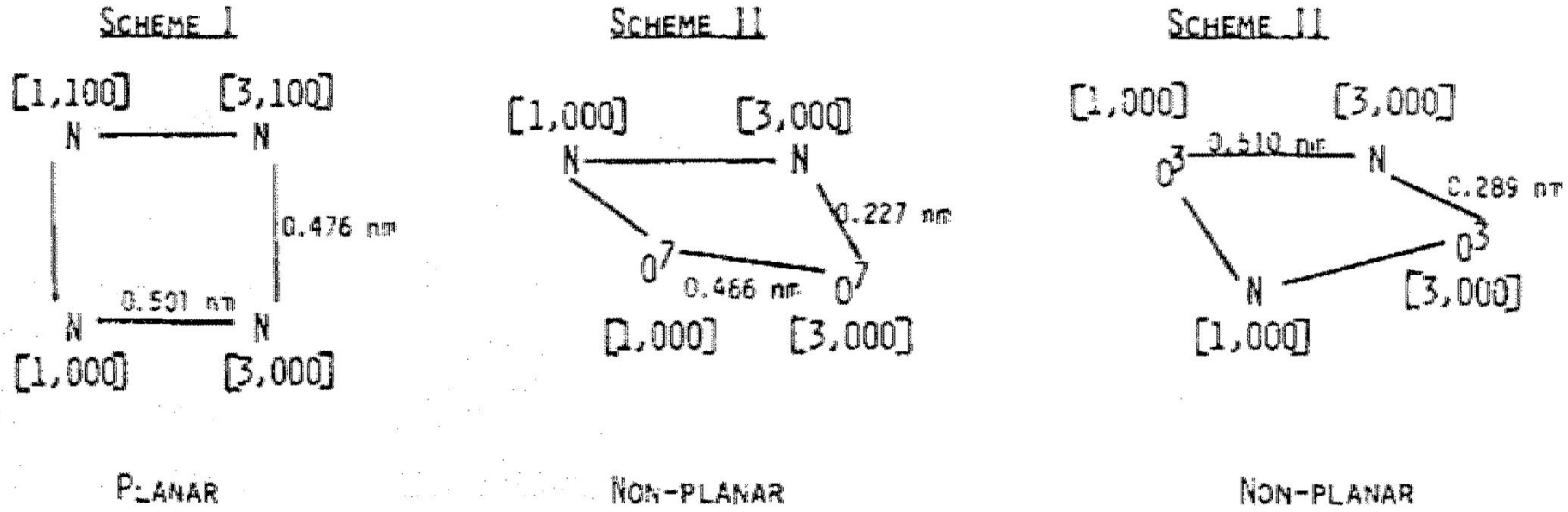
CHITOSAN and ADSORPTION



CHITOSAN and ADSORPTION

Models

- Bridge Model

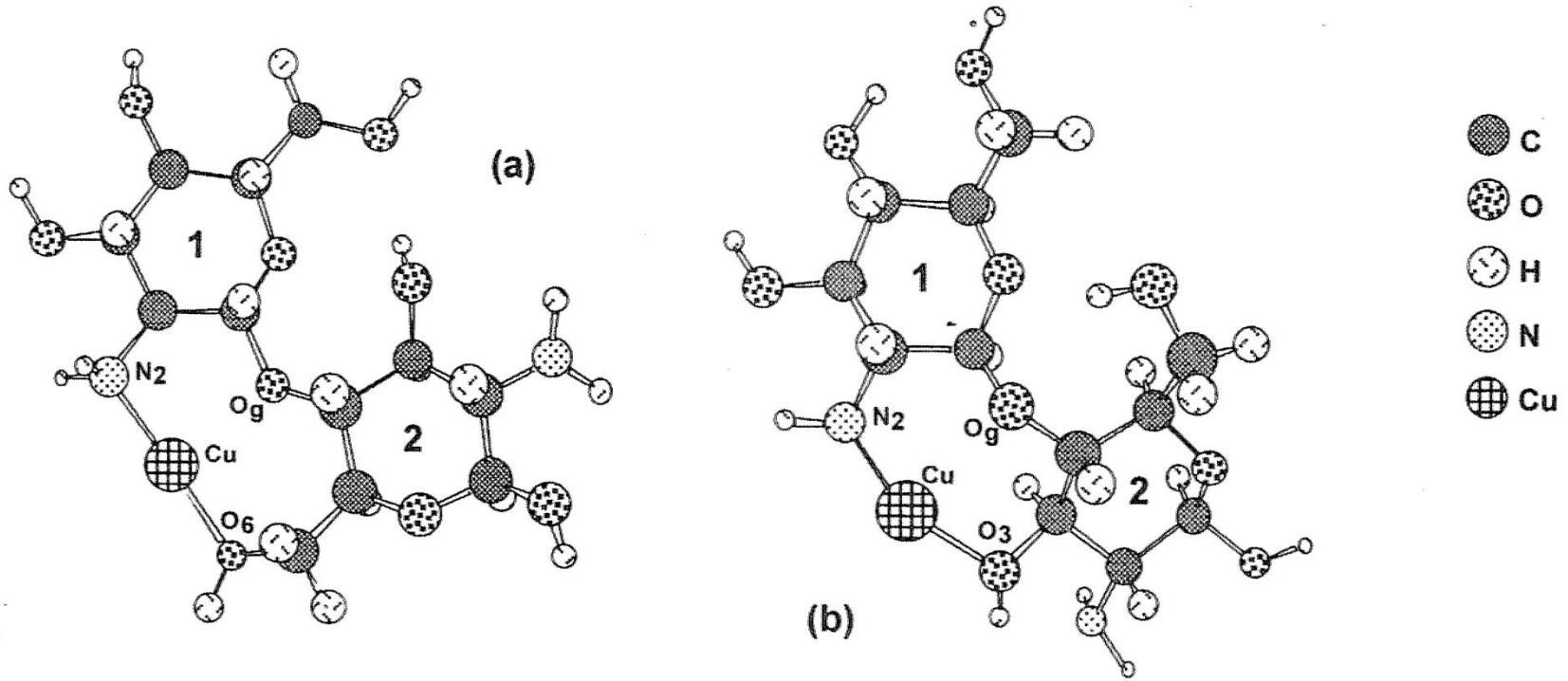


Schlick, Macromolecules (1986) 19, 192-195

- Pendant Model

CHITOSAN and ADSORPTION

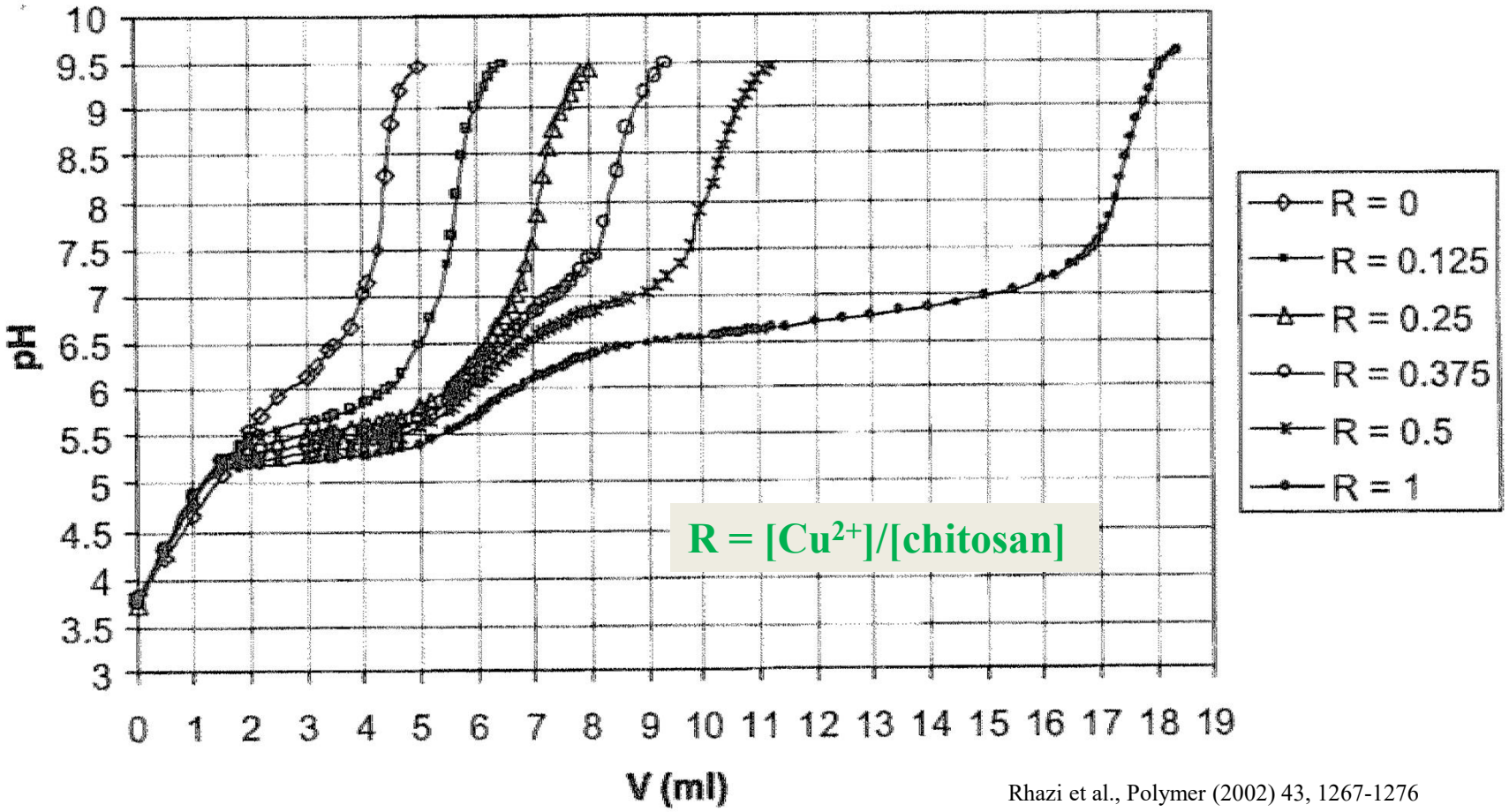
Coordination of Copper by DFT



Braier and Jishi, J. Mol. Struct. (Theochem) (2000) 499, 51-55.

CHITOSAN and ADSORPTION

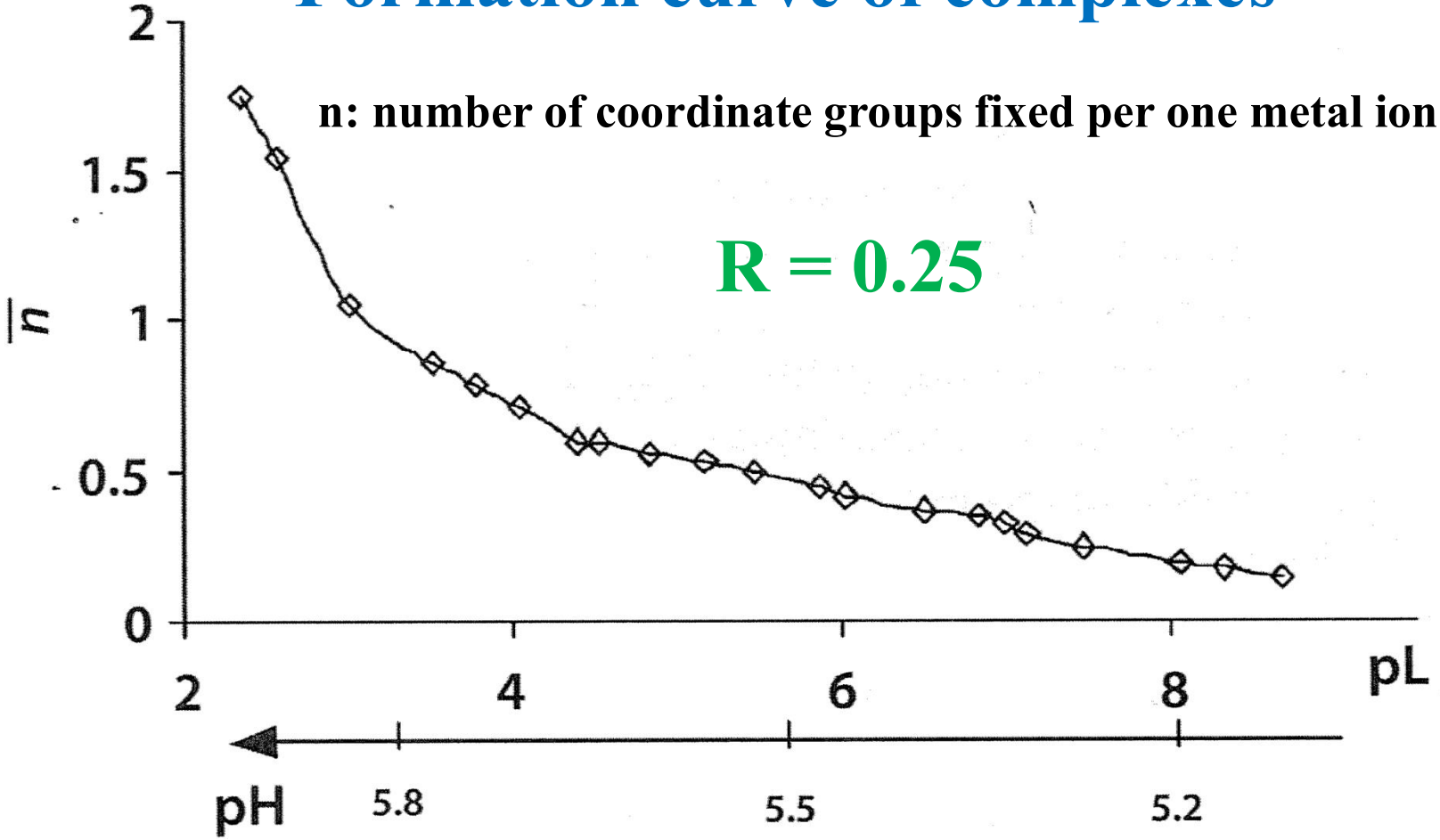
Neutralization of chitosan by NaOH in presence of Cu (II) ions



Rhazi et al., Polymer (2002) 43, 1267-1276

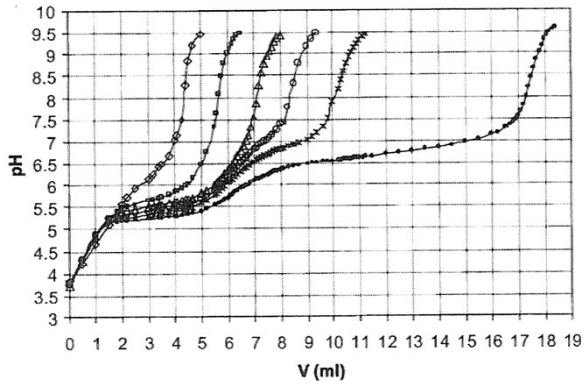
CHITOSAN and ADSORPTION

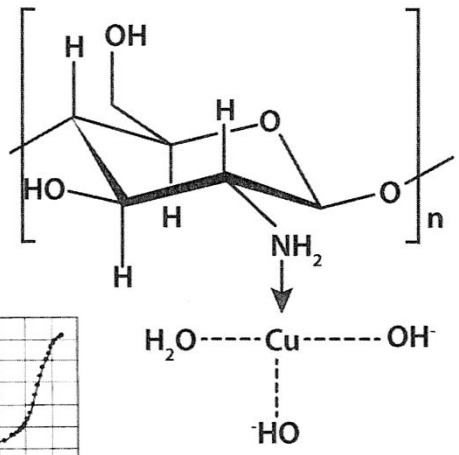
Formation curve of complexes

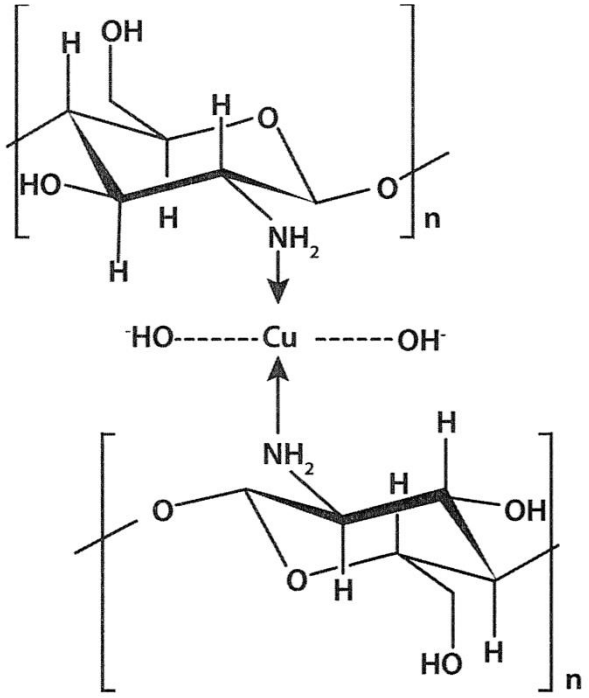


CHITOSAN and ADSORPTION

Cu-Chitosan complexes







pH 5.3

Type I

$[Cu(-NH_2)^{2+}, 2OH^-, H_2O]$

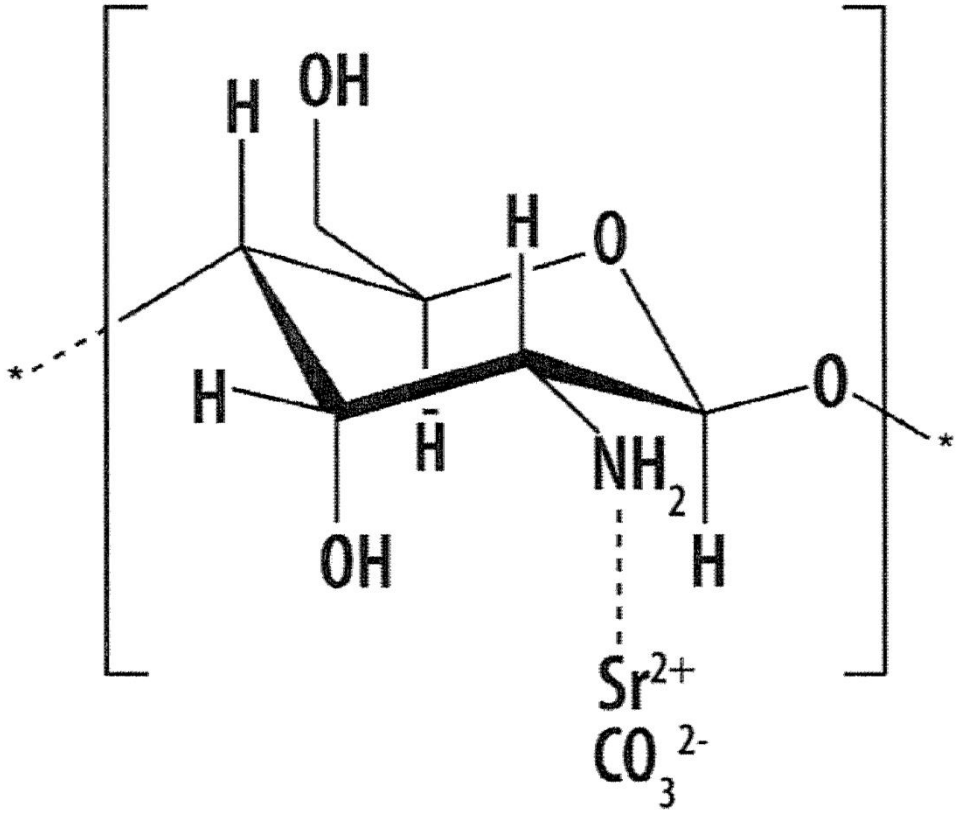
pH 5.8

Type II

$[Cu(-NH_2)_2^{2+}, 2OH^-]$

CHITOSAN and ADSORPTION

Complexes with Sr^{2+}



Piron and Domard, Int. J. Biol. Macromol. (1998) 23, 113-.

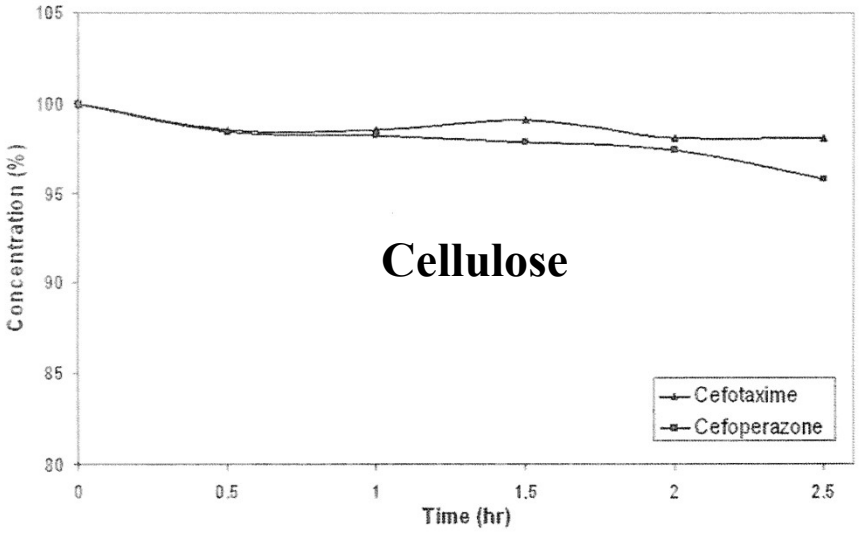
ADSORPTION of ORGANIC COMPOUNDS

One of the most serious environmental problems (persistence of organic contaminants within environment)

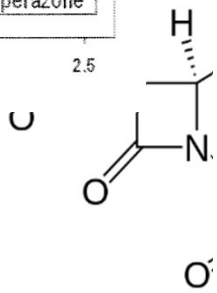
Major parameters:

- **Size of the molecule**
- **Chemical structure**
- **Hydrophilic or hydrophobic character**

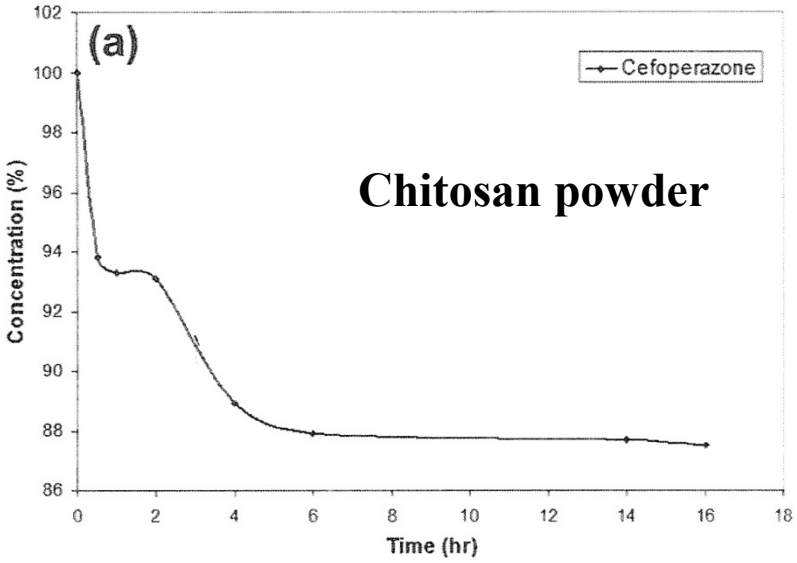
ADSORPTION of ORGANIC COMPOUNDS : DRUGS



Cellulose



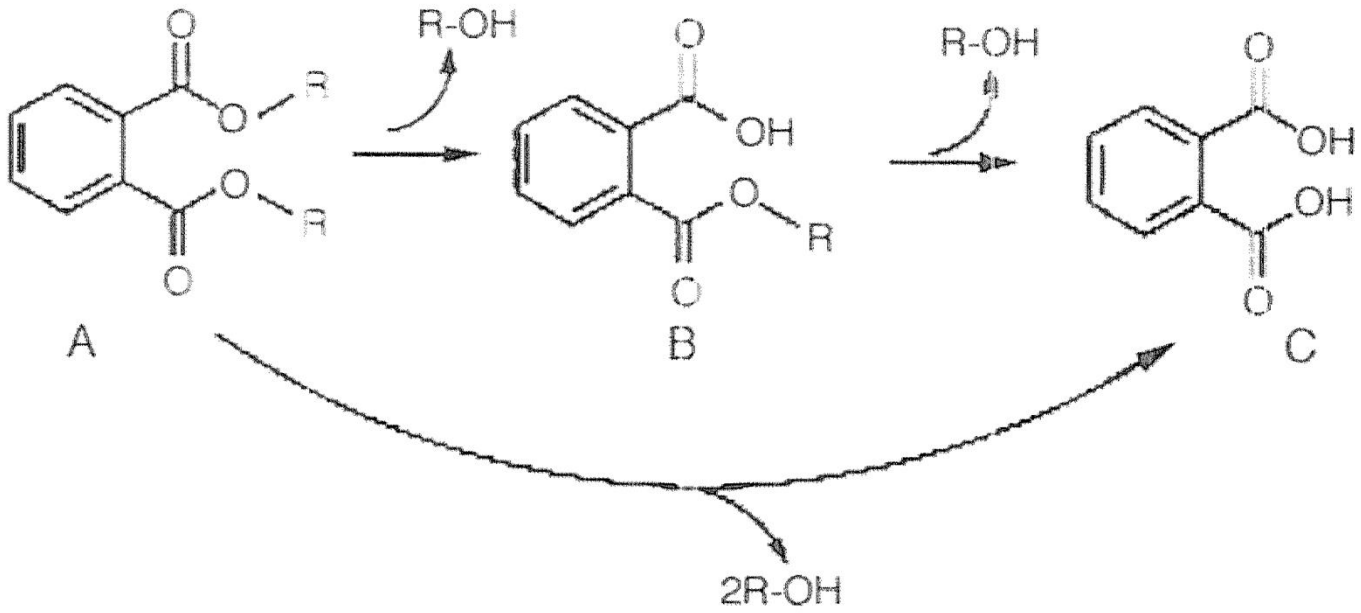
Cefoperaz



Chitosan powder

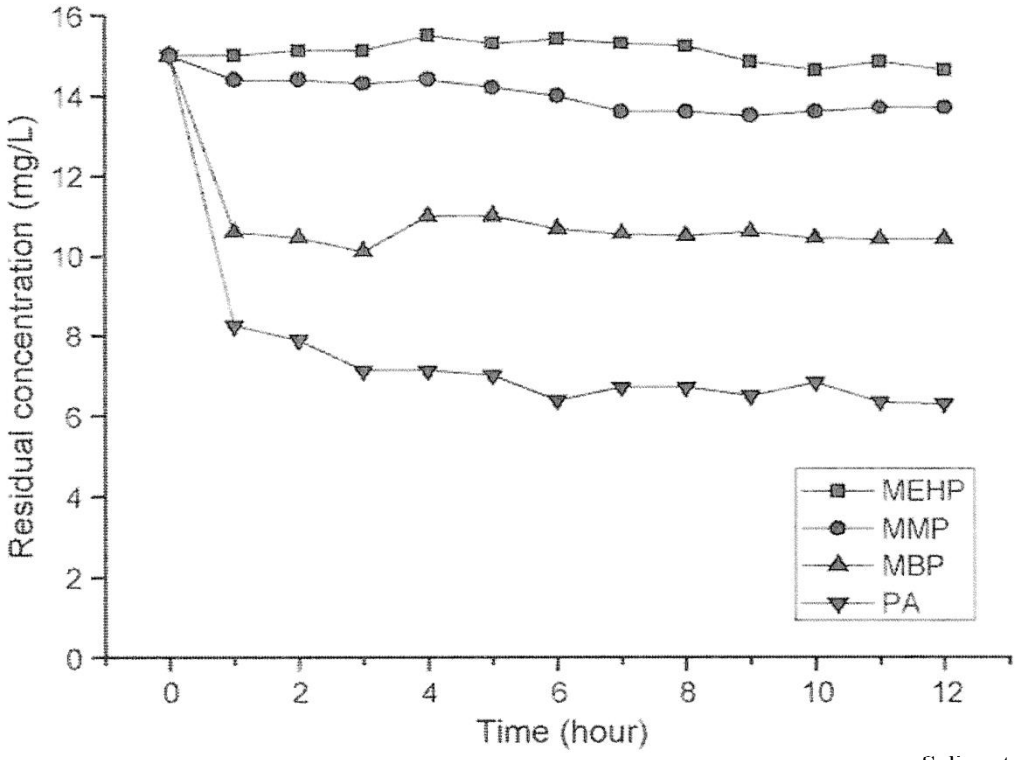
El-Shafey et al., J. Appl. Polym. Sci. (2014) 131, 40458

ADSORPTION of ORGANIC COMPOUNDS : ENDOCRINIAN DISRUPTORS



Salim et al., Carbohydr. Polym. (2010) 81, 640-644

ADSORPTION of ORGANIC COMPOUNDS : ENDOCRINIAN PERTURBATORS

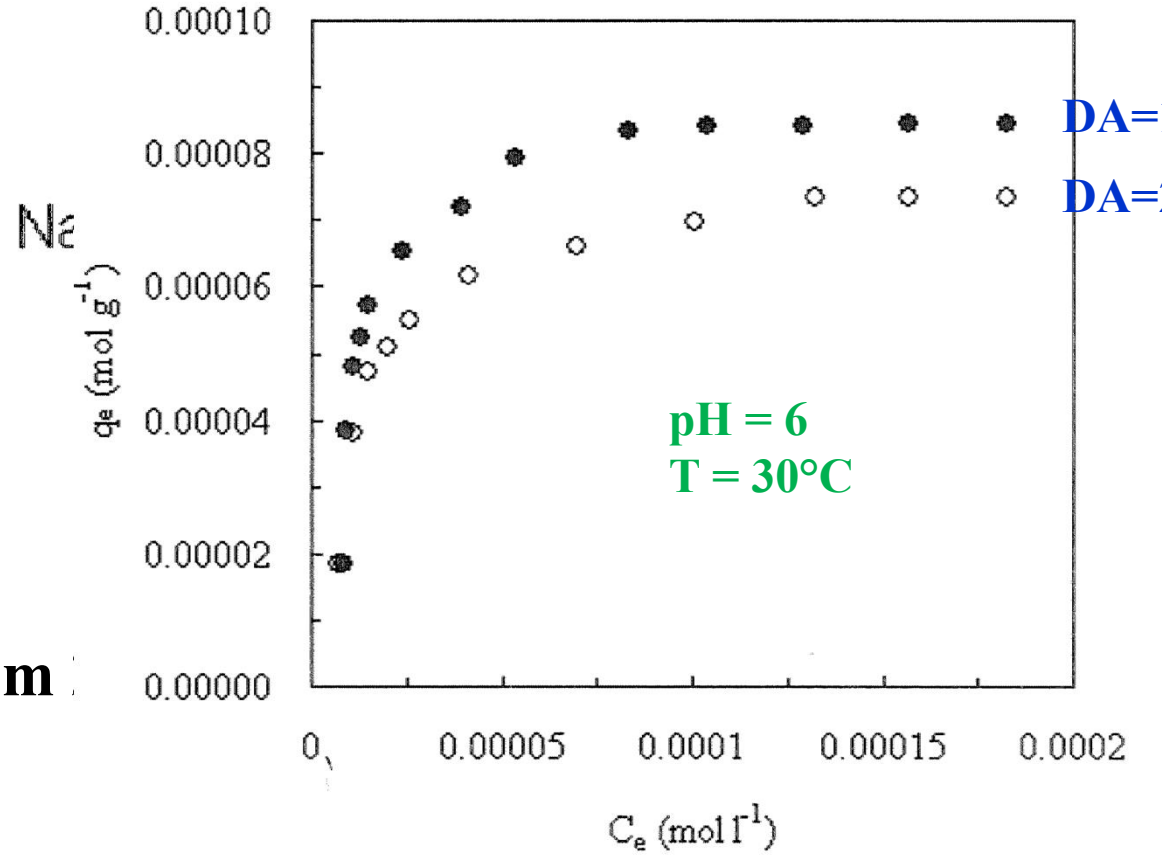


DA=15%
Mw=78,000 g/mol)

pH 7
Room temperature

Salim et al., Carbohydr. Polym. (2010) 81, 640-644

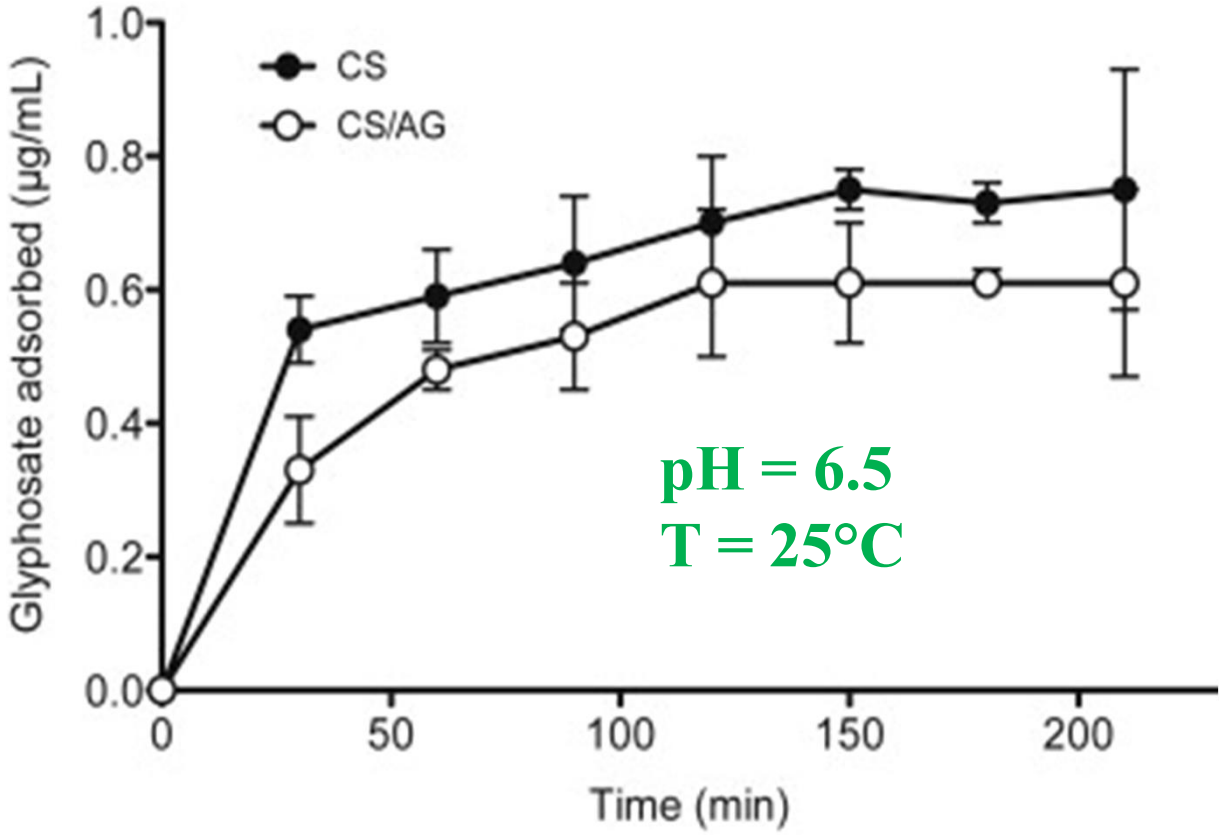
ADSORPTION of ORGANIC COMPOUNDS : DYES



Trisodium **fonate**

nt. Sci. (2005) 286, 433-439

ADSORPTION of ORGANIC COMPOUNDS : HERBICIDES



Carneiro et al., J. Environ. Manag. (2015) 151, 353-360

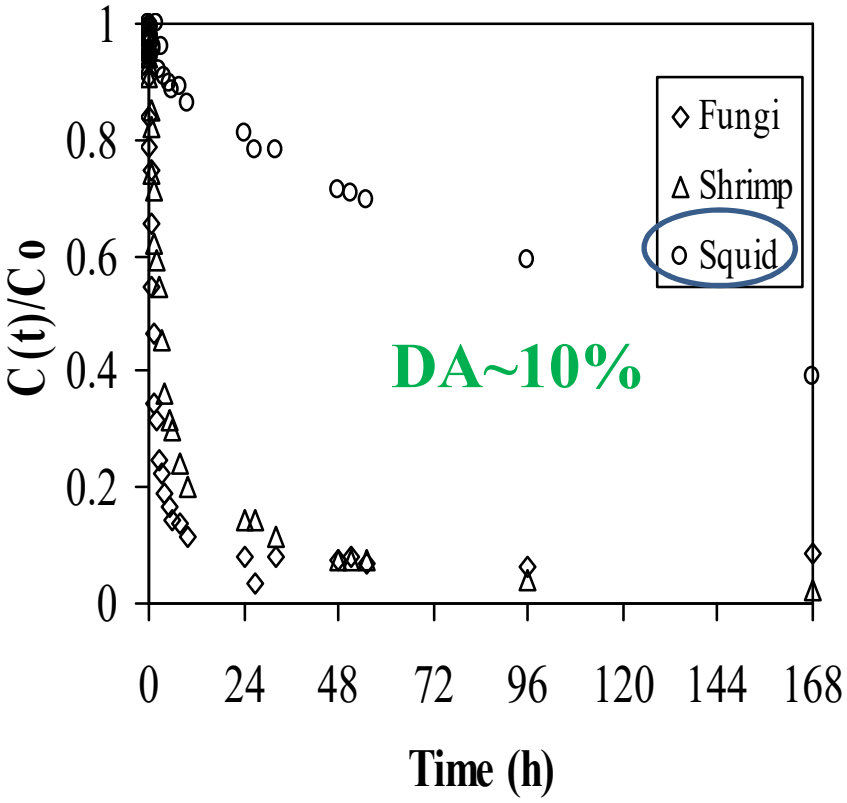
ADSORPTION in ACIDIC MEDIA

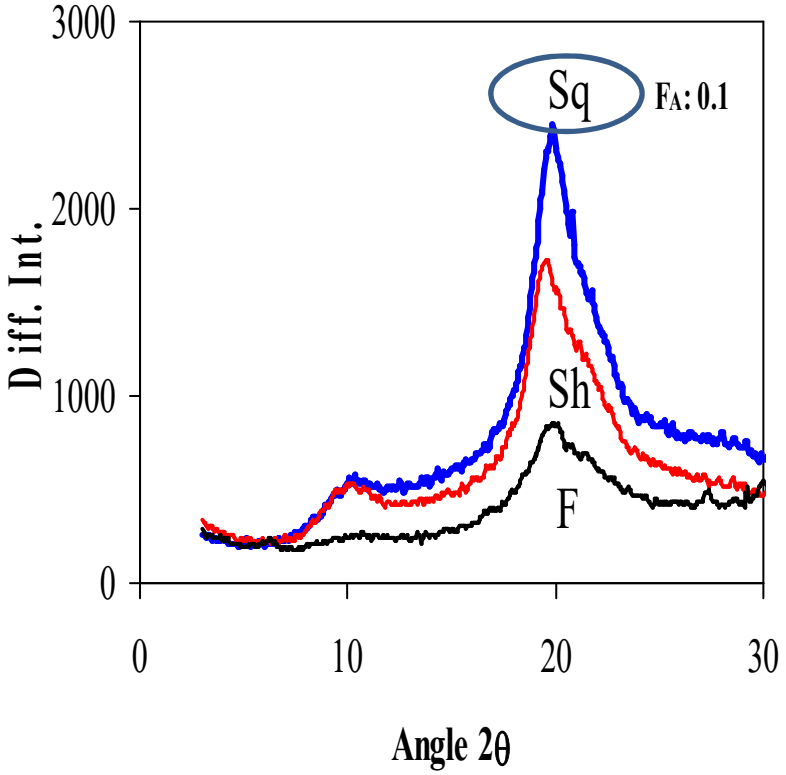
To use the ability of IONIZATION of amino groups and ELECTROSTATIC interactions

➔ CROSSLINKING of chitosan and preparation of beads….

Controlling Parameters : Cristallinity

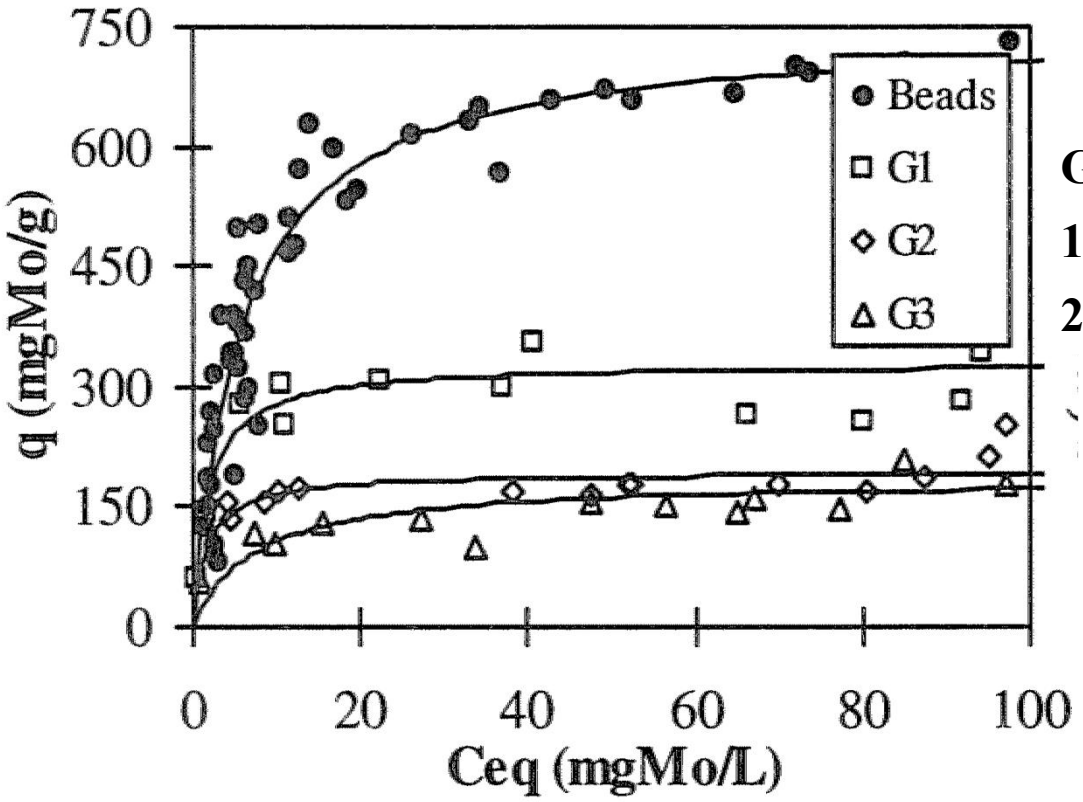
Pt(IV) Adsorption
(pH 2 on crosslinked materials)





Jaworska et al., Polym. Int. (2003) 52, 198-205

Controlling Parameters: Diffusion within chitosan crosslinked flakes



G1 < 125 µm

125 µm < G2 < 250 µm

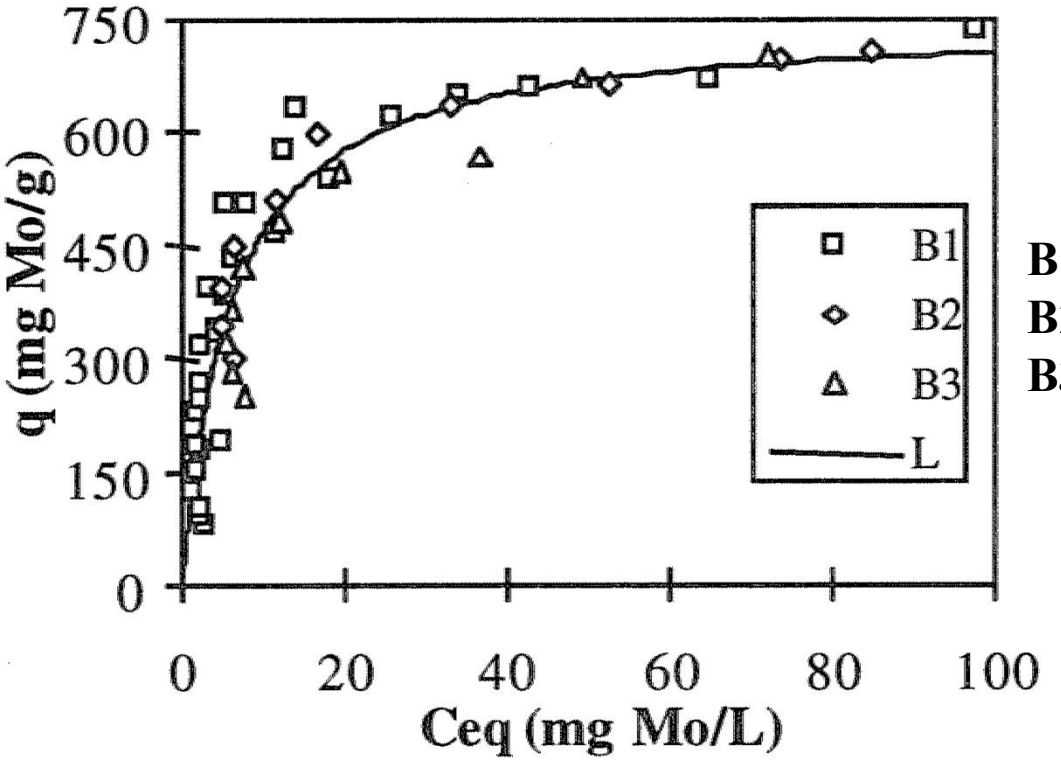
250 µm < G3 < 500 µm

pH 3

MoO_7^{6-}

Guibal et al., Ind. Eng. Chem. Res. (1998) 37, 1454-1463

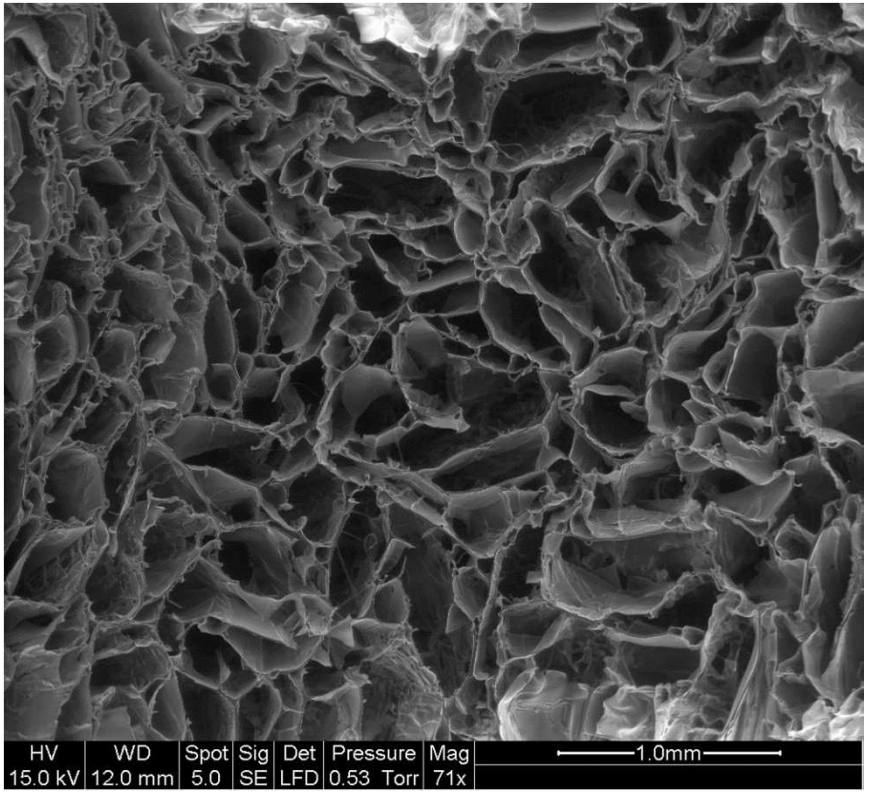
Controlling Parameters: Diffusion in gel beads



B1 = 0.95 mm
B2 = 1.6 mm
B3 = 2.3 mm

Guibal et al., Ind. Eng. Chem. Res. (1998) 37, 1454-1463

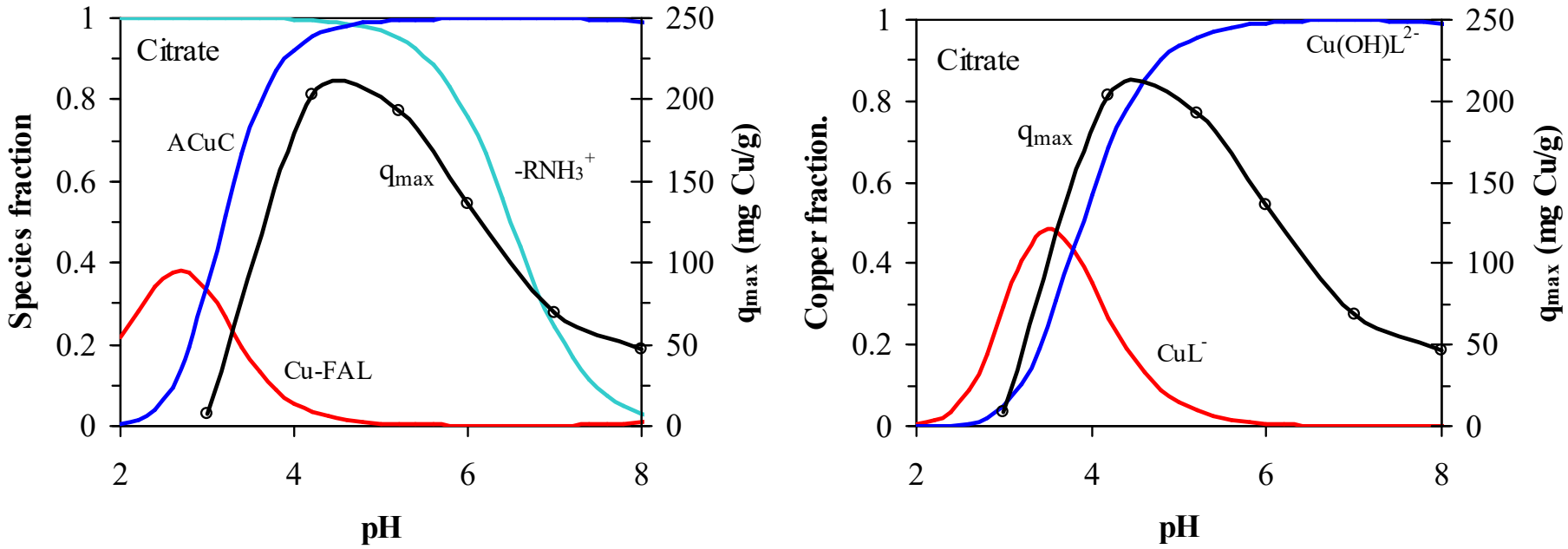
Controlling Parameters: Diffusion



Chitosan foam used for Pd(II) binding

Controlling Parameters : Metal speciation and pH

Copper sorption in presence of citrate (DA=13%, Mw=125,000 g/mol)



Guzman et al., Int. J. Biol. Macromol. (2003) 33, 57-65

CHITOSAN and

COAGULATION-FLOCCULATION

WHAT IS THE PRINCIPLE?

Coagulation:

to neutralize the surface charges in order to limit repulsion forces and allow aggregation

Flocculation of the aggregated matter in suspension

CHITOSAN BOTH COAGULANT AND FLOCCULANT

Coagulant

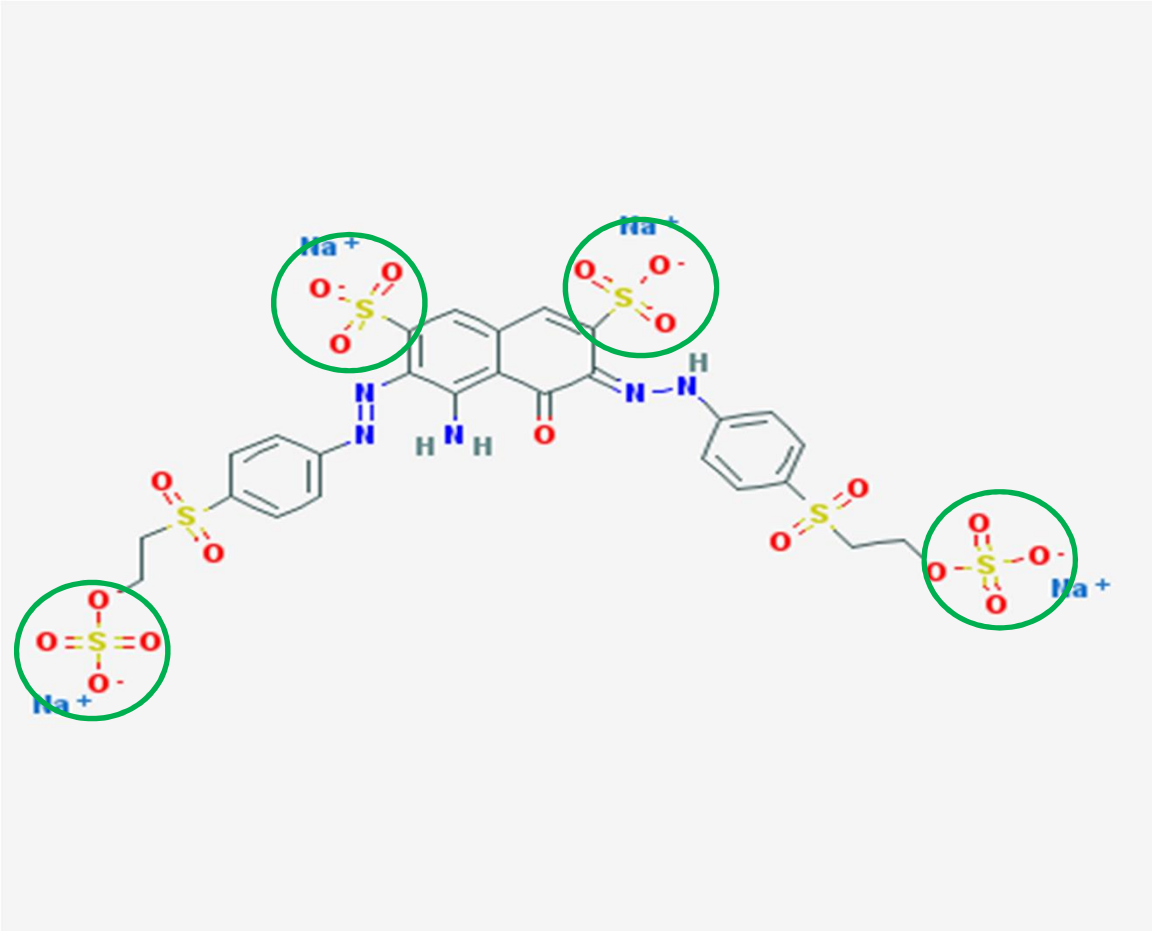
Solubility in acidic medium (pKa~6)

Presence of ionic charges in acidic solution

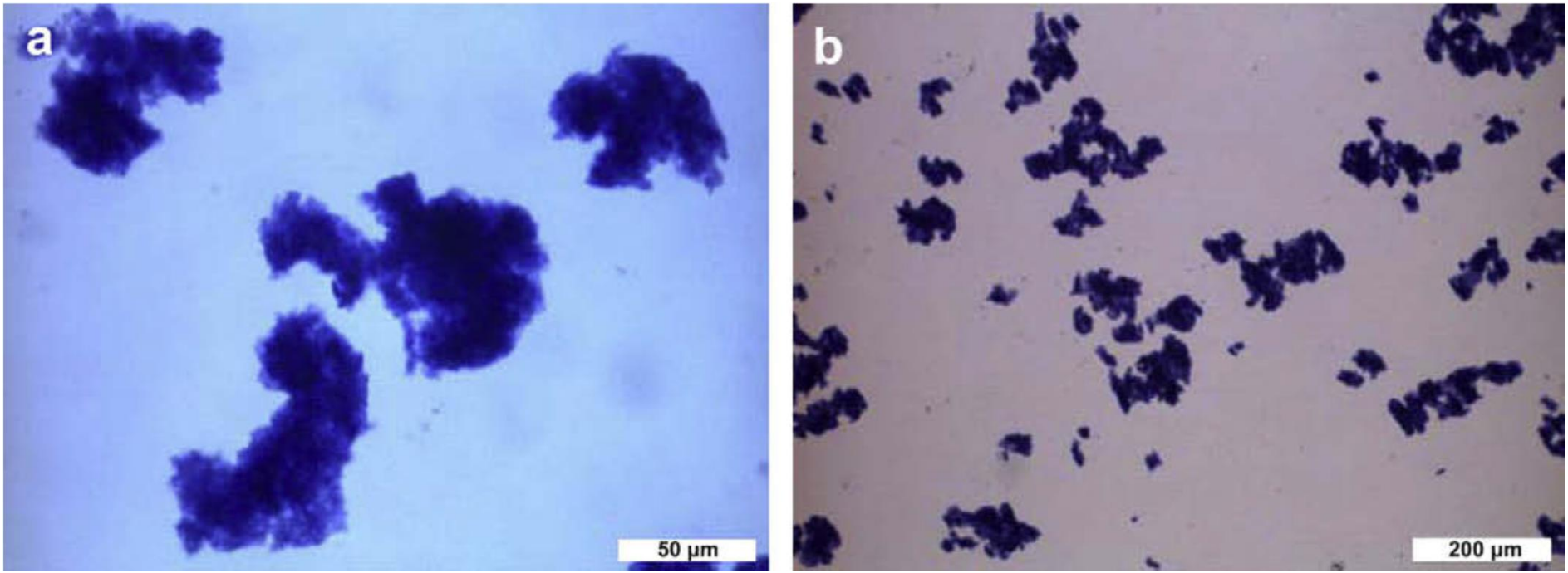
Flocculant

Due to high molecular weight

EXAMPLES : Dissolved contaminants as Reactive Black 5

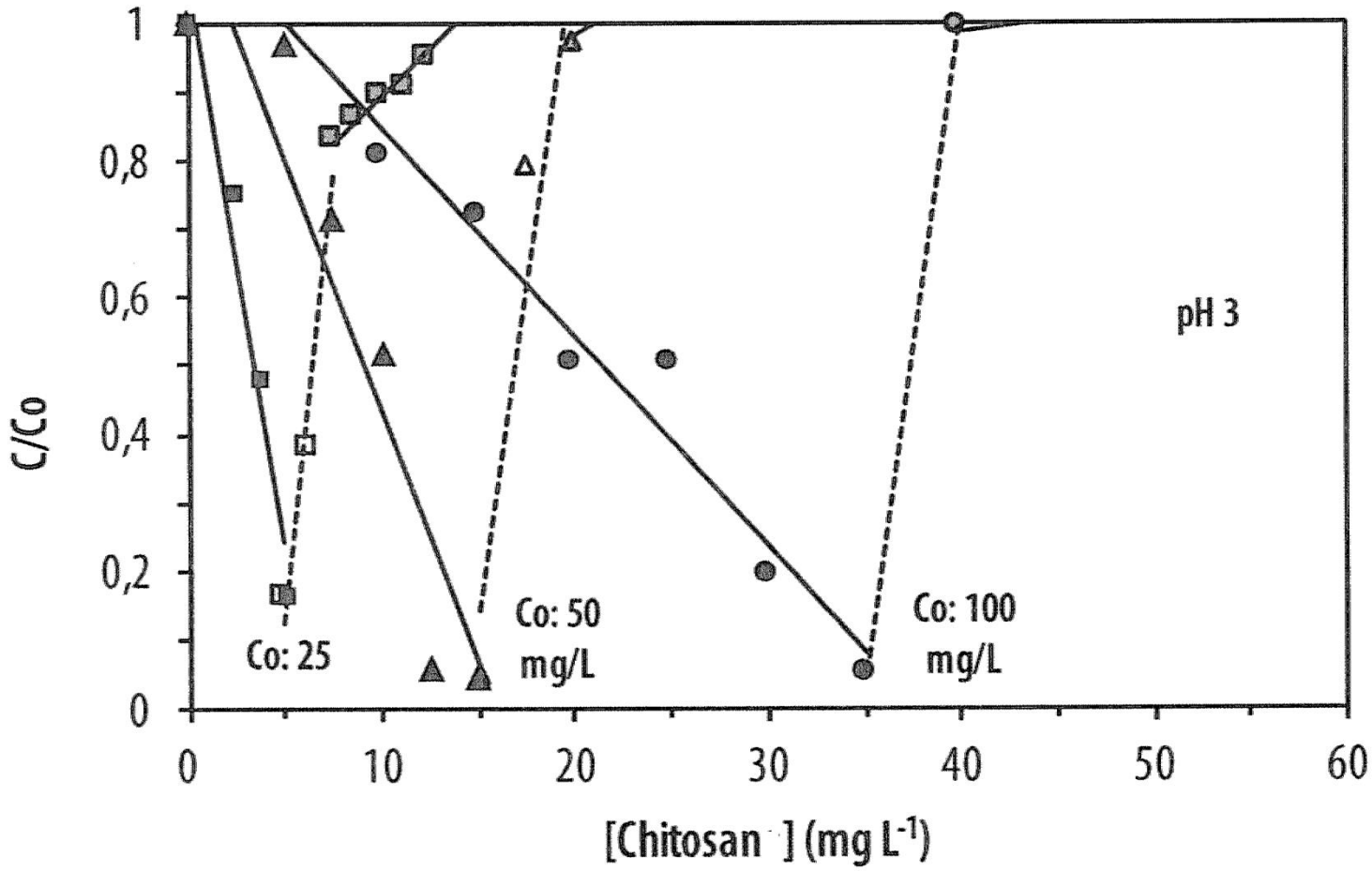


EXAMPLES : Dissolved contaminants as Anionic dye



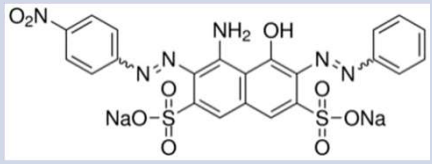
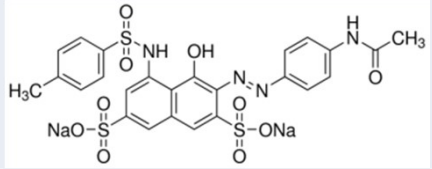
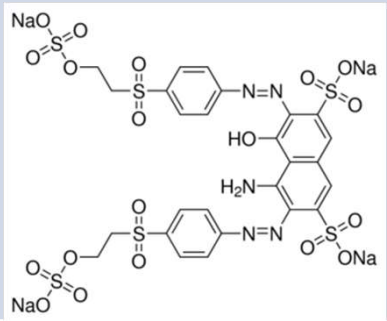
Szygula et al., J. Environm. Manag. (2009) 90, 2979-2986

Effect of Chitosan concentration

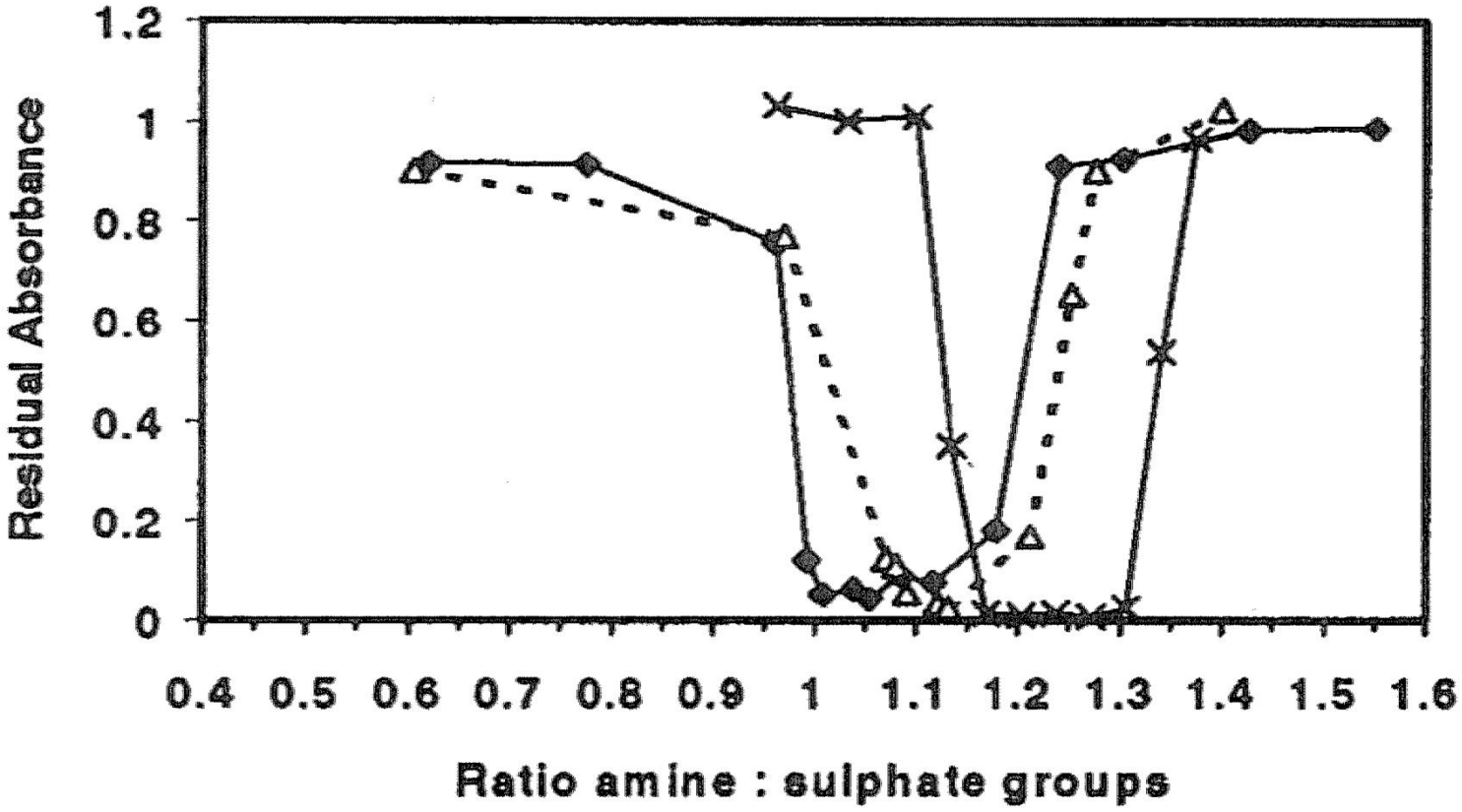


Guibal and Roussy., React. Funct. Polym. (2007) 67, 33-

DYES

Dye	Structure	Number of Sulfonic groups	[n] (mol dye/mol protonated amines)
Acid black 1		2	0.8-0.9
Acid violet 5		2	0.5-0.6
Reactive Black 5		4	0.2-0.3

EXAMPLES : Particulate contaminants as polystyrene latexes

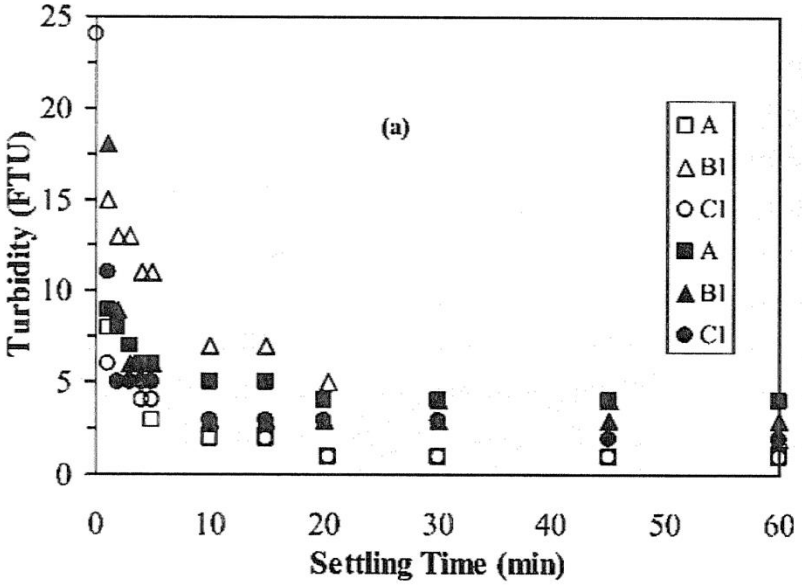


♦ : DA=14%; Δ : DA=33%; x : DA=57%

Ashmore and Hearn, Langmuir (2000) 16, 4906-4911

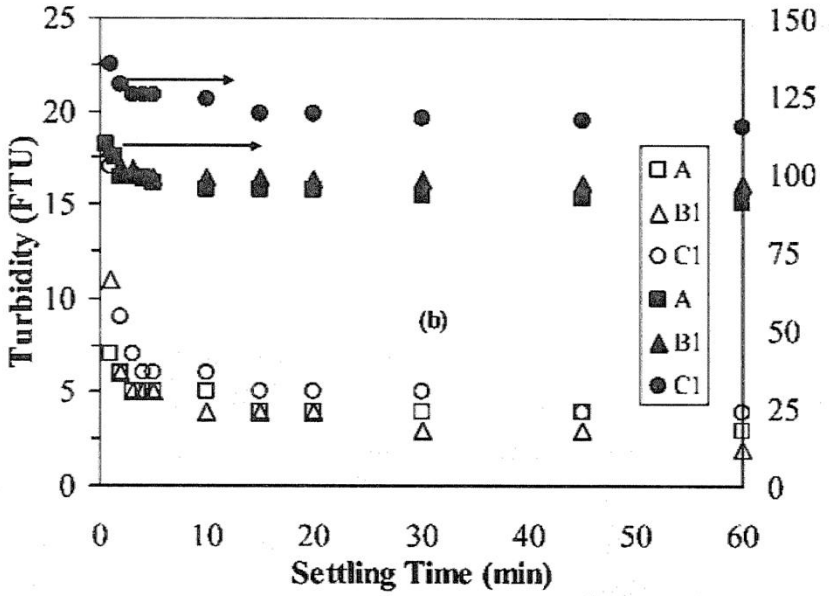
EXAMPLES : Mineral suspensions

Bentonite suspension and chitosan (0.17 mg/L; DA/M)
(A:22%/230,700; B1:10.5/308,300; C1:5/182,300)



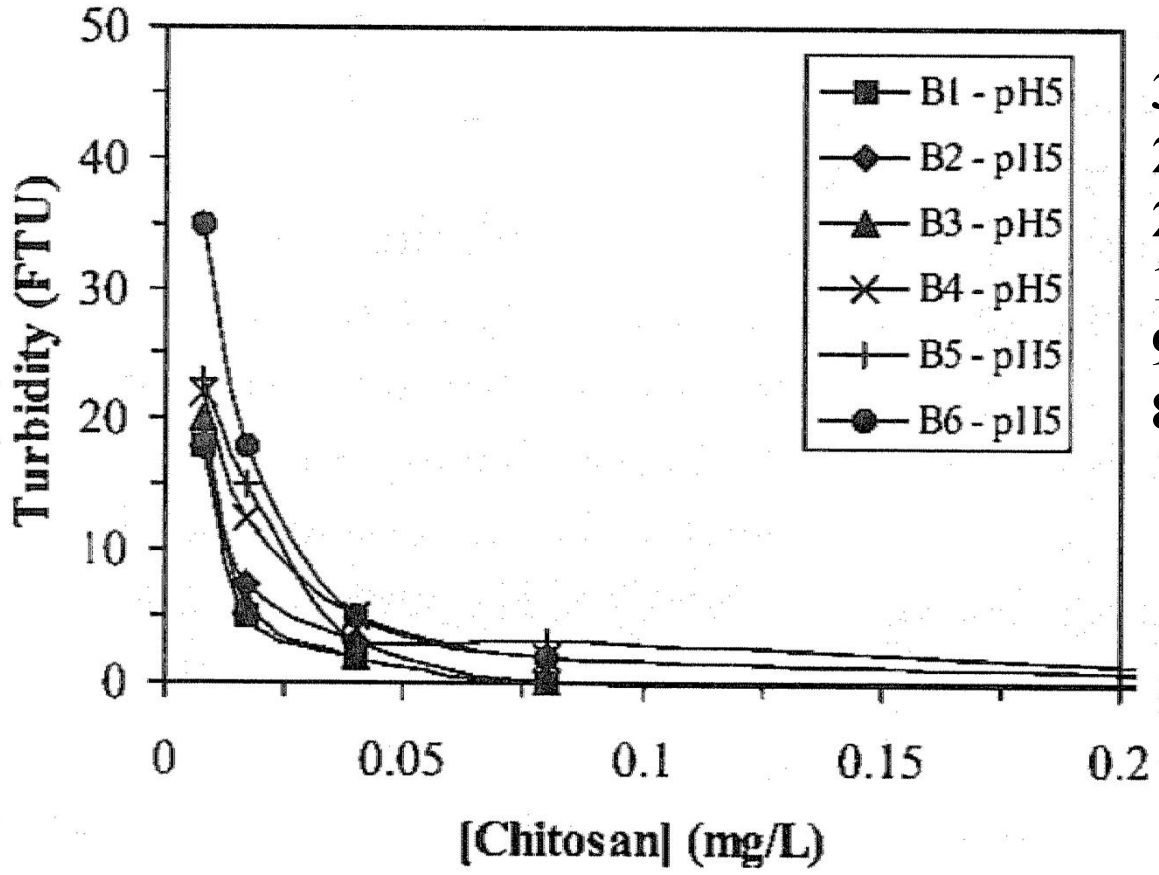
Tap water
pH 5 (open symbols),
pH 7 (closed symbols)

Demineralized water
pH 5 (open symbols),
pH 7 (closed symbols)



EXAMPLES : Mineral suspensions

Bentonite suspension and chitosan (DA = 10.5%) in tap water

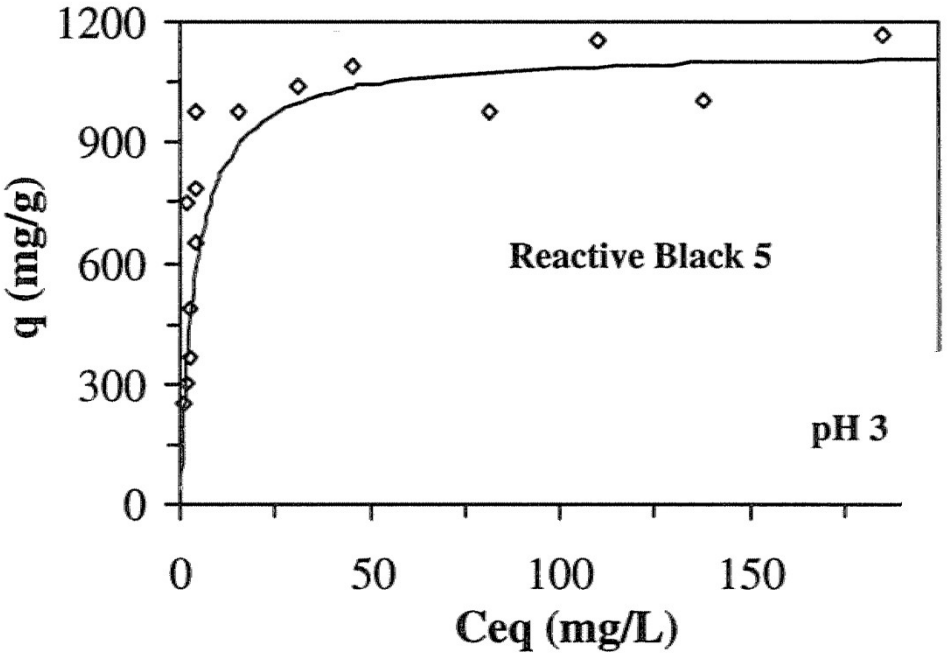


308,300 g/mol
235,200 g/mol
222,000 g/mol
155,000 g/mol
94,300 g/mol
80,100 g/mol

COMPARING ADSORPTION and

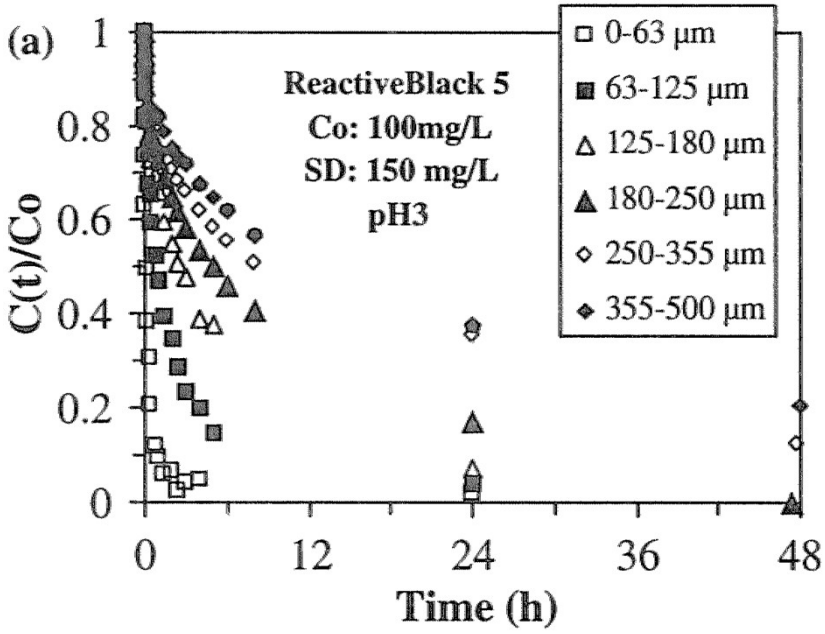
COAGULATION-FLOCCULATION

Chitosan interactions with RB5



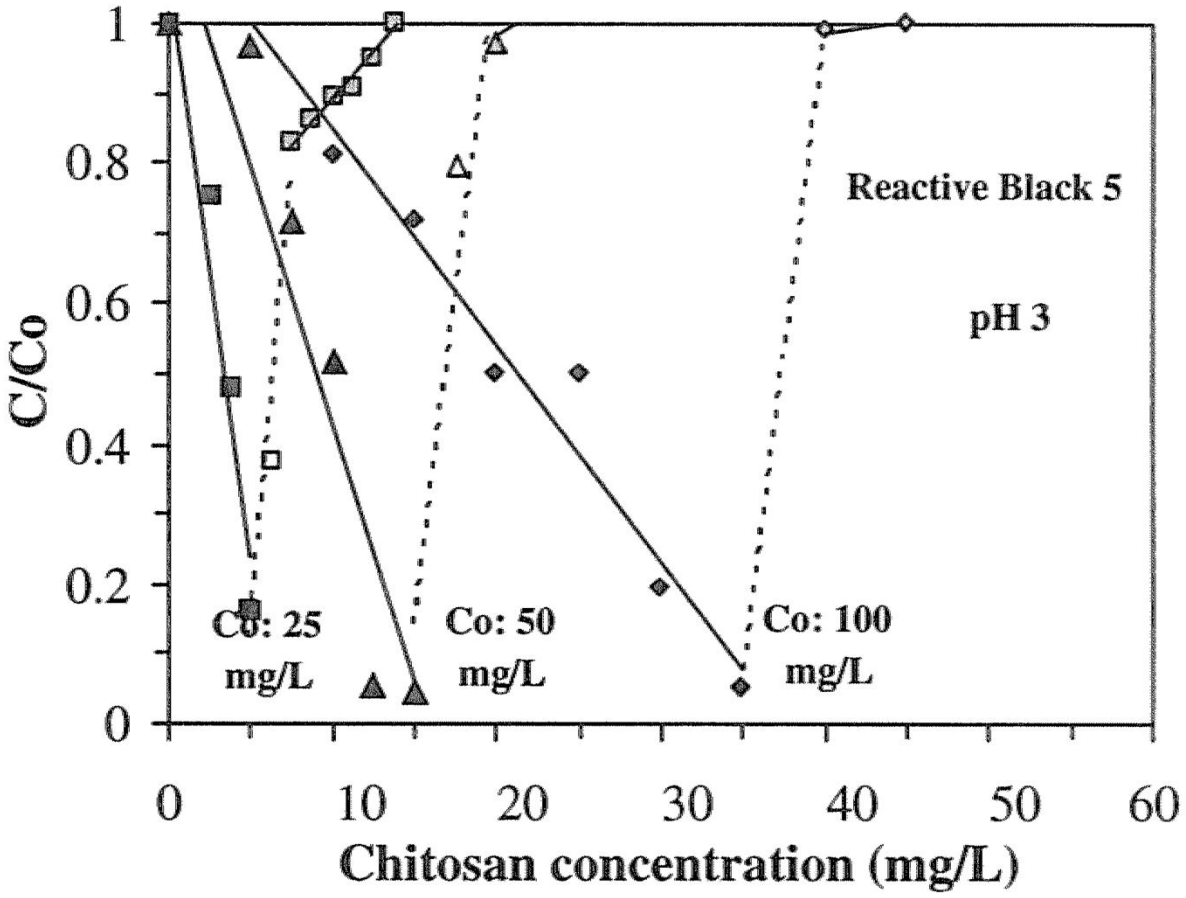
Maximal sorption capacity = 1100 mg dye.g^{-1}

➔ 7 mol of amino group for sorption of 1 mol of dye



Guibal et al., World J. Microbiol. Biotechnol. (2005) 21, 913-920

Chitosan interactions with RB5



Chitosan interactions with RB5

Chitosan quantity

Maximal sorption capacity = 1100 mg dye.g^{-1}

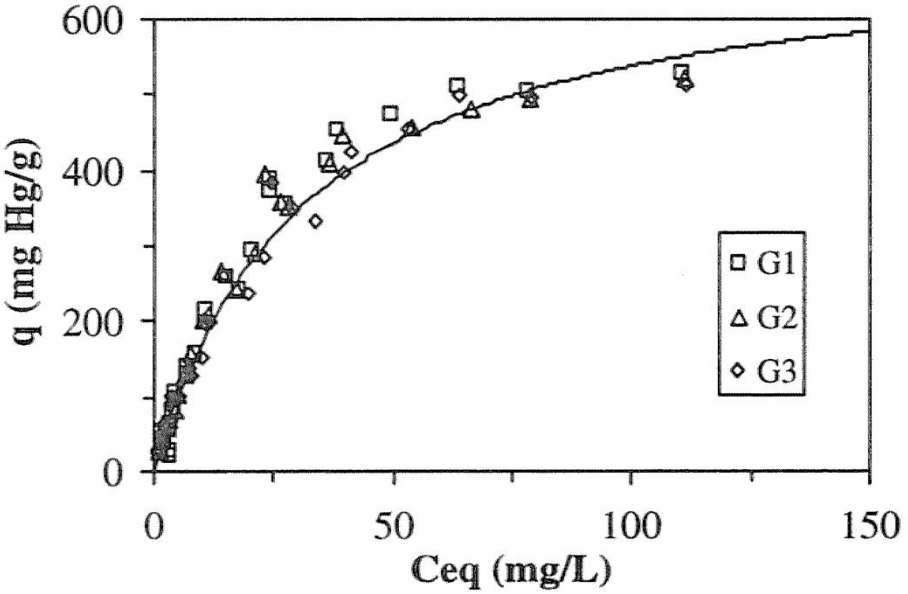
➔ 7 mol of amino group for sorption of 1 mol of dye

Dye Concentration (mg.L^{-1})	Chitosan concentration (for colour abatment) (mg.L^{-1})	[amine group mol]/[dye mol]
25	5	2
50	15	2.7
100	35	3.1

Kinetics

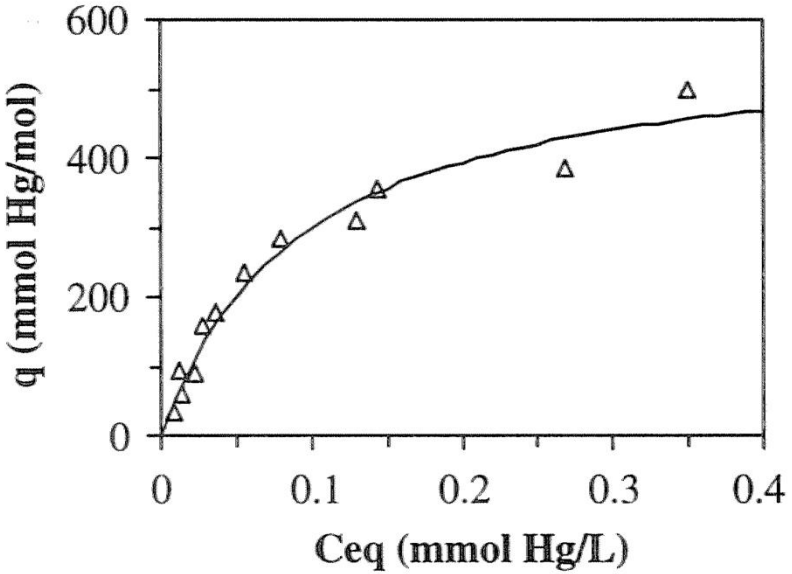
Chitosan interactions with Hg(II)

Sorption



pH 5

Coagulation-Flocculation



Guibal et al., World J. Microbiol. Biotechnol. (2005) 21, 913-920

Interest of Coagulation-Flocculation process

- **Better (or similar) efficiency**
- **Kinetics of the process (tens of minutes compared with few hours)**

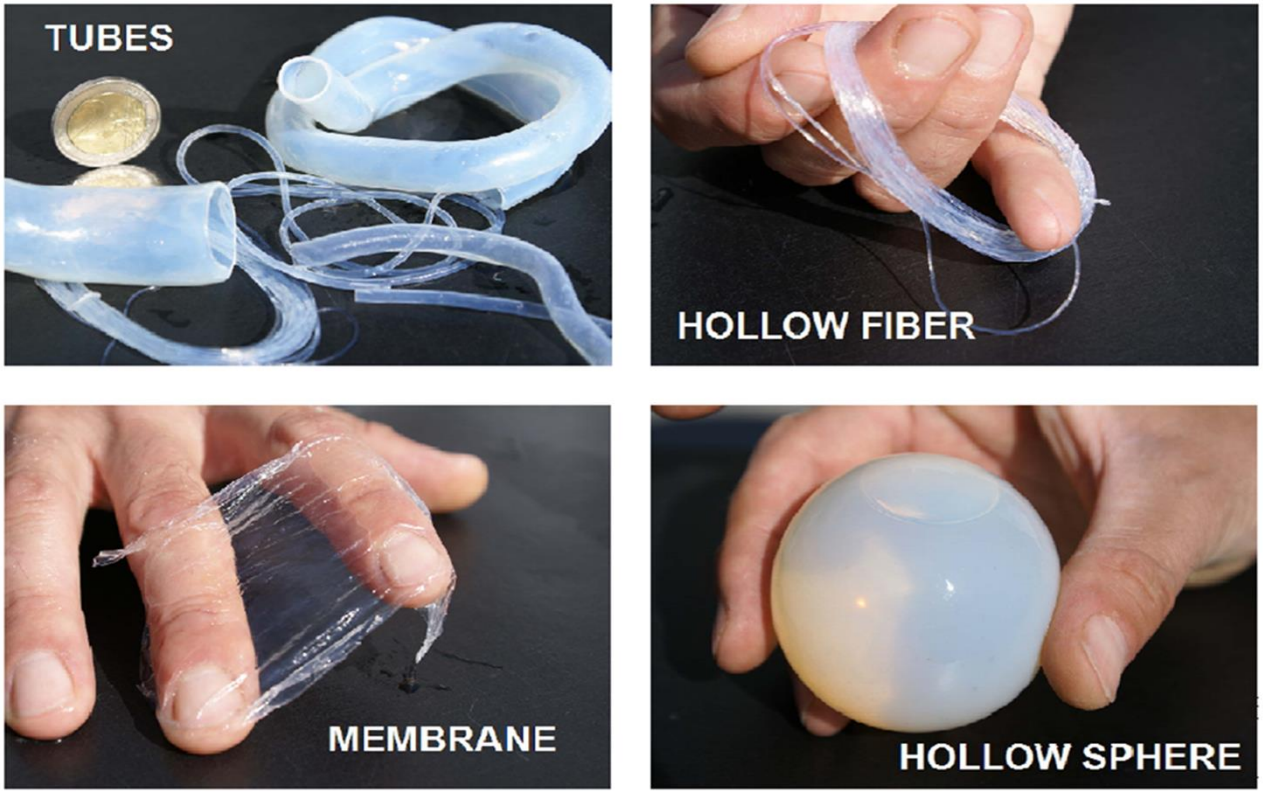
WHY?

WHY?

- **Dissolution of polymer leads to destruction of crystallinity**
- **Breakage of hydrogen bonds**

➔ BETTER ACCESSIBILITY of AMINO GROUPS

HOW APPLYING CHITOSAN?



But also foams, sponges (high porosity)…

CONCLUSION and PROSPECTS

Interest in using chitosan

- Abundant and renewable sources
- Under solid or liquid form
- Environment-friendly thermal degradation
- Ability to be chemically or physically modified, processed under different forms

But : - Material variability

- Cost

CONCLUSION and PROSPECTS

Design of new materials

- specific sorbents
- support for affinity chromatography
- heterogeneous (or supported) catalysis
- biosensors

Acknowledgments

IMT Mines Alès
École Mines-Télécom

T. Vincent
All students, PhD students and co-workers (Universidad Politecnica de Catalunya)

UNIVERSITE JOSEPH FOURIER
SCIENCES. TECHNOLOGIE. MEDECINE. GRENOBLE - ALPES

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

M. Rhazi
All students and PhD students

THANK YOU

OBRIGADO

Coagulation-Flocculation
Jar-test Apparatus