
# Synthesis of magnetic biochar for utilization in Fenton based process

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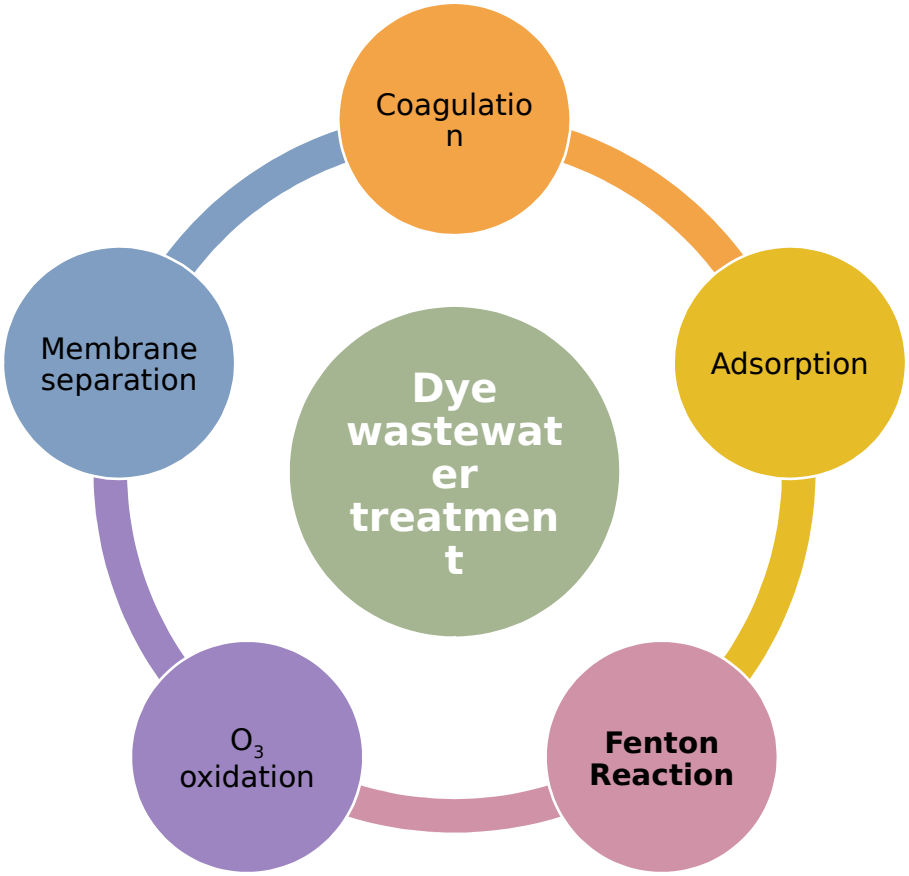
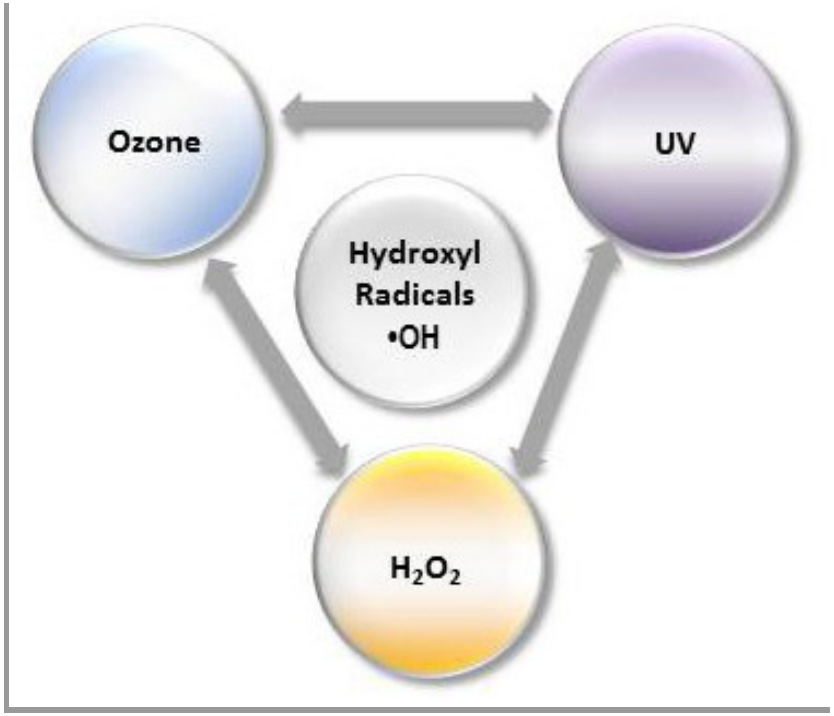
# Dye wastewater treatment

- Used in the textile, cosmetic, pharmaceutical and food industries
- High volumes of wastewater during  operation
- Complex structure, resistant to biodegradation



# Advanced Oxidation Process




- Based on chemical oxidation by forming very reactive species such as **hydroxyl radicals (·OH)**
- Degrades organic pollutants completely to harmless chemicals, mainly $CO_2$ and $H_2O$
- Feasible option for biologically persistent wastewater
- Widely recognized as highly efficient treatments for recalcitrant wastewater

# Fenton Process

- The chemical oxidation of organic compounds by $H_2O_2$ using **Fe ions** as a catalyst

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OH_2^{\bullet}$$

Particularly attractive because of

- the low costs
- the lack of toxicity of the reagents
- the simplicity of the technology

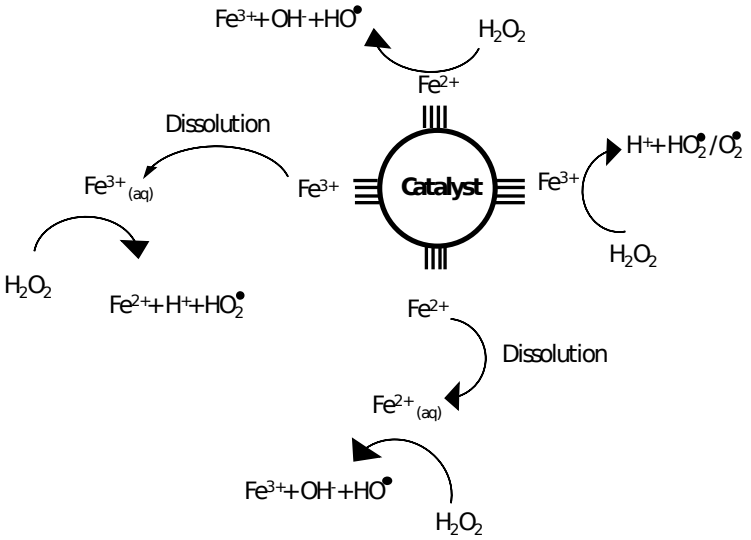
# Fenton Process

Disadvantages of homogeneous catalysis

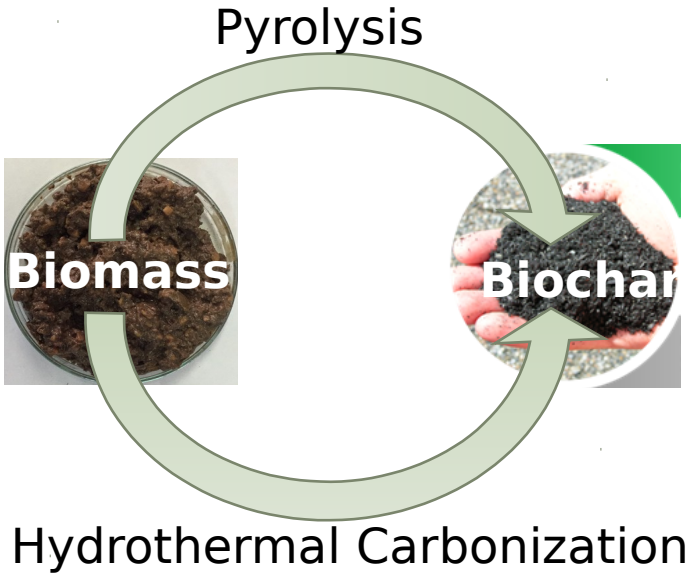
- 50–80ppm of ions needed in solution
  - *above* environmental regulations to dump directly into the environment => [Fe]max =2 ppm
  - the removal/treatment of the sludge-containing metal ions at the end of treatment
- Not recyclable

Pure Metal oxides; poor stability, inert activity, etc.

**Heterogeneous catalyst**



# Biochar

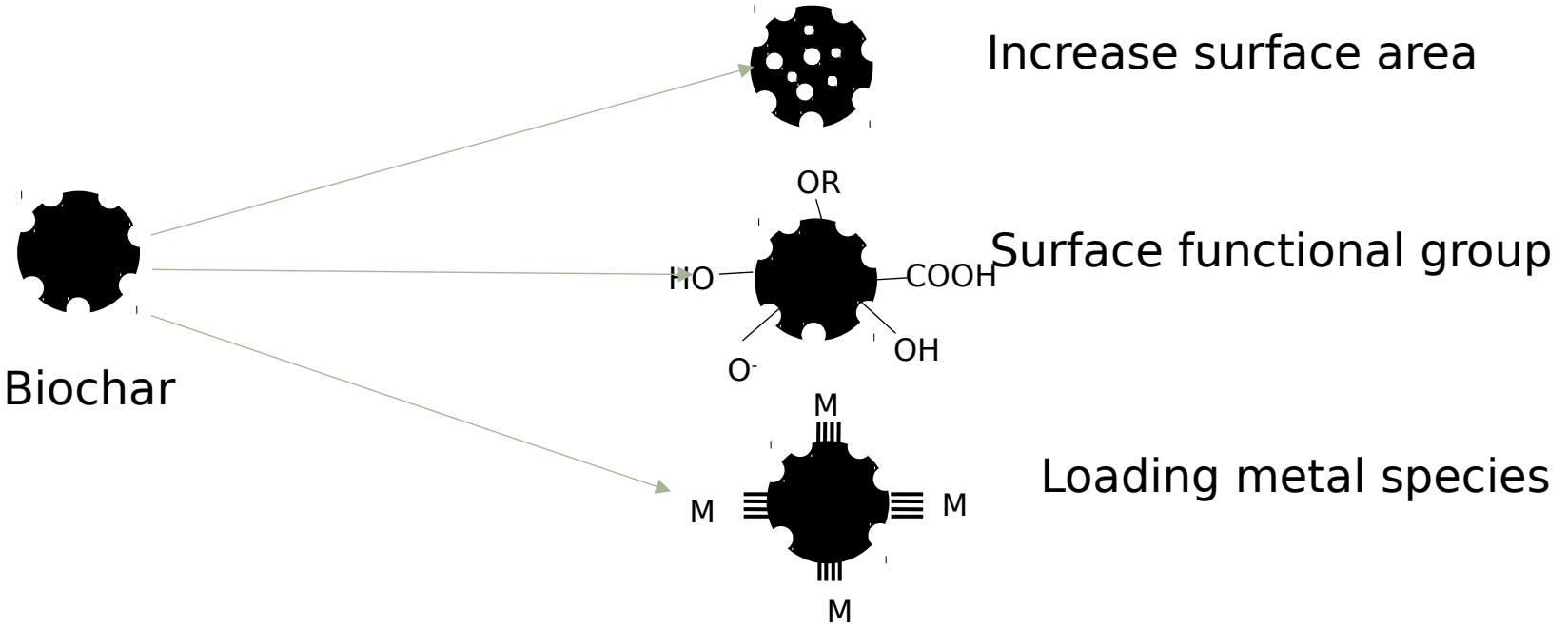



Biochar for wastewater treatment

-Adsorbent

- support for oxidation catalyst

**Modification/activation**



# PURPOSE

**Decolorization of wastewater containing methylene blue via Fenton process in presence of Fe doped biochar**


- Synthesis and characterization of Fe loaded biochars
- Catalyst screening
- Parametric study on Methylene blue removal

# ANALYSIS

## termination of Methylene blue (MB) removal

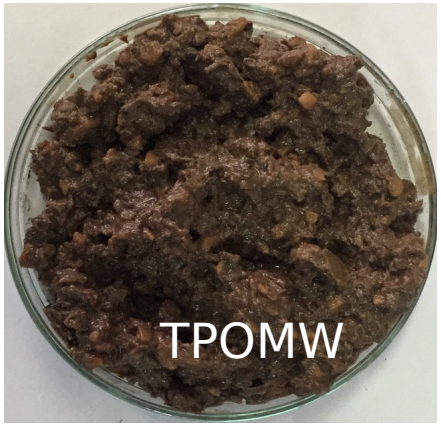
- Performed by measuring the absorbance of the methylene blue concentration at the maximum absorbance wavelength of each compound in a UV/VIS Spectrophotometer ( Varian Cary 100 Bio)
- The wavelengths λ =664 nm for MB,
- Removal efficiency (de-colorization) was calculated by

$$\text{MB Removal}(\%) = \frac{m_0 - m_f}{m_0} \times 100$$

where $m_0$ and $m_f$ were initial and final concentration of MB

# MATERIALS AND METHODS

**Biomass:** Two phase olive mill waste(TP)




**Fe source**:

-$FeSO_4$(Fe),

-Red Mud (RM): Fe rich ( containing 38% $Fe_2O_3$) waste sludge from aluminum company

-Acidified Red Mud (ARM): Dissolved in 10 % HCl solution

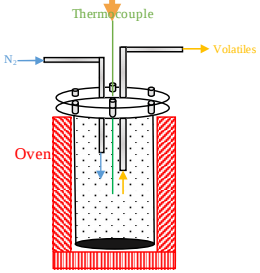
Properties of TPOMW, %

| | |
|---|---|
| Moisture | 66.4 |
| *Proximate analysis, wt % (db)* | |
| Ash | 3.8 |
| Volatile matter | 68.5 |
| Fixed carbon | 27.7 |
| *Ultimate analysis, wt % (db)* | |
| *C* | 51.47 |
| *H* | 7.02 |
| *N* | 1.09 |
| *S* | 0.13 |
| *O* | 36.51 |

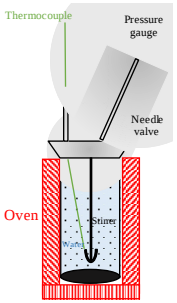
# MATERIALS AND METHODS

$TP_{dry}$ + Fe source in solution

mpregnation in oven
at 110 °C overnight




**Pyrolysis** at 500
nd 700 °C for 1 hour




**Hydrothermal carbonization (HTC)**
at 220 °C for 1 hour

Filtrated,washed and
dried in oven
at 110 °C overnight

| | | |
|---|---|---|
| | Pyrolysis | 60.2 |
| | Pyrolysis | 55.7 |
| | HTC | 49.6 |
| | Pyrolysis | 68.9 |
| | Pyrolysis | 57.2 |
| | HTC | 81.7 |
| | Pyrolysis | 72.0 |
| | Pyrolysis | 61.3 |

***Magnetic properties***

**based on initial biomass amount

# MATERIALS AND METHODS

## enton Reaction Experiments

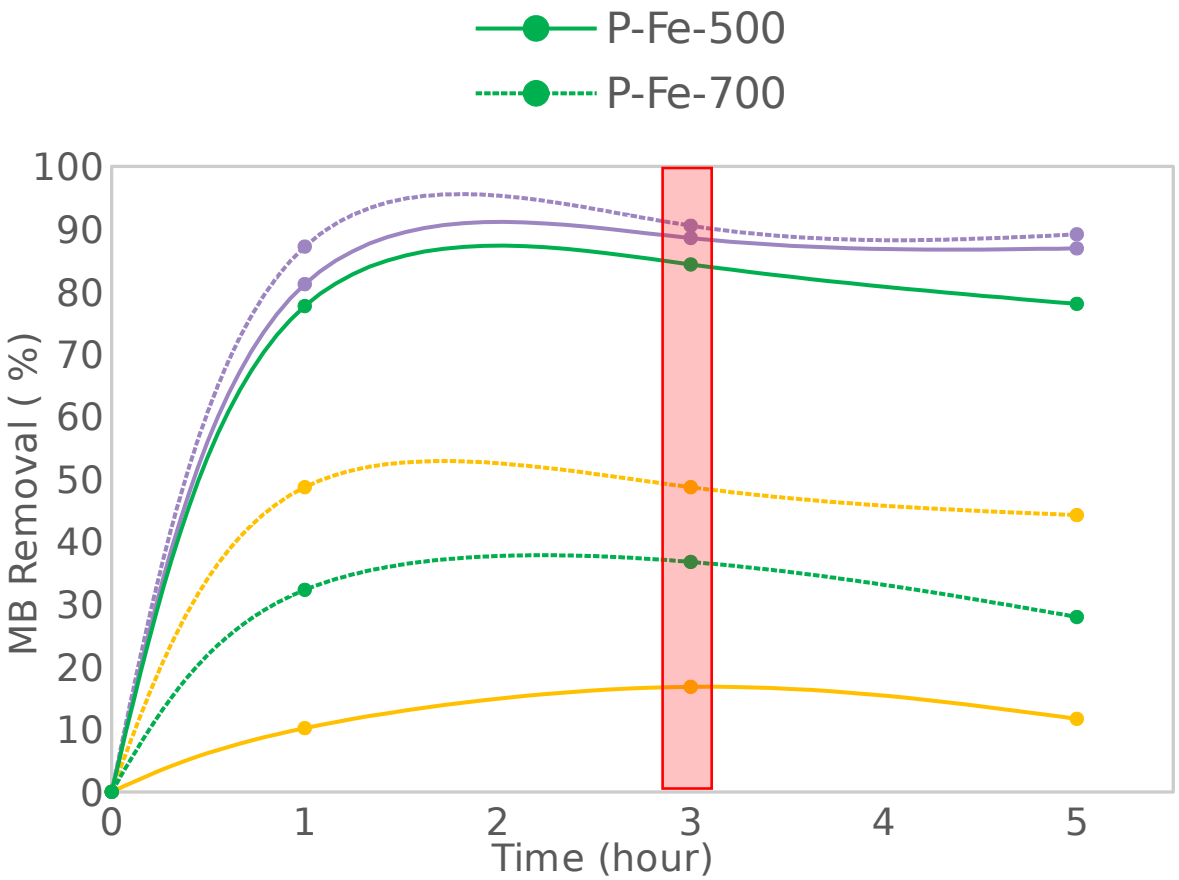
Batch experiments

- 250 ml erlenmayer flask
- 150 rpm shaking

**Tested parameters**

- Catalyst type
- Day light and under dark
- Concentration of $H_2O_2$
- pH
- MB concentration

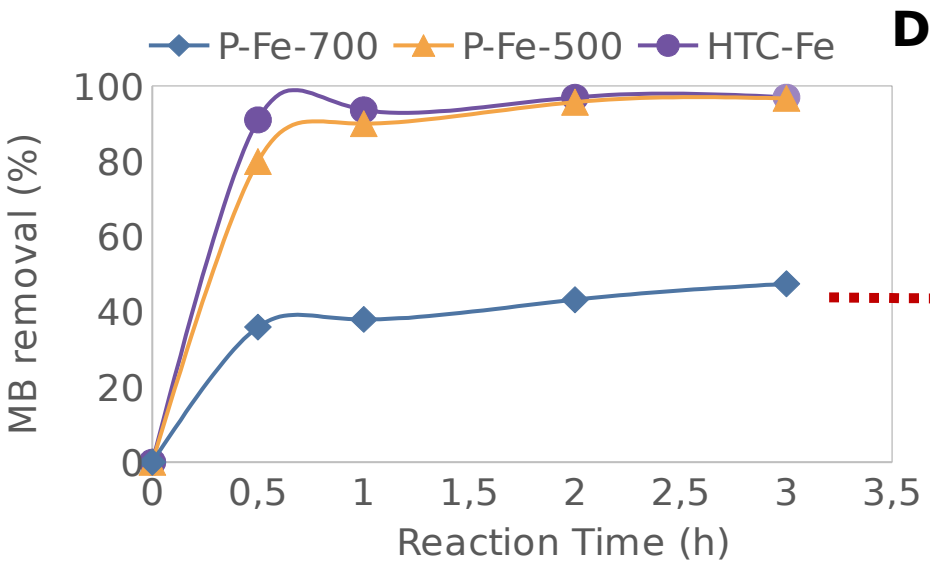
# RESULTS-Comparison of Fe source

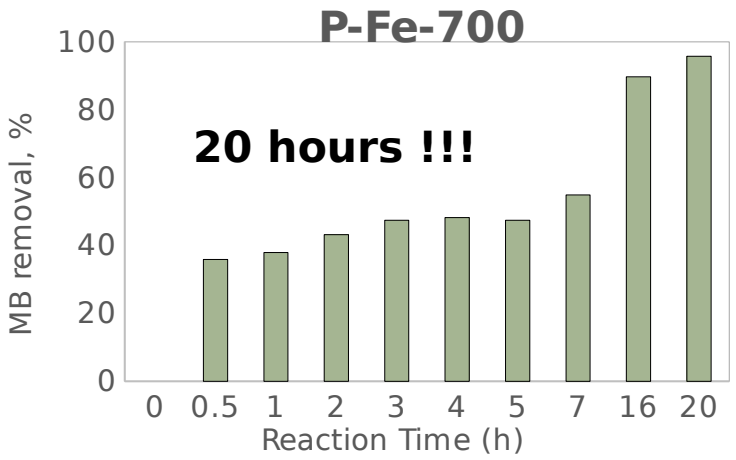


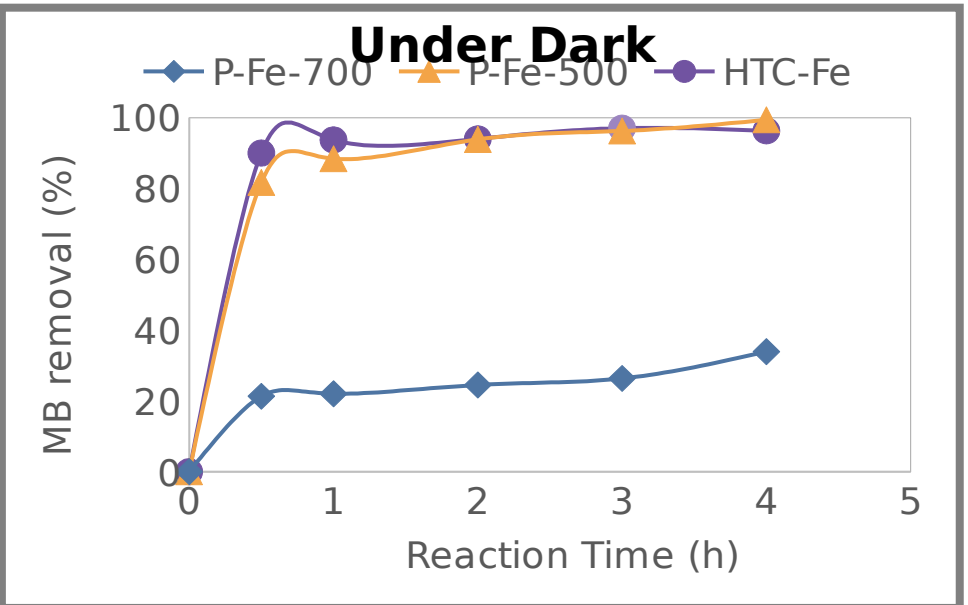

- RM based biochars had low activity.
- The use of ARM instead of RM improved the removal of MB.
- Pyrolysis temperature for Fe based biochars had significant effect.

Conditions: 100 ppm MB, 10 mM $H_2O_2$, daylight, 150 rpm shaker, pH was adjusted to 3

# RESULTS- $FeSO_4$ based catalyst

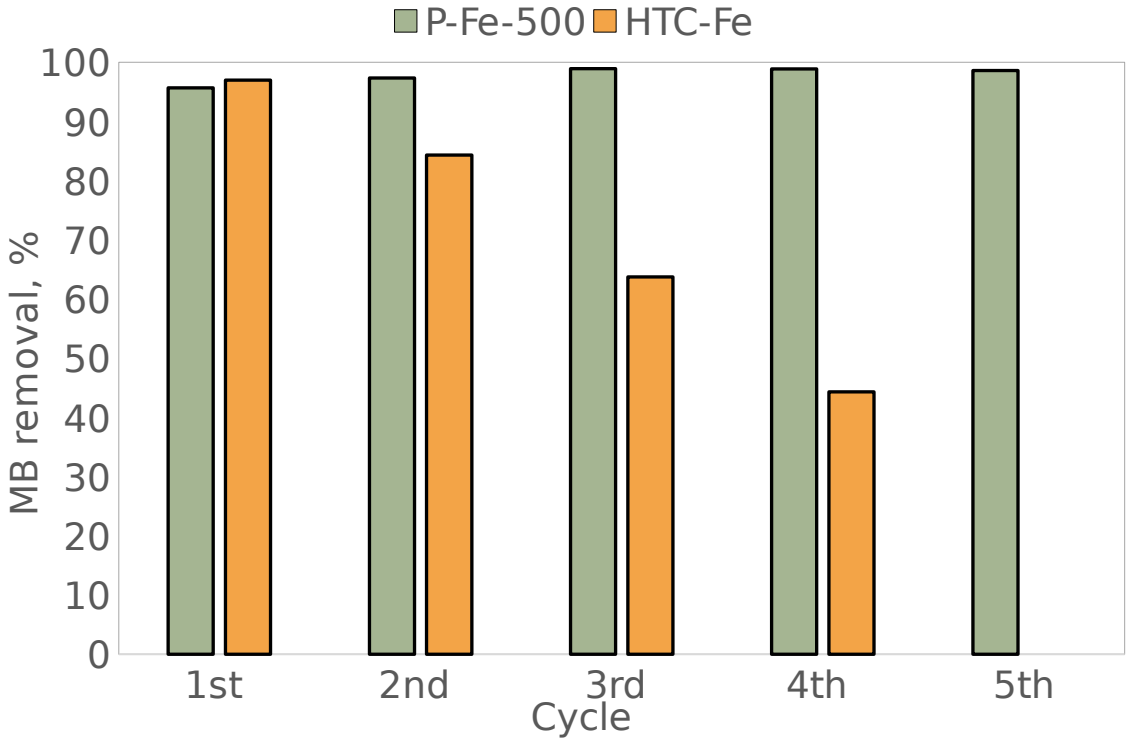


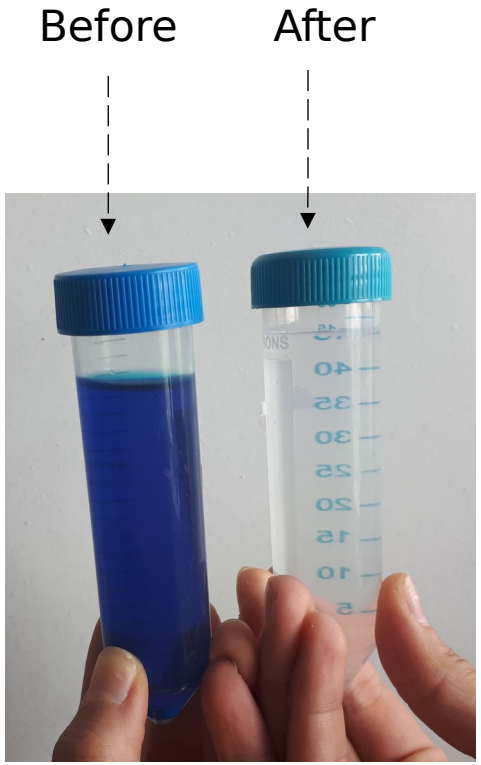




| Fe content of effluent water, ppb | |
|---|---|
| P-Fe-500 | 128 |
| P-Fe-700 | 4 |
| HTC-Fe | 357 |

# RESULTS- Cyclic usage of catalyst




Fenton oxidation with P-Fe-500




- No activity losses in case of P-Fe-500 after 5 cycle.

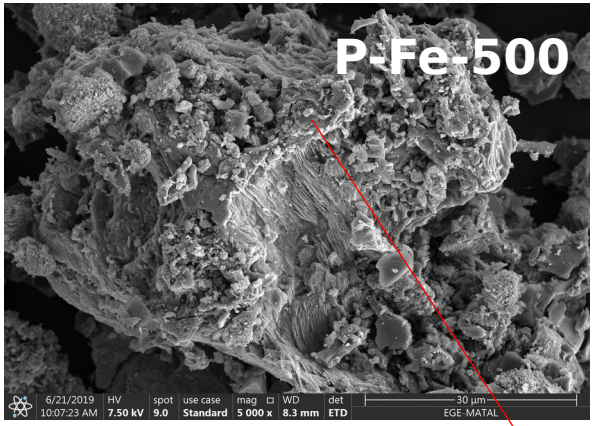
Conditions: 50 ppm MB, 10 mM $H_2O_2$, daylight, 150 rpm shaker, no pH adjustment ( ~3.5)

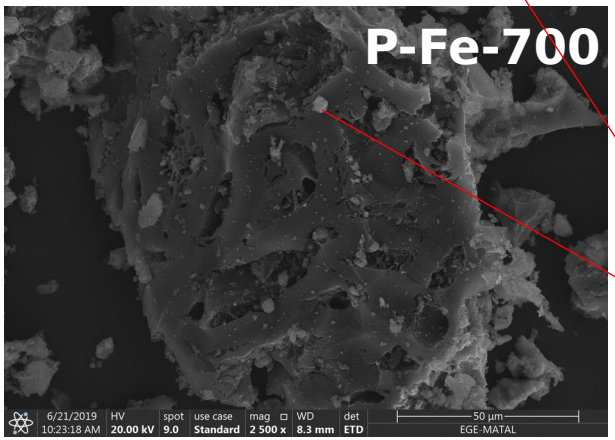
# RESULTS- $FeSO_4$ based catalyst

## Inorganic content, %

| | P-Fe-500 | P-Fe-700 | HTC-Fe |
|---|---|---|---|
| **Fe** | 22.02 | 25.86 | 1.35 |
| **Al** | 0.06 | 0.07 | 0.07 |
| **Si** | - | 0.02 | 0.03 |
| **Mg** | 0.09 | 0.11 | - |
| **Na** | 0.29 | 0.32 | 0.12 |
| **Ca** | 0.27 | 0.32 | 0.09 |
| **K** | 3.22 | 4.01 | 0.11 |

## SEM images



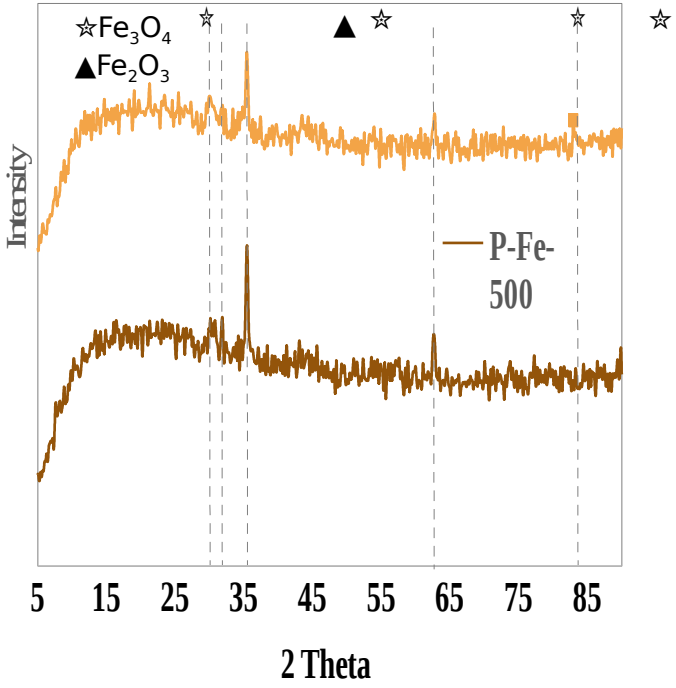



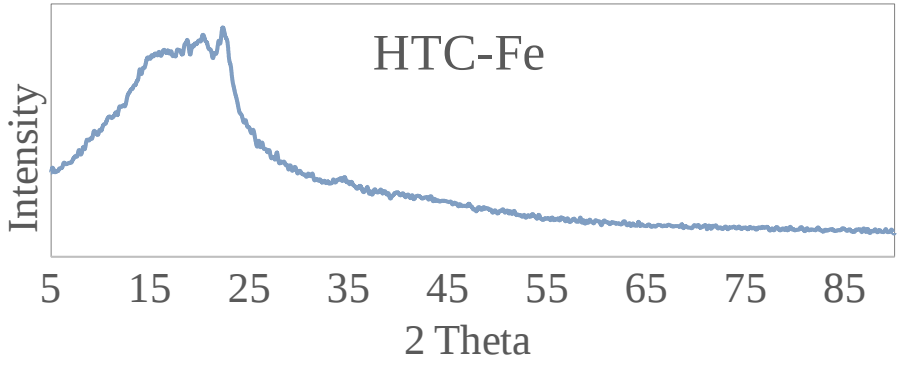

Iron particles

- Loading of Fe failed by hydrothermal carbonization

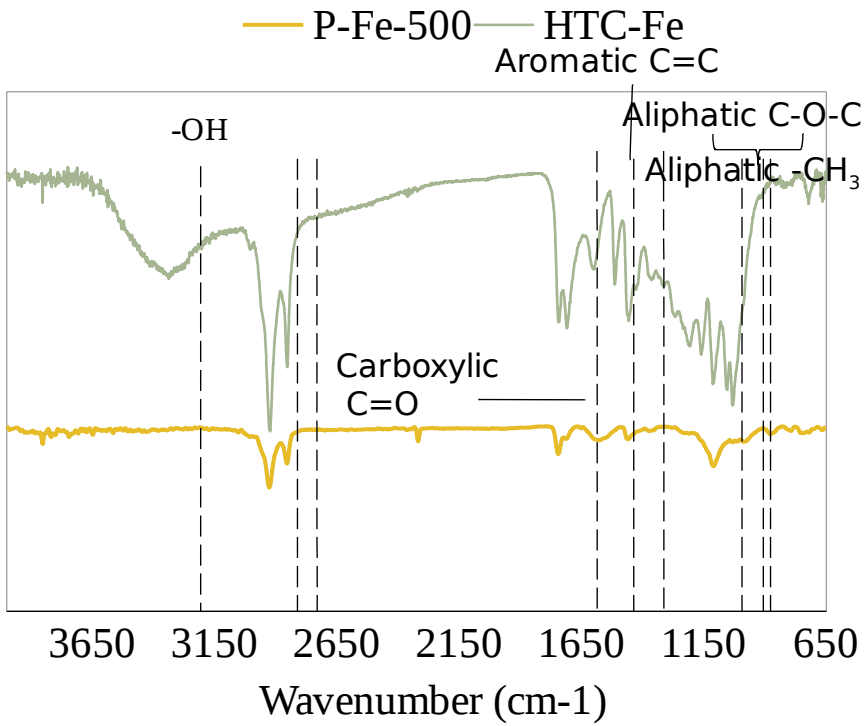
# RESULTS- $FeSO_4$ based catalyst

## XRD pattern



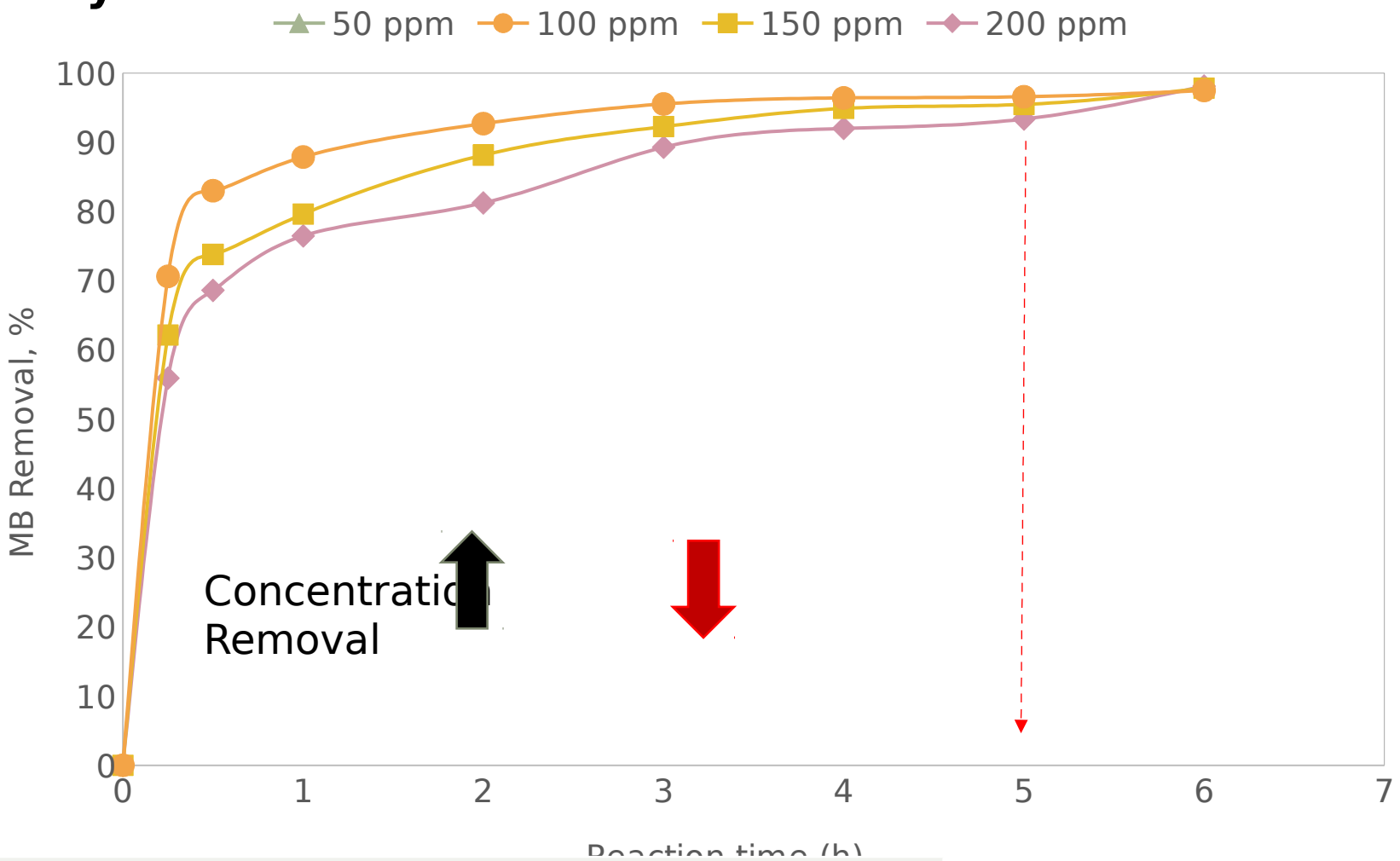

## FTIR spectrum



# RESULTS- Parametric study

**MB concentration: 50, 100, 150 and 200 ppm**

**Catalyst**: P-Fe-500

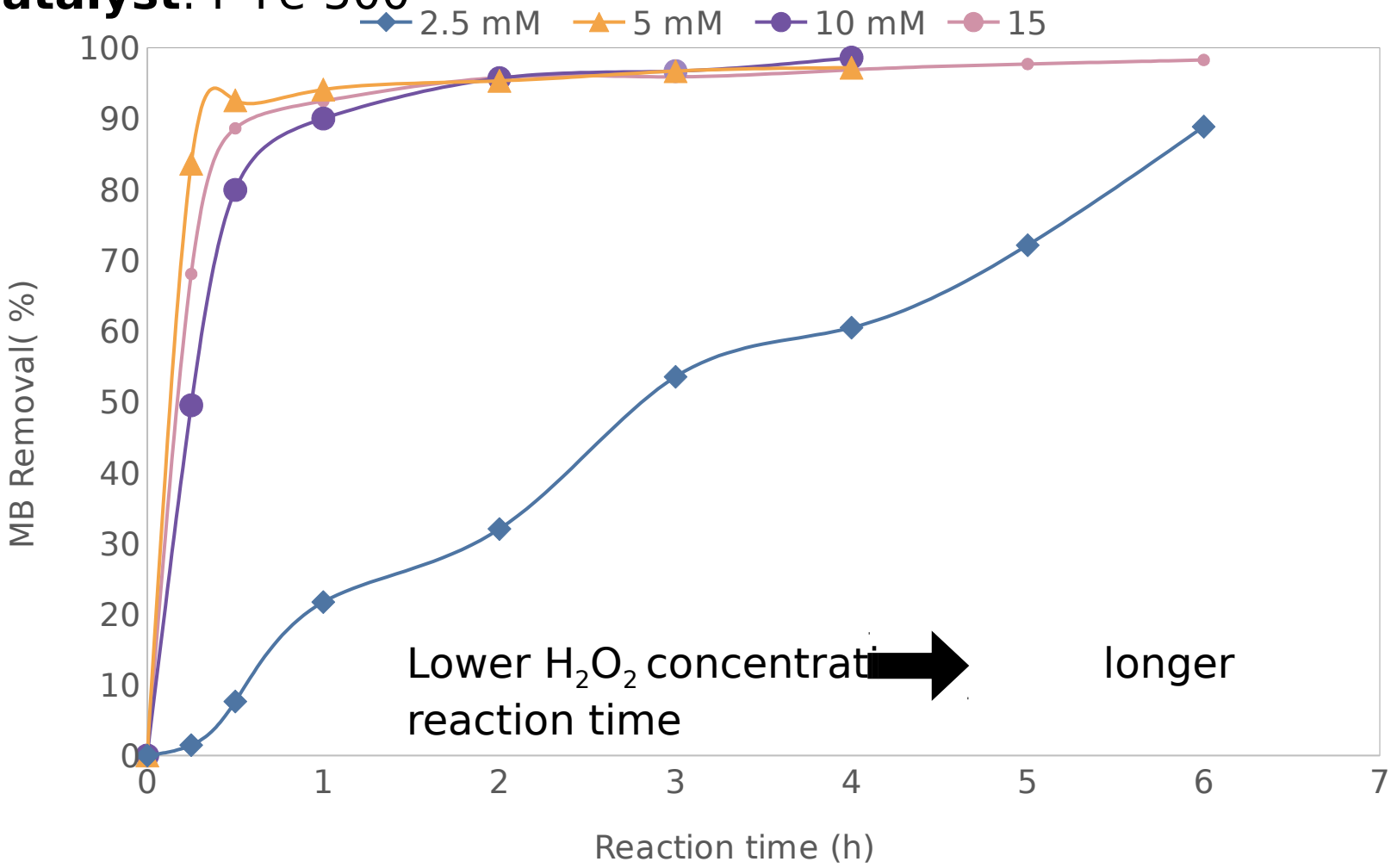



Conditions: 10 mM $H_2O_2$, daylight, 150 rpm shaker, no pH adjustment ( ~3.5)

# RESULTS- Parametric study

**Initial $H_2O_2$ concentration: 2.5, 5, 10 and 15 m M**

**Catalyst**: P-Fe-500

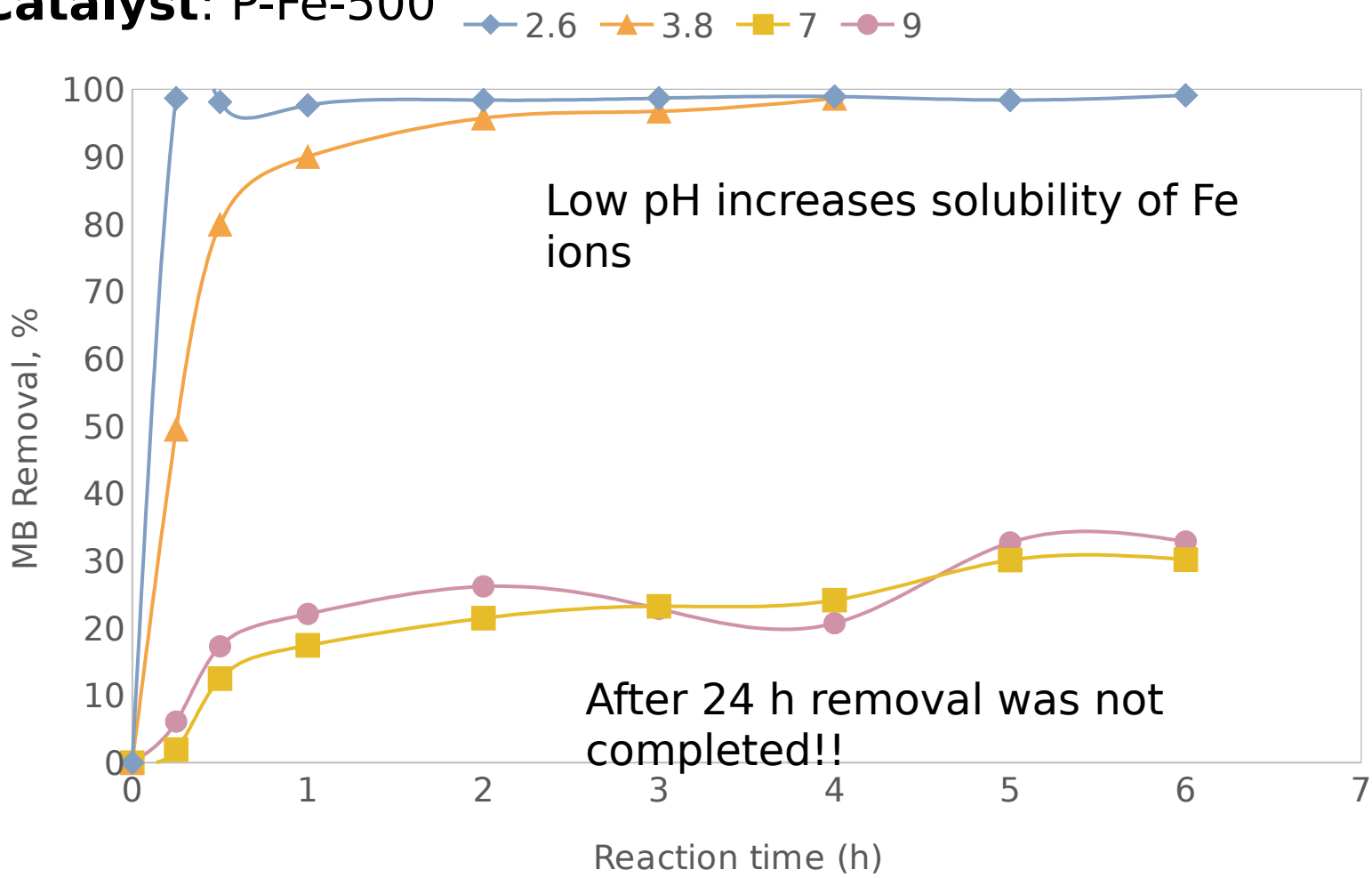



Conditions: 50 ppm MB, daylight, 150 rpm shaker, no pH adjustment ( ~3.5)

# RESULTS- Parametric study

**pH: 2.5, 3.6 (natural pH of MB), 7 and 9**

**Catalyst**: P-Fe-500




Conditions: 50 ppm MB, 10mM $H_2O_2$ concentration, daylight, 150 rpm shaker,

# Conclusion

-Fenton oxidation of MB was achieved with the catalysts prepared by TP.

-Release of Fe faciliates degradation of MB.

-P-Fe-500 had the highest activity stability in 5 cycles. Fe concentration in effluent water is acceptable for direct dumping.

-pH is most effective parameter, which affect the solubility of Fe in wastewater.

-Biochars obtained by pyrolysis showed magnetic properties whereas magnetic biochar could not produced by HTC.

-Biochar obtained from pyrolysis at lower temperature showed higher activity than that at higher temperatures.

- ❖ Ongoing studies focus on red mud to produce effective and stable catalyst,

  independent from different pH.

- ❖ In future work, different pollutants can be tested in their natural pH.

# THANK YOU FOR LISTENING…

Special Thanks…

- PhD candidate Gulen Tekin
- Dr. Dogan Tac
- Dr. Raif Ilkac
- Berkay Leskeri