Reactive Micro/Nano Encapsulation: A Way to High Performance Polymer Materials

Zlatan Denchev

i3N - Institute for Polymers and Composites, University of Minho, Guimaraes, Portugal

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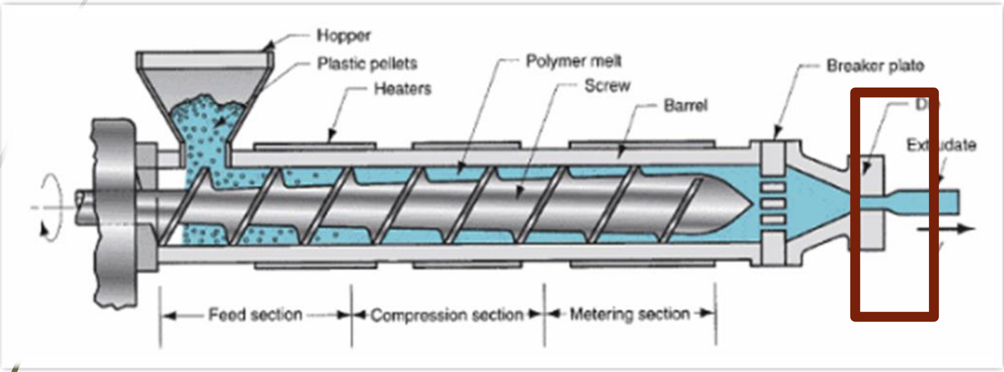
Outline

1. Reactive *versus* melt processing of thermoplastic polymers
2. Reactive microencapsulation by anionic polymerization of lactams
3. Reactive microencapsulation with PA6:
   - Hybrid PA6 composites and laminates
   - Immobilization of proteins
   - Controlled release of vitamins
4. Reactive microencapsulation with PA4:
   - Molecular imprinting of proteins
5. Conclusions

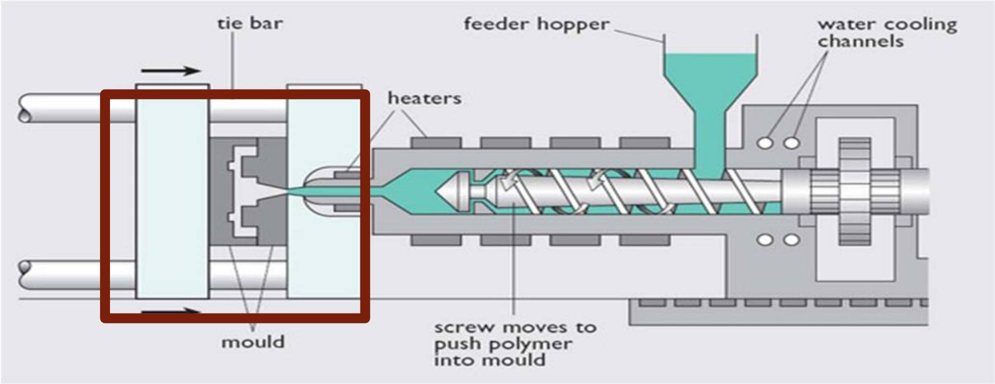
monomer → polymer → additivation & granulation → shaping + multiplication

Melt processing techniques: the shaping device works with ready-made polymer

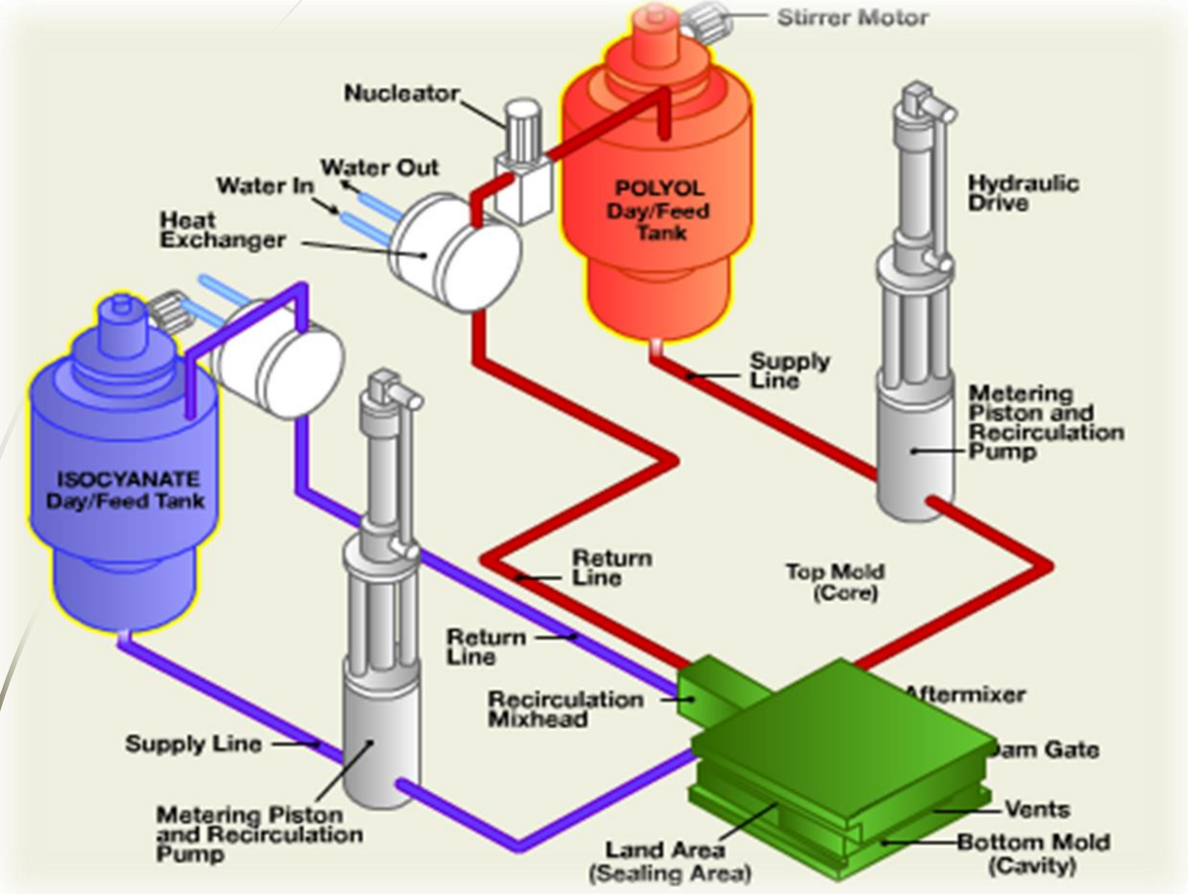
Extrusion



Injection

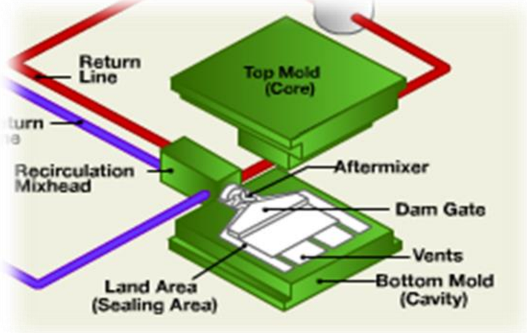


monomer → shaping + multiplication

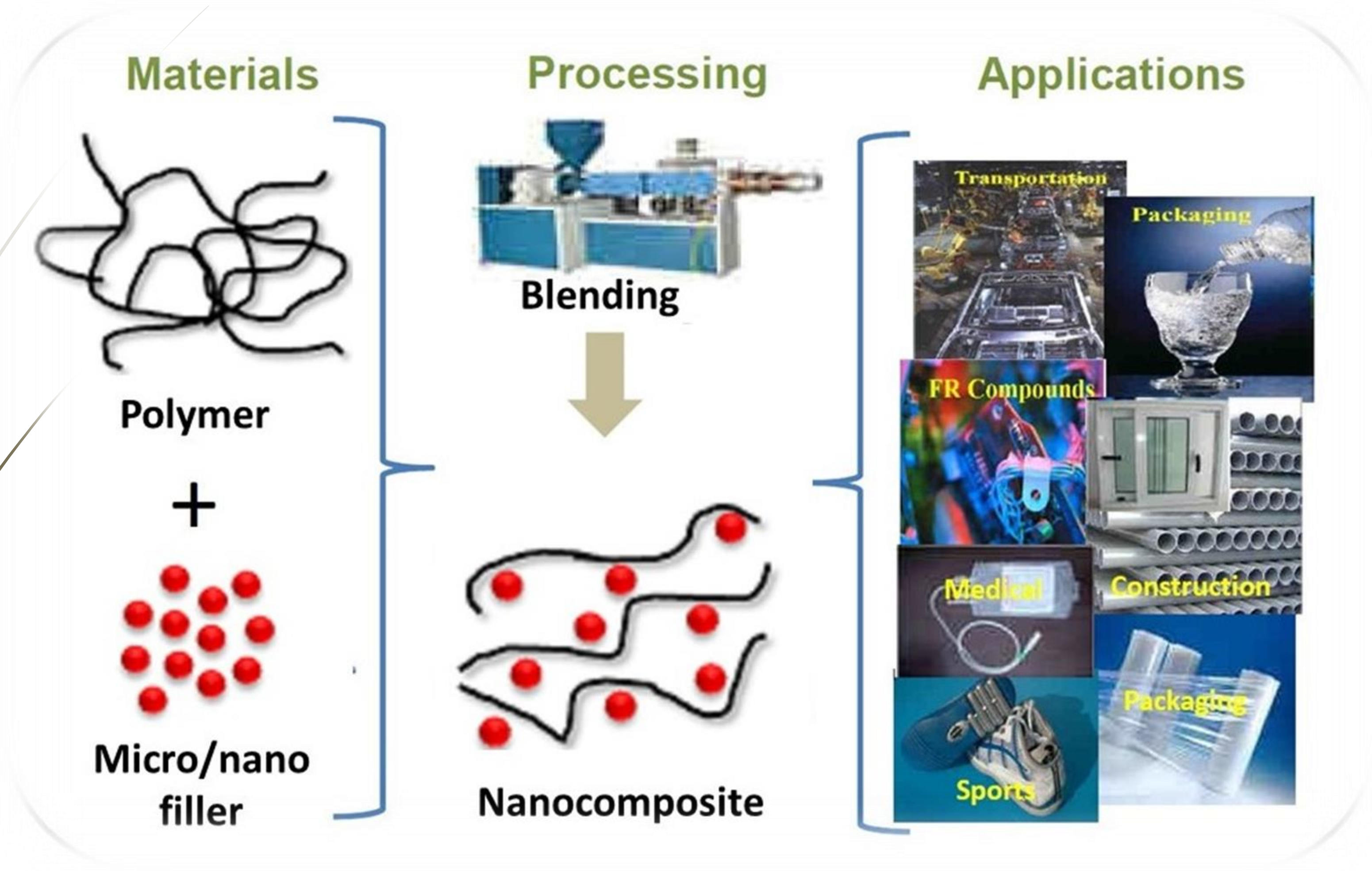


Reactive processing techniques: the polymer is formed in the shaping device

PUR mold



Polymer composites → **matrix polymer + reinforcement (particulate, fibrous, etc.)**



melt processing

↓

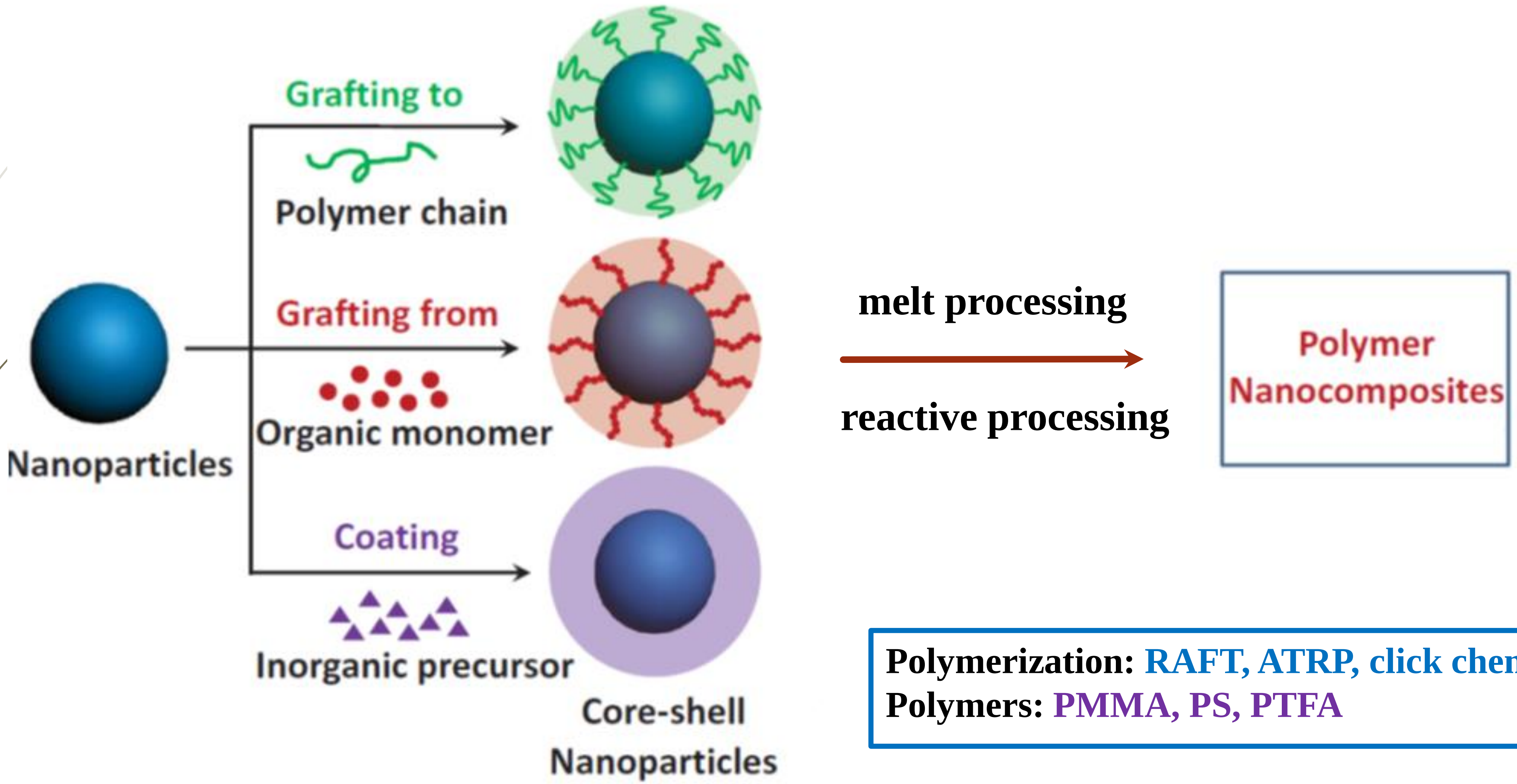
aggregation of of reinforcement

↓

insufficient mechanical properties

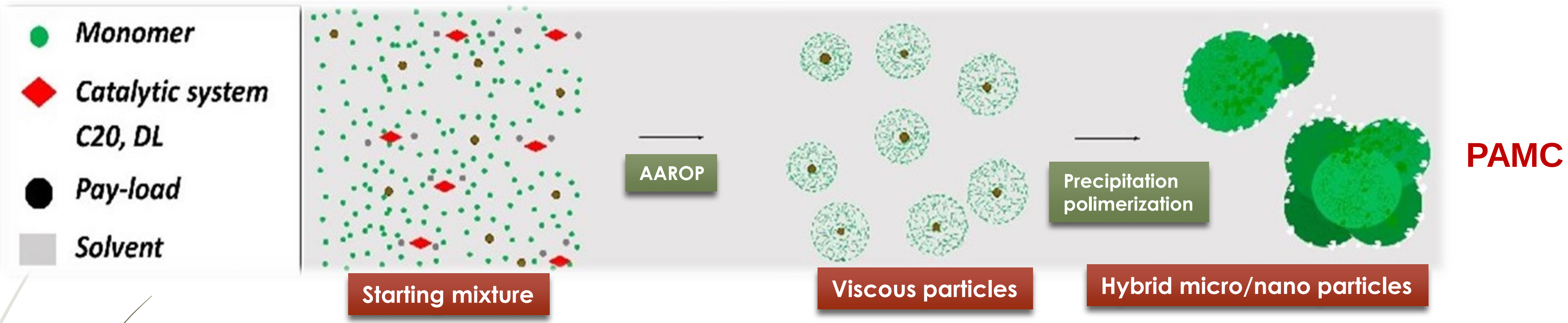
The "Reactive" Core-Shell Nano-Architecture Strategy

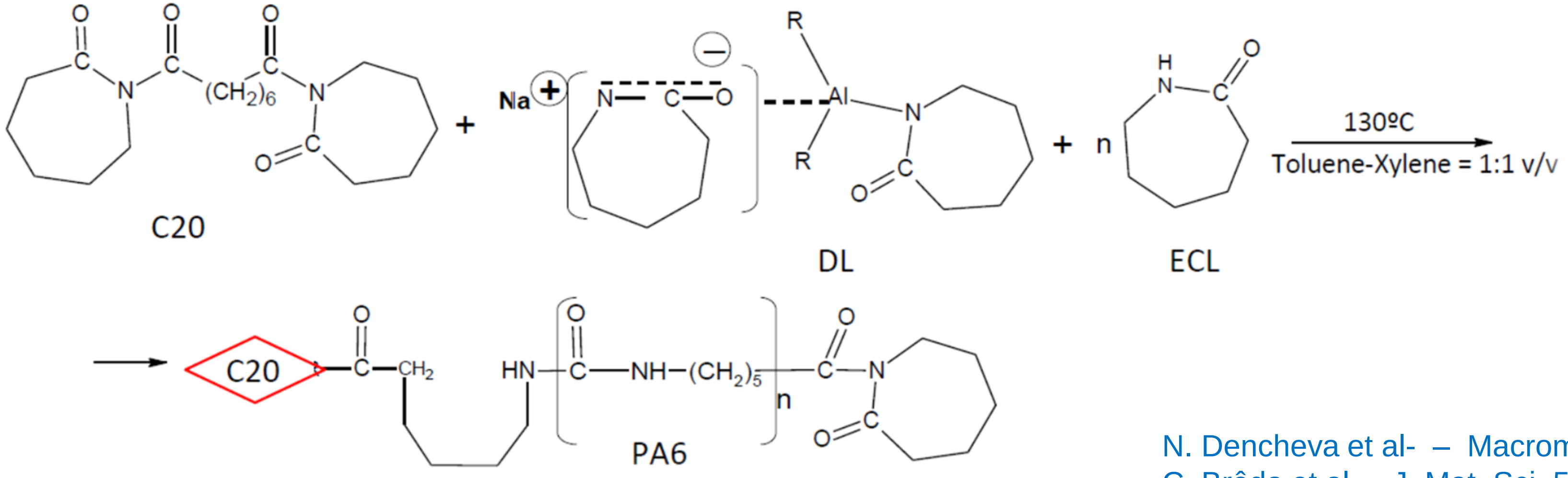
X. Huang and P. Jiang, Adv. Mater. 2015, 27, 546



Polymerization: RAFT, ATRP, click chemistry
Polymers: PMMA, PS, PTFA

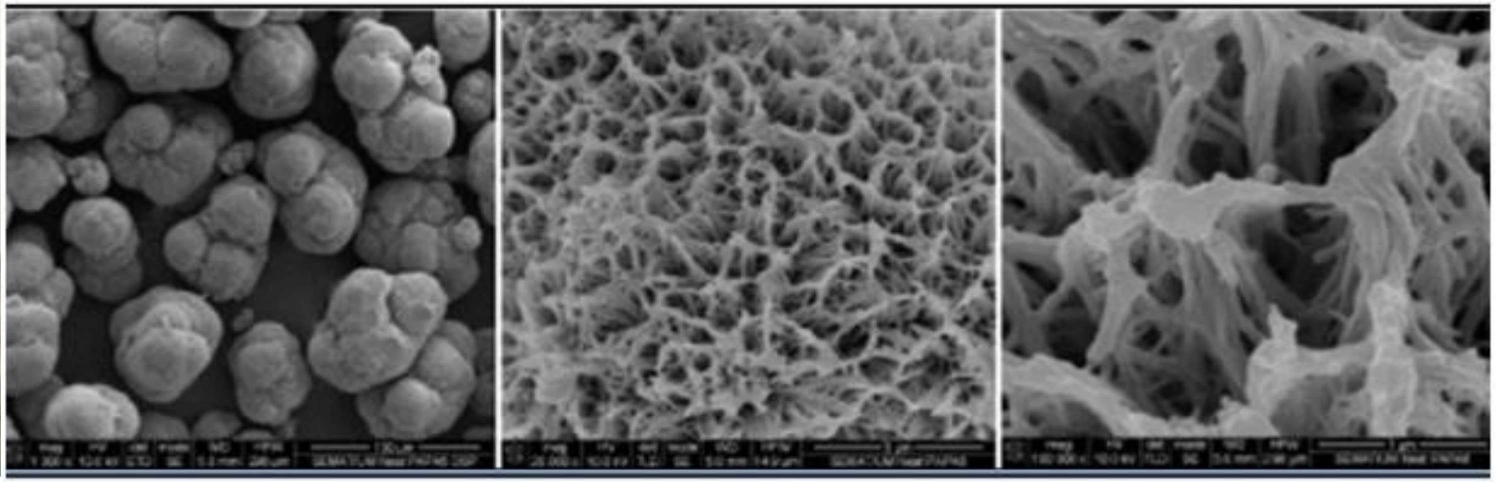
Polyamide Core-Shell Micro/Nanocapsules through AAROP

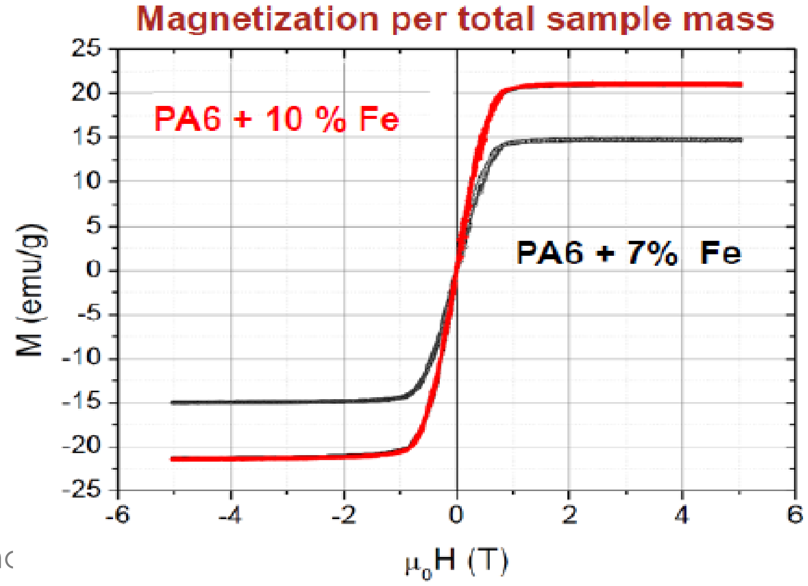




N. Dencheva et al- – Macromol. Mat. Chem. 301:119 (2016);
C. Brêda et al. – J. Mat. Sci. 51:10534 (2016)
F. Oliveira et al. – Polym. Lett. 10:160 (2016).

Morphology and Properties of Polyamide Micro/Nanocapsules



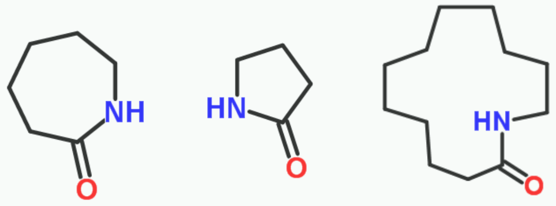


Sizes: from 300-400 nm to 50-100 µm;
Porosity: open pores, diam. 5-500 nm;
Payload in the core of the PAMC (EDX)

Fe and Fe_3O_4 loaded PAMC are sensitive to magnetic fields

Core-Shell Micro/Nanocapsules through AAROP

Lactams used:



Payloads used:
Metals and metal oxides: Cu, Mg, Al, Ag, Zn, Fe, Fe_3O_4, Sb_2O_3
Carbon allotropes: CB, CNT, CNF, GR, GN
Bioactive compounds: bovine serum albumin, B12, enzymes

- **High strength semicrystalline polyamide shells**
- **Mild polymerization conditions – down to 40°C**
- **Controllable size of PAMC**
- **Controllable open porosity**
- **Loading of PAMC with two or more fillers**
- **Magnetic PAMC**
- **Polyamide shell rich of functional groups (C=O, N-H)**
- **Scale-up for industrial process**

Two general ways for versatile applications of loaded PAMC

Loaded PAMC

melt processing
(CM, IM, EXTR)

Composites and laminates with tailored mechanical, electrical and magnetic properties, one-polymer composites

Macro sized, for technical applications

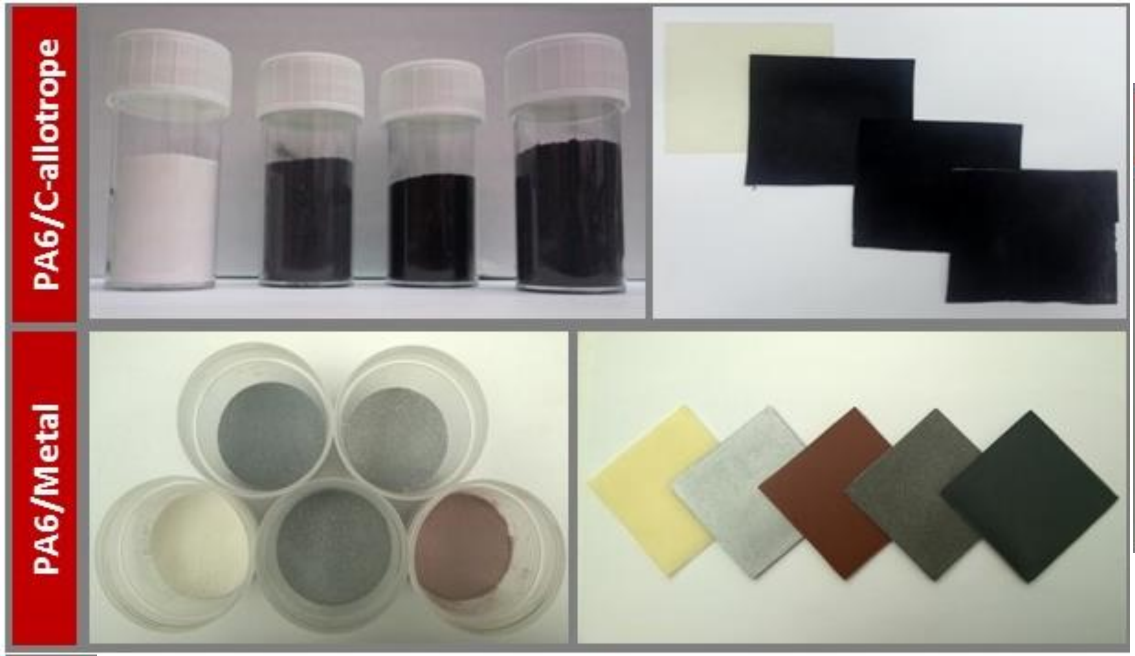
free-standing particles

Drug delivery systems, molecular imprinted systems, green catalysts, smart, stimuli-responsive systems

Micro/nanosized, for biomedical applications

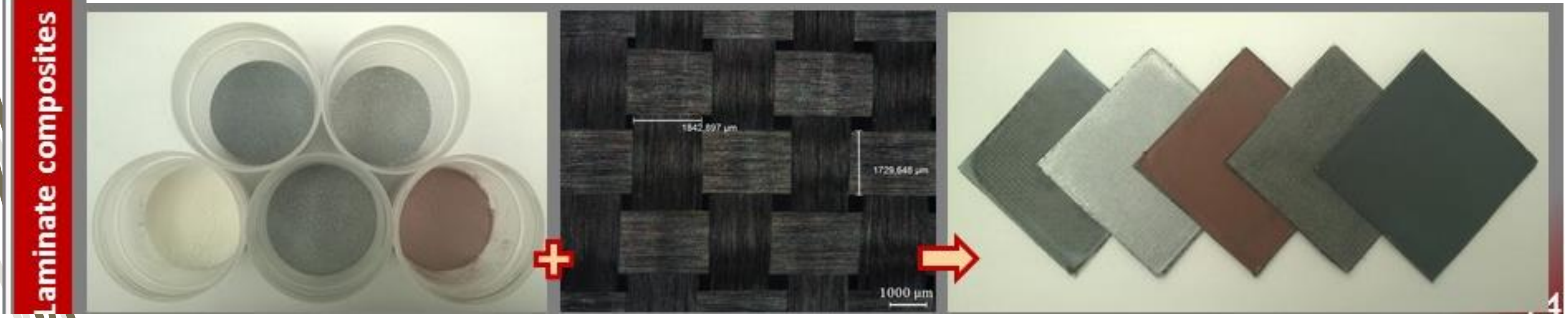
Melt-processing of Loaded PA6 Micro/Nanocapsules to Advanced Composites

Hybrid composite materials from single- and dual-core PAMC



PA6 hybrids

Up to 30 % metal & carbon allotrope



Carbon fiber hybrid laminates

Up to 50 % textile volume fraction

Hybrid composite materials - properties

PA6 hybrids

Electrical conductivity:

Improvement with 9 orders of magnitude in respect to the neat PA6 matrix

Magnetic properties:
depending on the Me load

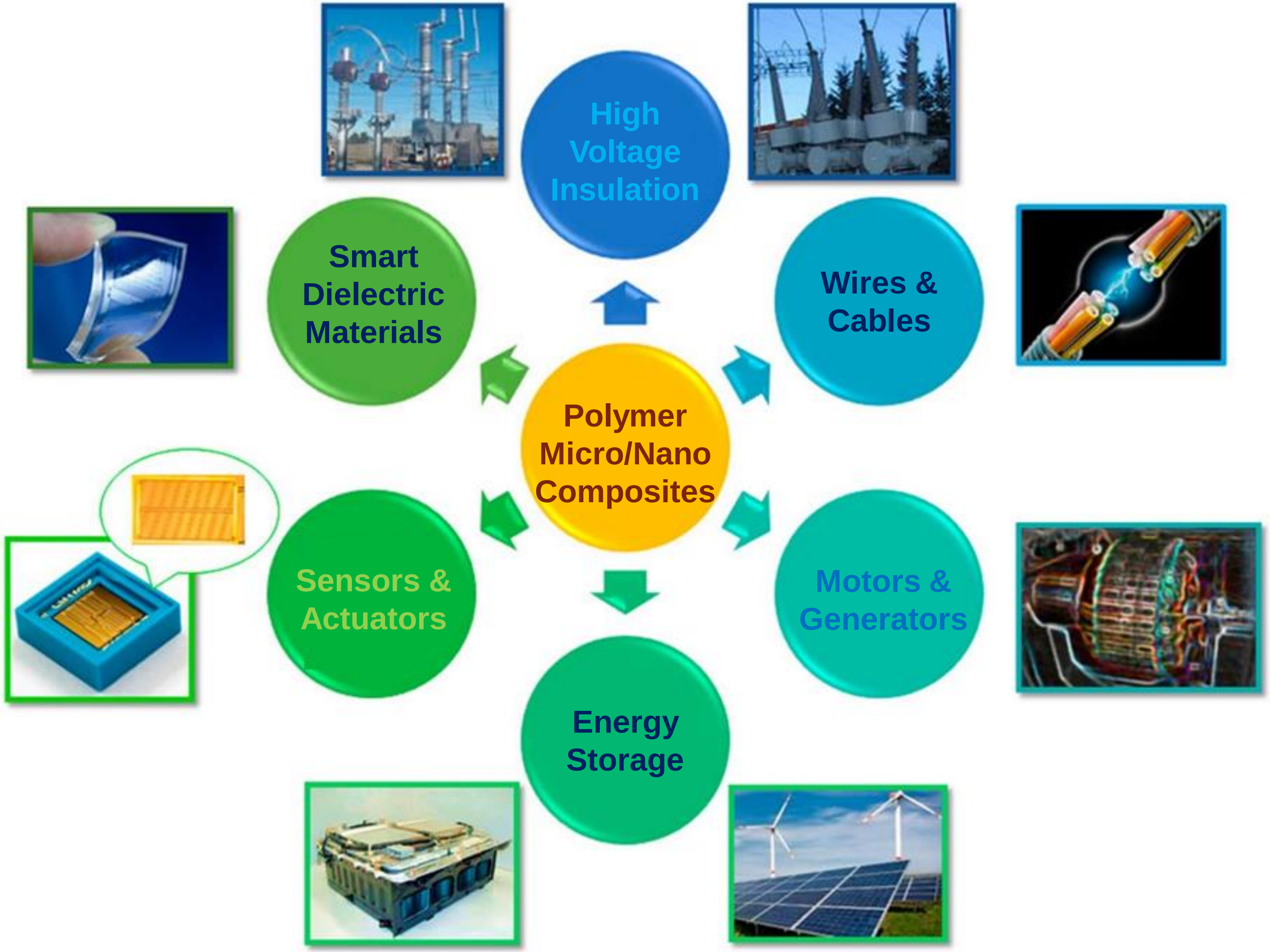
Carbon fiber hybrid laminates

Young's modulus:
Improvement Factor
150 ÷ 250%

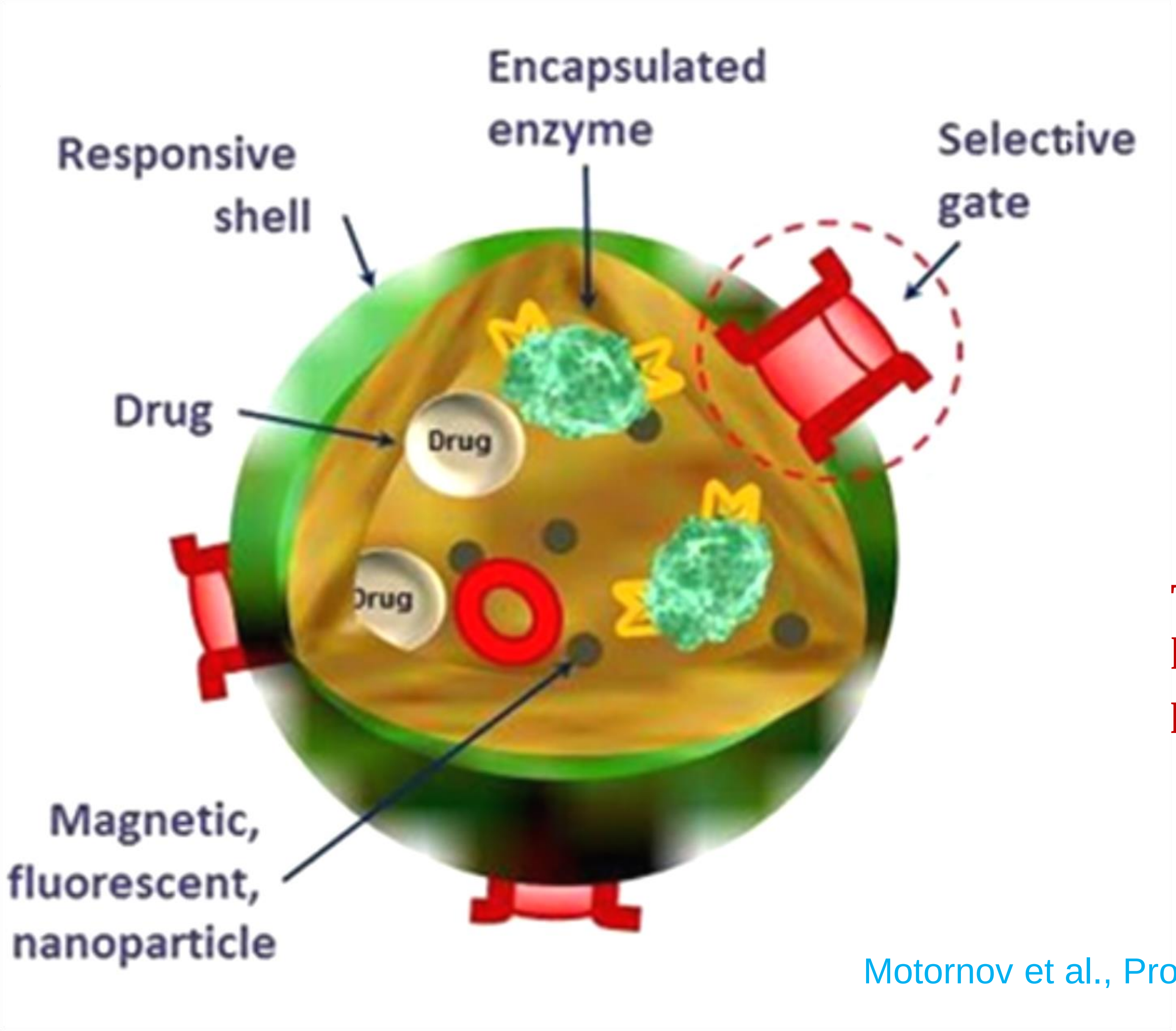
Tensile strength:
Improvement Factor
260 ÷ 370%

Magnetic properties:
depending on the Me load

Industrial Applications of Molded Polymer Micro/Nanocomposites



Applications of Loaded Micro/Nanocapsules



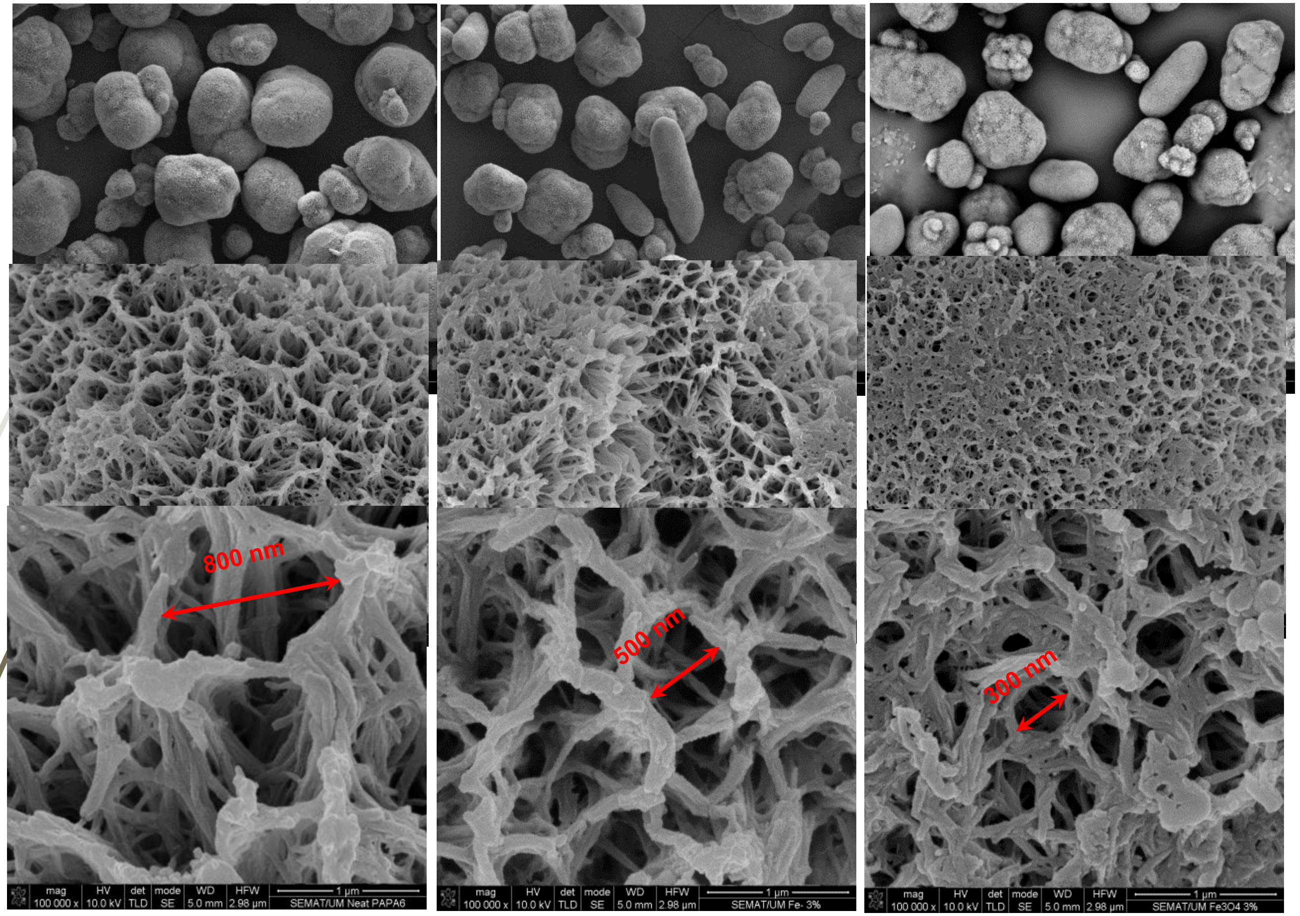
The ultimate smart, living cell-like particle

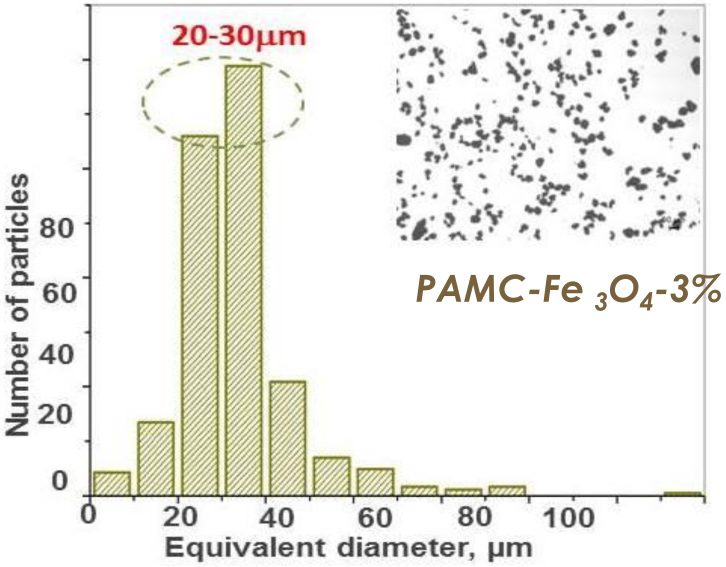
Motornov et al., Prog. Polym. Sci. 35 (2010), 174

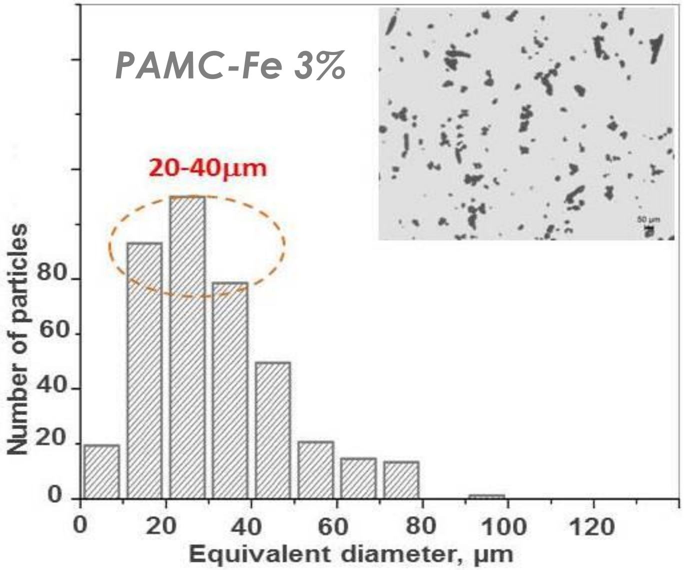
Magnetic and pH Responsive PA6 Microparticles for Protein Immobilization

1. Solution/precipitation AAROP of ECL + Fe or Fe_2O_3

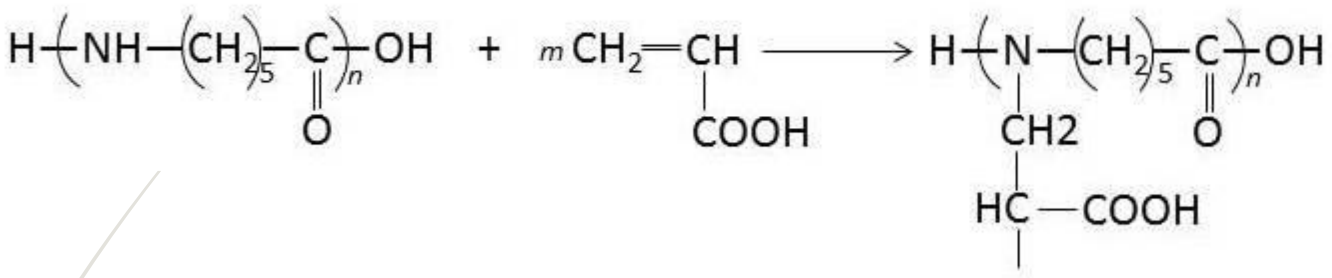
PAMC | PAMC-Fe 3% | PAMC-Fe_3O_4-3%





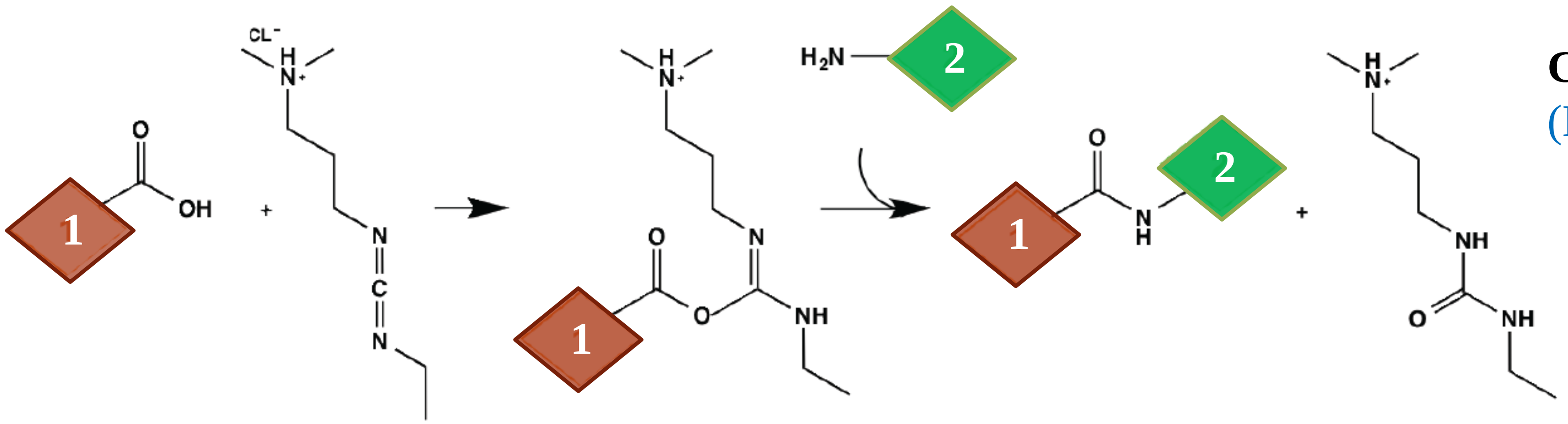


2. Functionalization with polyacrylic acid branches (grafting from)



Conditions: Radical polymerization in toluene/H_2O, 90ºC, BPO initiator, t = 90 min

3. Chemical bonding of the protein (2) to the activated COOH group of PAMC-F (1)

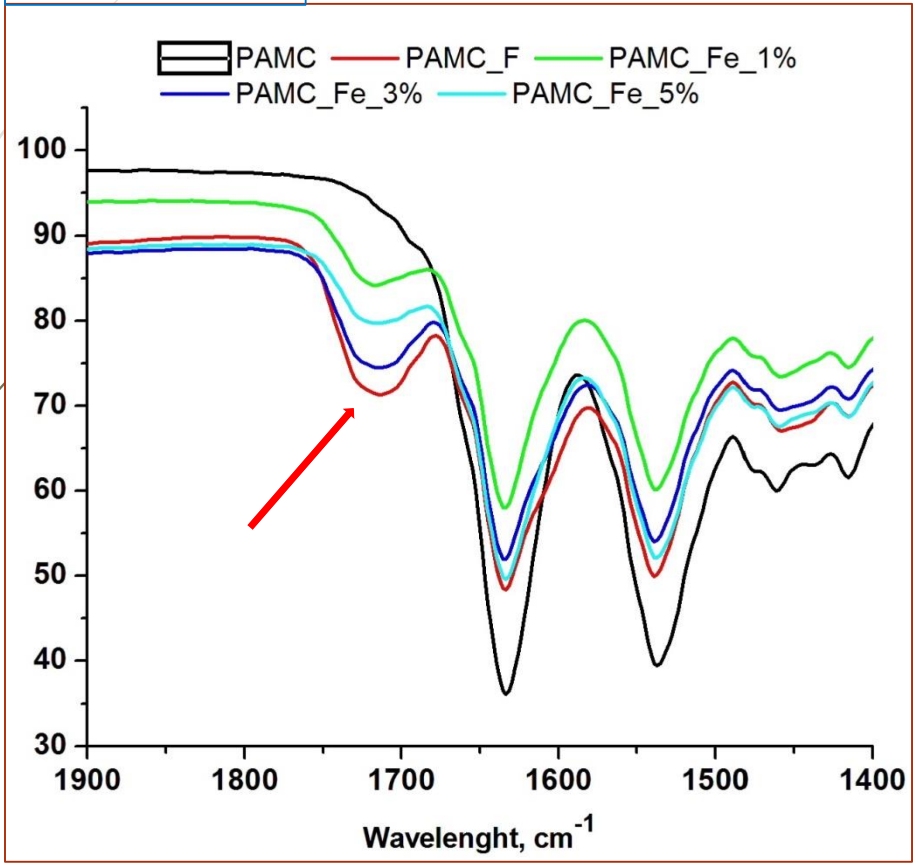


Conditions: pH = 4.7 (H_2O, MES), 25ºC

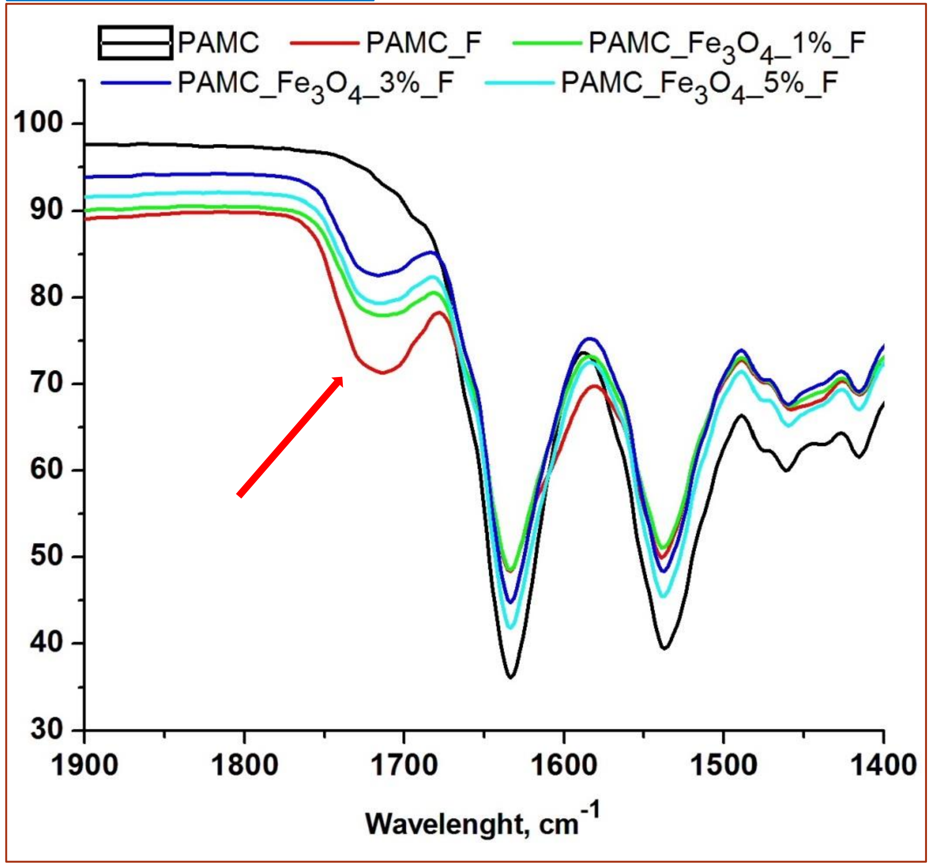
RM Molnar et al, Colloid. Polym. Sci (2009 287:739)

FTIR of functionalized PAMC

PAMC-Fe-F



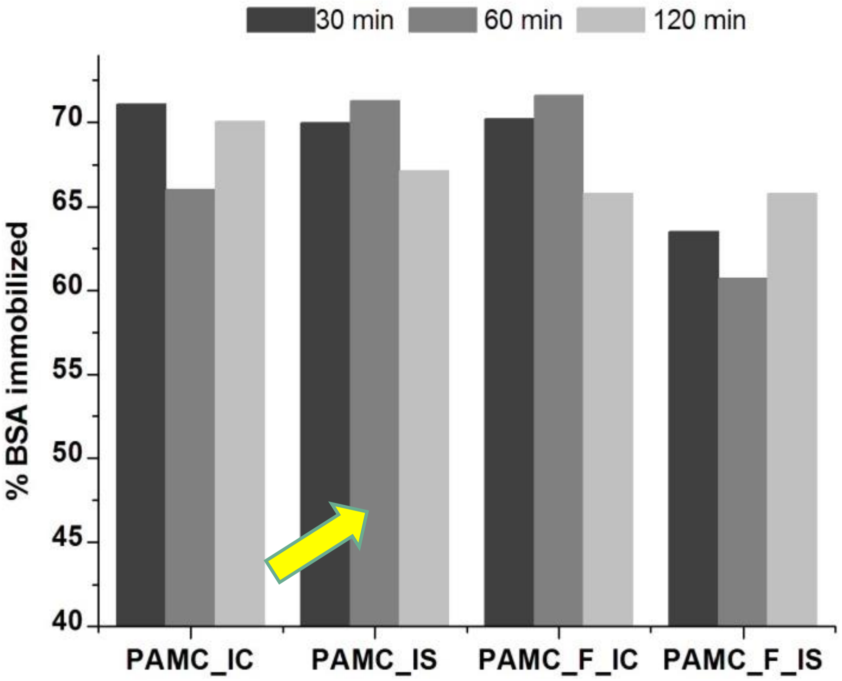
PAMC-Fe_3O_4-F



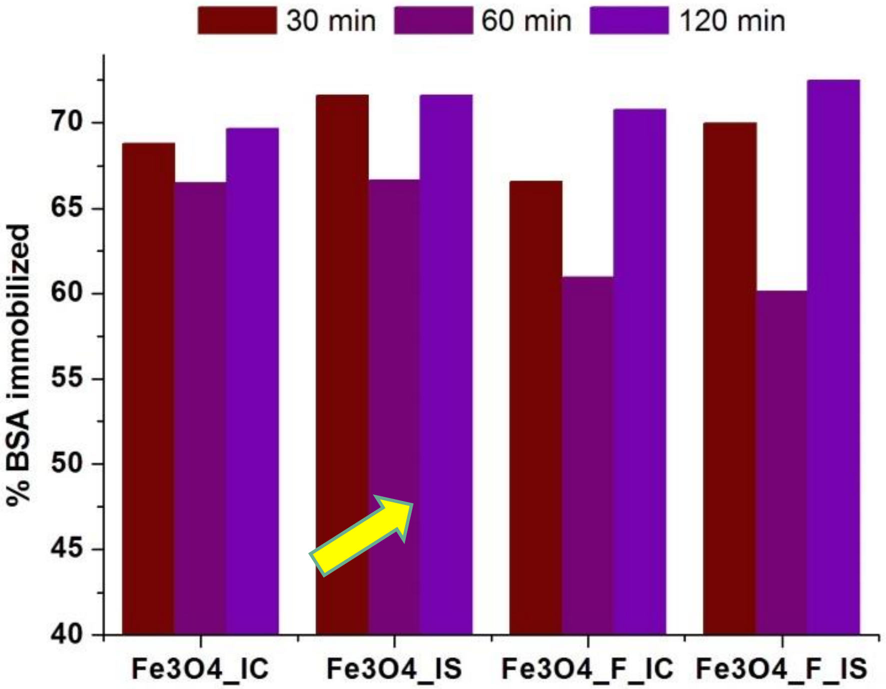
Immobilization of bovine serum albumin protein (BSA)

Conditions:
Incubation of 100 mg PAMC for 30 min to 2 days at 37ºC, pH = 4.7 (MES buffer)
Determination of the immobilized BSA: UV-VIS, at 562 nm, bicinchoninic acid intermediator;
Samples: IC=carbodiimide activated COOH; IS= no carbodiimide; F – functionalization with PAA

% BSA immobilized up to 2 hours



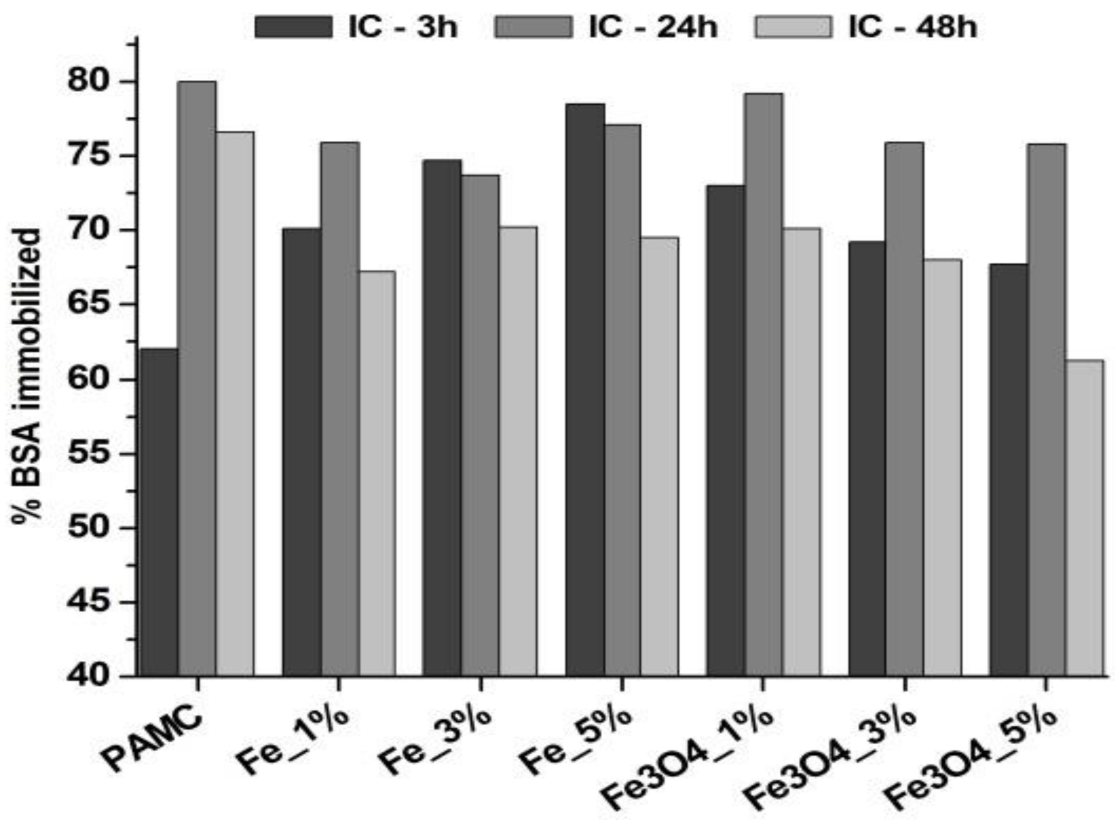
PAMC

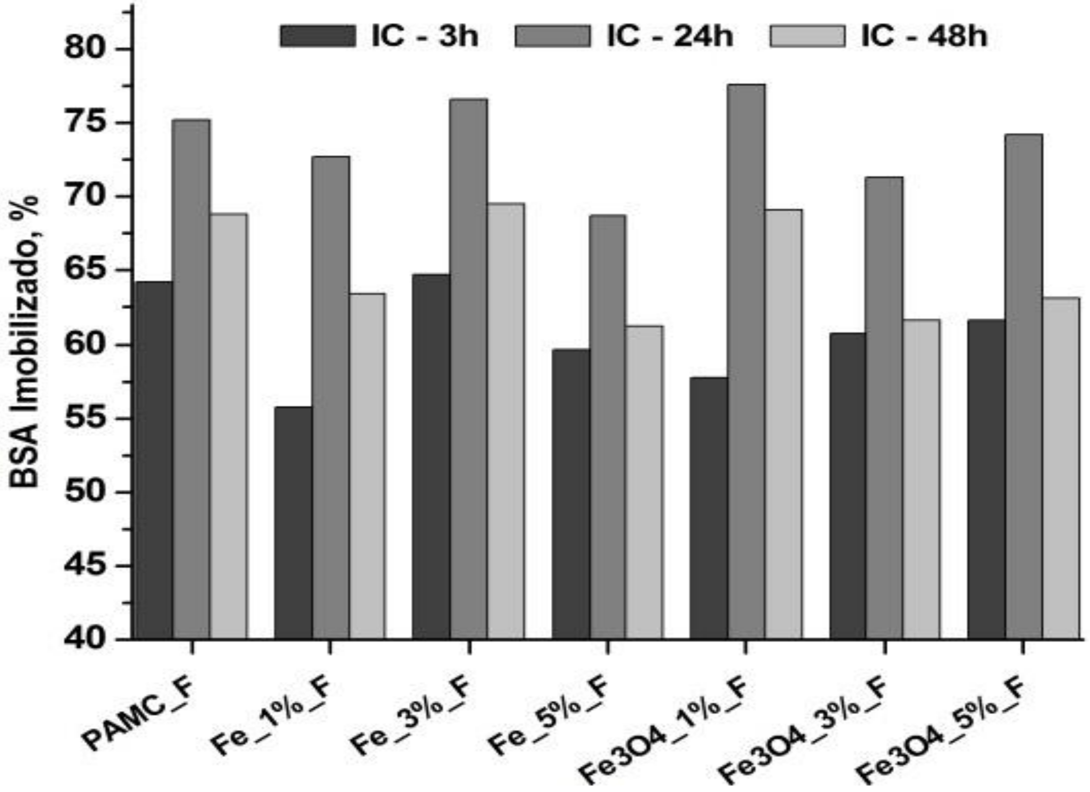


PAMC + Fe_3O_4, 3%

Immobilization of bovine serum albumin protein (BSA)

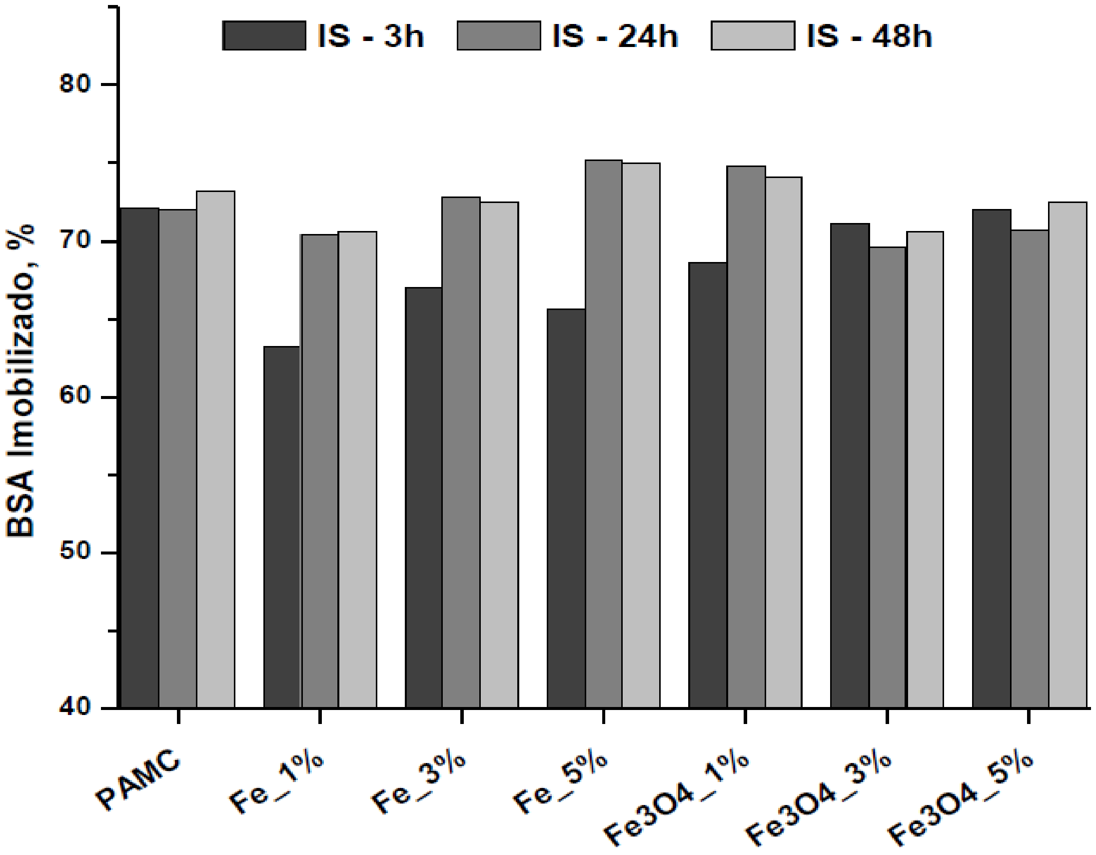
Samples: IC=carbodiimide activated COOH, without and with PAA functionalization

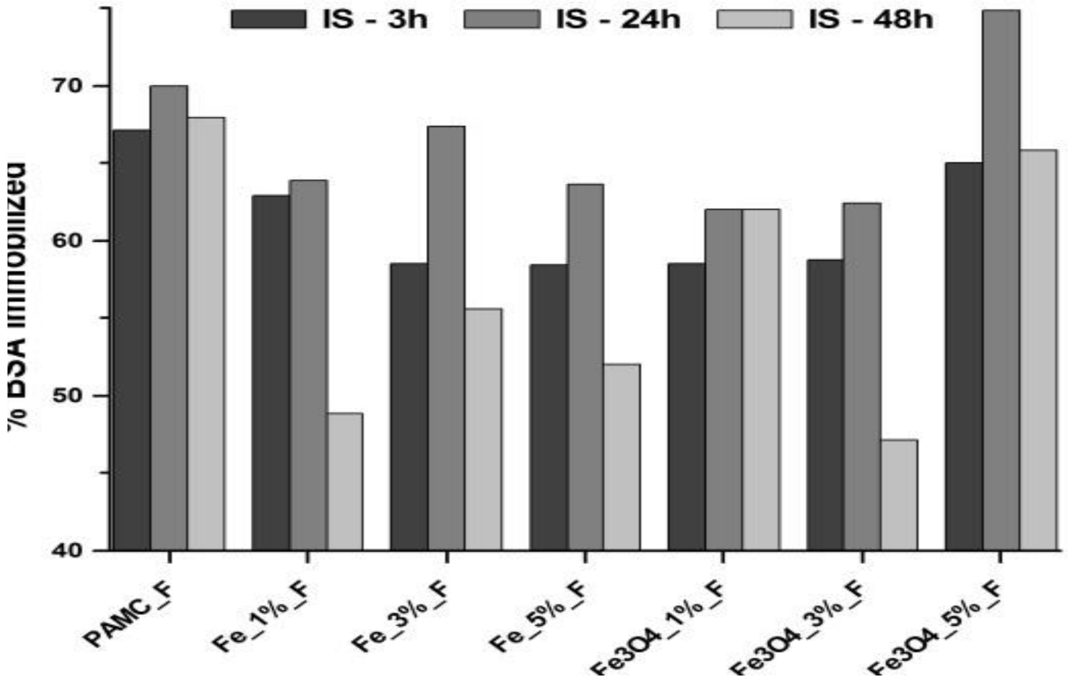




Immobilization of bovine serum albumin protein (BSA)

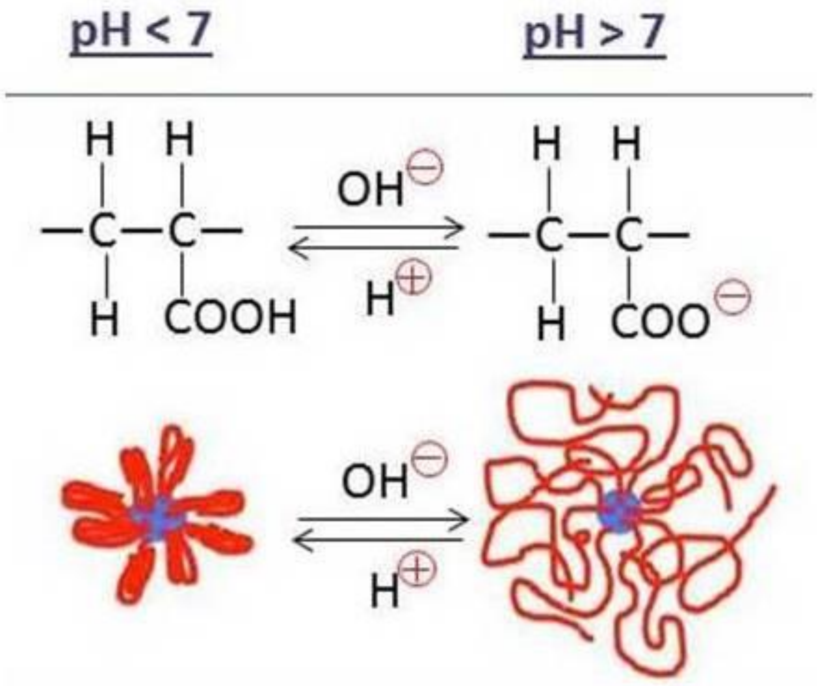
Samples: IS= no carbodiimide activation of COOH, without and with functionalization

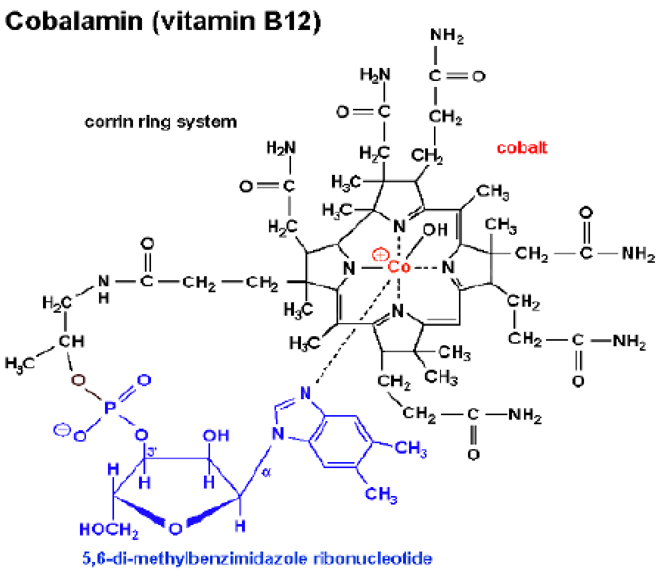


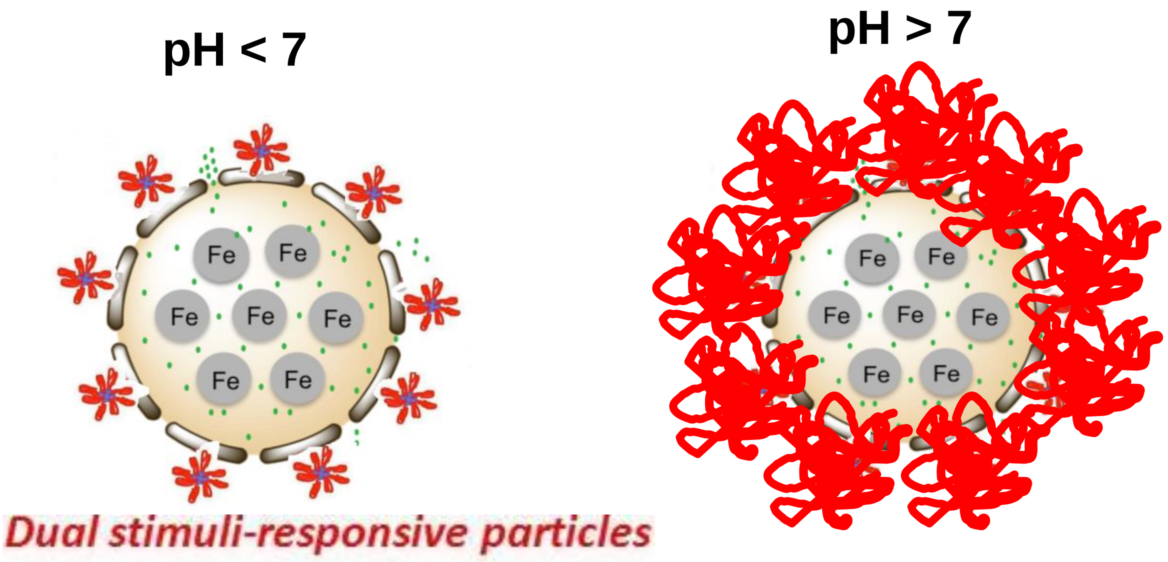


Immobilization and pH Controlled Release of Vitamins B12

Immobilization of vitamin B12 on functionalized PAMC



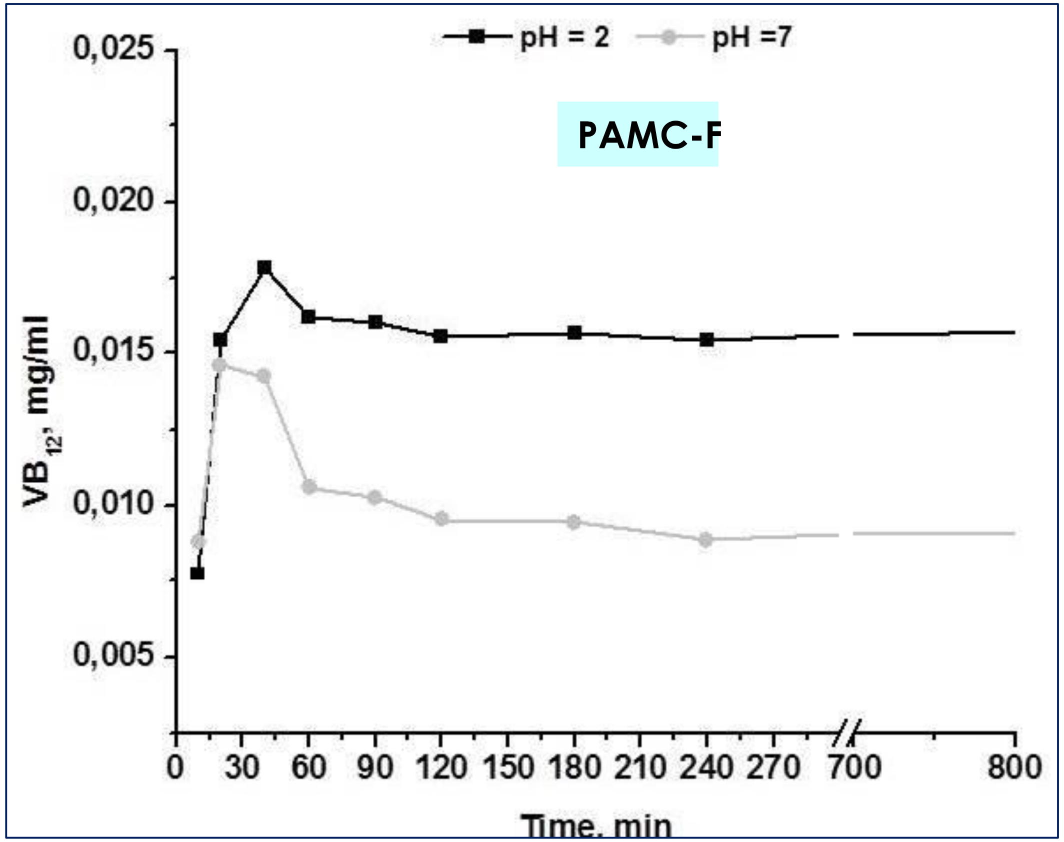


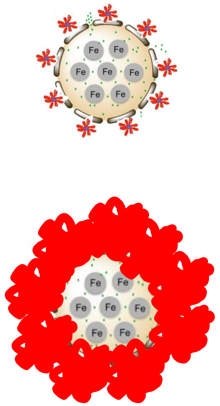


Conditions: Incubation of 100 mg PAMC in 0.2 mM/L solution of B12 for 24 h/37ºC; pH = 2.0 (phosphate buffer)

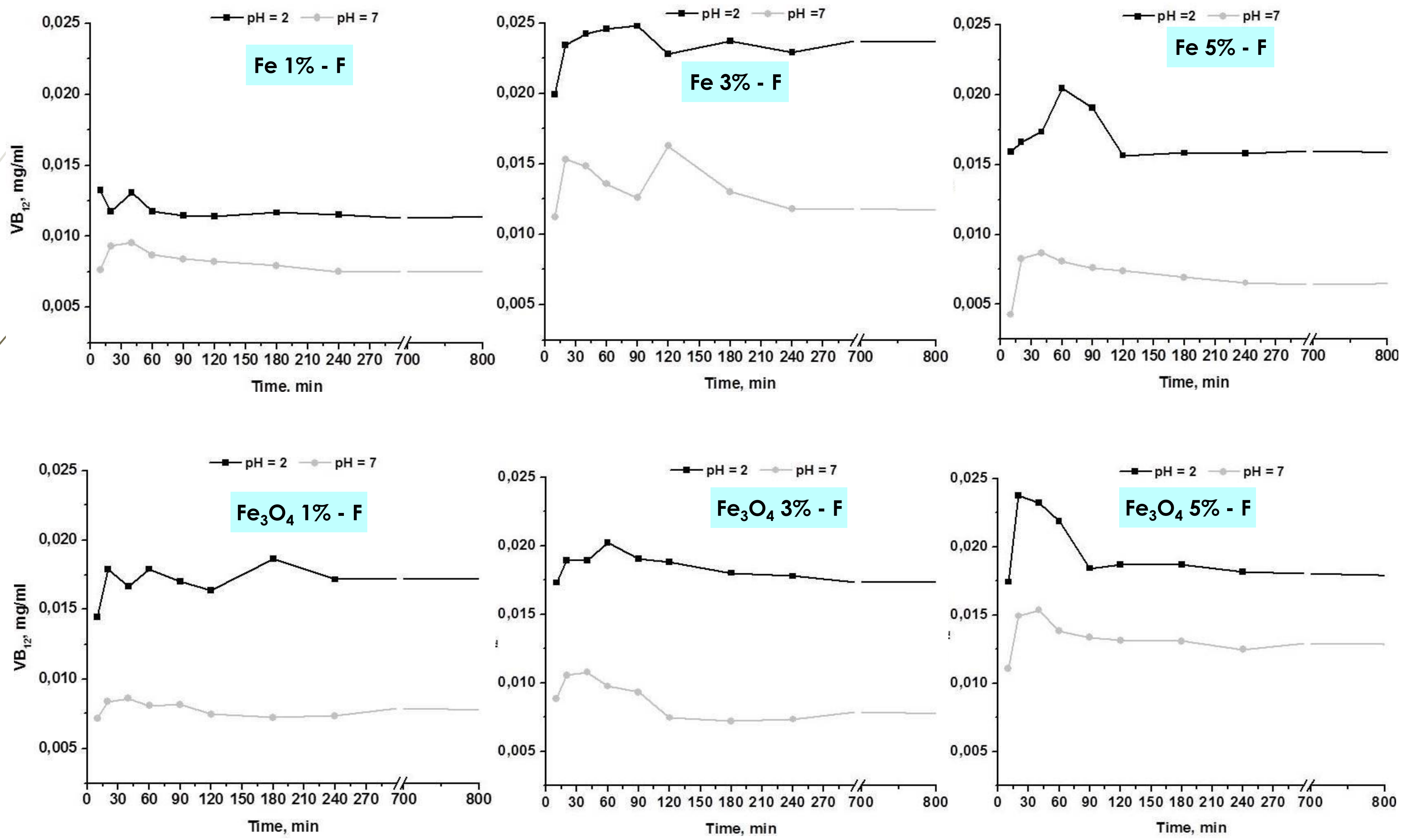
Release experiments – PAMC-F/Vitamine B12

Conditions: pure phosphate buffer at pH = 2 or pH = 7; Time: 30-800 min/37ºC;
Determination of B12: UV-VIS, peak of B12 at 361 nm



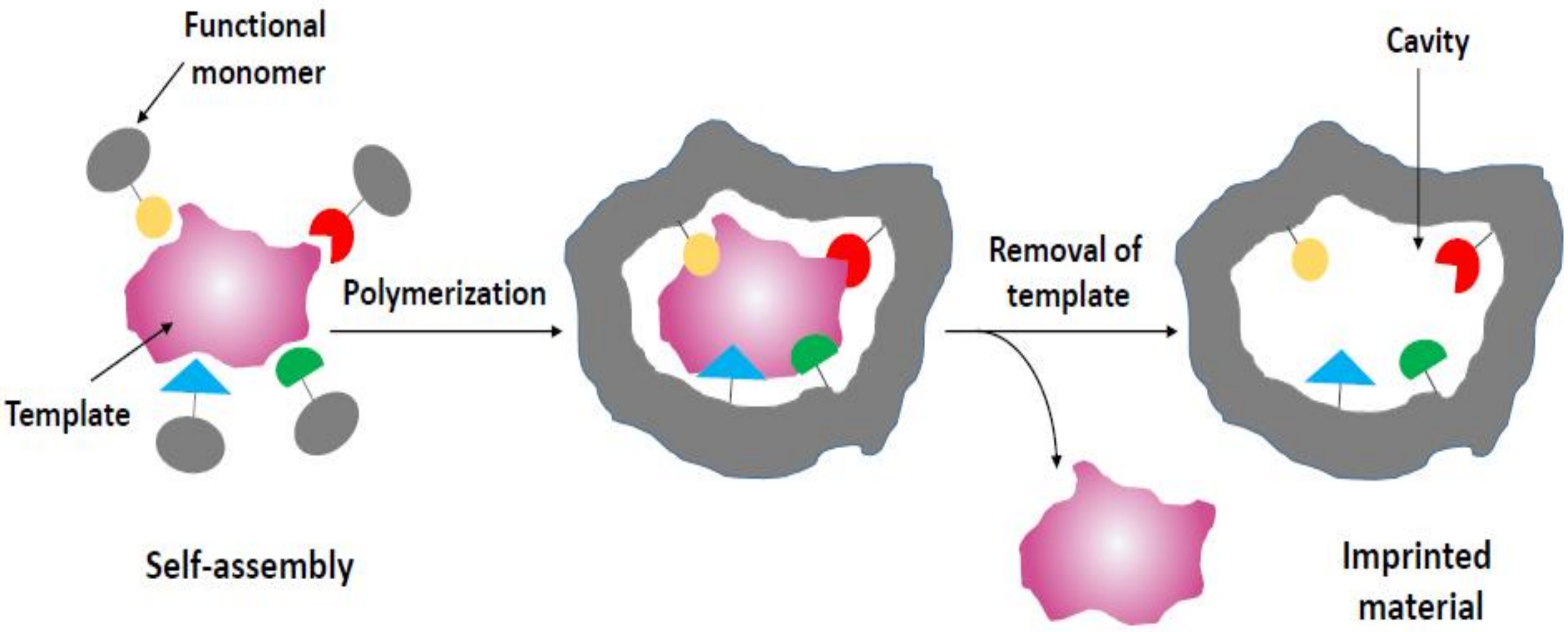


Release experiments – PAMC-F/Vitamine B12



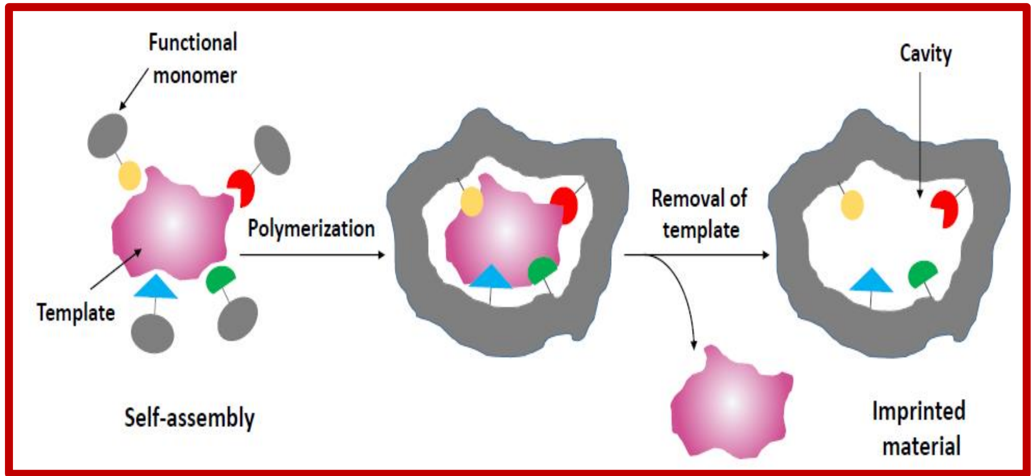
Molecularly Imprinted Magnetic PA4 Particles for Protein Recognition

Molecular imprinting – general scheme

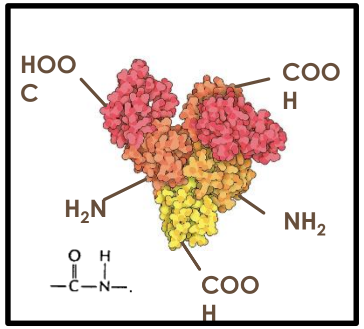


Non-covalent Imprinting

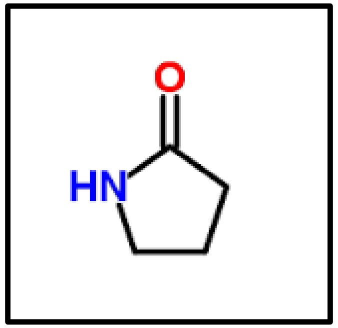
Molecularly imprinted PA4 particles



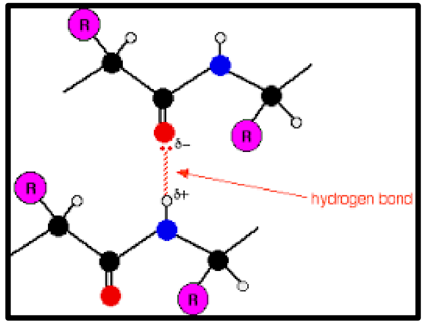
Template:
Bovine Serum Albumin (BSA)



Functional monomer:
2-pyrrolidone (PD)



PD:BSA Self-assembly
by **hydrogen bonds:**



Conditions:

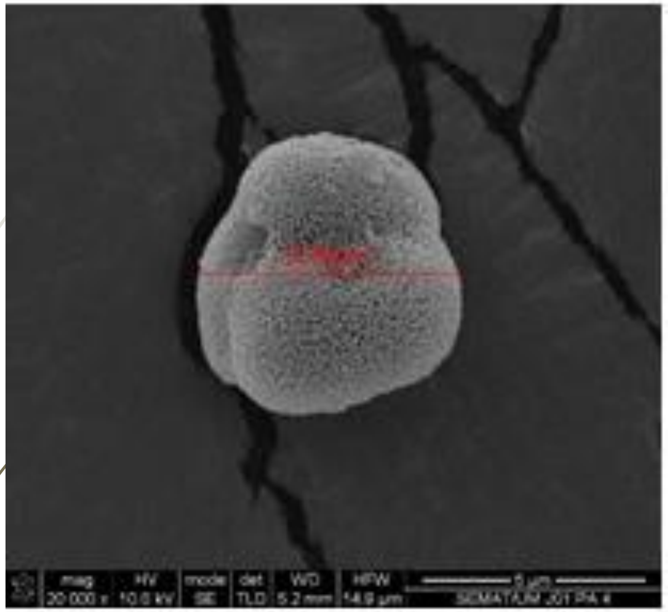
AAROP + magnetic particles (Fe, F_e3O_4)
Catalytic system**:**
DL+C20
40ºC; no solvent.

Samples

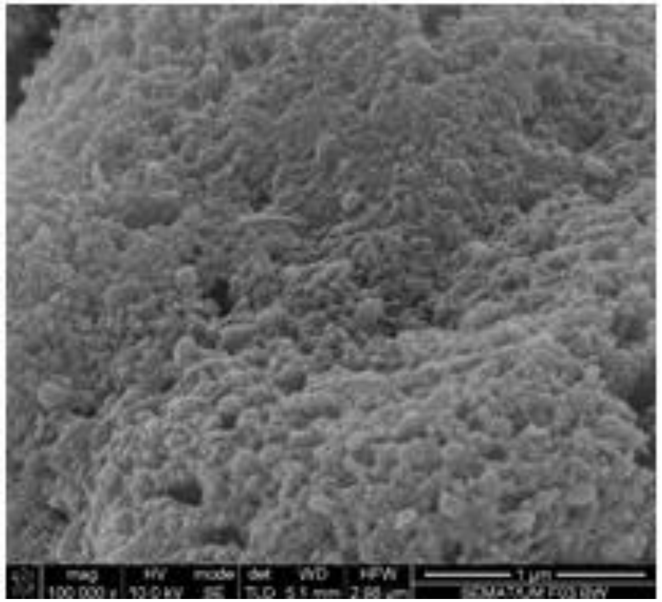
MIP:	**NIP:**
PPD@BSA	PA4
PPD-Fe 1%@BSA	PA4-Fe 1%
PPD-Fe_3O_4 1%@BSA	PA4-Fe_3O_4 1%
PPD-Fe_3O_4 0.1%@BSA	PA4-Fe_3O_4 0.1%

Particle surface topography by SEM

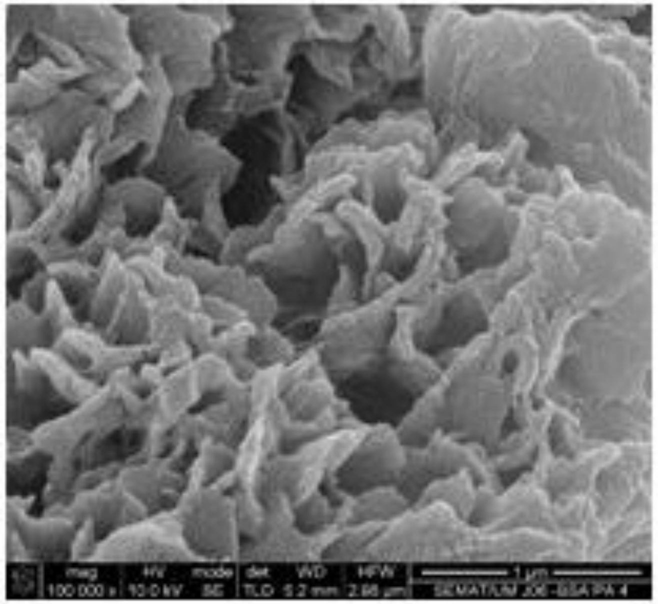
Sample: PPD-Fe_3O_4 1.0%@BSA



Typical size and form

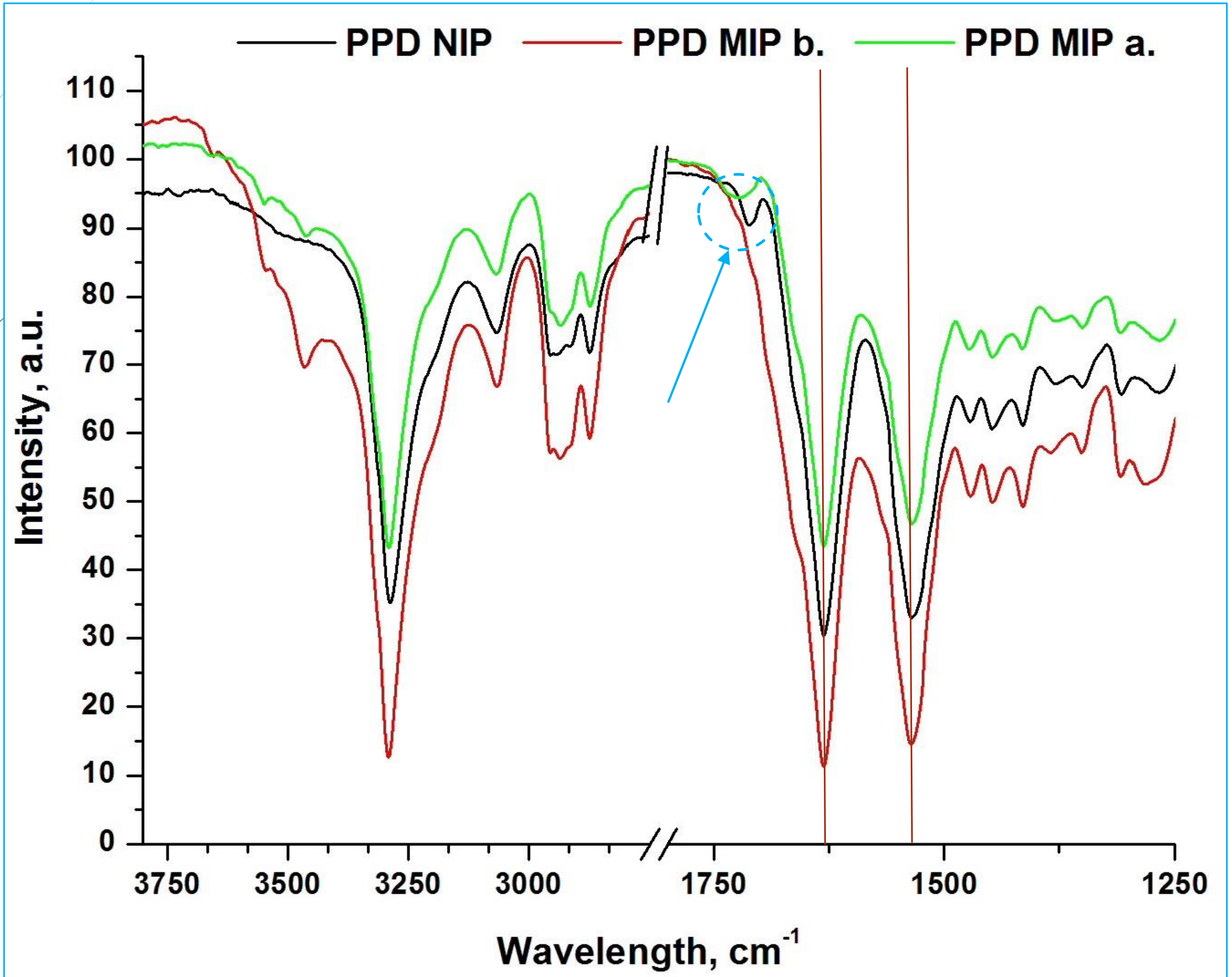


Before washing of BSA



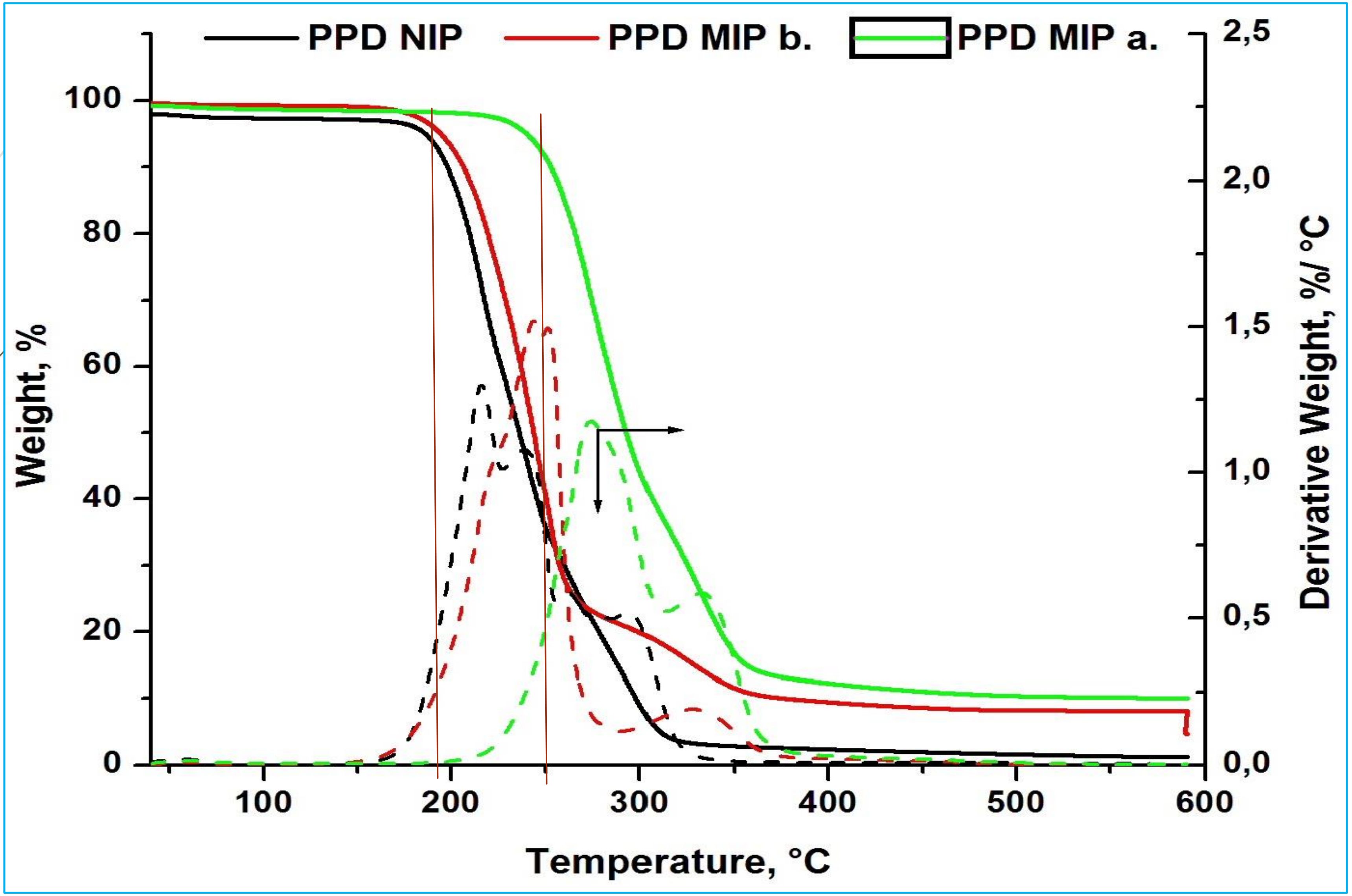
After washing of BSA

MIP/NIP characterization



FTIR (ATR)

MIP/NIP characterization

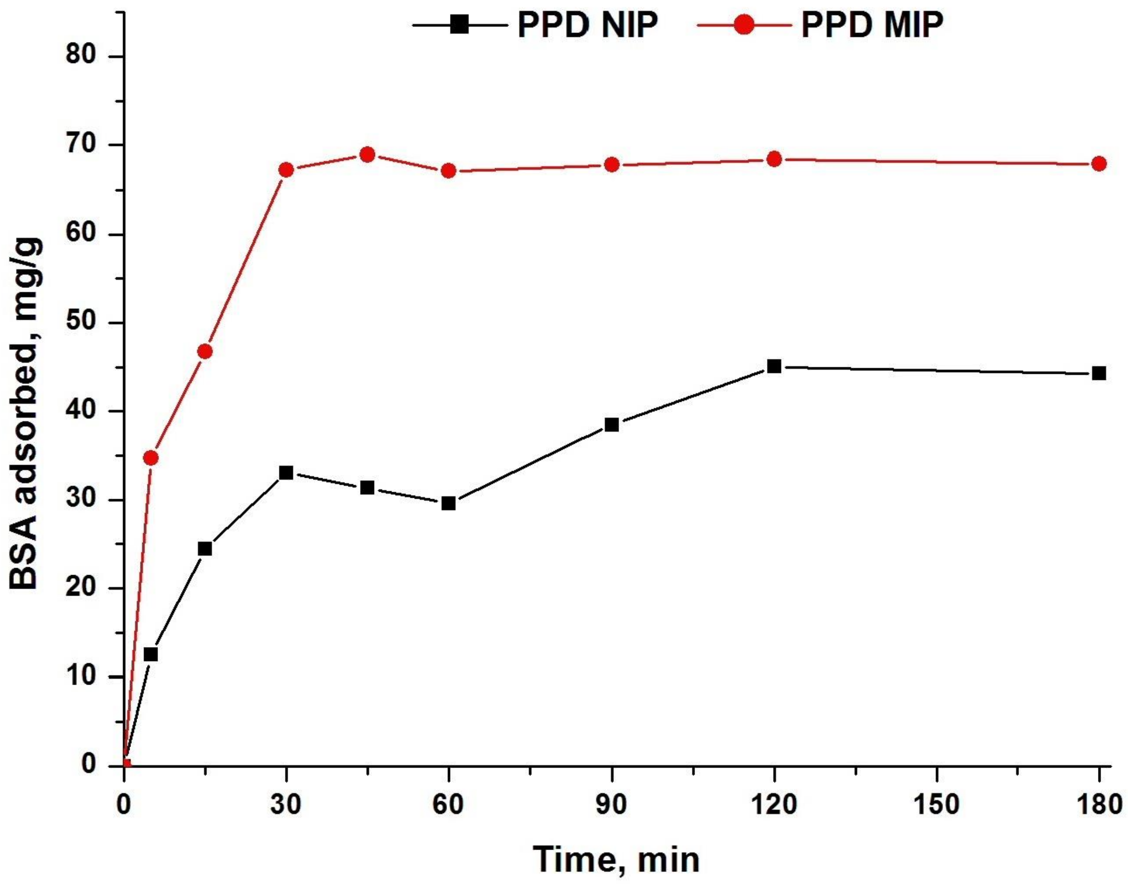


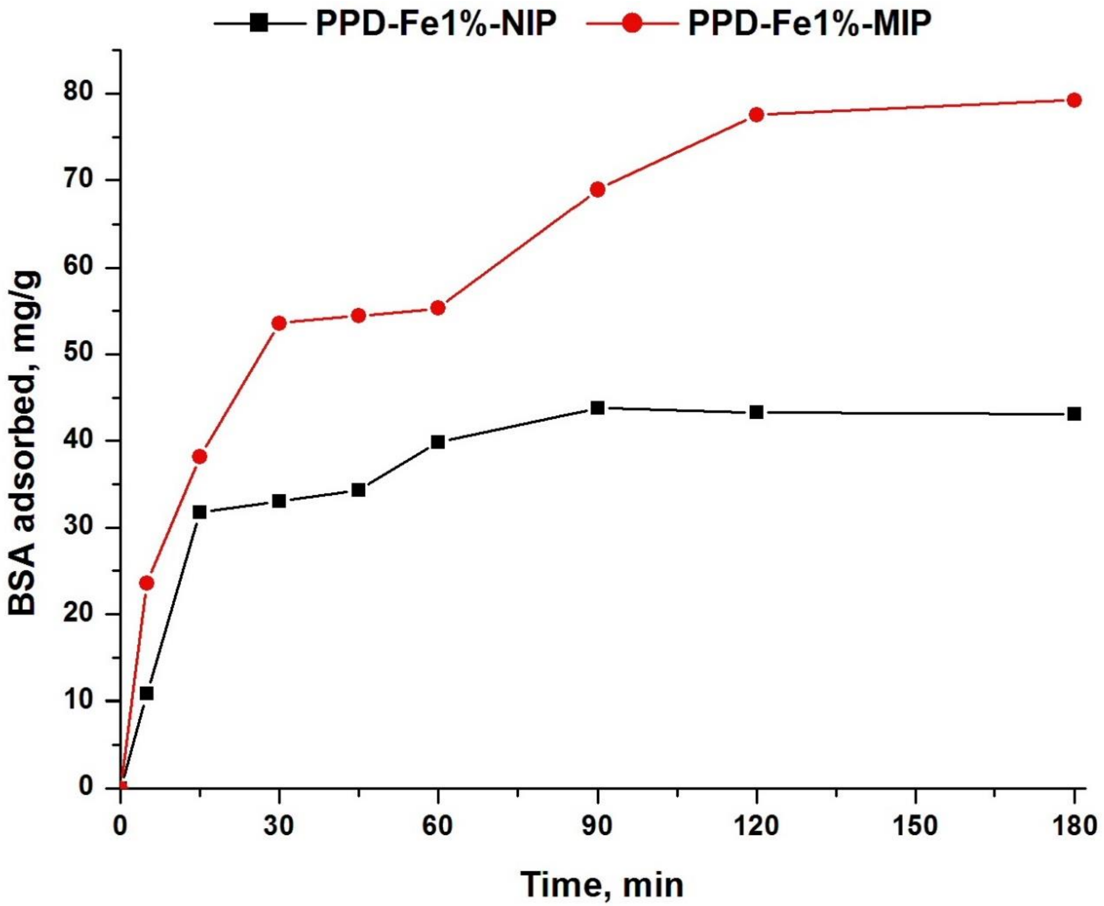
TGA

$T^{id}_{MIP} > T^{id}_{NIP}$

Absorption capacity Q in MES buffer

100 mg MIP/NIP in 1 wt% BSA (aq.)
Incubation: 3 h/37ºC; pH = 4





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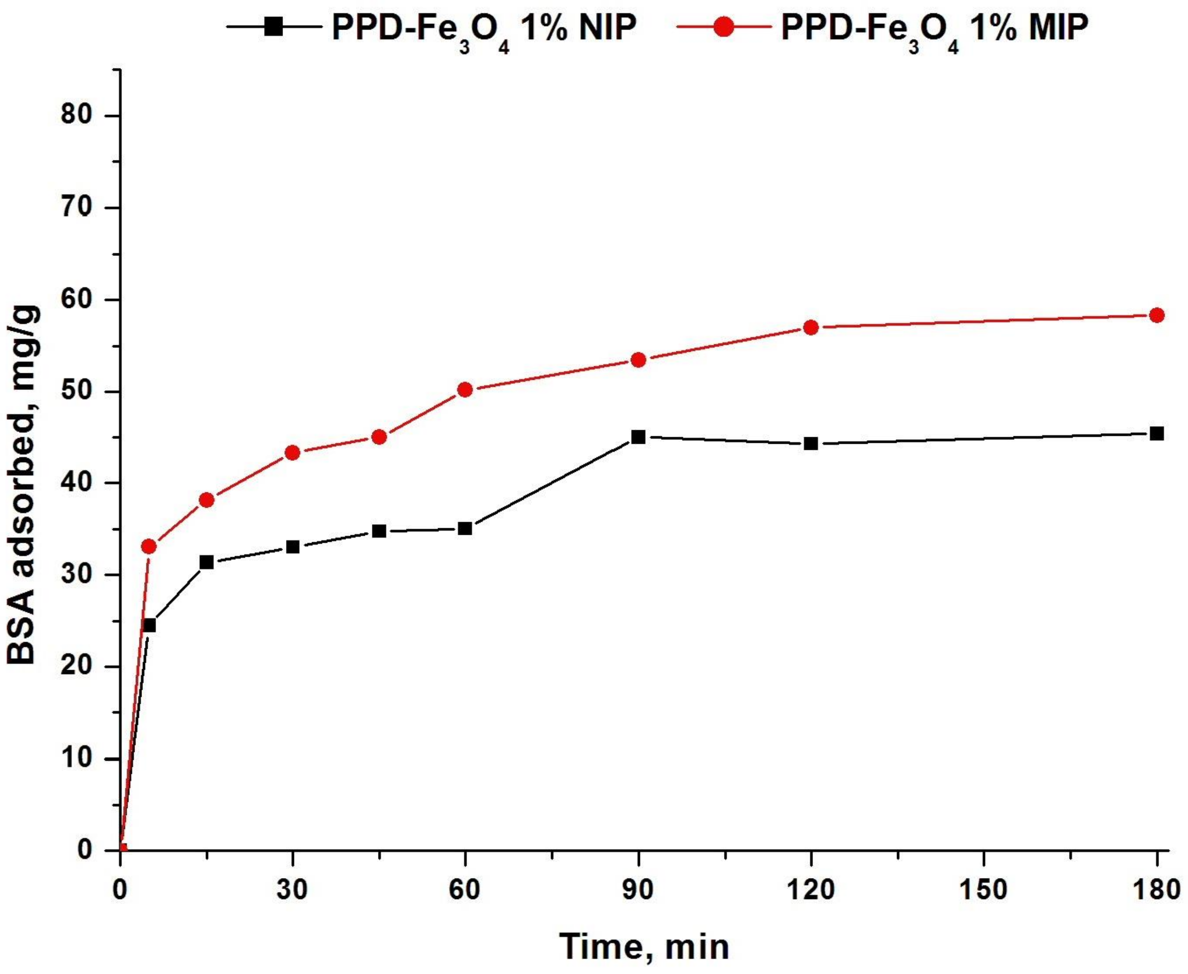
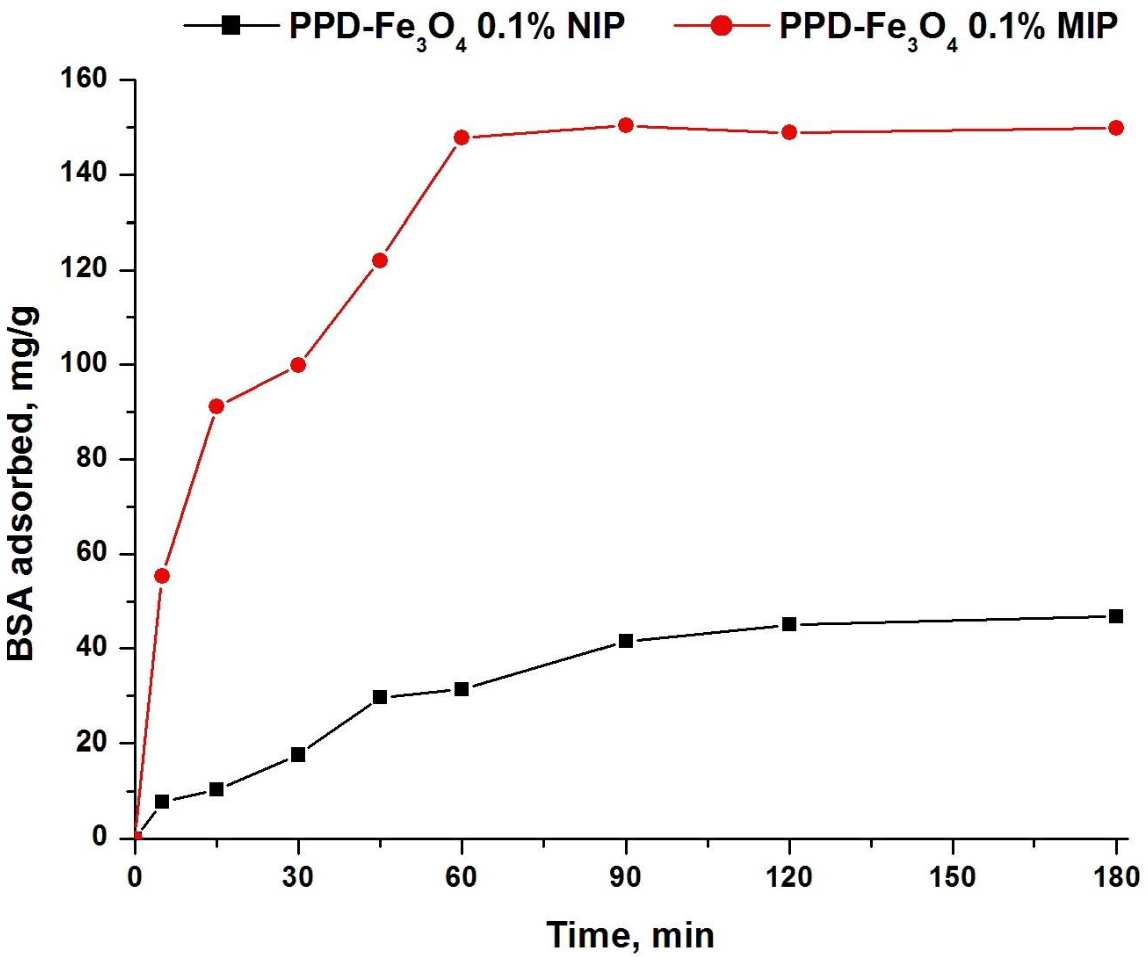
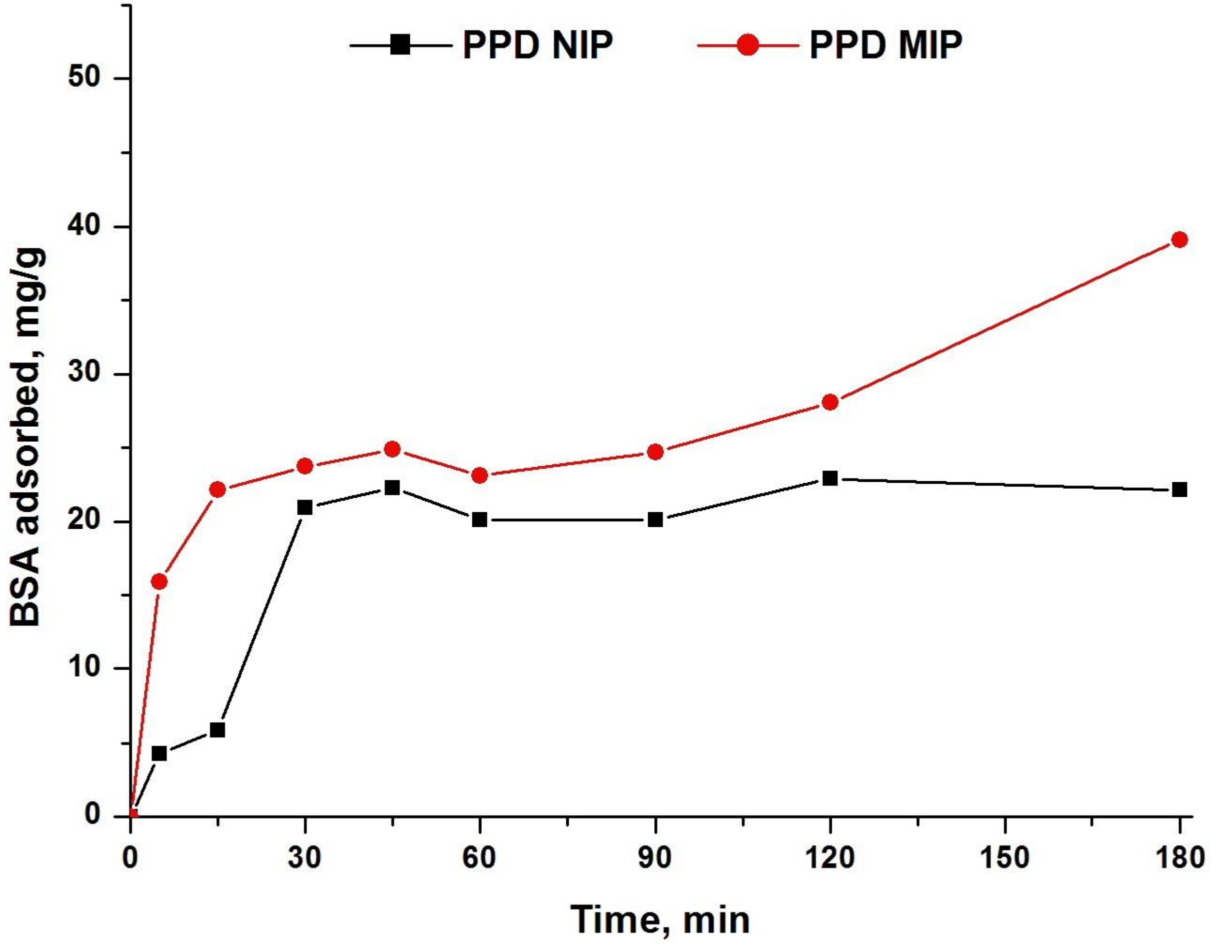
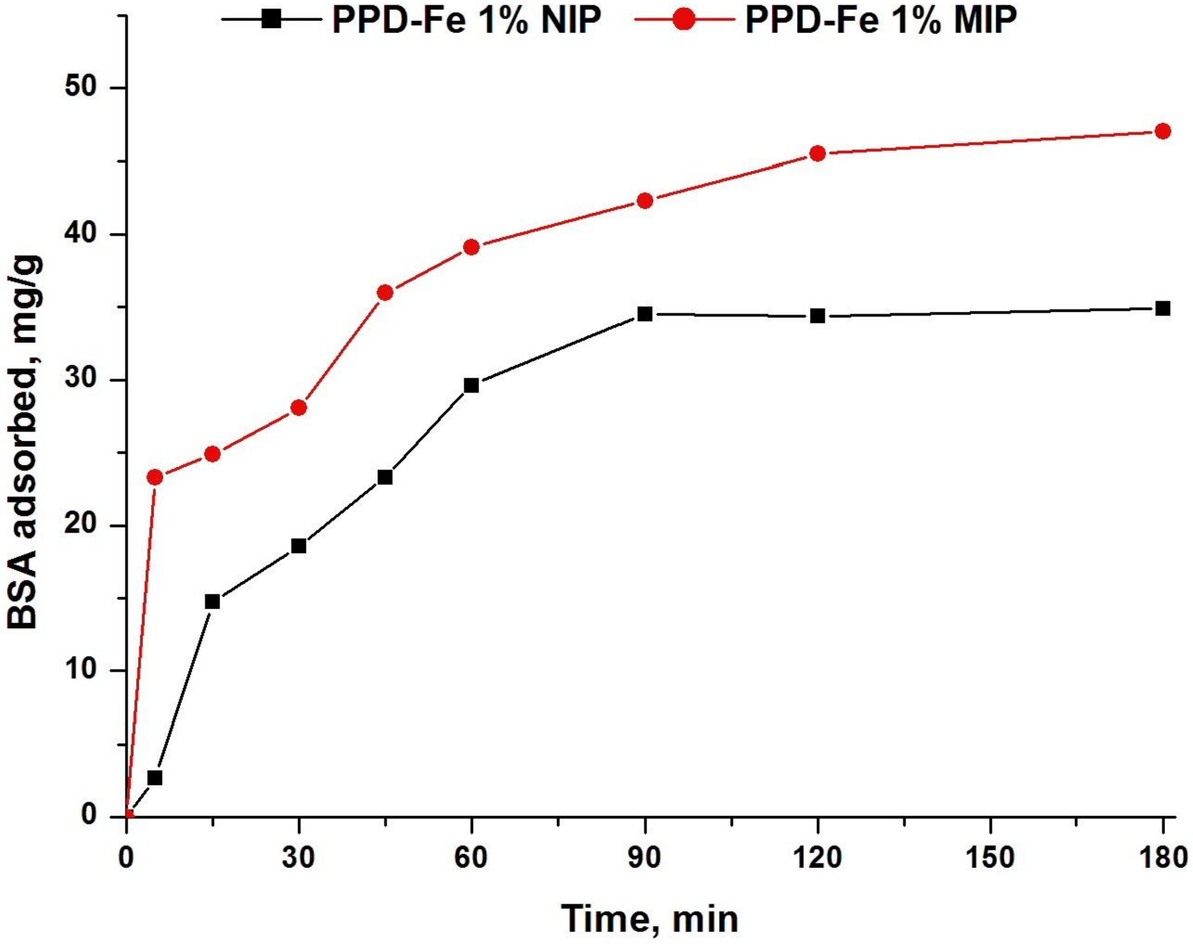




Absorption capacity Q in PBS

100 mg MIP/NIP in 1 wt% BSA (aq.)
Incubation: 3 h/37ºC; pH = 7





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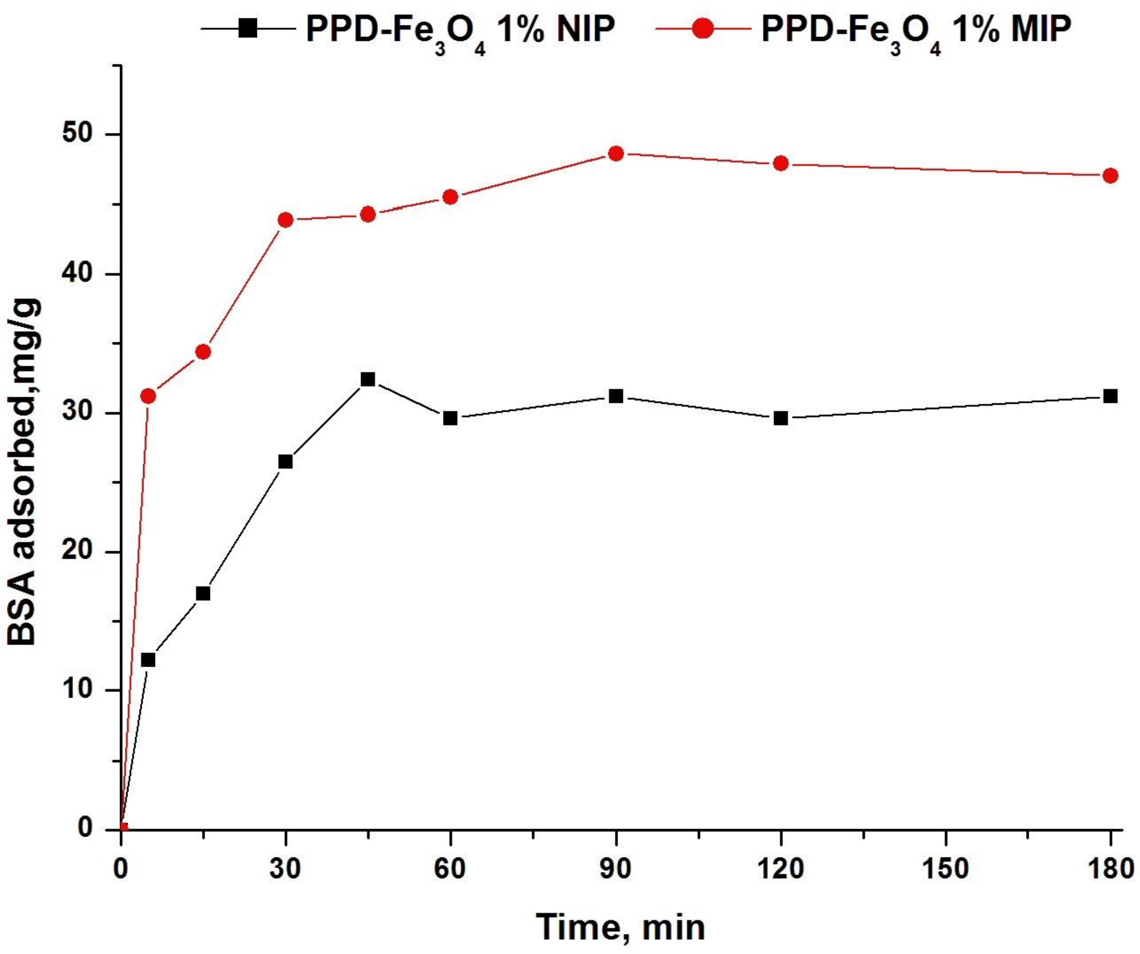
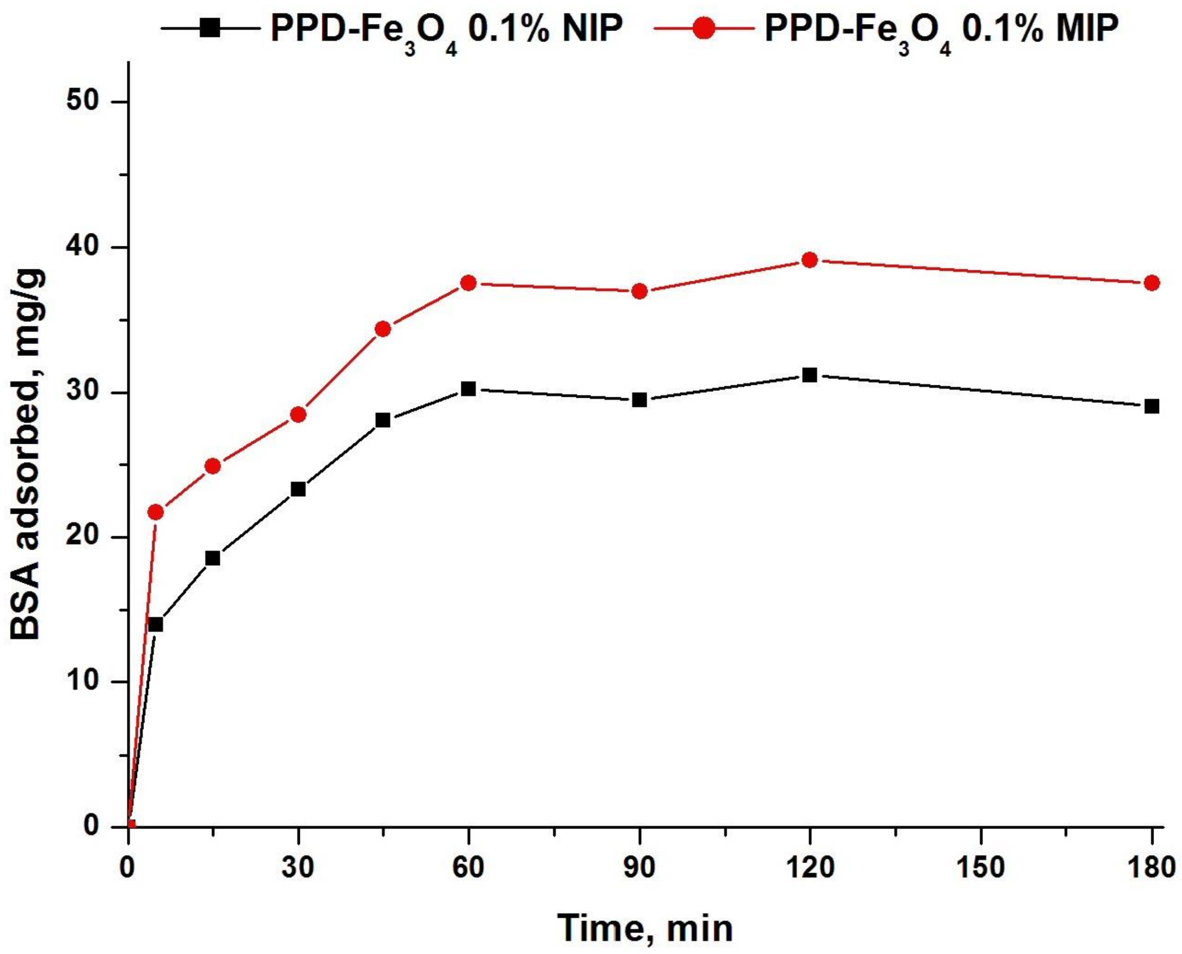
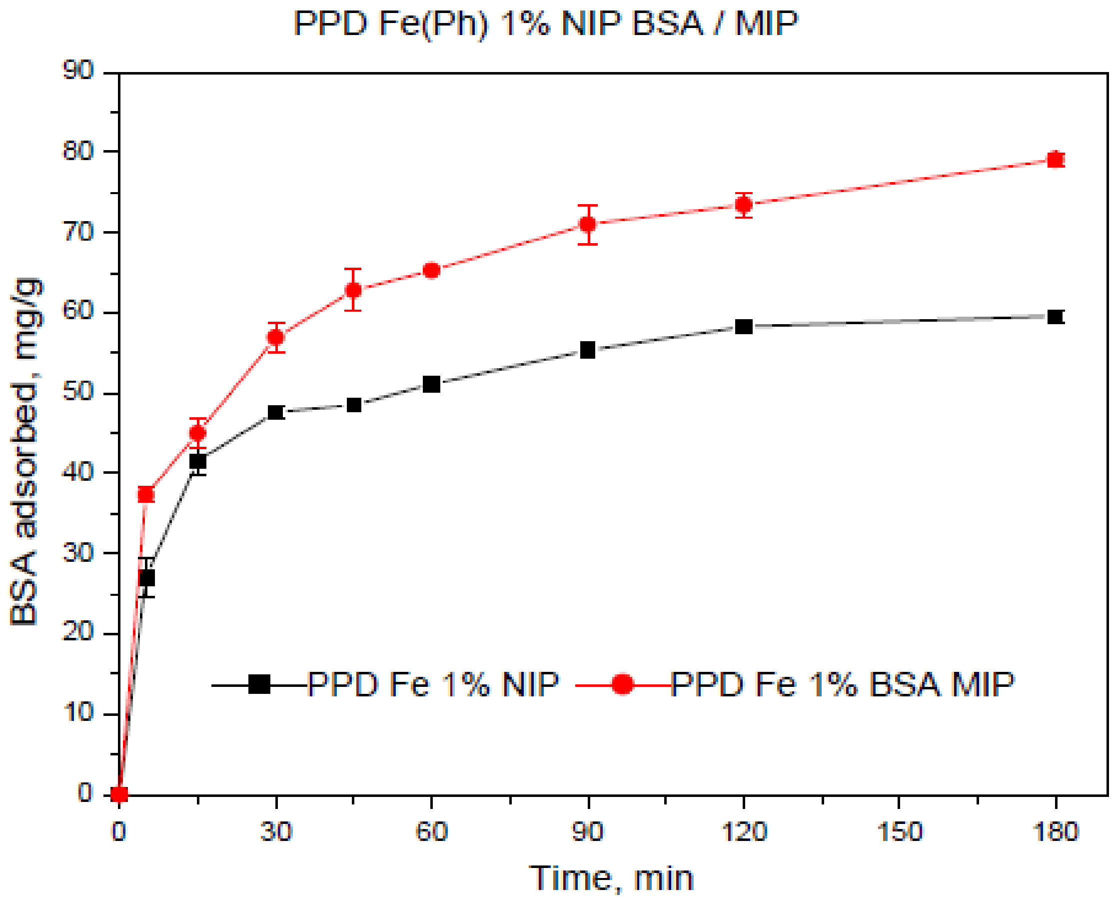


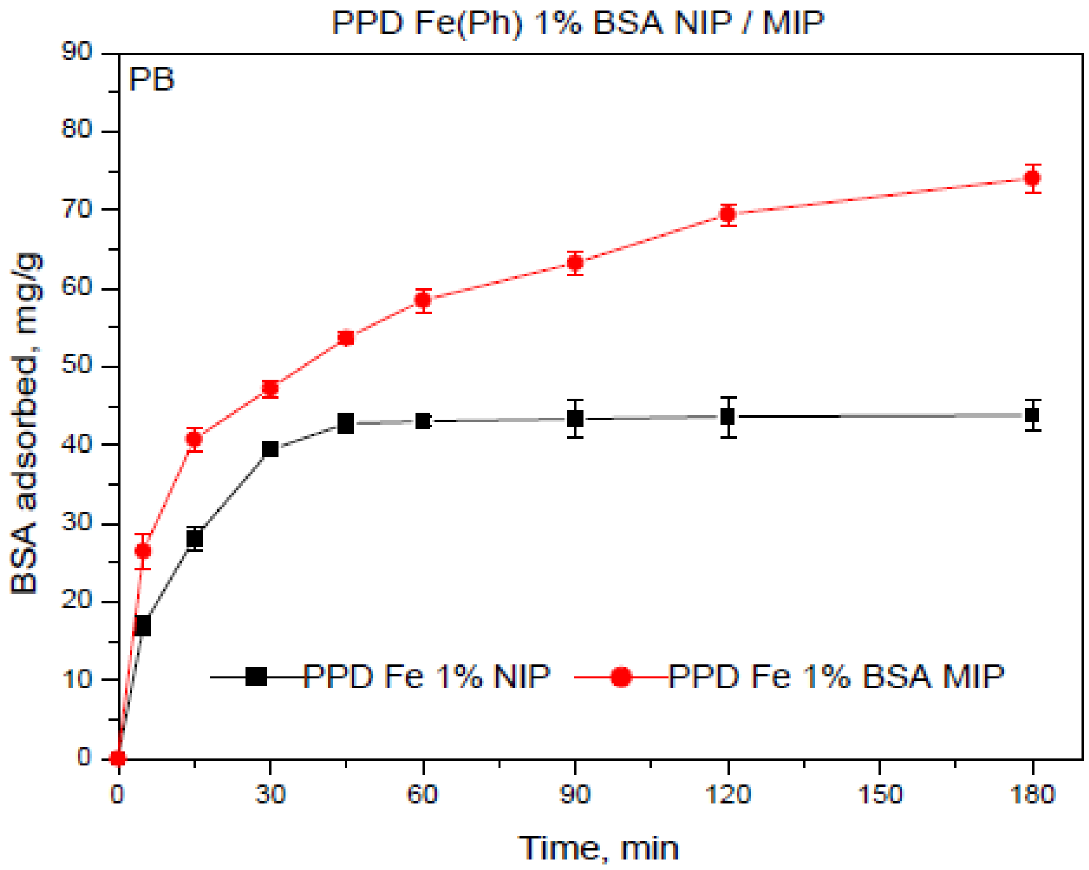


Absorption capacity Q of PA4 containing -PO_4 treated Fe

MES buffer 0.1 M pH 4

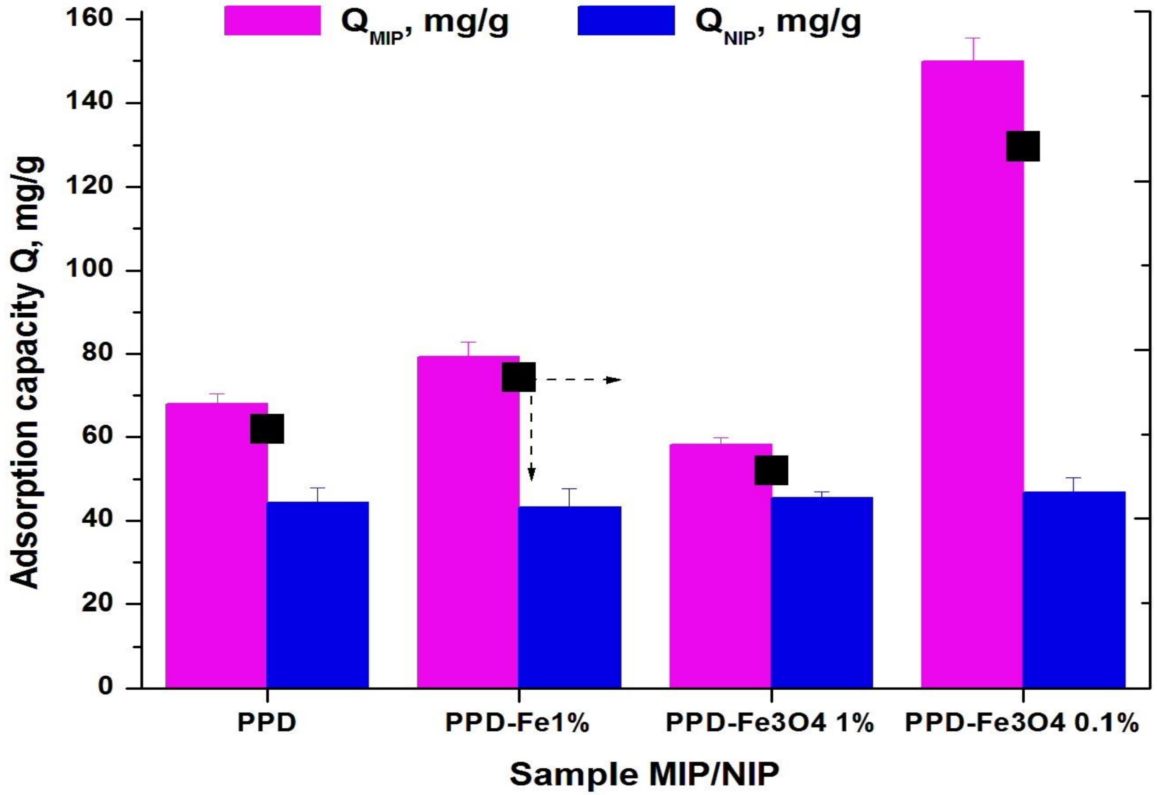


PBS 0.1 M pH 7

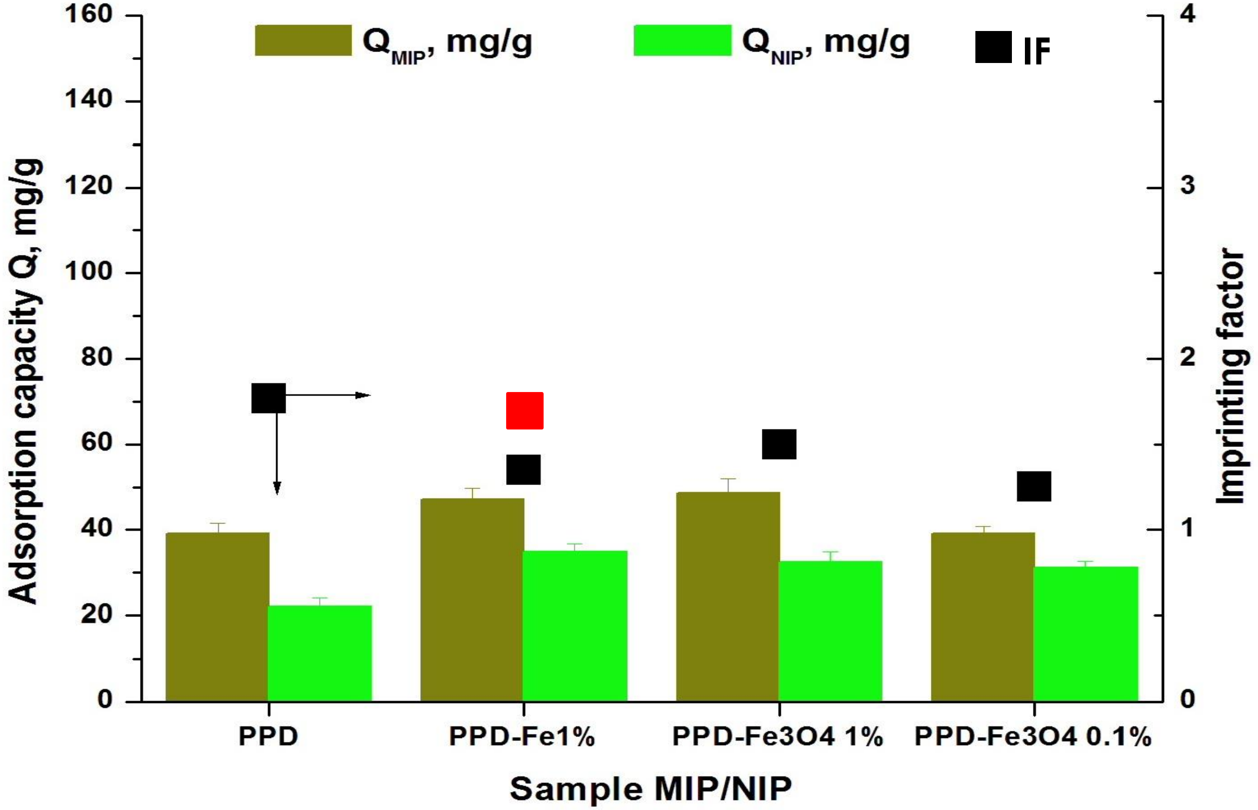


Absorption capacity Q - imprinting factor IF

In pH 4 (MES buffer)



In pH 7 (PBS)



$$IF = Q_{MIP} / Q_{NIP}$$

Conclusions

Reactive microencapsulation by anionic polymerization of lactams can produce loaded polyamide microcapsules with adjustable properties that can be transformed into PA6-based hybrid composites or used as free standing smart particles.

The magnetic polyamide microcapsules can be used for immobilization or selective recognition of proteins;

After functionalization by polyacrylate acid grafted chains, the magnetic microcapsules can be used as dually responsive drug delivery systems sensitive to pH and magnetic field.

TSSiPRO NORTE-01-0145-FEDER-000015

NORTE2020

Strategic projects UID/CTM/50025/2013 and LA25/2013-2014

COMPETE 2020

PORTUGAL 2020

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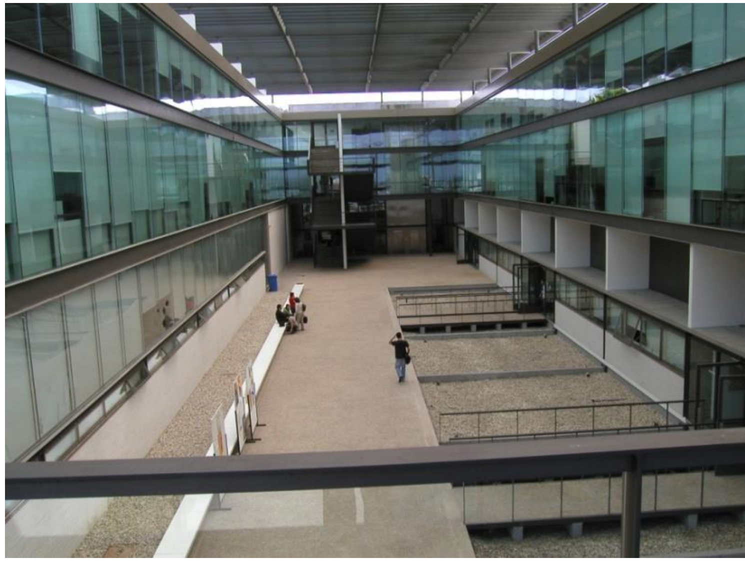
20 anos FCT Fundação para a Ciência e a Tecnologia

SFRH/BSAB/130271/2017

20 anos FCT Fundação para a Ciência e a Tecnologia

The “Micro/Nano Encapsulation” Team

Elina Marinho
Clara Cano
Nadya Dencheva
Filipa Oliveira
Joana Rompante
Joana Braz
Filipa Castro
Shafagh Tochidi



Thank you!

University of Minho