NANOTECHNOLOGY APPLICATIONS FOR TREATMENT: COST EFFECTIVE AND RAPID TECHNOLOGIES; SMART MATERIALS OR ACTIVE SURFACE COATINGS

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Why Nanomaterials?

- Ability to manipulate, control and build materials at the atomic and molecular level
- Provide novel affinity, capacity, and selectivity because of their unique physical, chemical and biological properties.
- Create large structures with new molecular organization that will facilitate recovery

Types of Nanomaterials for Environmental Treatments

- 1. Smart modified surfaces or membranes
- 2. Nanostructured materials
- 3. Molecularly imprinted polymers
- 4. Nanoscale Biopolymers

Smart Surfaces or Membranes

Active Membranes for Heavy Metal Removal

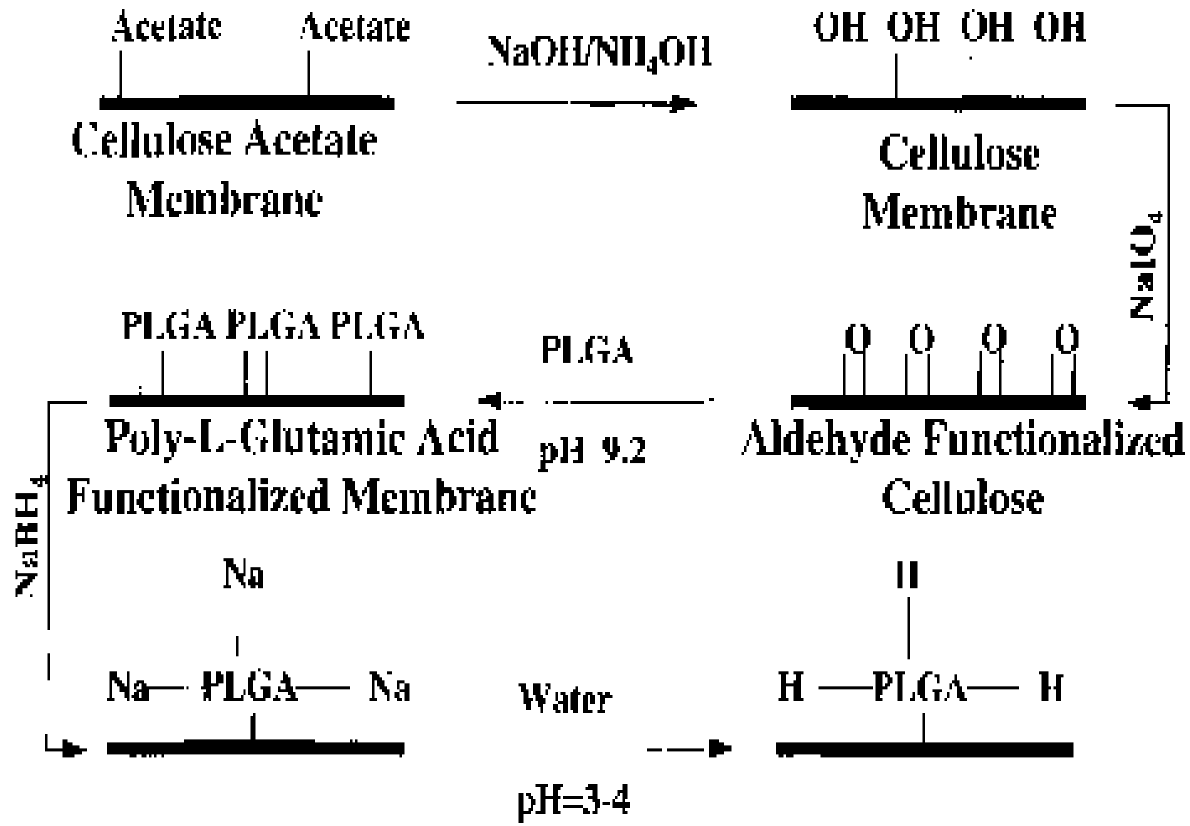


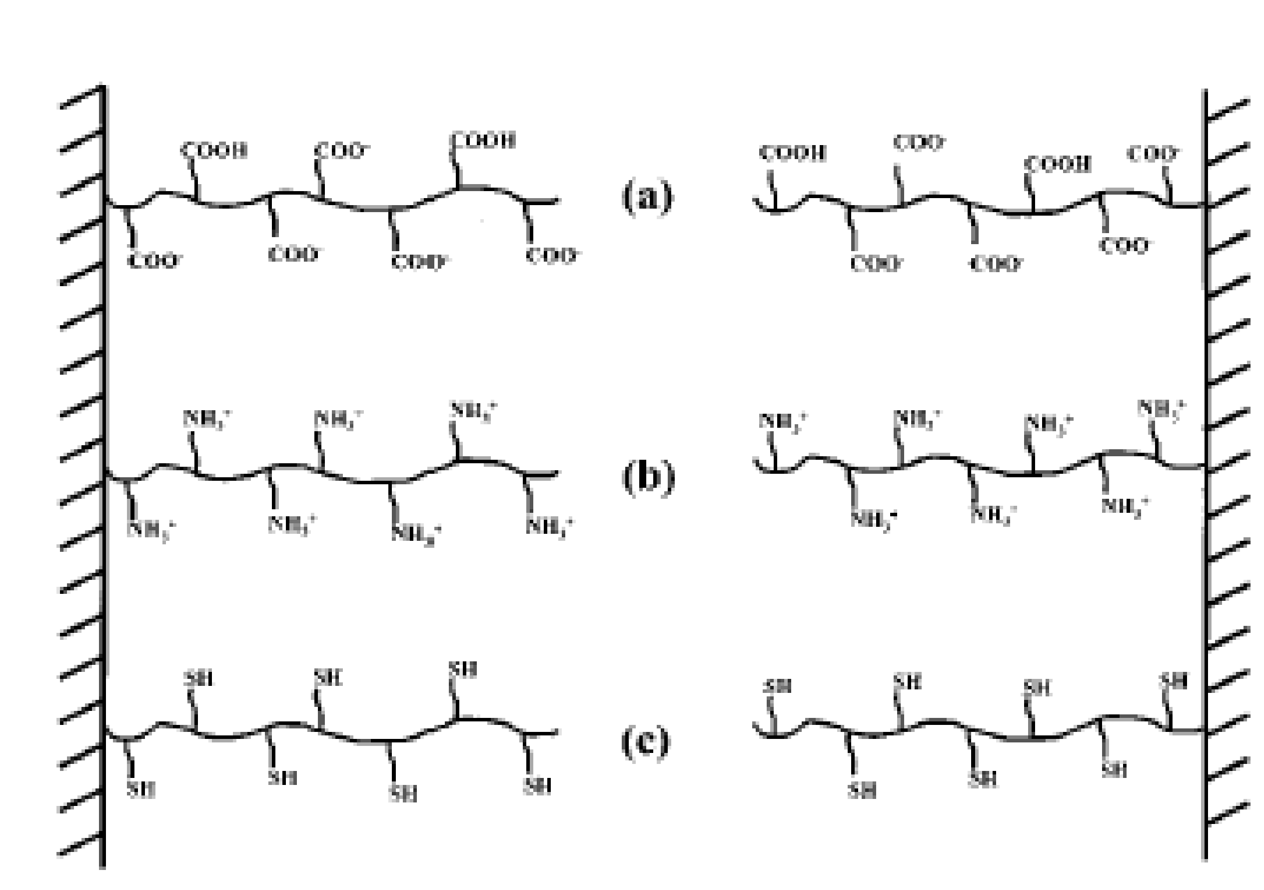
Fig. 3. Functionalization and derivatization steps for cellulose acetate microfiltration membranes.

Types of modifying peptides

poly-L-glutamate
or aspartate

poly-L-lysine or
arginine

poly-L-cysteine



Ritche et al. ES&T 2001

Metal Chelating Behavior

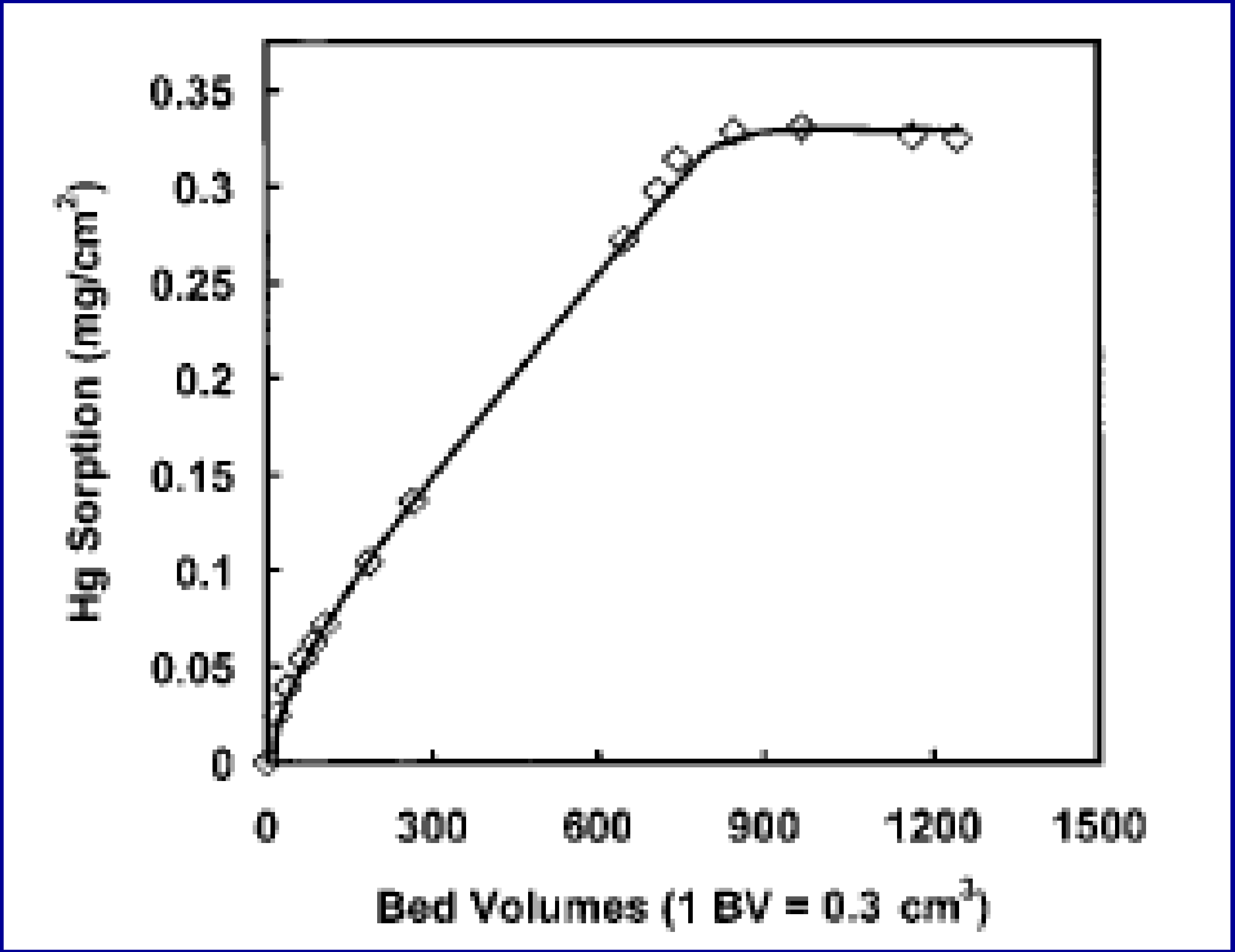
TABLE 3. Metal Complex Stability Constants (log *K*) of Various Metals with Amino Acids[a]

	aspartic acid	glutamic acid	cysteine
Ca^{2+}	1.6	1.4	NA[b]
Cd^{2+}	4.4	3.8	10.1[c]
Cu^{2+}	8.9	8.3	NA[b]
Ni^{2+}	7.2	5.6	9.7
Pb^{2+}	5.9[d]	4.4[e]	12.2
Hg^{2+}	NA[b]	NA[b]	14.2

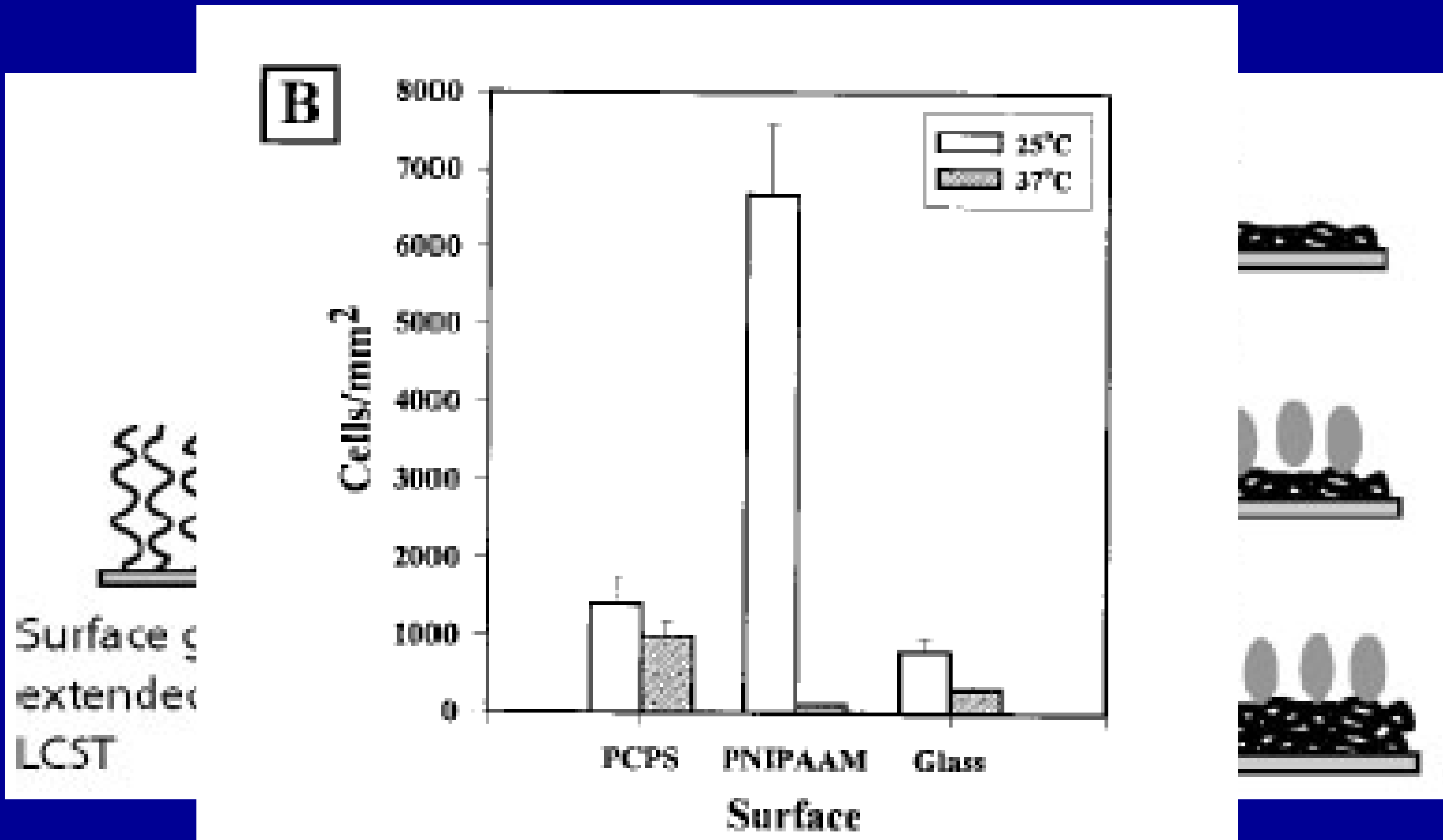
[a] Data taken from ref *20*. All stability constants at 25 °C and 0.1 M ionic strength (μ) except where noted. [b] Not applicable, NA. [c] 37 °C and $\mu = 0.15$ M. [d] $\mu = 1.0$ M. [e] $\mu = 0.5$ M.

poly-L-lysine or arginine - oxyanion such as As

Results with poly-cysteine membrane



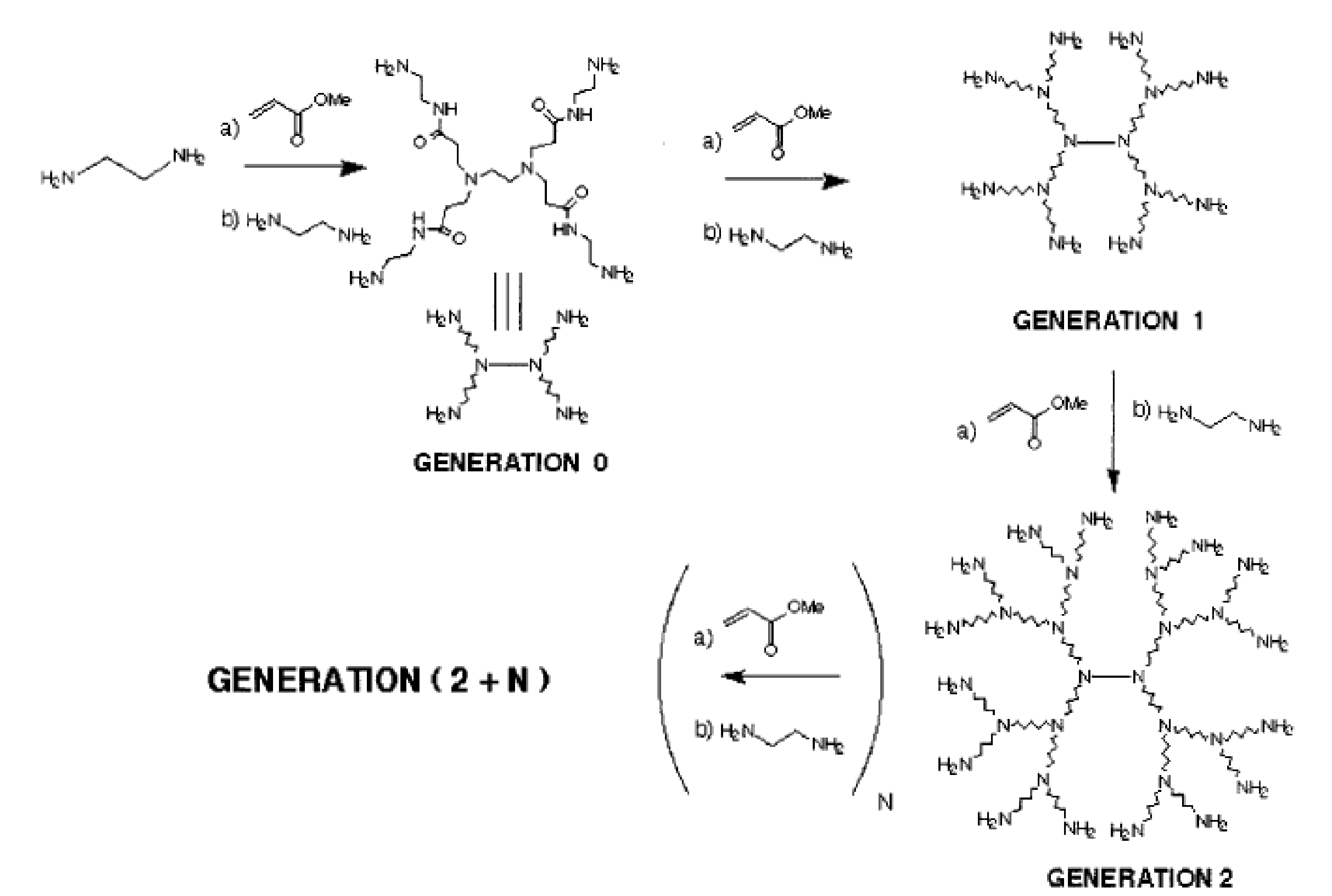
Tunable Surfaces for Biofouling



Ista et al. Appl. Environ. Microbiol. 1999

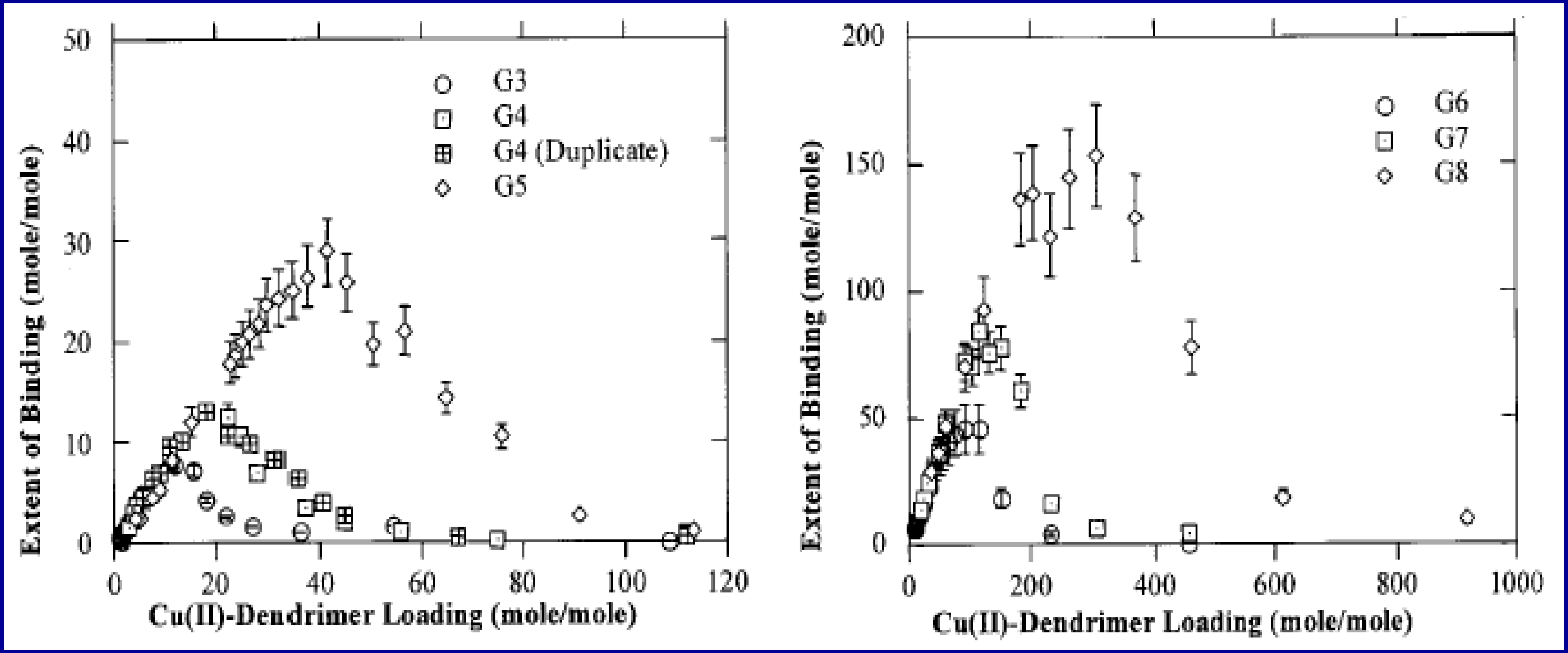
Nanostructured Materials

Poly(amidoamine) Dendrimers

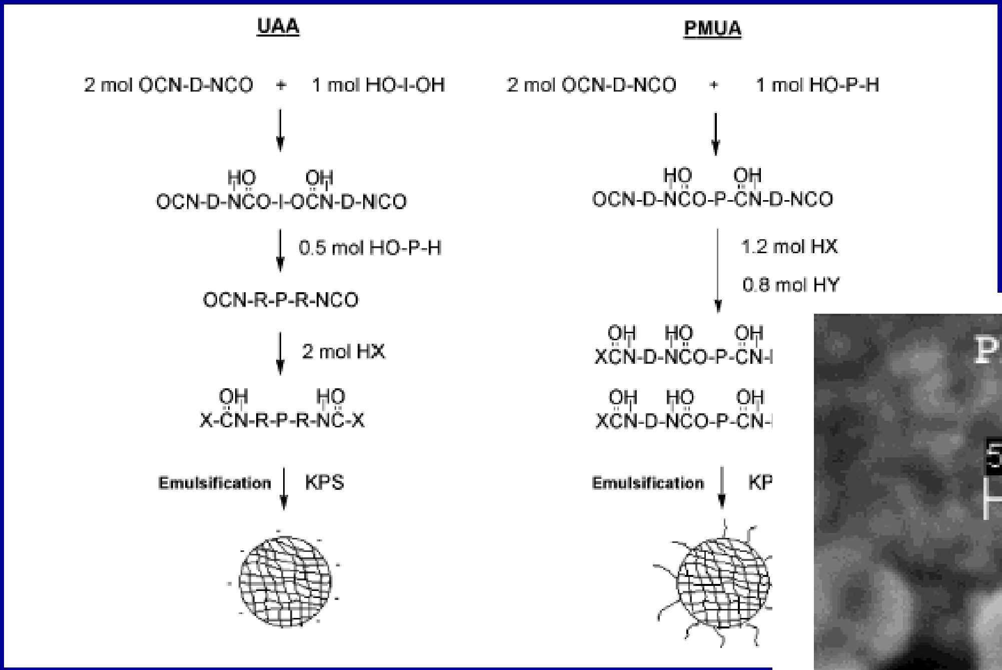


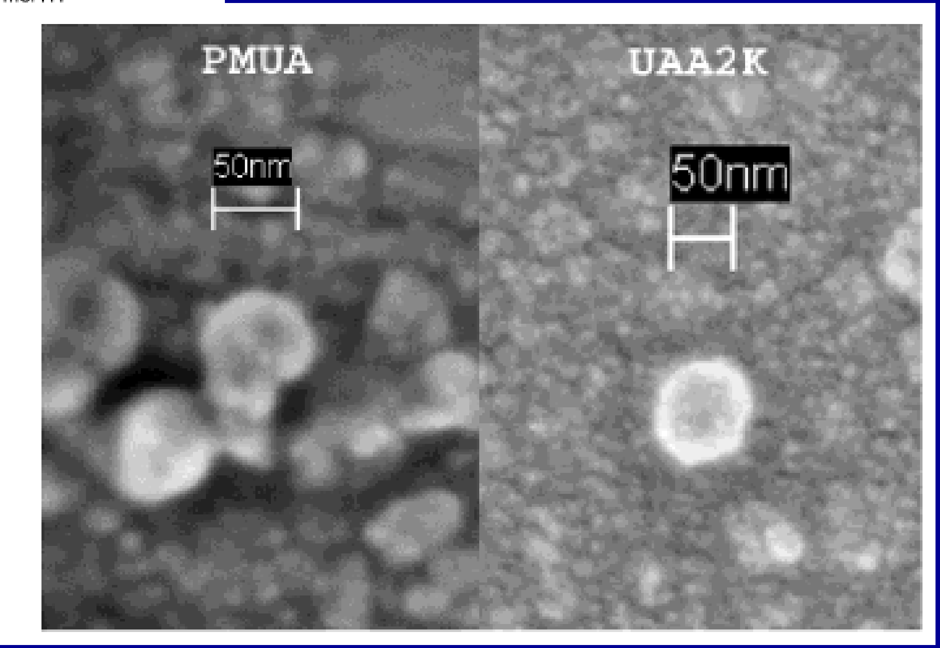
Diallo et al. ES&T 1999

Binding properties



Polymeric Nanoparticles





Tungittiplakorn et al. Appl. Environ. Microbiol. 2004

Enhance PAH Desorption

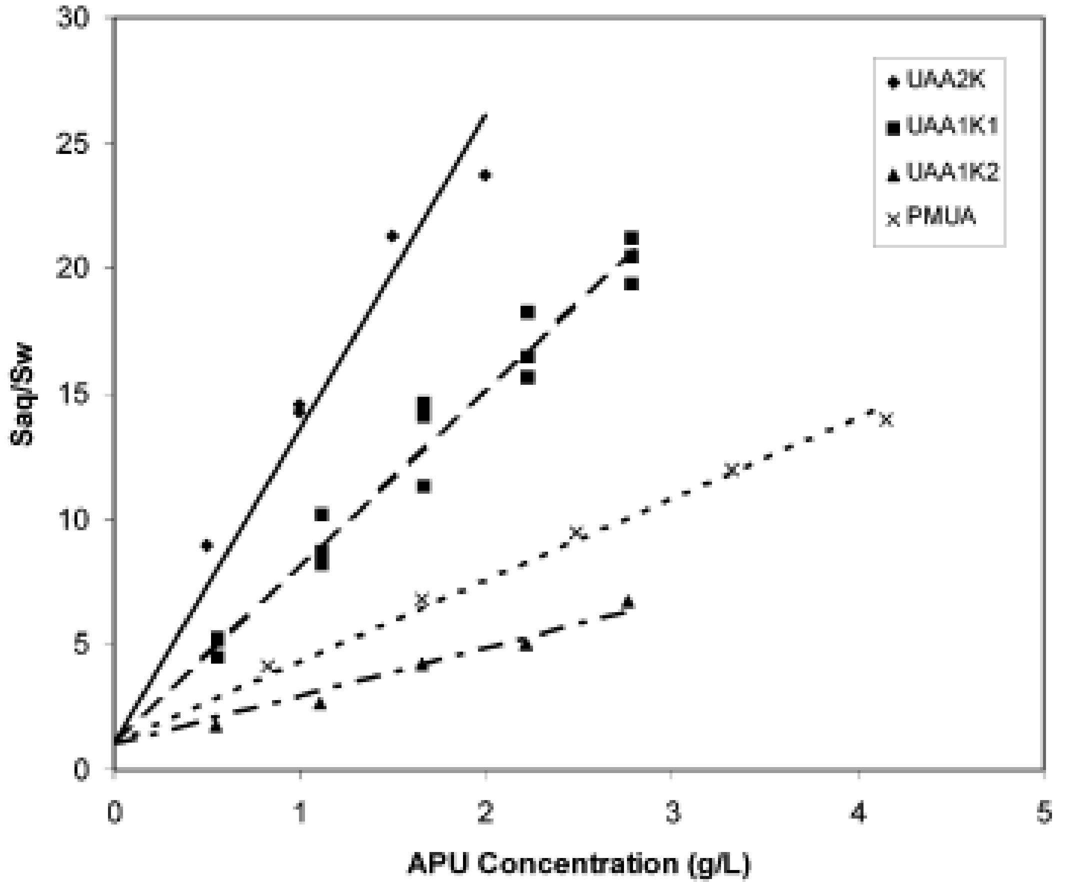
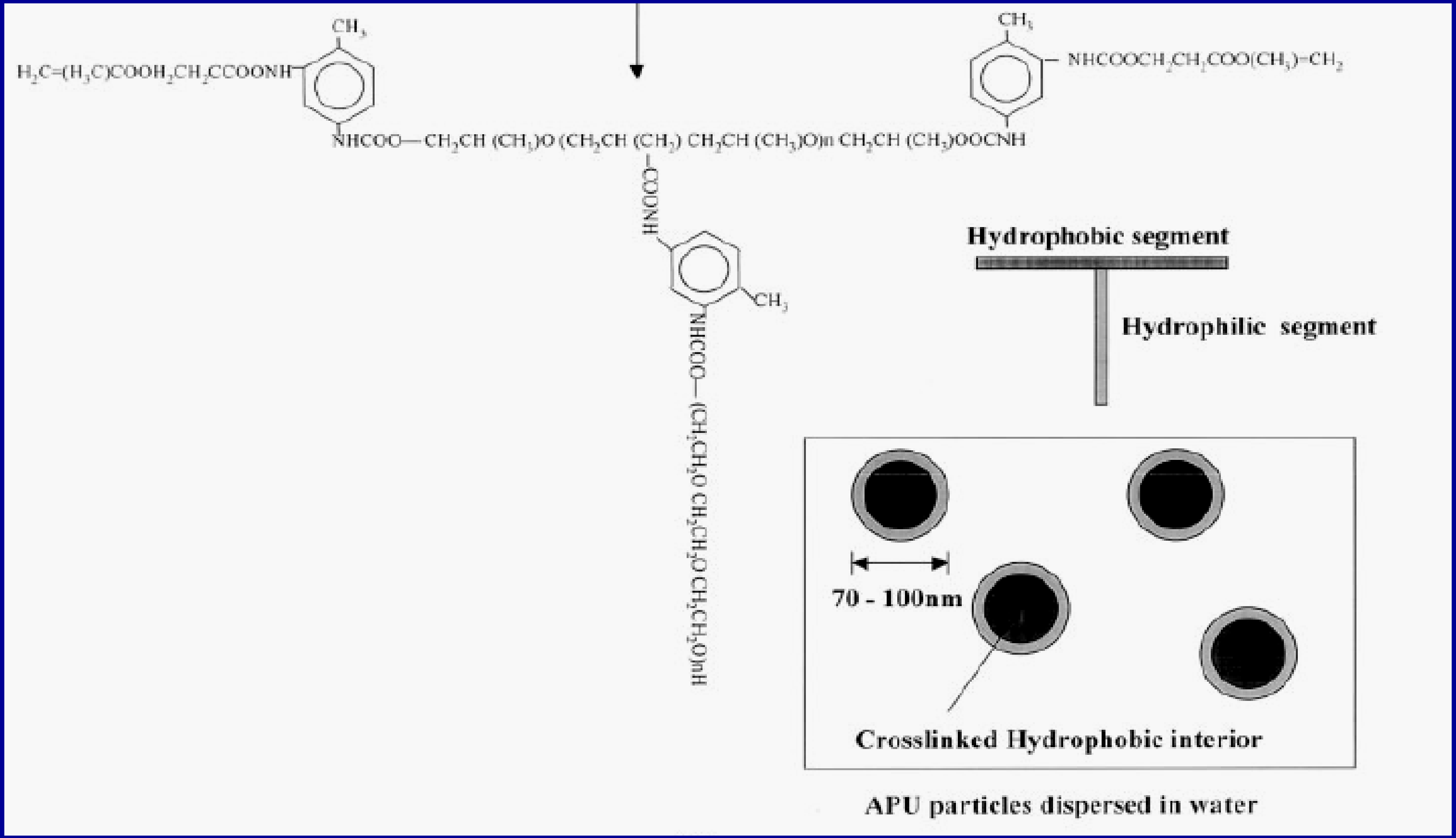


FIGURE 4. Apparent solubility of PHEN as a function of APU particle concentration.

Amphiphilic Polyurethane Nanoparticles

Kim et al. Journal of Applied Polymer Science 2004



90 nm in size

Enhanced PAH Solubility

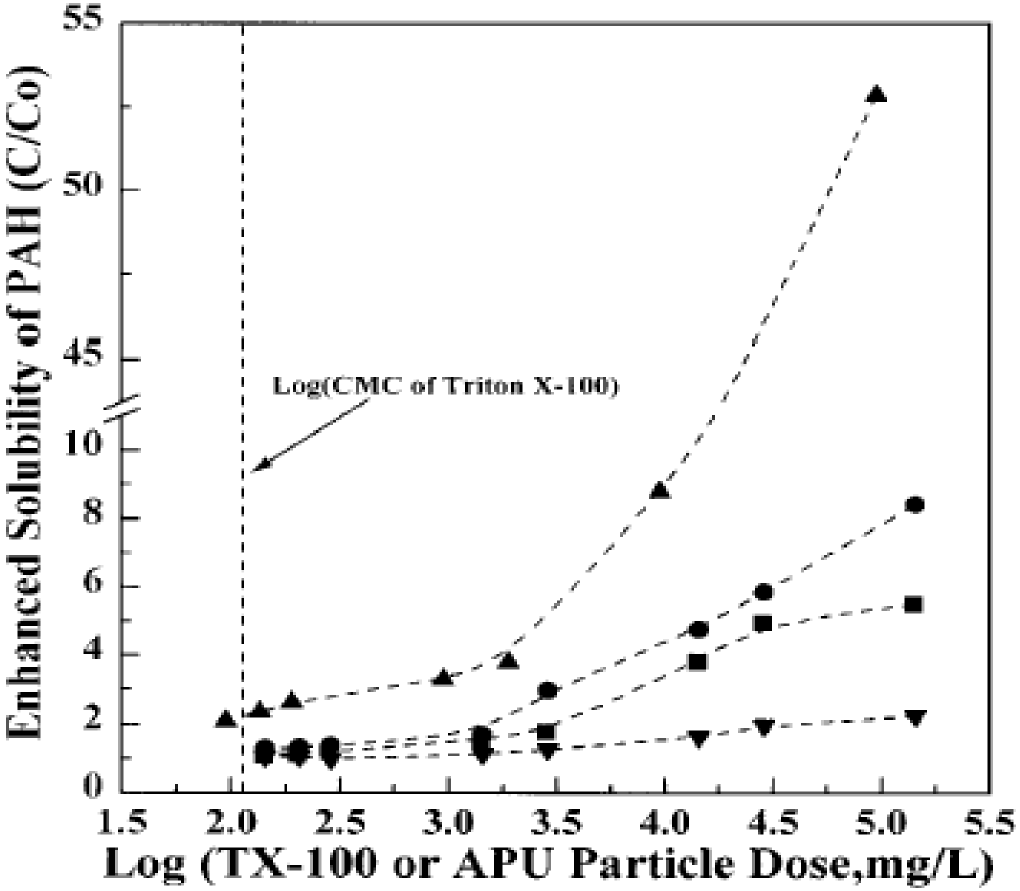
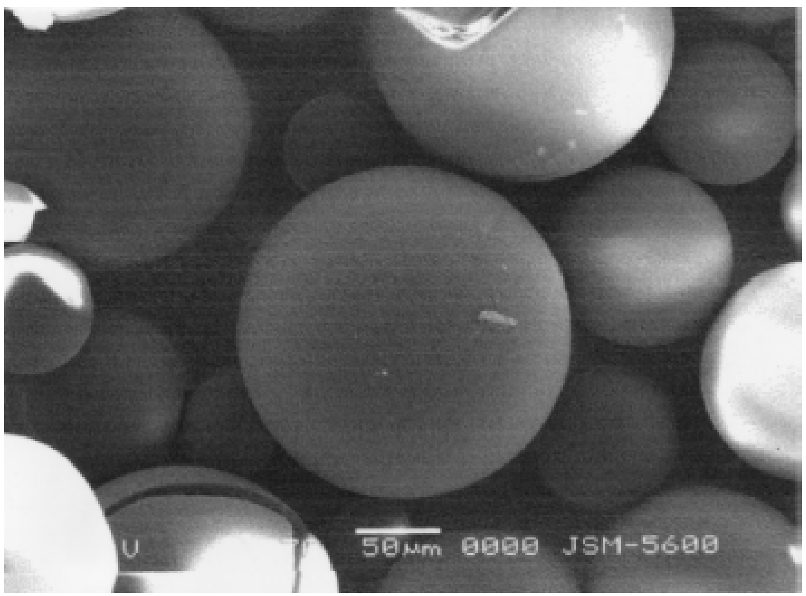


Figure 3 Enhanced solubility of phenanthrene in the aqueous phase in the presence of Triton X-100 or APU particles: (▲) Triton X-100, (▼) APU700-2, (■) APU700-3, and (●) APU1000

PHEMA Beads
containing N-Methacryloylhistidine



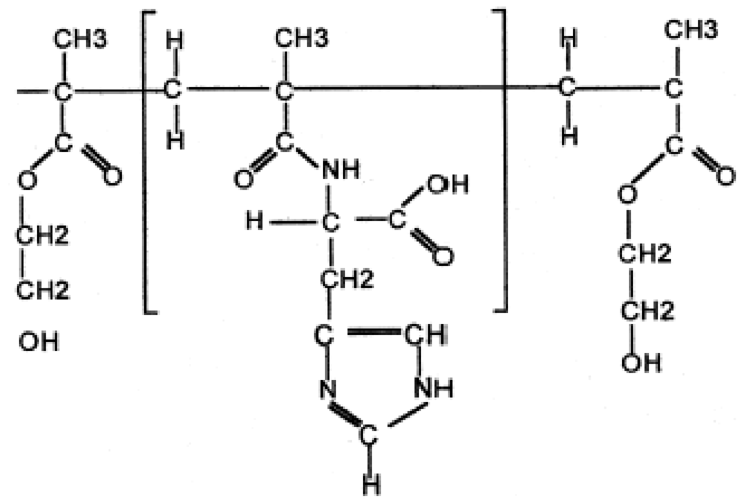


Figure 2. Molecular formula of p(HEMA-MAH) beads.

Say et al. Macromol. Mater. Eng. 2002

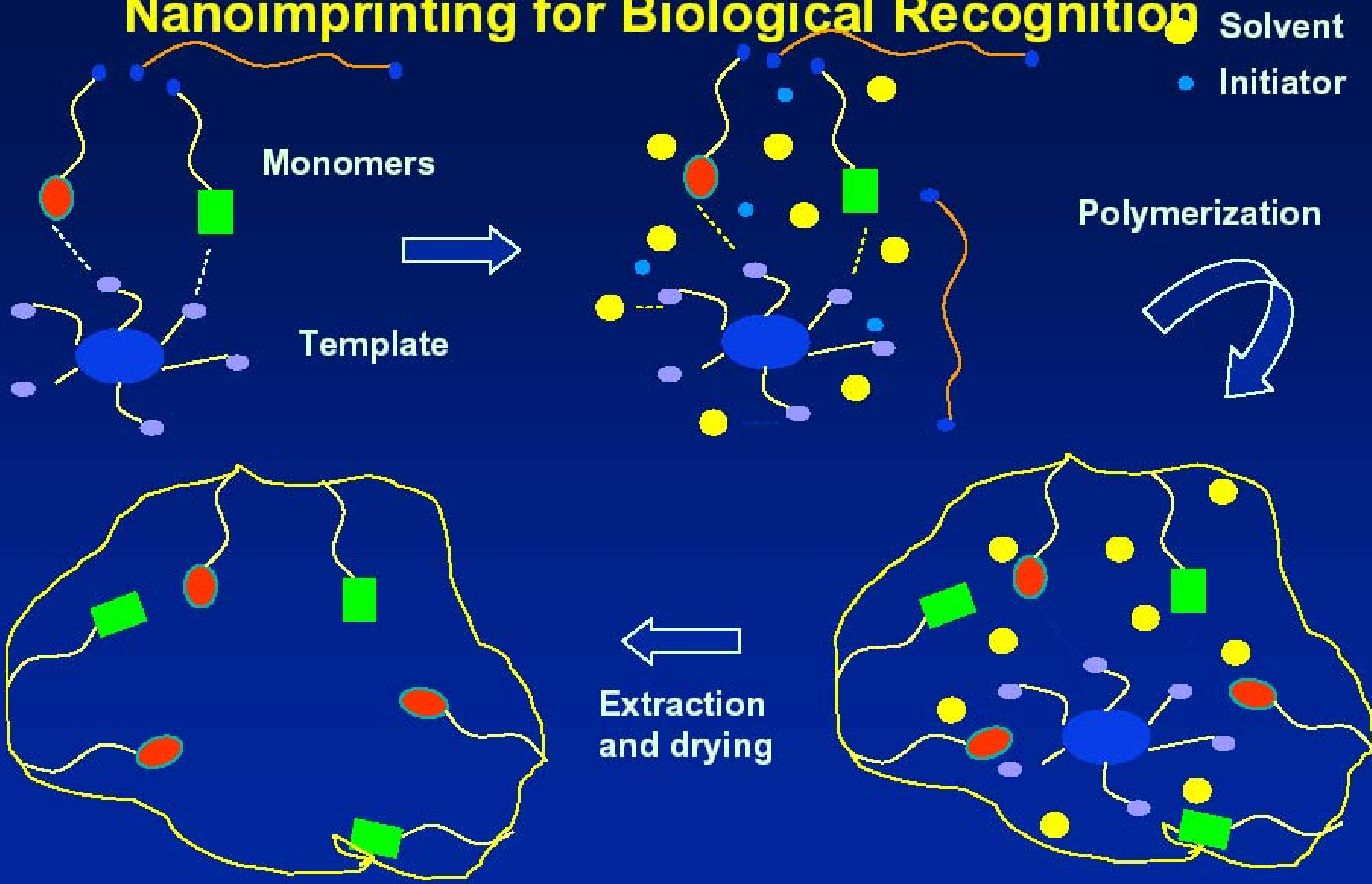
Metal Removal

Table 2. Heavy metal ions adsorption capacity of p(HEMA-MAH) beads after repeated adsorption-desorption cycle. Initial concentrations of metal ions 50 mg/L; pH: 6.0; temperature: 20 °C.

Cycle no	Cu(II)		Pb(II)		Cr(III)		Hg(II)		Cd(II)	
	Adsorption mg/g	Desorption %	Adsorption mg/g	Desorption %	Adsorption mg/g	Desorption %	Adsorption mg/g	Desorption %	Adsorption mg/g	Desorption %
1	122.7 ± 9.5	96.5 ± 4.8	714.1 ± 9.5	95.6 ± 4.5	468.8 ± 8.2	96.5 ± 6.0	1234.4 ± 11.4	94.5 ± 5.8	639.4 ± 8.6	97.6 ± 9.5
2	121.5 ± 8.8	98.2 ± 4.1	713.5 ± 8.8	97.4 ± 5.0	468.4 ± 8.5	98.2 ± 7.8	1232.2 ± 10.6	93.2 ± 6.1	638.2 ± 8.8	96.4 ± 9.0
3	121.4 ± 8.3	97.8 ± 4.9	712.6 ± 8.9	96.2 ± 5.1	468.1 ± 8.7	98.7 ± 7.1	1230.0 ± 11.3	92.8 ± 6.9	637.9 ± 8.9	95.2 ± 9.1
4	121.0 ± 9.2	96.5 ± 4.3	712.0 ± 9.8	96.4 ± 5.9	467.2 ± 9.5	97.4 ± 7.4	1229.4 ± 12.2	98.9 ± 7.3	637.0 ± 9.2	93.4 ± 9.9
5	120.7 ± 9.7	99.1 ± 4.5	711.6 ± 9.6	97.3 ± 6.1	465.6 ± 9.6	96.8 ± 7.8	1229.0 ± 12.7	97.5 ± 7.5	636.5 ± 9.0	96.3 ± 9.1

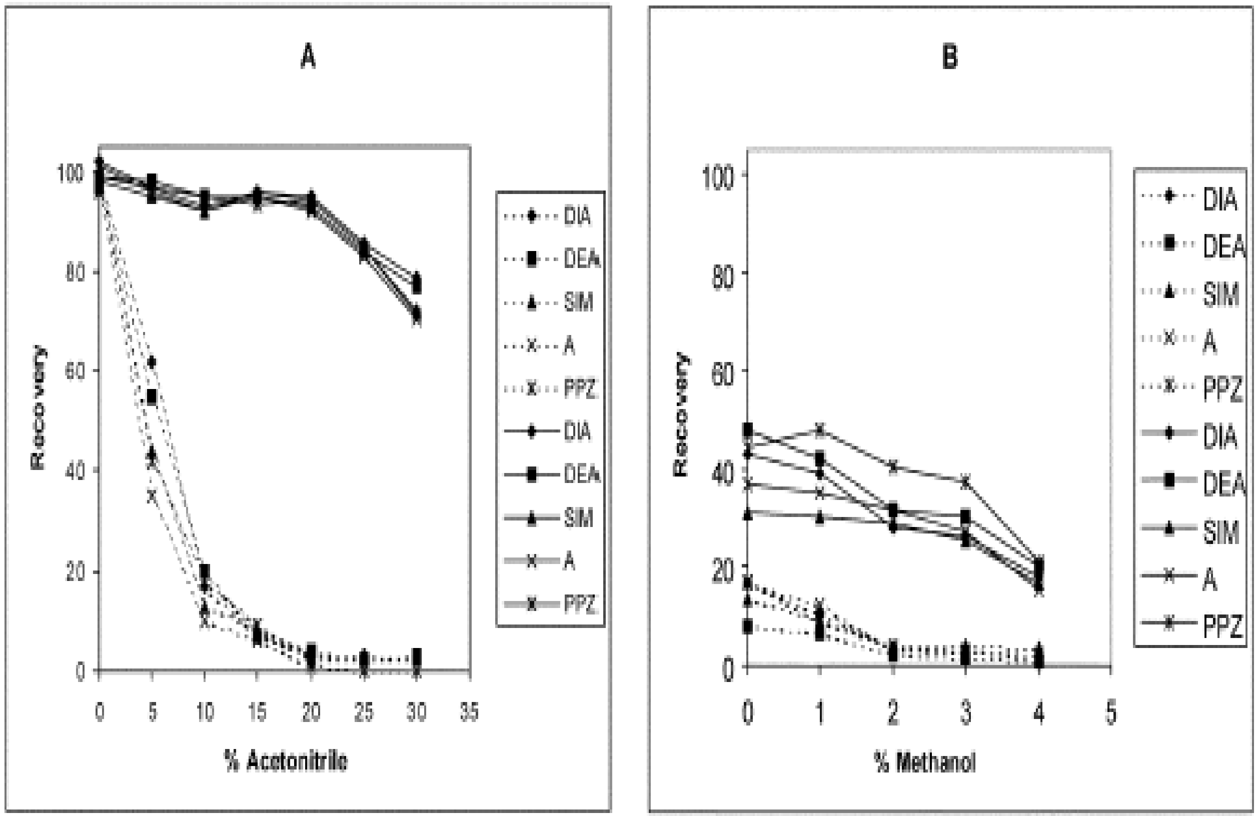
Molecularly Imprinted Polymers

Nanoimprinting for Biological Recognition



Atrazine-Imprinted Polymers

Fig. 1 Variation of the recoveries obtained for triazines (500 ng mL^{-1}) loaded in toluene (A) or in acetonitrile (B) on imprinted (*solid lines*) and non-imprinted (*dashed lines*) polymers as a function of the percentage of acetonitrile or methanol present in the washing solution

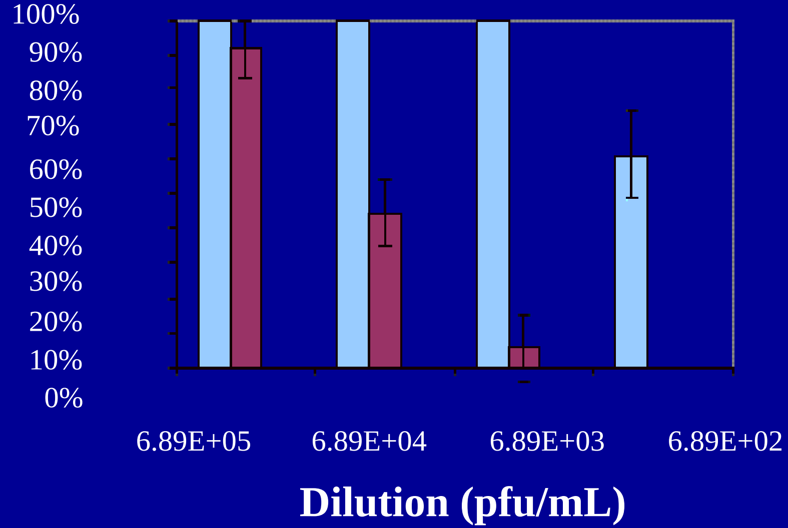


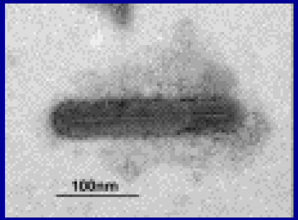
Cacho et al. Anal Bioanal Chem 2002

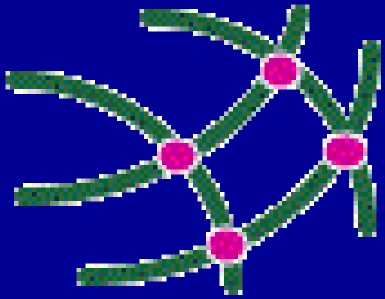
Imprinted Polymers for Virus Removal

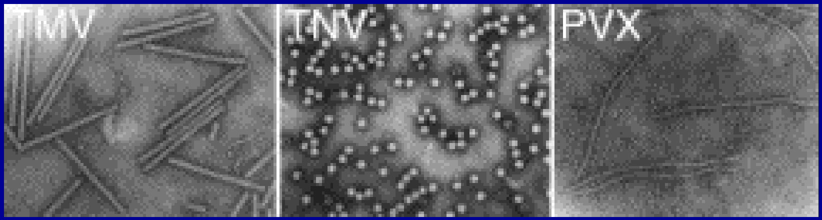
Infection Frequency of

Spodoptera frugiperda 9 (Sf9) cells









Reactive Polymer Hydrogel for Phosphate Removal

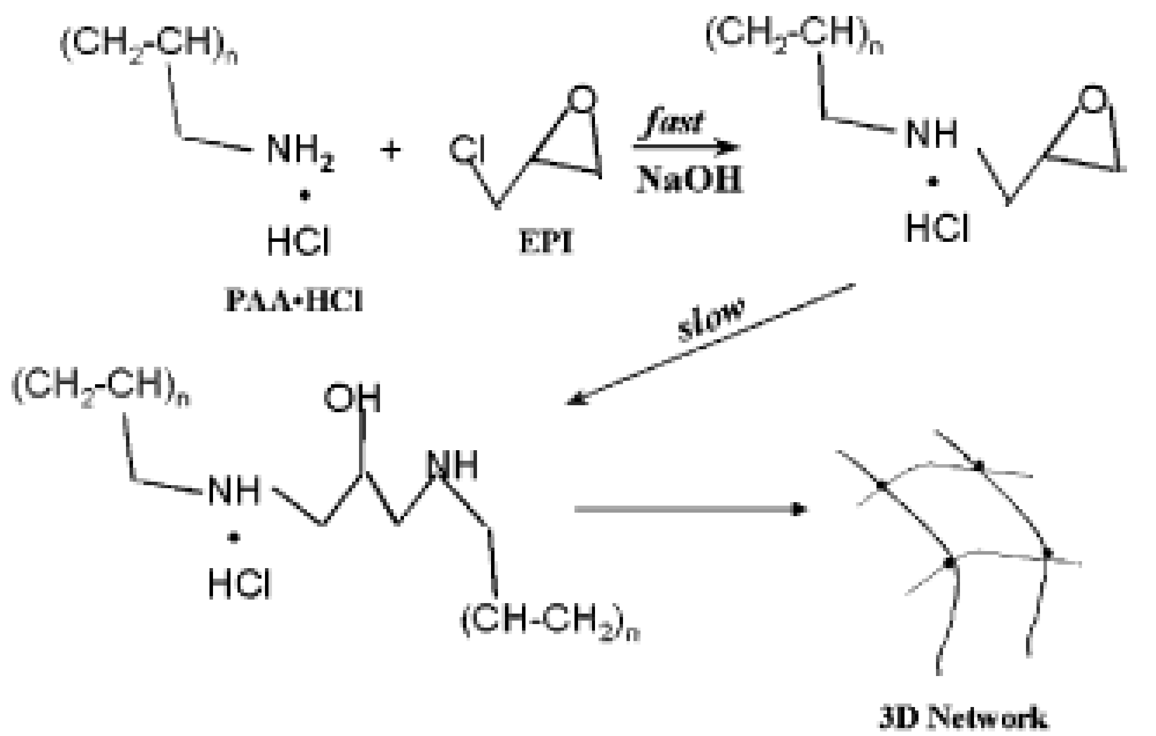


FIGURE 1. PAA·HCl Hydrogel synthesis by chemical cross-linking with EPI cross-linker.

Kiofinas et al. ES&T 2003

Efficiency of Removal

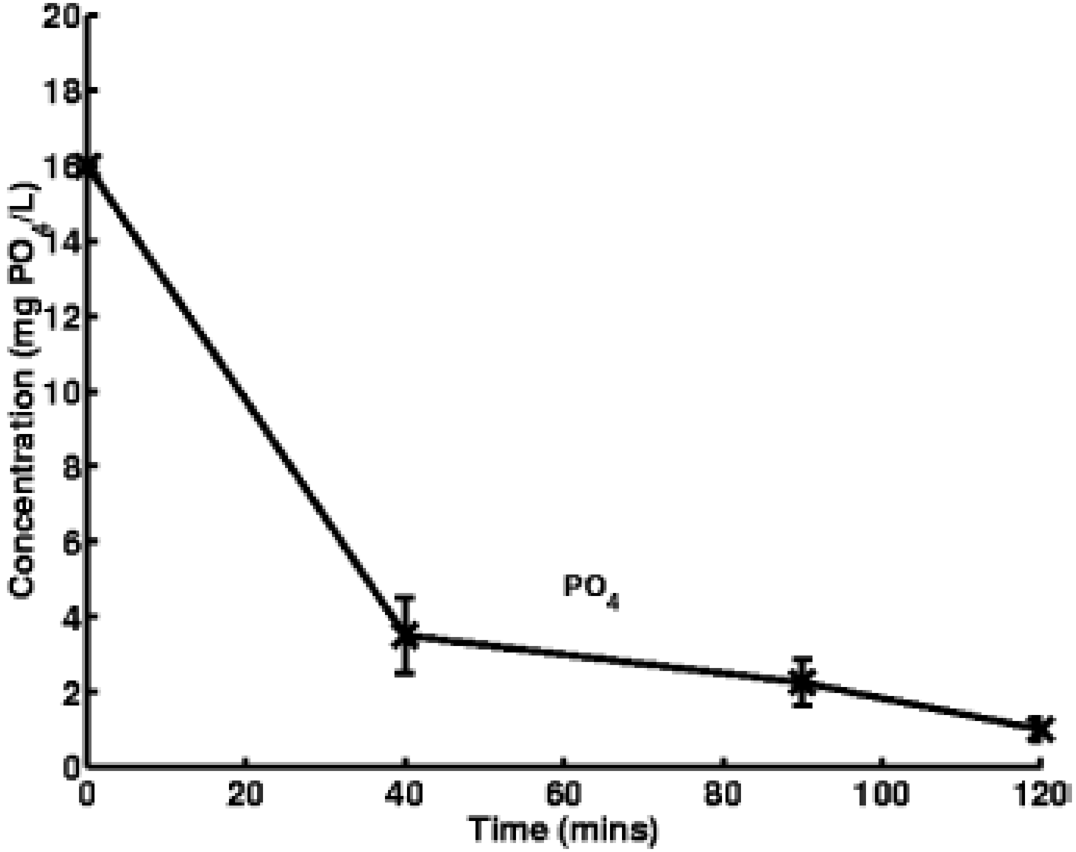


FIGURE 2. PO_4^{3-} binding from aquaculture wastewater using PAA·HCl hydrogels.

Perchlorate Removal

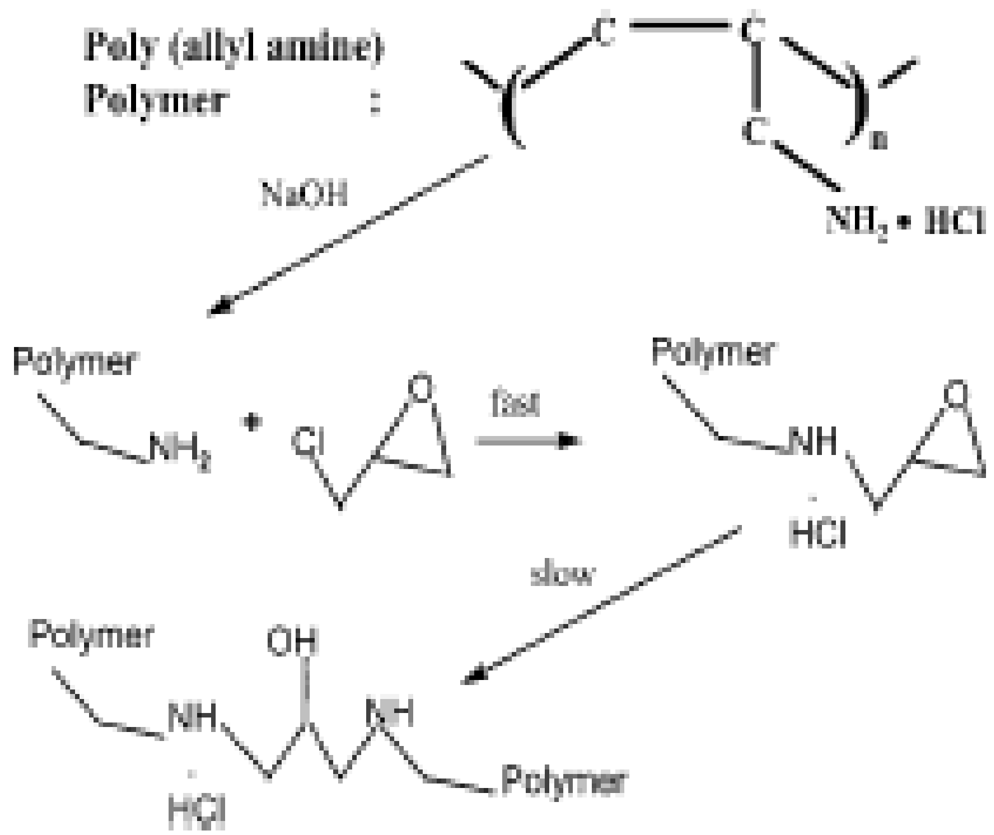


Figure 1 Hydrogel synthesis by chemical crosslinking with EPI.

Kioussis et al. Journal of Applied Polymer Science 2001

Efficiency of Removal

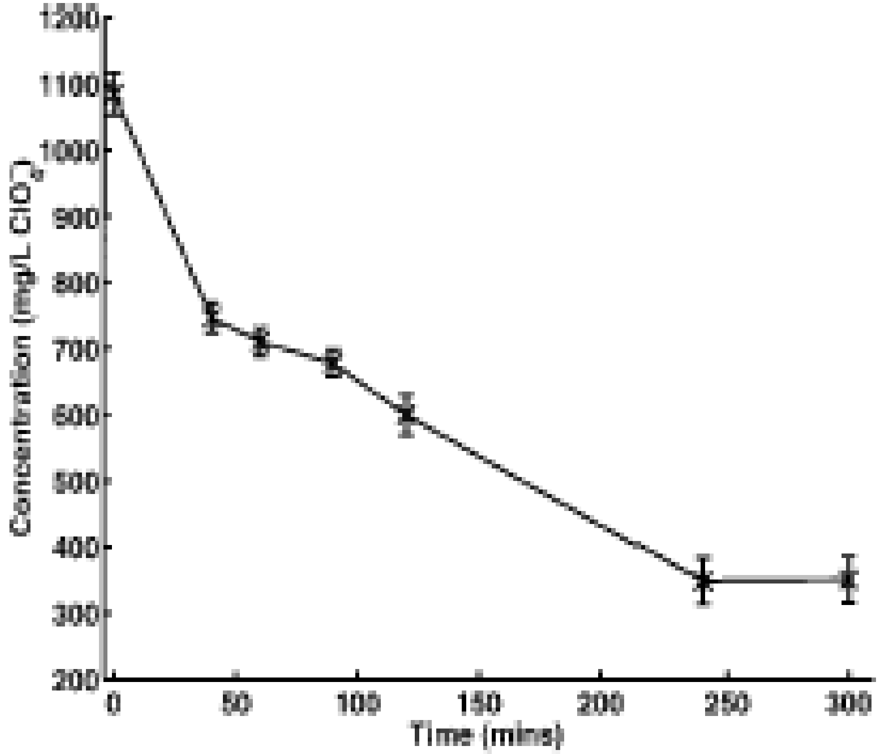


Figure 2 Measurement of ClO_4^--binding capacity of PAA·HCl gel in AP standard solution. PAA·HCl concentration: 20% w/v, M_w = 9750 g/mol; NaOH: 0.28 g/g PAA·HCl; EPI: 1.88×10^{-3} mol/g PAA·HCl.

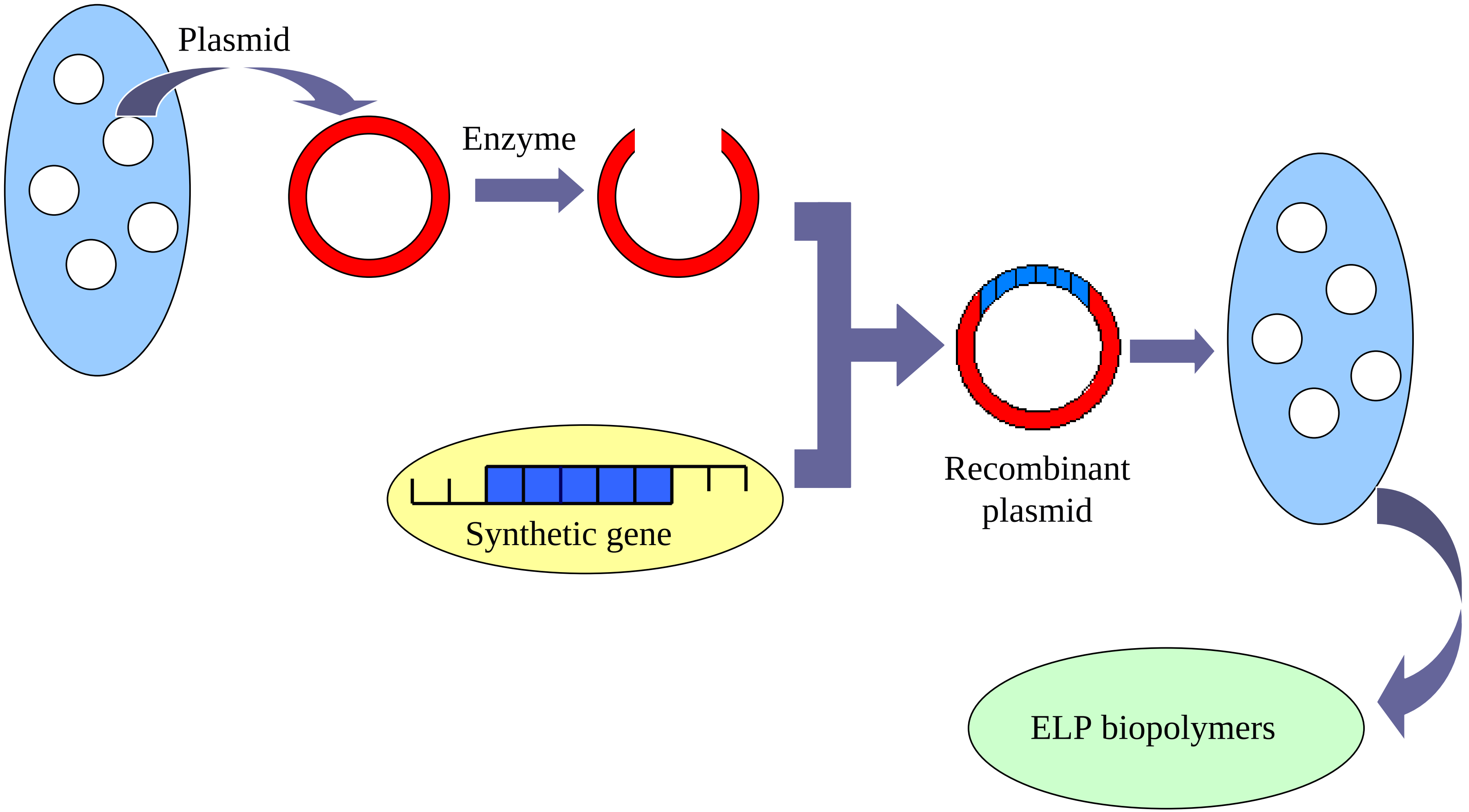
Tunable Biopolymer with Metal-Binding Property

Elastin Domain **Metal Binding Domain**

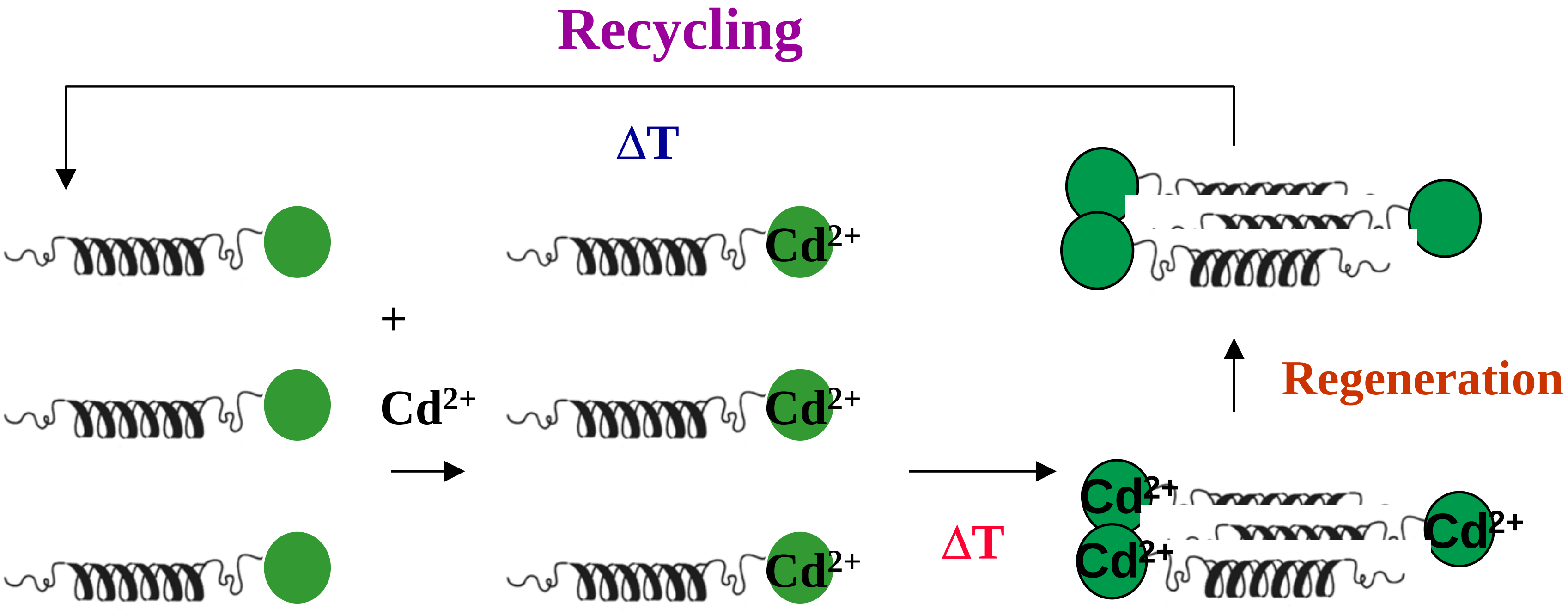
Fine tune affinity with different binding sequence

Fine tune ΔT by controlling amino acid sequence and no. of repeating unit $(VPGXG)_n$

Genetic and Protein Engineering Methodology

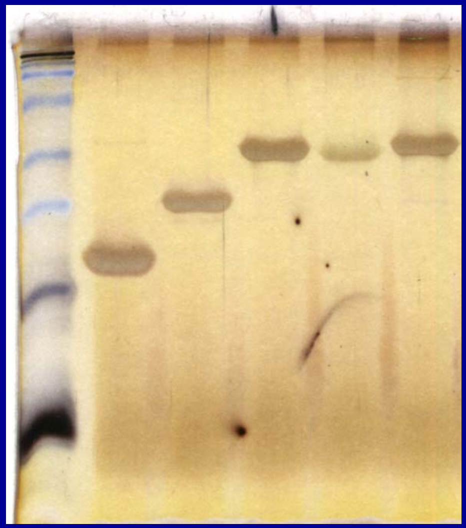


Metal Removal



Production of Biopolymers

Biopolymer	Protein yield (mg/3 L)
Ela38H6	289
Ela58H6	295
Ela78H6	207
Ela78	191
Ela78H12	168



A, Ela38H6

B, Ela58H6

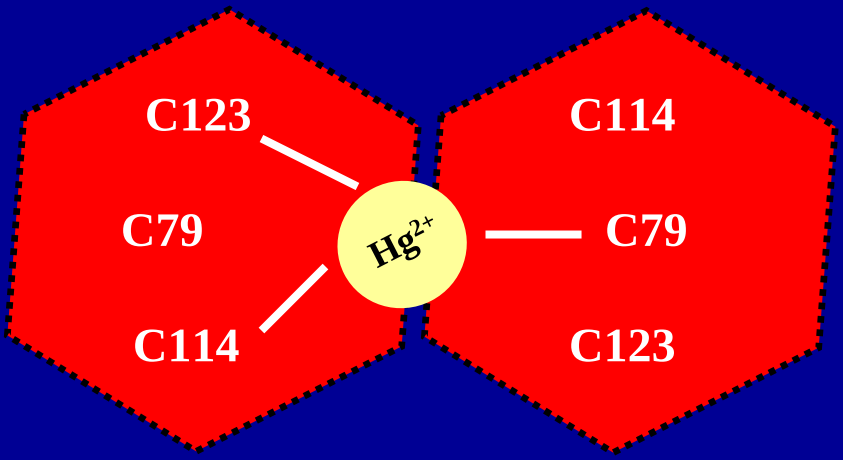
C, Ela78H6

D, Ela78

E, Ela78H12

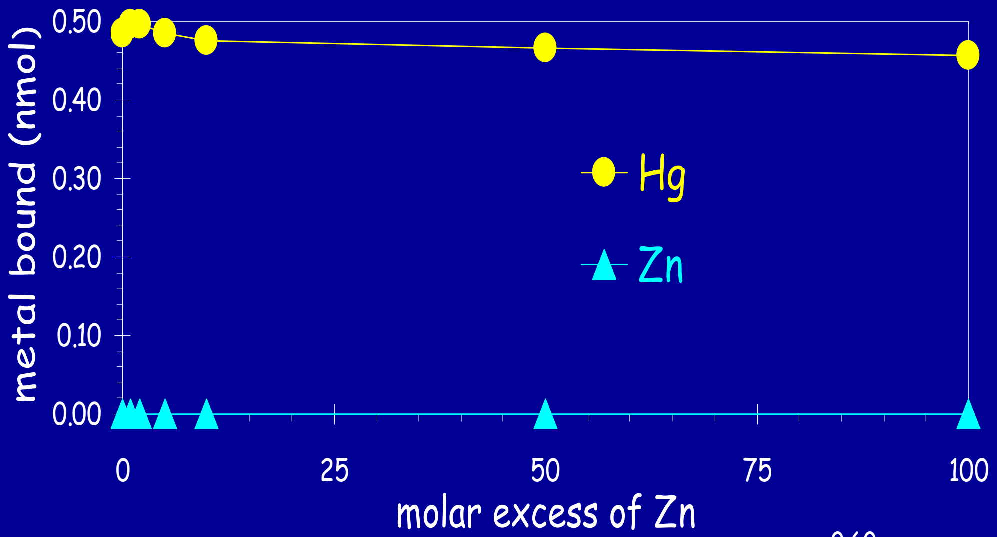
Kostal et al. *Marcomolecules*, 34, 2257-2261, 2001

MerR can serve as a specific mercury binding domain

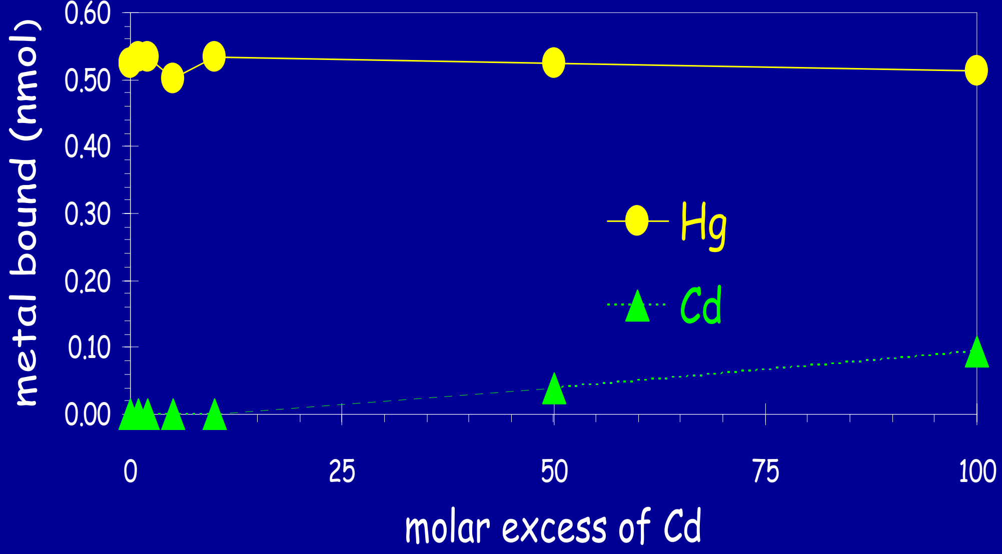


MerR-Hg complex

Selective Binding of Mercury by Ela153-MerR Biopolymer



Acidic waste water (pH 4)



Kostal et al. ES&T 2003

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Exploratory Research: Nanotechnology