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SYNTHESIS OF A MOLECULARLY IMPRINTED CORE-SHELL PHOTOCATALYST

Ivana Gabelica[1], Floren Radovanović-Perić[2], Gordana Matijašić[2], Lidija Ćurković[1]

[1]Sveučilište u Zagrebu Fakultet strojarstva i brodogradnje, Ivana Lučića 5, 10000 Zagreb

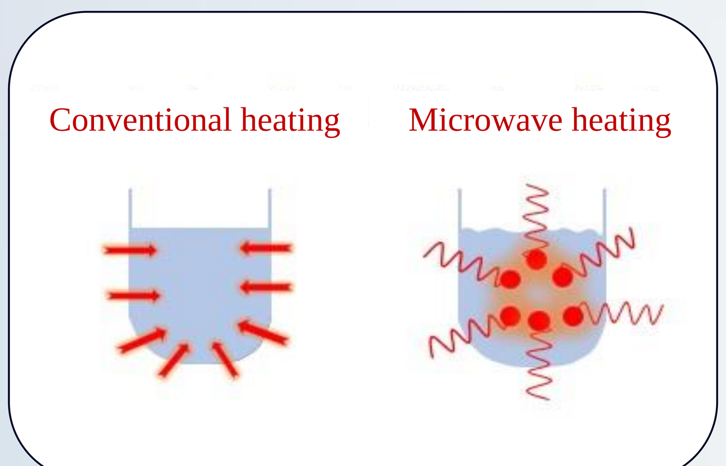
[2]Sveučilište u Zagrebu Fakultet kemijskog inženjerstva i tehnologije, Trg Marka Marulića 19, 10000 Zagreb

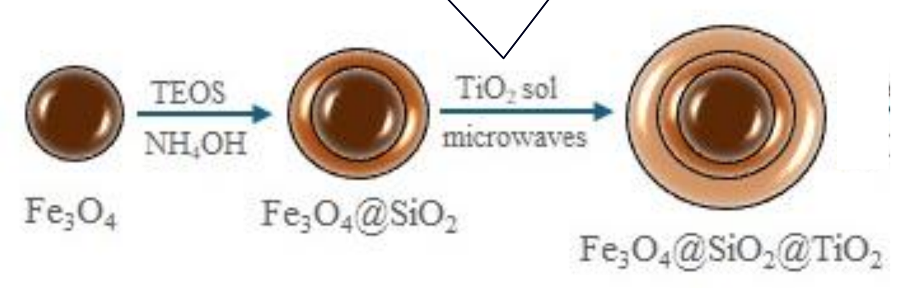
ABSTRACT

In recent decades, pharmaceutically active compounds have been recognized as emerging pollutants because of their continuous release and persistence in the aquatic environment, even at low concentrations. Therefore, extensive research has been done into developing effective removal strategies. One of them is photocatalytic degradation, as a part of advanced oxidation processes (AOP). The main drawback of commercial photocatalysts is their separation from the solution. For this purpose, a magnetic nanostructured core-shell photocatalyst with a molecular imprint of sulfamethoxazole was prepared via microwave-assisted synthesis. The magnetite core was coated with a protective layer of SiO_2 and a photocatalytic layer of molecularly imprinted TiO_2. Microwave radiation enables fast and uniform heating rate, rapid nucleation and growth of particles, shortens reaction time and enables energy savings, while the magnetite core enables easy separation by an external magnet as well as the posibility for reuse. The molecularly imprinted TiO_2 layer possess specific cavities designed for the target molecule (imprint) that will improve the efficiency of the extraction process, thus creating an synergystic effect of photocatalysis and extraction.

MATERIALS AND METHODS

- The synthesis of magnetic nanostructured core-shell photocatalyst was conducted via microwave heating. The heating of the sample in the microwave reactor is ensured from the inside to the outside without heating the surrounding elements, which ensures uniform heating, in contrast to conventional heating where the heating is done from the outside to the inside.
- TiO_2 sol was prepared prior to synthesis according to previous work with molar ratio: TIP:PrOH:AcAc:HN = 1:35:0.63:0.015





MAGNETIC NANOSTRUCTURED CORE-SHELL PHOTOCATALYST

- Persistence in the aquatic environment
- Difficulty separating the photocatalyst from the solution after photocatalysis

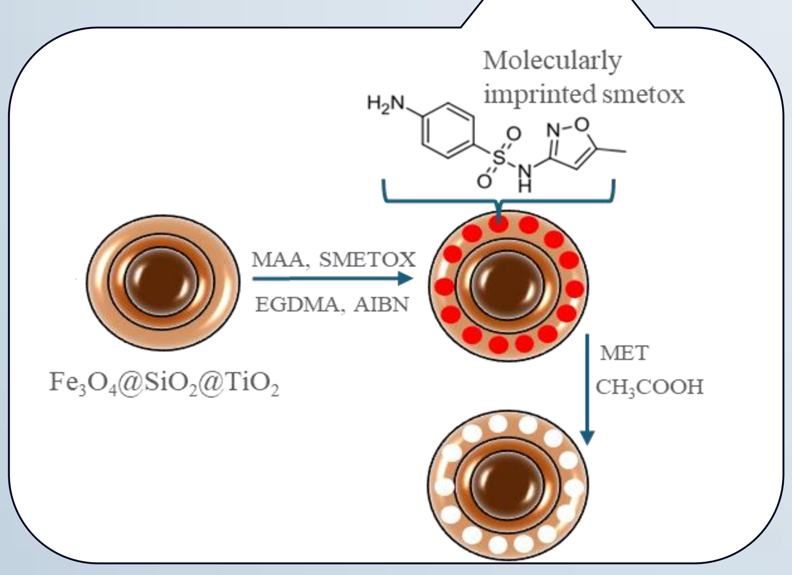
PHARMACEUTICALLY ACTIVE COMPOUNDS

- Easy separation by external magnet
- Posibility of reuse
- Synthesis time shortened, energy savings, higher yields

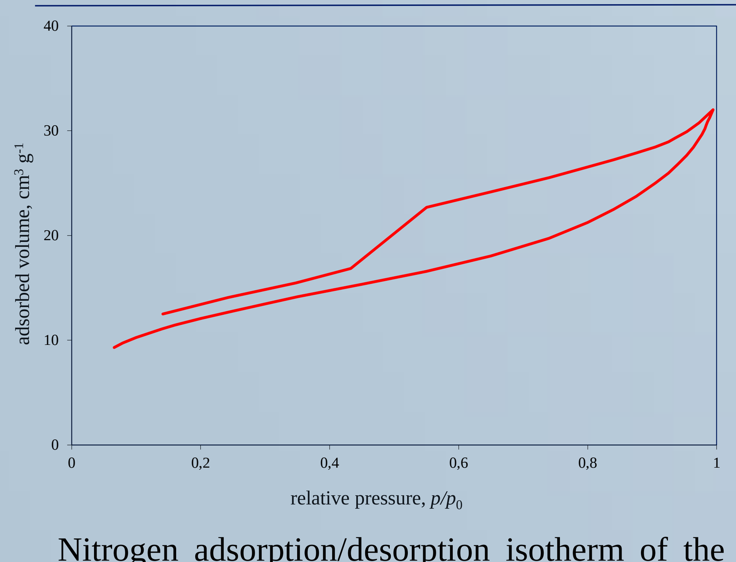
- Improving the efficiency of the extraction process
- Synergystic effect of photocatalysis and extraction

MOLECULARLY IMPRINTED PHOTOCATALYST

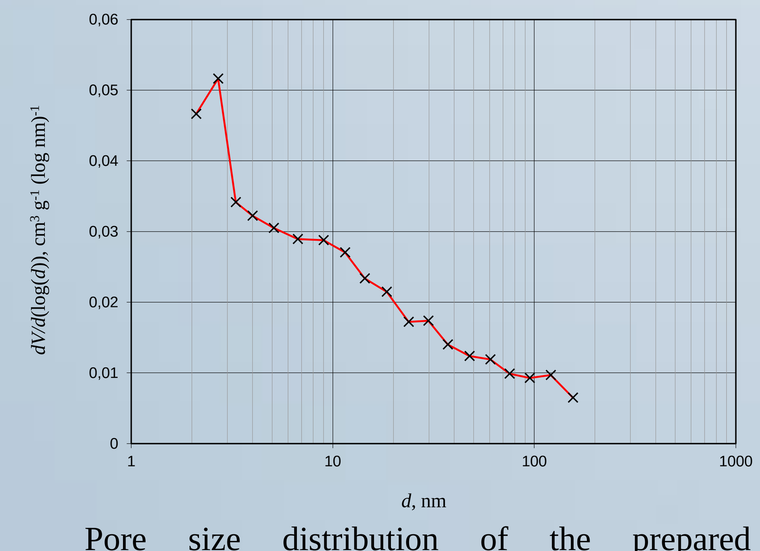
- The core-shell nanoparticles were added to the polimerization mixture containing the pollutant (sulfamethoxazole), functional monomer (methacrylic acid), crosslinker (EGDMA) and iniciator (AIBN)
- The suspension was placed in the microwave reactor
- The obtained particles were collected by centrifugation, the template was removed by washing with methanol containing 10% acetic acid (V/V), until no template could be detected from the solvent using UV spectrometric measurement



CHARACTERIZATION



Nitrogen adsorption/desorption isotherm of the prepared molecularly imprinted core-shell photocatalyst



Pore size distribution of the prepared molecularly imprinted core-shell photocatalyst

Specific surface area, S_{BET}, $m^2\ g^{-1}$	Average pore diameter, $d_{average}$, nm
44.1	4.3

HRZZ Croatian Science Foundation

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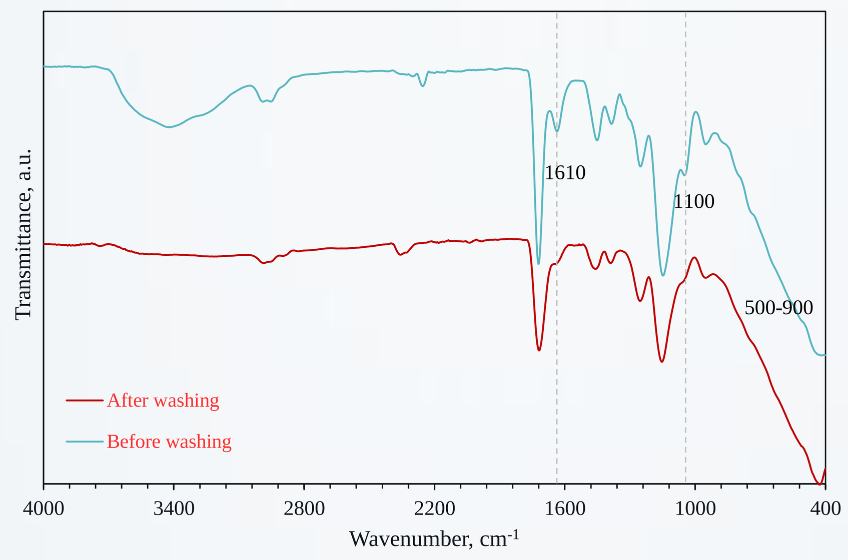
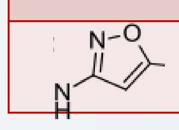
CHARACTERIZATION

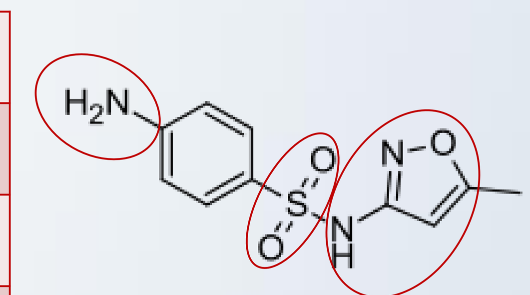


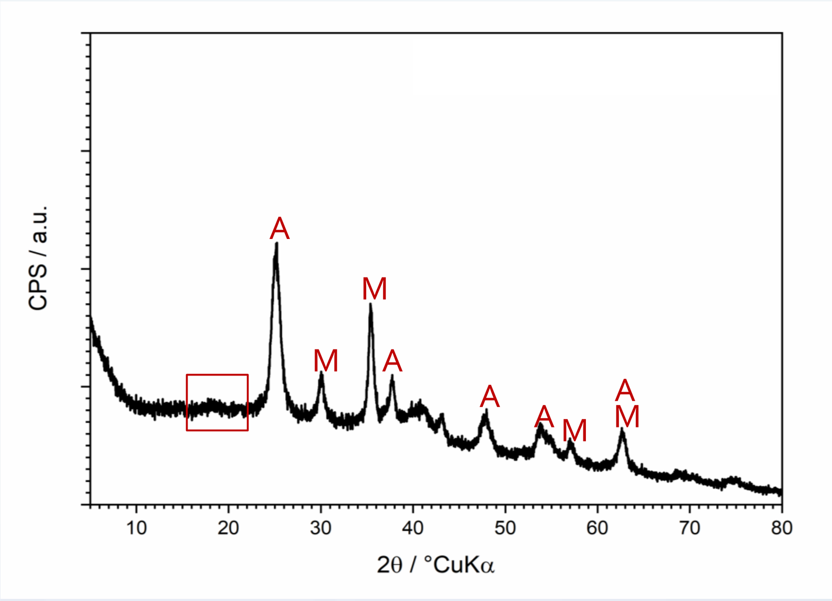
FTIR spectra of the prepared molecularly imprinted core-shell photocatalyst

- The absence of bands characteristic for sulfamethoxazole indicates that the template was succesfully washed

Characteristic bands of the prepared molecularly imprinted core-shell photocatalyst

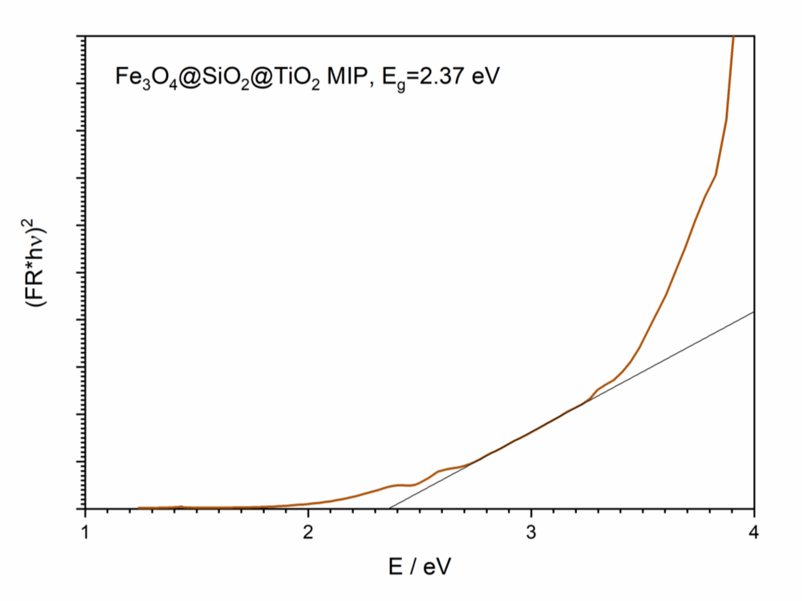
Ti-O-Ti	500-900
Fe-O	550
Si-OH	950
O=S=O	1100
C=N	1610
$-NH_2$	3300
	3200-3500





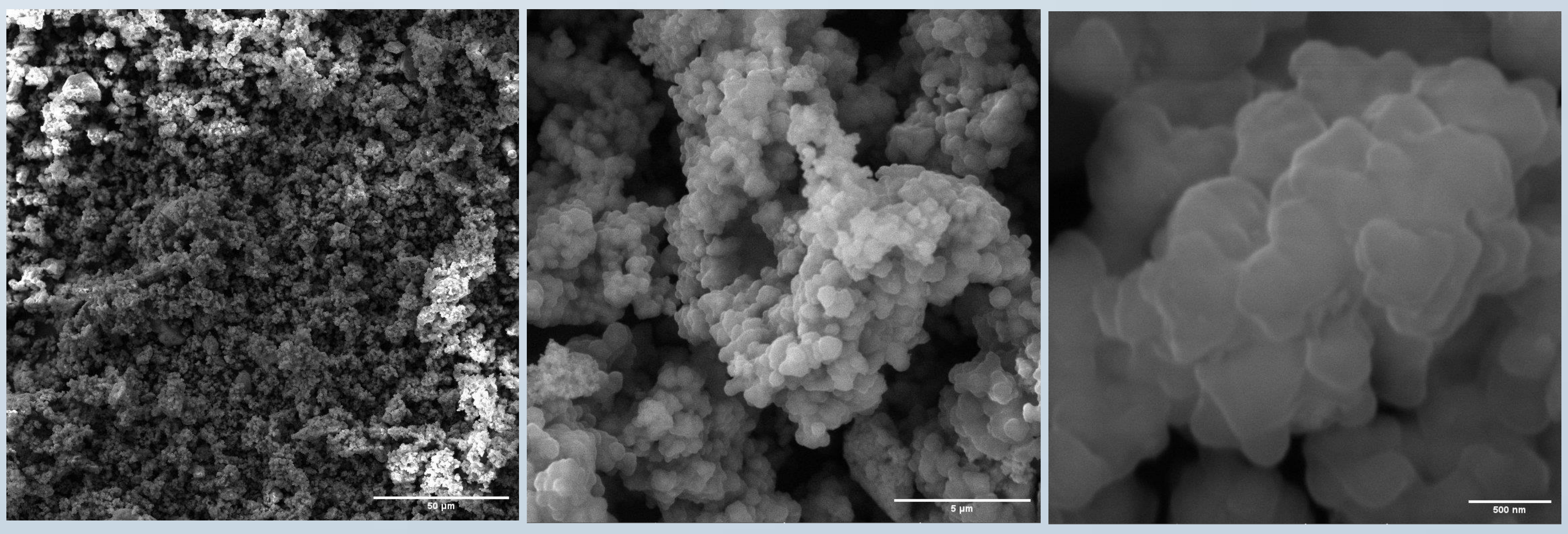
Diffractogram of the prepared molecularly imprinted core-shell photocatalyst

- The XRD analysis showed anatase as the main phase (ICDD PDF#21-1272)(marked with A) and magnetite as minor phase (Fe_3O_4) (ICDD PDF#19-0629) (marked with M)
- A barely visible hump centered around 2θ of 26° characteristic of amorphous silica was evidenced, confirming the presence of the SiO_2 phase (highlighted with red square)



Diffuse reflectance spectroscopy of the prepared molecularly imprinted core-shell photocatalyst

- Bandgap was determined by the slope of the Taucs plot which was obtained from the data and is shown on the graph



SEM images with different magnifications of the prepared molecularly imprinted core-shell photocatalyst

CONCLUSIONS

- Based on the characterization presented results, it can be concluded that a molecularly imprinted core-shell photocatalyst was succesfully synthesized via microwave-assisted synthesis
- The obtained particles have a 44.1 $m^2\ g^{-1}$ specific surface area and an average pore diameter 4.3 nm
- Bandgap was determined by diffuse reflectance spectroscopy and amounts 2.37 eV
- FTIR spectra confirmed the presence of characteristic bands for $Fe_3O_4@SiO_2@TiO_2$ as well as the absence of bands characteristic for sulfamethoxazole which indicates that the template was succesfully washed
- XRD analysis confirmed anatase as the main crystalline phase, magnetite as the minor crystaline phase and traces of amorphous silica
- SEM images showed microporous structure which can enhance photocatalytic activity, as well as round shaped particles which can indicate core-shell structure of the obtaines photocatalyst