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Immobilization of a Carbonic Anhydrase Enzyme onto Flame Spray Pyrolysis-Based Silica Nanoparticles for Promoting CO_2 Absorption into a Carbonate Solution for Post-combustion CO_2 Capture

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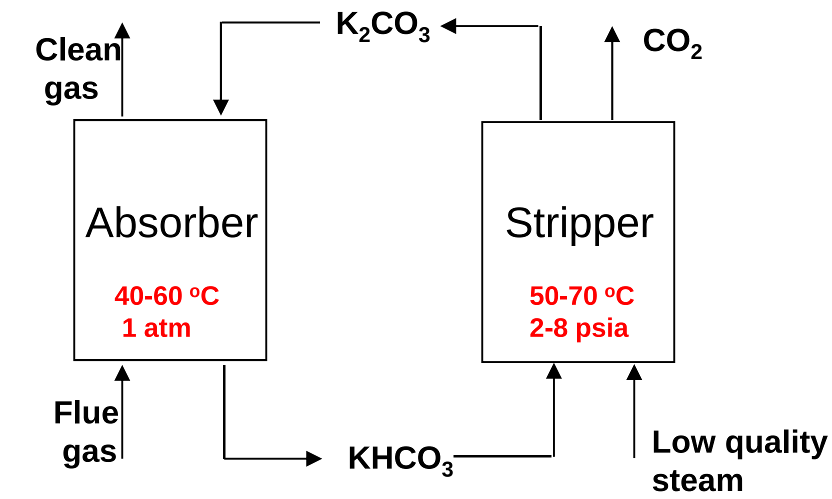
Outline of the presentation

- Background
- Synthesis and characterization of silica nanoparticle
- Preparation of immobilized enzymes
- Evaluation of immobilized enzymes
- Conclusions

Background

Features of IVCAP



Absorber:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$

Stripper:

$$2KHCO_3 \xrightarrow{Heat, Vaccum} K_2CO_3 + CO_2 \uparrow + H_2O$$

Integrated Vacuum Carbonate Absorption Process (IVCAP) for CO_2 capture

- Low T/P stripping
  - at 2-8 psia, 50-70 ^{0}C, allowing use of low quality steam from power plant
  - Energy use reduced by 20-30% compared to MEA-based processes
- Biocatalyst (*Carbonic anhydrase*) to promote absorption rate

Enzyme immobilization

Advantages:

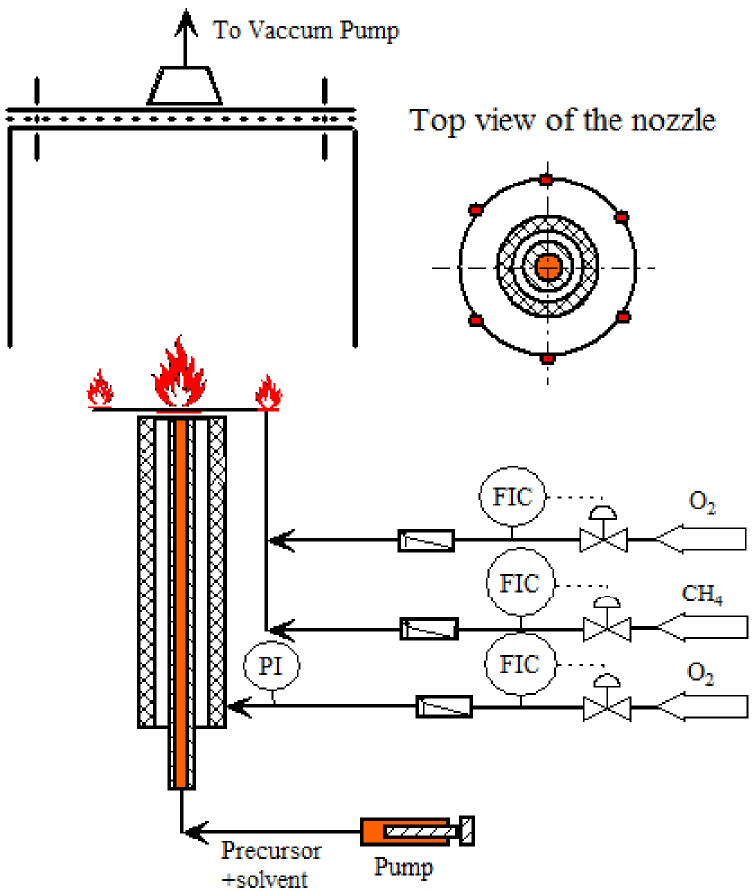
- Improve enzyme stability
- Reduce enzyme elution in a flow system

Support materials:

- Macro-porous particles (e.g., Controlled pore glass (CPG), 100 nm pore, SA=25 m^2/g, 200-400 mesh)
- Meso-porous particles (e.g., activated carbon, 40-60 mesh)
- Non-porous nanoparticles (e.g., silica)

Synthesis and characterization of silica nanoparticles

Synthesis of silica nanoparticles by flame spray pyrolysis (FSP)



Schematic of FSP experimental set-up

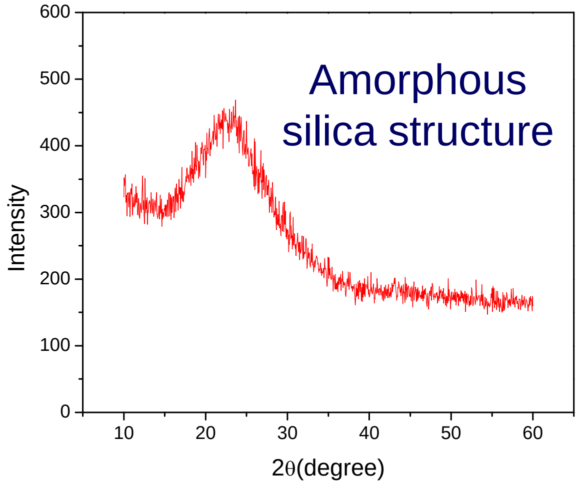
Advantages:

- Easy to scale up
- Controlled sorbent properties (size, composition, etc)
- Suitable for massive production
- Waste-free

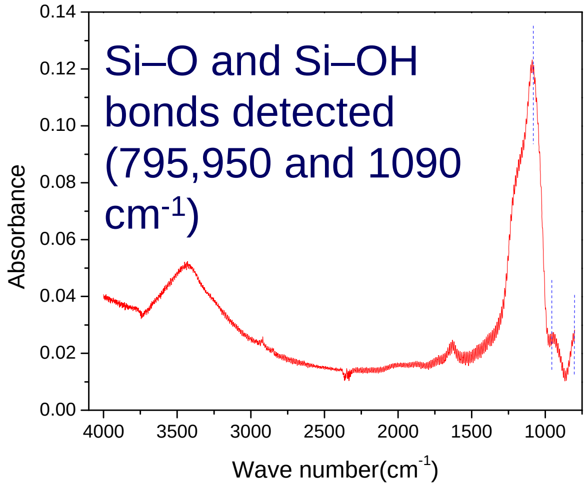
Synthesis conditions:

- Precursor: TEOS
- Solvent: Xylene
- Volumetric ratio of TEOS and xylene: 1:1
- Liquid feed rate: 1 ml/min
- Dispersion gas: O_2 (4.46 l/min)
- Premixed combustion gas: O_2 (0.42 l/min) and CH_4 (0.41 l/min)

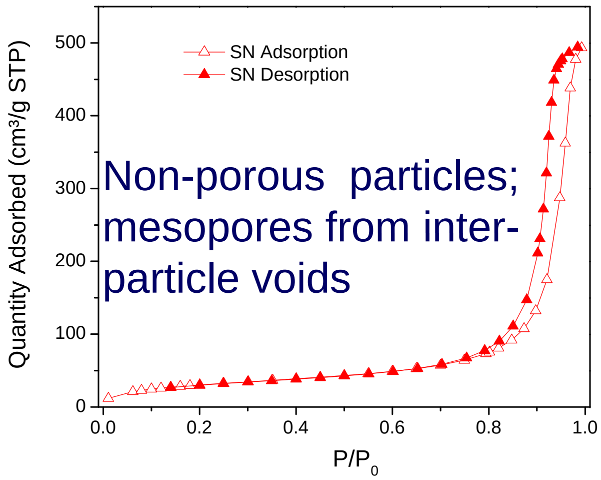
Characterization of silica nanoparticles



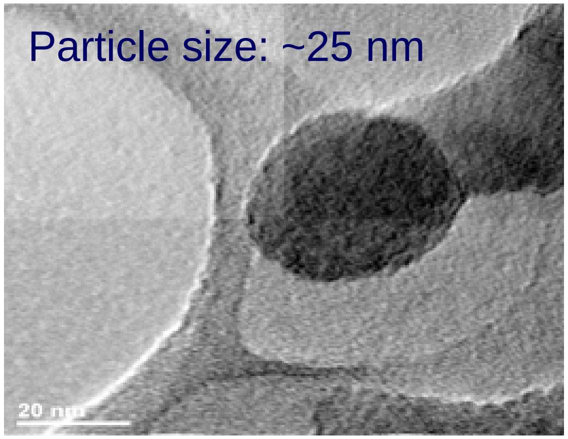
XRD patterns of FSP silica nanoparticles



FTIR spectrum of FSP silica nanoparticles



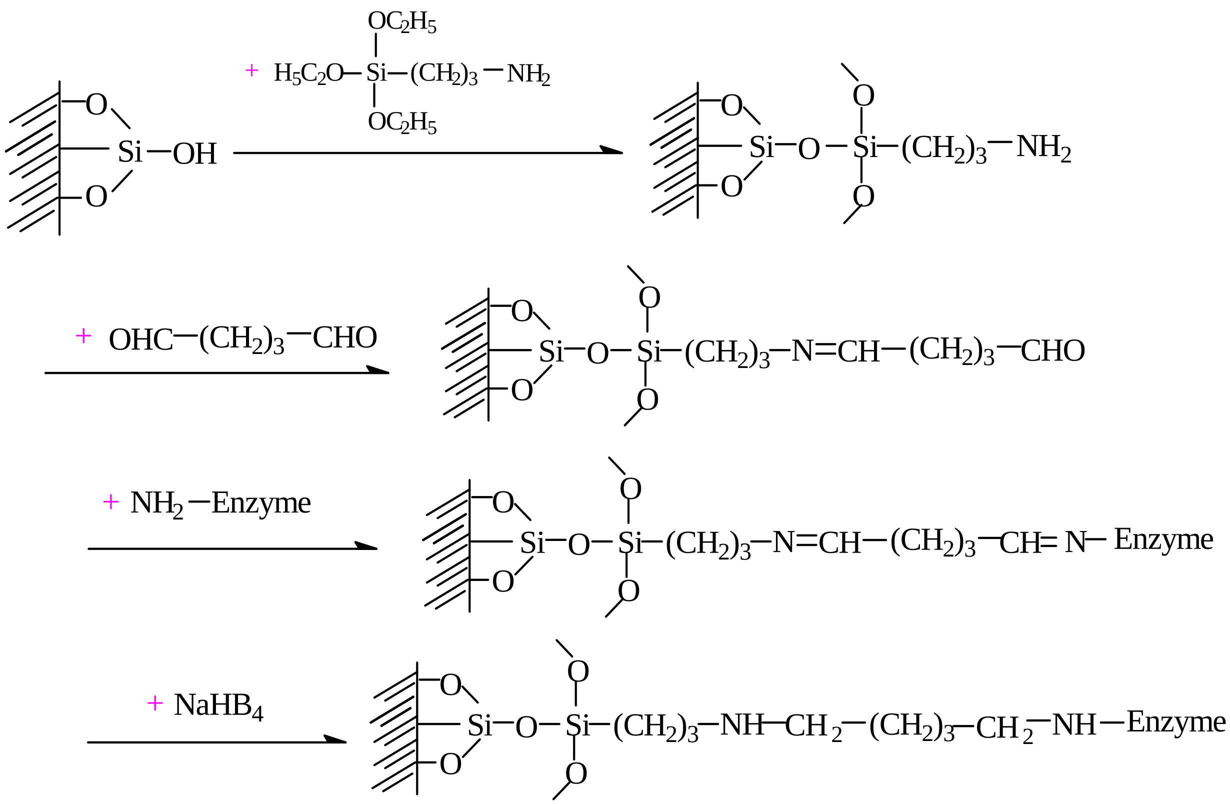
N_2 adsorption isotherms (-196 ^oC)

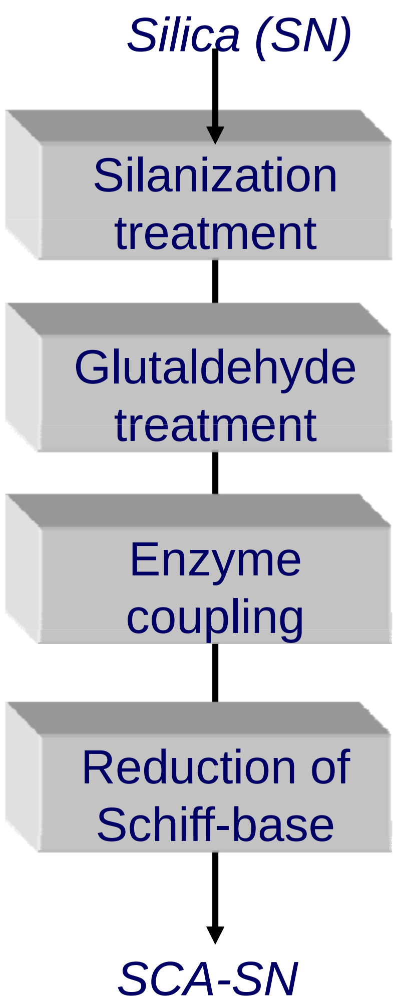


TEM image of FSP silica nanoparticles

Preparation of immobilized enzymes

Procedure of CA immobilization onto silica nanoparticles





SCA: A commercial bovine Carbonic Anhydrase from Sigma-Aldirich

Theory of enzymatic kinetics for CO_2 absorption

For pseudo-first order gas absorption in a stirred cell reactor:

$$R = -\frac{V_G}{A \times R_{gas} T}\frac{dP_i}{dt} = k_L \sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} \times \left(C^* - C^b\right) \qquad \text{where} \qquad C^* = \frac{P_i}{He_i}$$

When C^b is negligible, we obtain:

$$Ln\left(\frac{P_{i,0}}{P_i}\right) = \sqrt{k_L^2 + Dk_{ov}}\,\frac{RTA}{V_G He_i}\Delta t$$

Without an enzyme $\quad k_{ov} = k_{H_2O} + k_{OH^-}[OH^-]$

With an enzyme $\quad k_{ov} = k_{H_2O} + k_{OH^-}[OH^-] + k_{SCA}[SCA]$

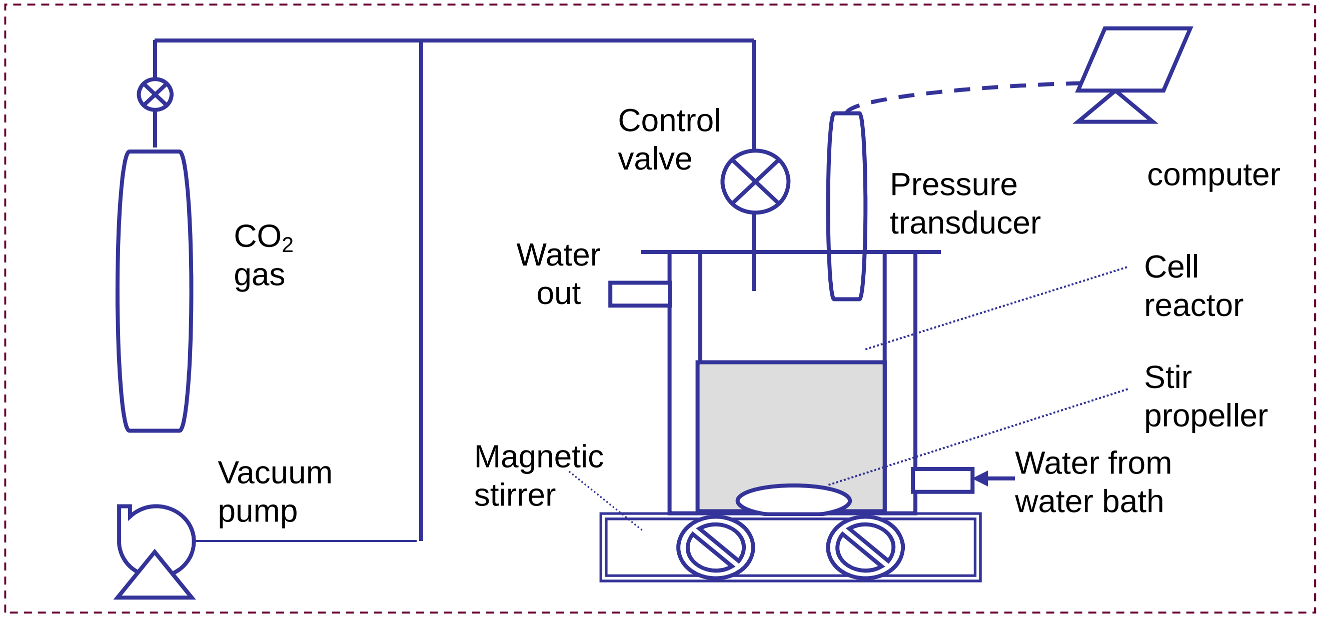
$$k_{SCA} = \frac{k_{cat}}{K_m}$$

The criterion of a pseudo-first order reaction is given by:

$$C^*\left(\frac{1}{a} + \frac{2}{b}\right)\left[\sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} - 1\right] << 1$$

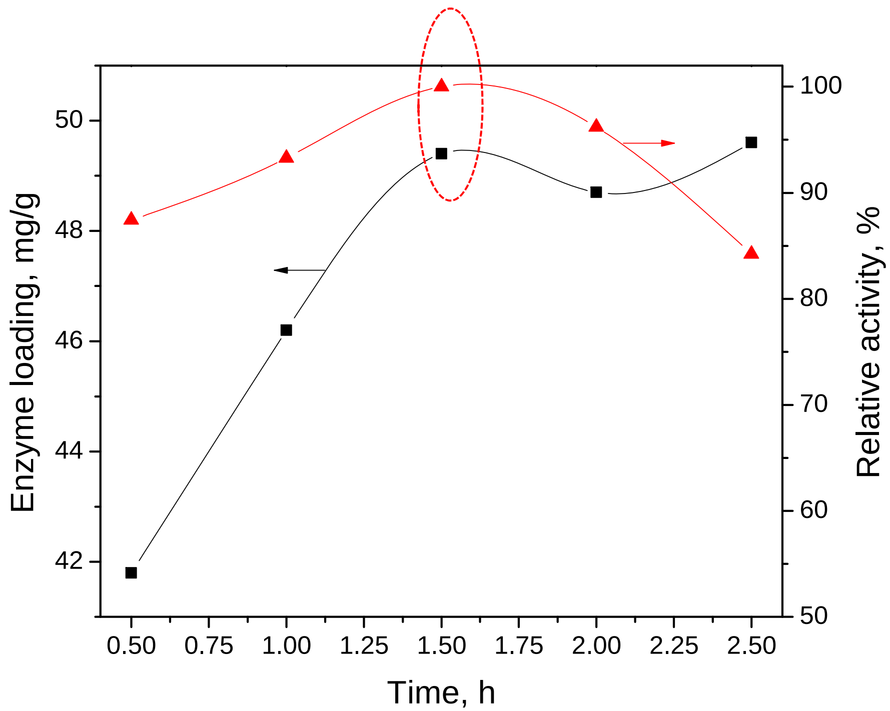
$$IF = \frac{k_{SCA}(IM)}{k_{SCA}(free)}$$

A stirred cell reactor for enzyme activity assay



- 15 ml of 0.1M carbonate-bicarbonate solution (pH10.0) mixed with free or immobilized SCA
- Profile of CO_2 pressure change vs. time recorded to estimate K_{SCA}

Determination of optimal condition for SCA enzyme immobilization



Profile of the SCA enzyme loading and activity over immobilization time

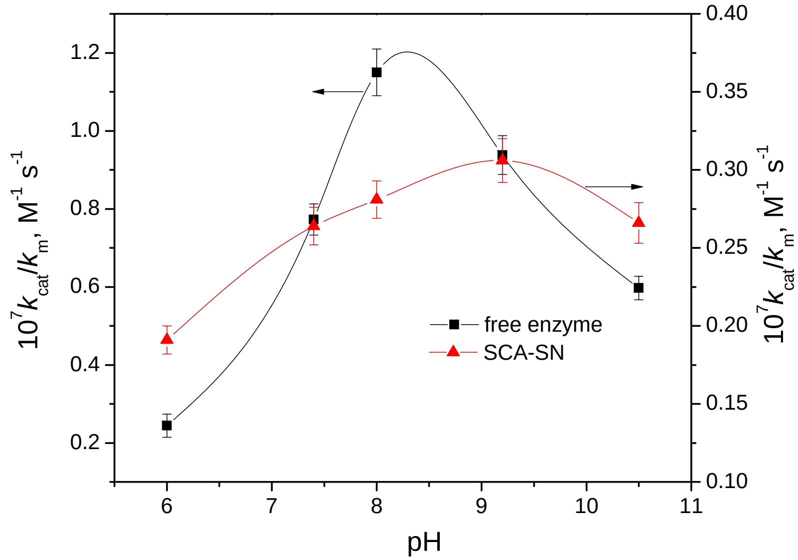
Loadings and activities of the immobilized SCA enzymes prepared at different pH conditions

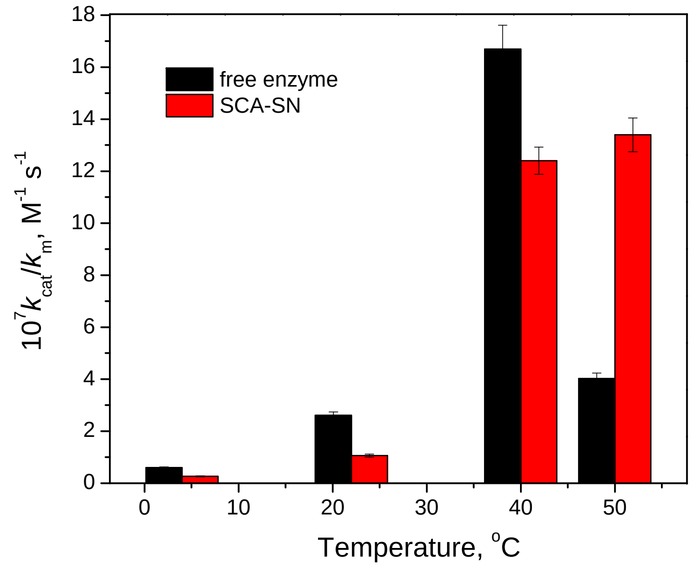
pH	Enzyme loading, mg/g	IF, %
10	22.3	16.5
8	**49.4**	**44.6**
7	33.2	18.9
5	22.6	14.3

Optimal immobilization time of 1.5 hr and pH of 8

Evaluation of immobilized enzymes

Activity of SCA-SN under different pH and temperature conditions





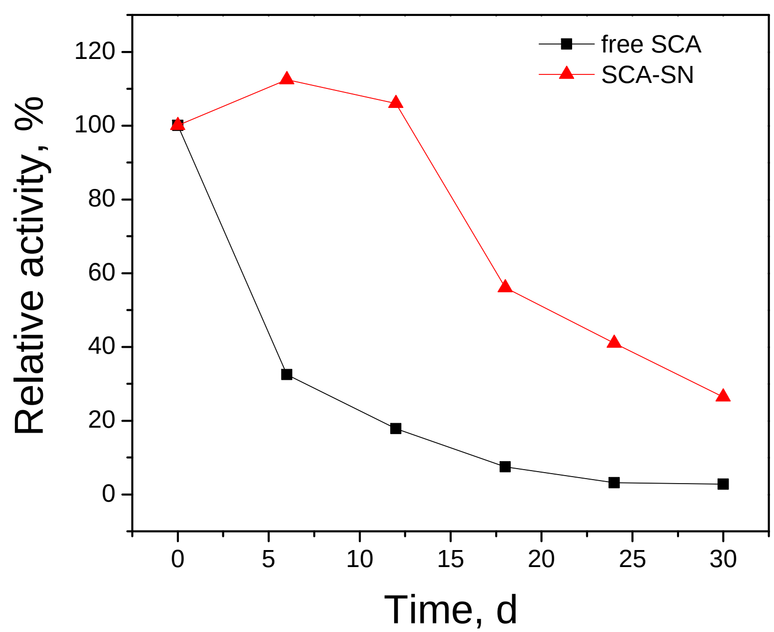
Effect of pH on the activities of free and immobilized enzymes at 4 ºC

Effect of temperature on the activities of free and immobilized enzymes at pH10.5

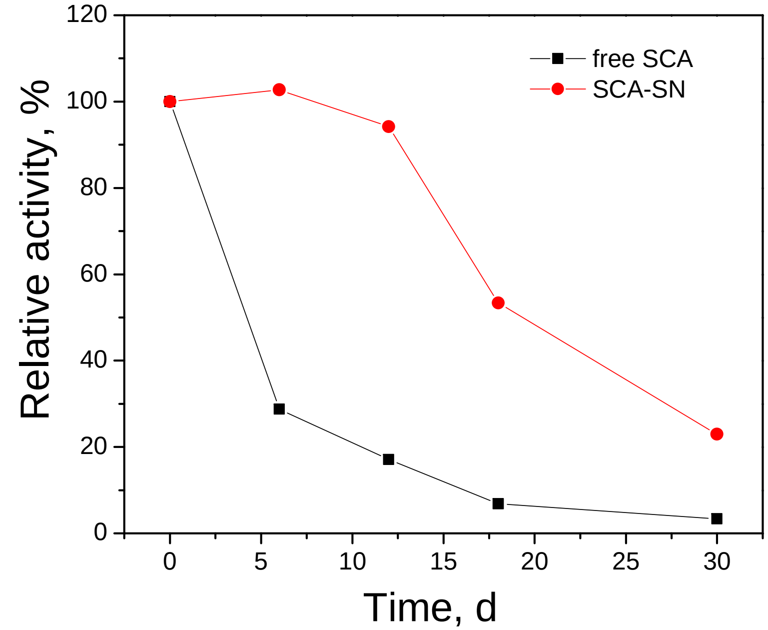
(Enzyme loading onto the silica support: **49.4 mg/g)**

Immobilized enzymes exhibited high activities under the typical conditions of the IVCAP process (pH=10.5, T=50 ºC)

Stability of SCA-SN at 50 °C



Thermal stability of immobilized SCA at 50 °C



Chemical stability of immobilized SCA in the presence of SO_4^{2-}, NO_3^-, and Cl^- anions at 50 °C

Both thermal and chemical stabilities of the enzyme improved via immobilization

Conclusions

- Amorphous nonporous silica nanoparticles (25 nm) synthesized by an FSP method
- SCA successfully immobilized onto the FSP silica nanoparticles (49.4 mg SCA /g silica support)
- Kinetic parameters (k_{cat}/k_m) of immobilized enzymes determined using classic Danckwerts absorption theory with reaction
- Immobilized enzymes exhibited higher activities at the typical conditions of the IVCAP process.
- Immobilized enzymes exhibited significantly improved stability compared to their free counterpart.

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Thank you for your attention!