Preparation, structural and photocatalytic characterization of a synthetic kaolinite and its nanocomposites

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Abstract:

Clay minerals are natural, abundant and widely used industrial raw materials. Kaolinite is a 1:1 type, layered phylloaluminosilicate, constituted by Si^{4+}-centered tetrahedral (T) and Al^{3+}-centered octahedral (O) layers. Kaolinite has a strong potential as innovative, environmental-friendly photocatalyst, due to its not yet understood photocatalytic activity. Photocatalytic investigations require clean samples, free of mineral contaminants. Natural kaolinite is obtained through mining of kaolin. The mineral composition and varying properties of kaolin significantly influence their catalytic activity, and therefore pose an adverse impact on their catalytic investigations. Laboratory synthesis of kaolinite offers a way to obtain kaolinite with the desired properties and purity.

In the present work, the laboratory synthesis and evaluation of a synthetic kaolinite and its TiO_2 nanocomposites are reported. The hydrothermal synthesis method was chosen to minimize pollutants. The effect of the applied acid concentration and liquid phase ratio were investigated. The synthesized kaolinites were characterized by XRD, FTIR-ATR, TG/DTG/DTA. The mineral composition, the presence and crystallinity (Hinckley, Stoch, Range-Weiss indices) of kaolinite were determined by XRD. Fourier transform infrared spectroscopy was utilized to identify kaolinite vibrations. Thermal stability, mineral purity and dehydroxilation was determined by TG/DTG/DTA. The morphology and elemental composition maps of the best sample was investigated by TEM-EDX.

Sol-gel method and thermal treatment were used to prepare synthetic kaolinite-TiO_2 nanocomposites with varying surface concentrations of TiO_2. The composites were characterized by XRD and FTIR-ATR.

The photocatalytic activity of the samples were investigated by the aqueous degradation of an oxalic acid test compound upon 365nm UV irradiation.

Keywords: Synthetic kaolinite; hydrothermal synthesis; structural characterization; synthetic kaolinite-TiO_2 nanocomposite; photocatalytic activity

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Synthesis of synthetic kaolinite and its TiO_2 composite

Hydrothermal synthesis procedure was selected;

kaolinite formation proceeds via boehmite transformation

$$2\ Al(OH)_3 \rightarrow 2\ AlO(OH) + 2\ H_2O$$

$$2\ AlO(OH) + 2\ SiO_2 + 2\ H_2O \rightarrow Al_2Si_2O_5(OH)_4 + H_2O$$

The effects of HCl concentration and reagent (solid-liquid) ratio is investigated

Synthetic kaolinite-TiO_2 composites were formed via sol-gel synthesis of $Ti(OH)_4$ and subsequent thermal treatment

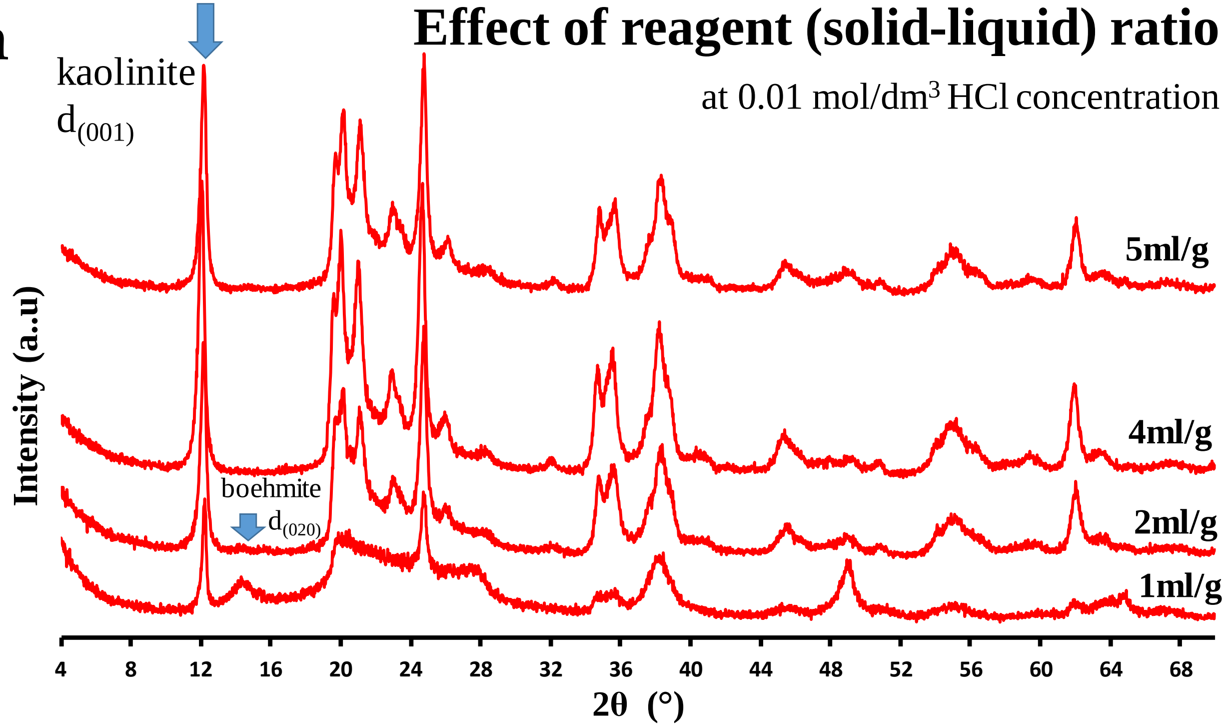
$$Ti(OH)_4 \rightarrow TiO_2 + 2\ H_2O$$

Results and Discussion (XRD)

Boehmite-Kaolinite transformation rate affected by reaction parameters

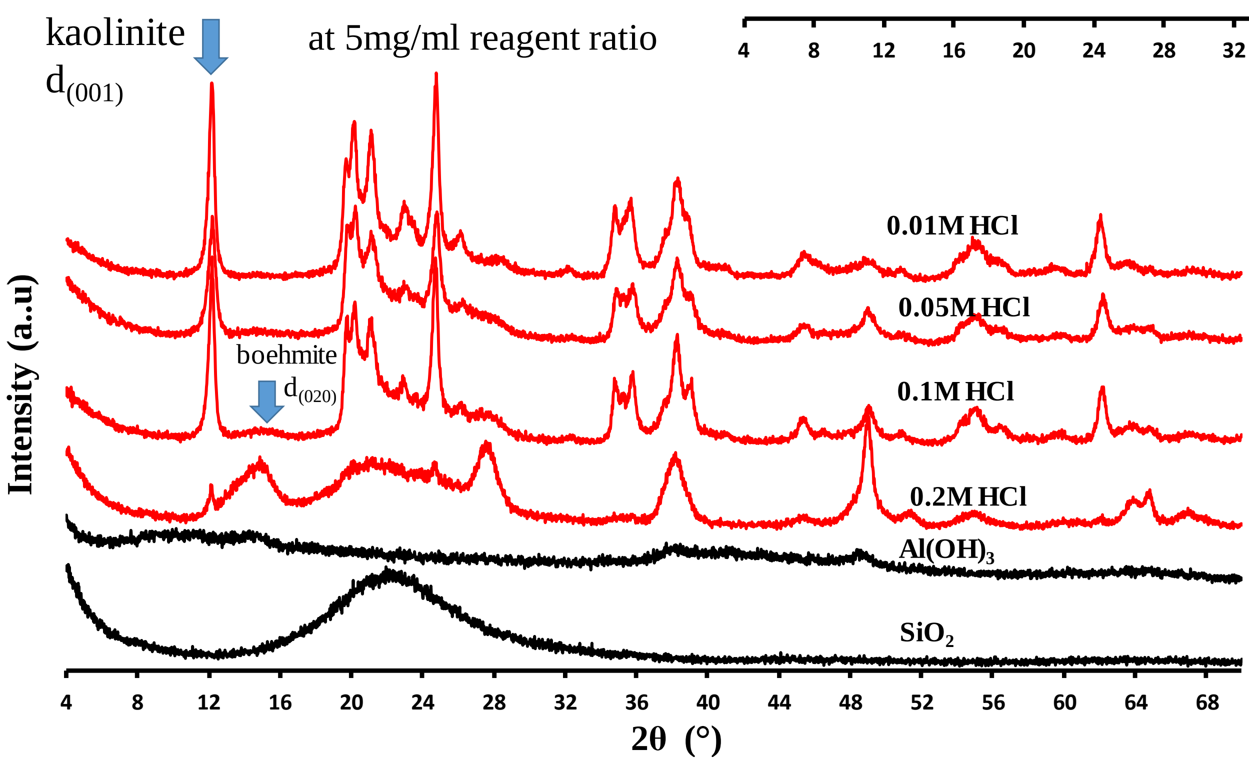
Effect of reagent (solid-liquid) ratio

at 0.01 mol/dm^3 HCl concentration



Effect of HCl concentration

at 5mg/ml reagent ratio



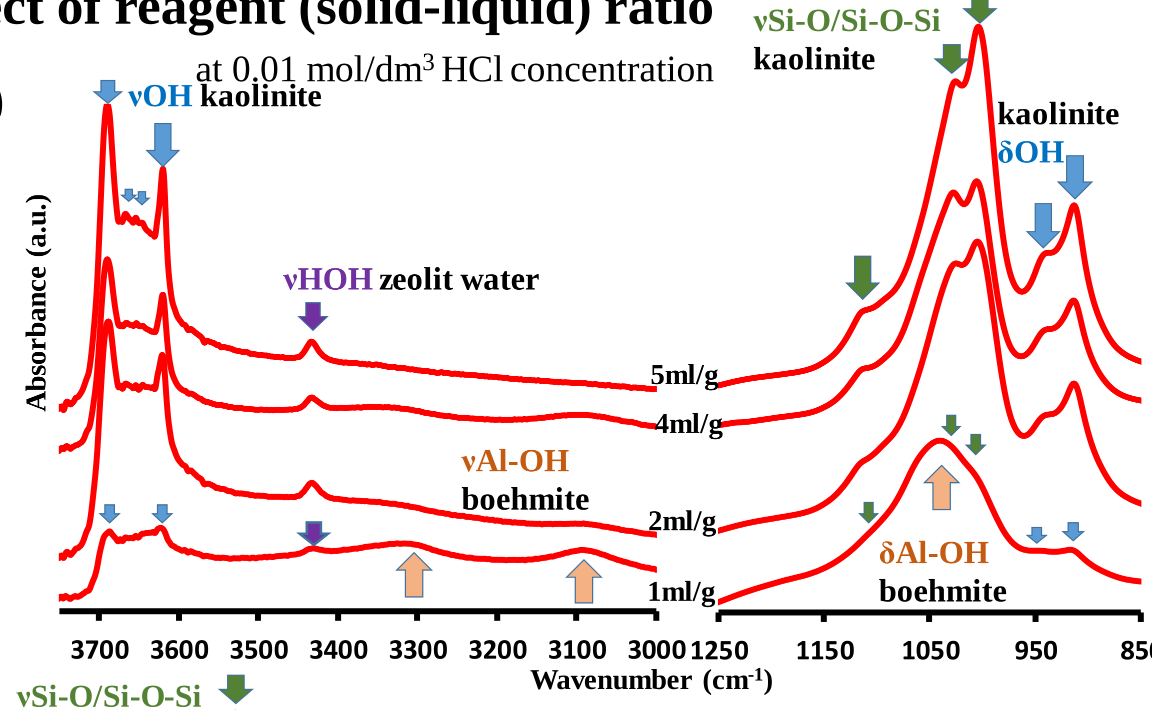
Crystallized kaolinite reflections are well identifiable

Results and Discussion (FTIR-ATR)

Boehmite-kaolinite transformation rate affected by reaction parameters

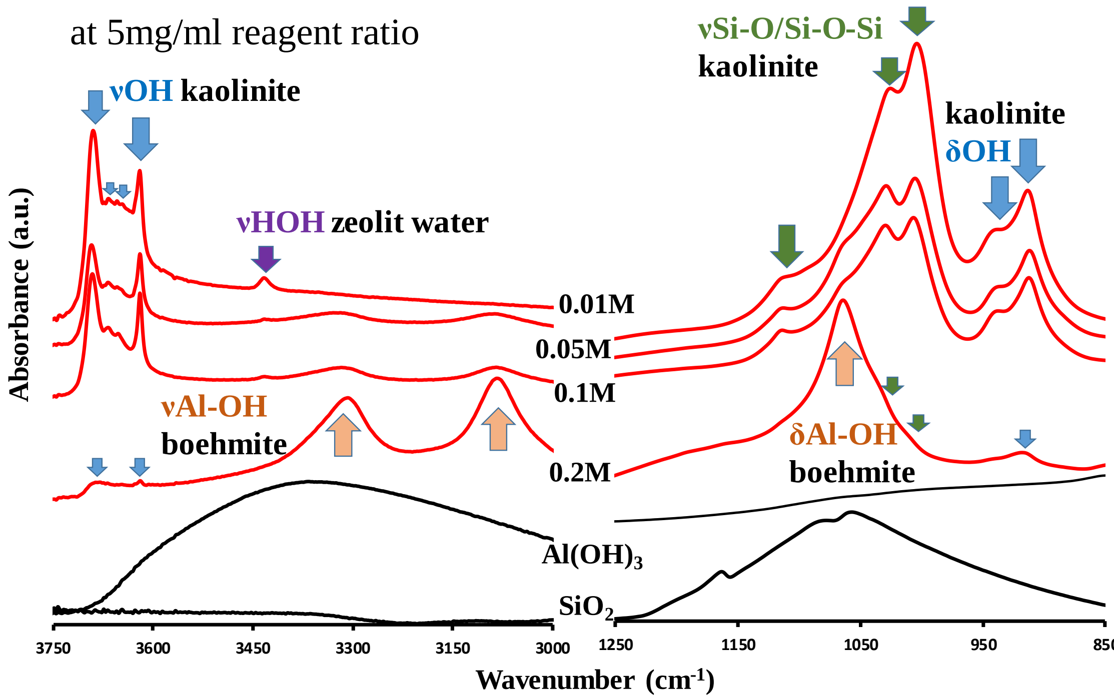
Effect of reagent (solid-liquid) ratio

at 0.01 mol/dm^3 HCl concentration



Effect of HCl concentration

at 5mg/ml reagent ratio



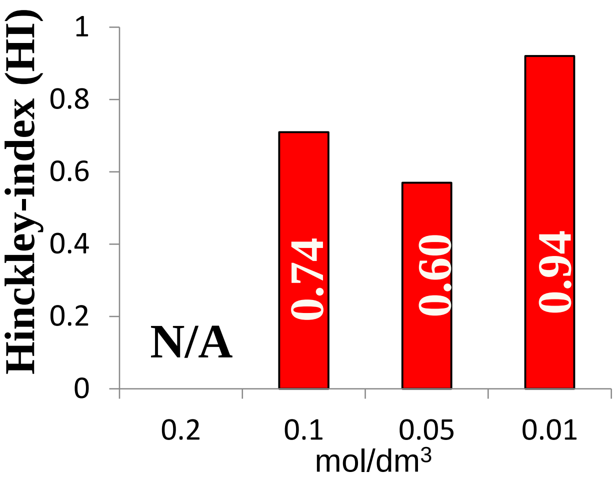
Kaolinite structural vibrations are well identifiable

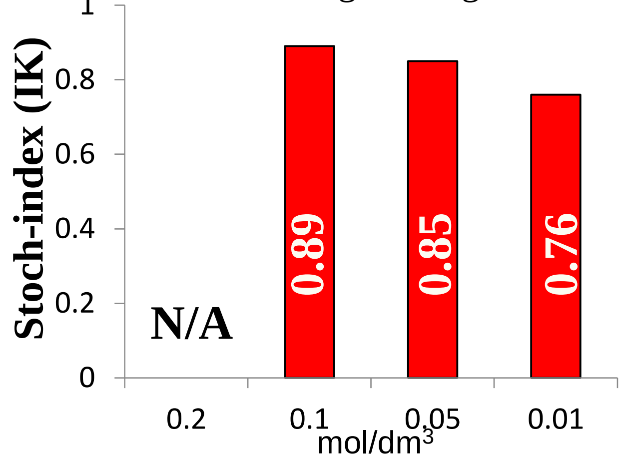
Results and Discussion: Crystallinity (calculated from XRD)

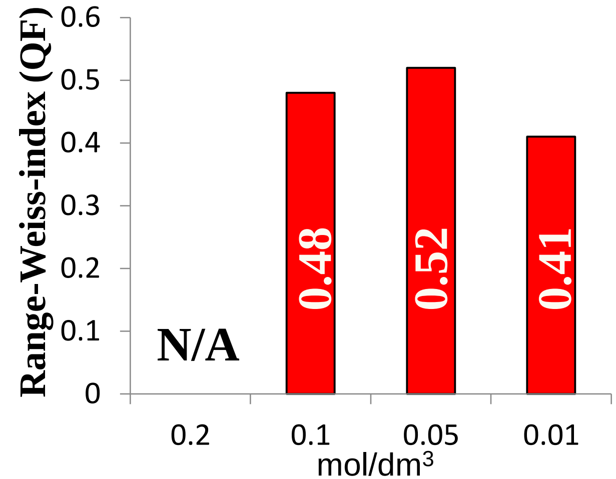
Well-ordered/moderately-ordered kaolinite crystal structures observed

Effect of HCl concentration

at 5mg/ml reagent ratio

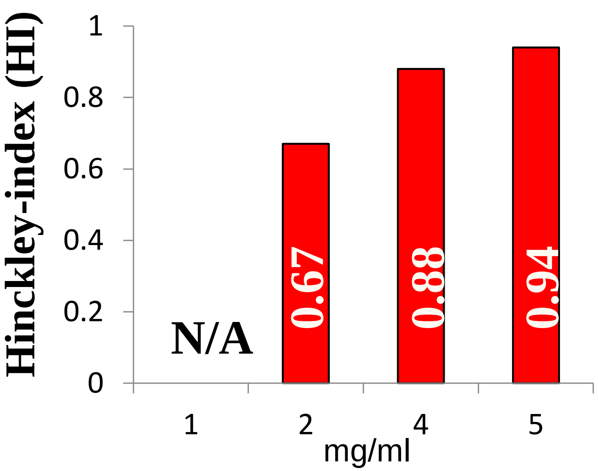


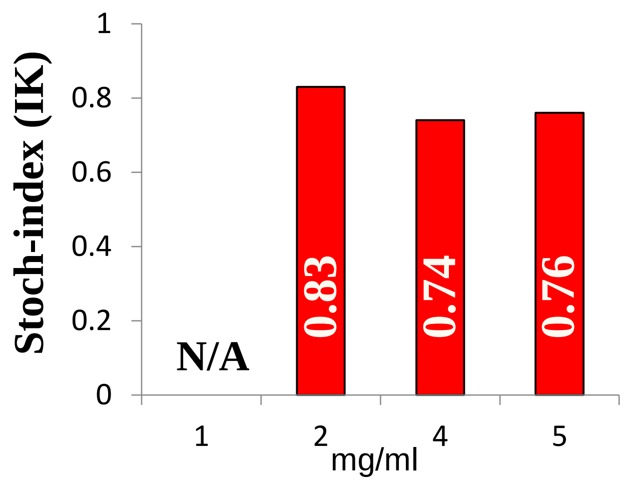


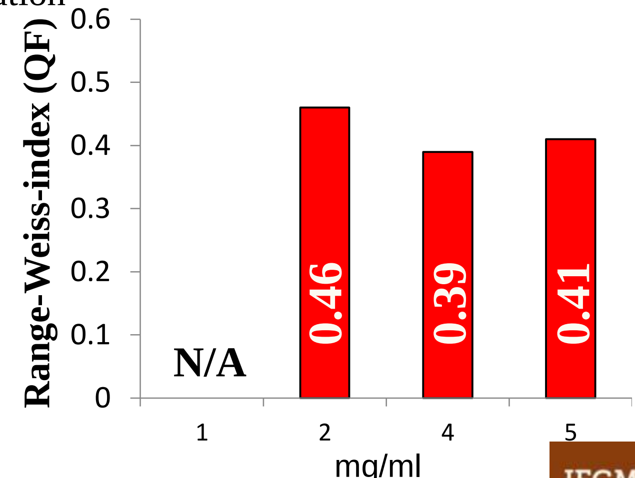


Effect of reagent (solid-liquid) ratio

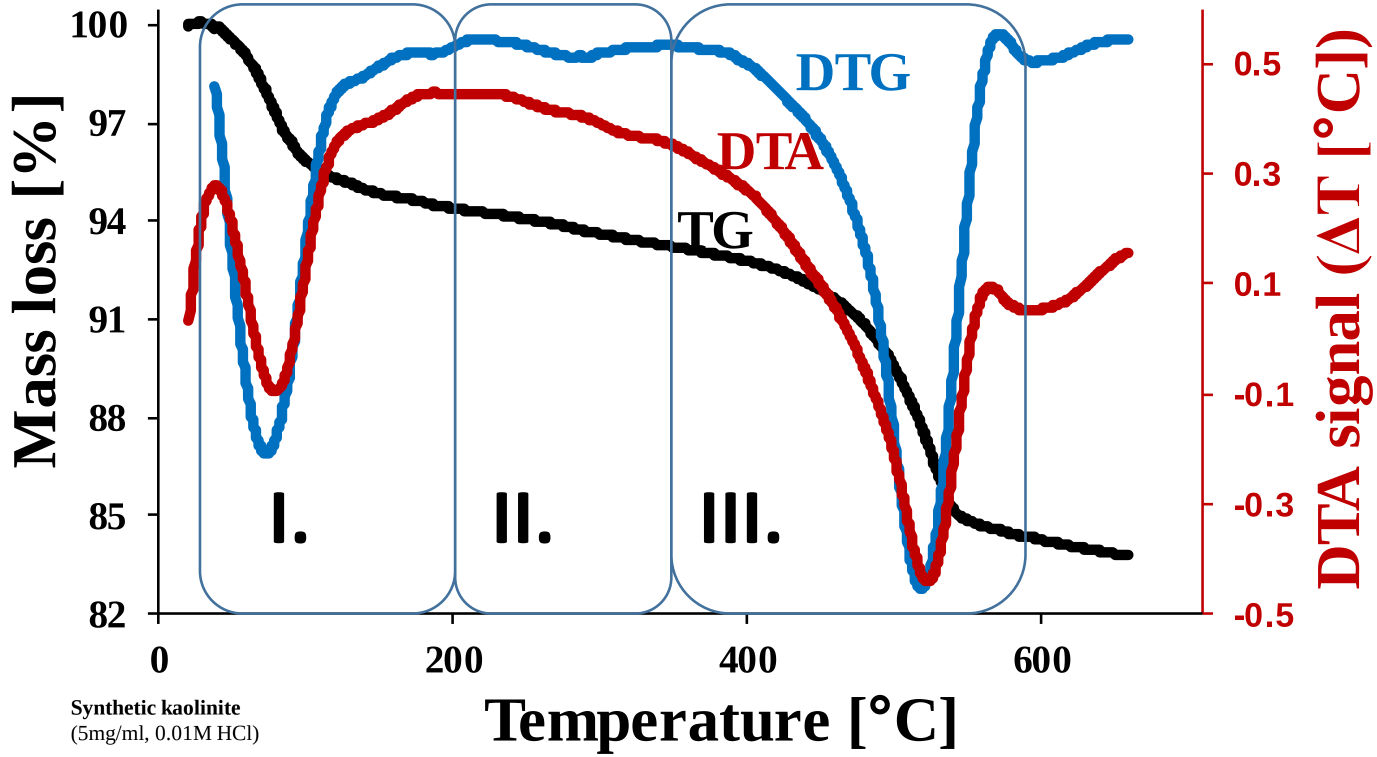
at 0.01 mol/dm^3 HCl concentration







Results and Discussion (Thermal analysis)



Synthetic kaolinite
(5mg/ml, 0.01M HCl)

3 thermal processes were identified:

I. 20-200°C – dehydration of adsorbed water

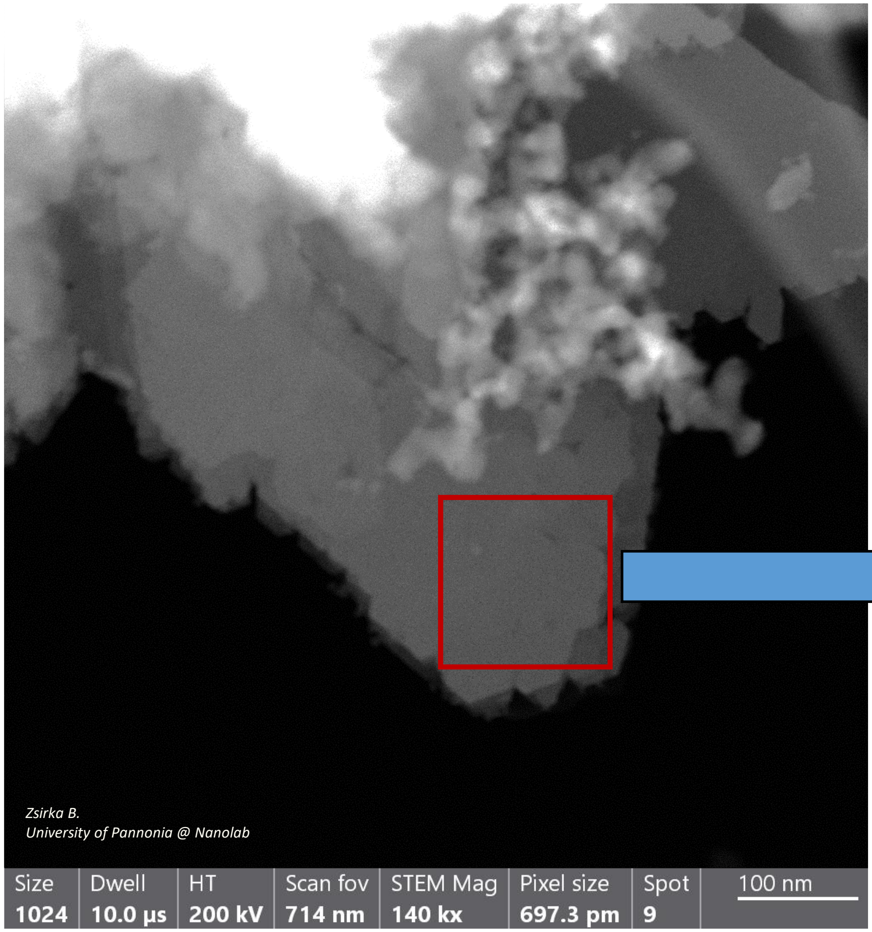
II. 200-360°C – dehydration of zeolite water

III. 360-600°C – thermal dehydroxilation of kaolinite TO structure (can partially overlap with boehmite dehydroxilation)

Thermal dehydroxilation indicates crystalline kaolinite with minor impurities

$$Al_2[Si_2O_5](\mathrm{OH})_4 \rightarrow Al_2O_3 + 2\ SiO_2 + 2\ H_2O$$

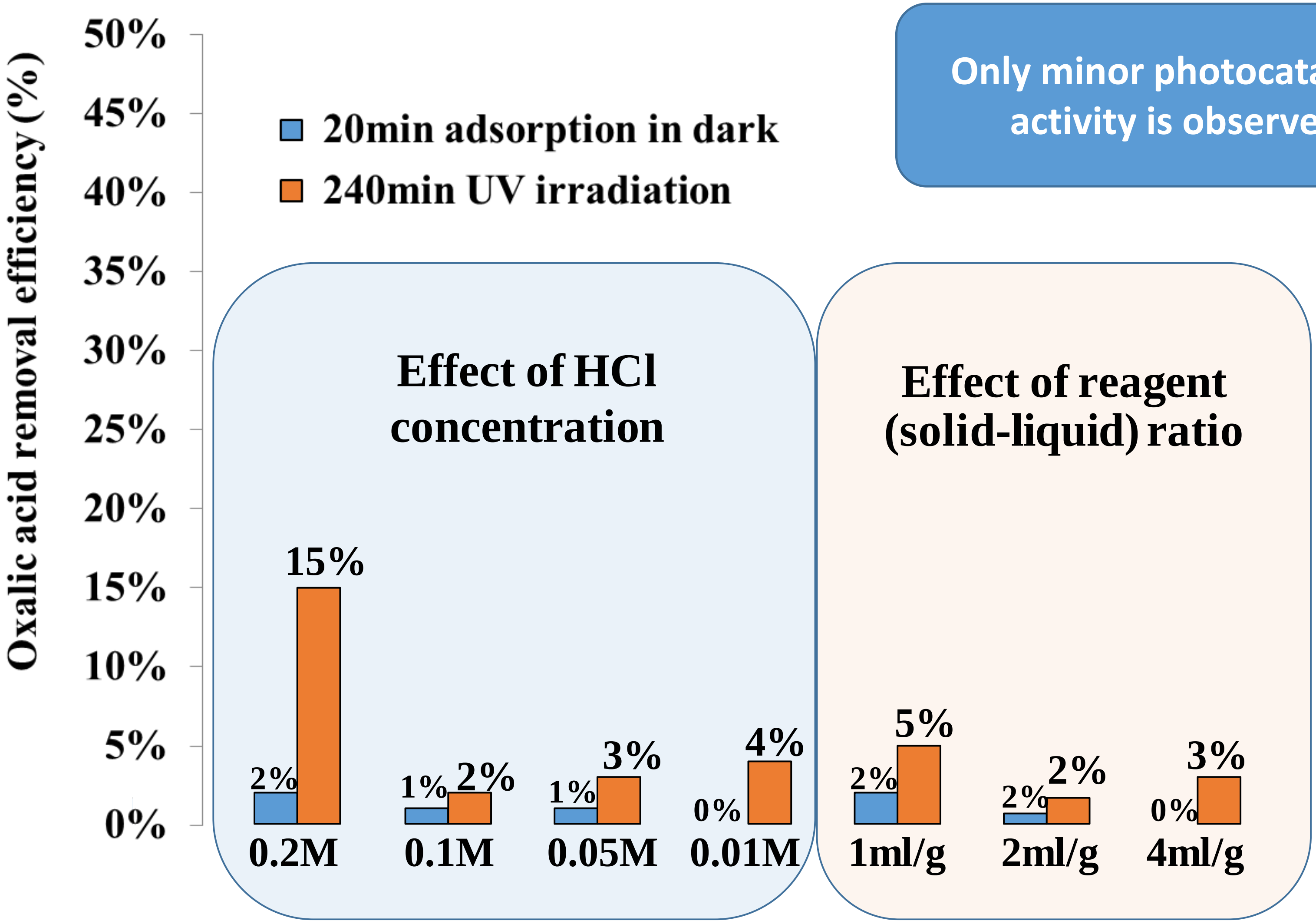
Results and Discussion (TEM-EDX)



TEM-EDX confirms the presence of kaolinite pseudo-hexagons

Element	EDX analysis results	
	Atom%	Mass%
O	67.16 ± 6.72	54.32 ± 3.43
Al	16.76 ± 3.71	22.86 ± 4.74
Si	16.07 ± 3.49	22.82 ± 4.62

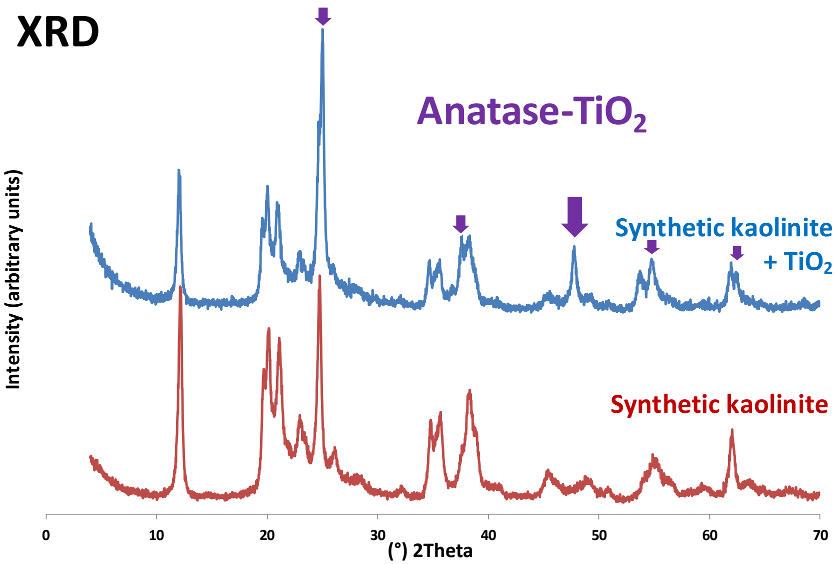
Results and Discussion (Photocatalytic activity)



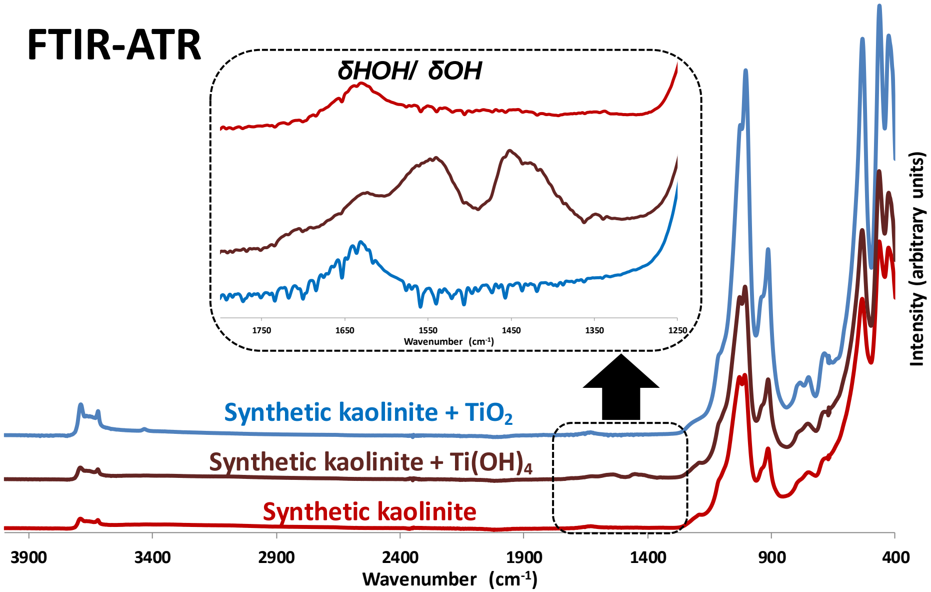
Only minor photocatalytic activity is observed

Results and Discussion (Synthetic kaolinite+TiO_2)

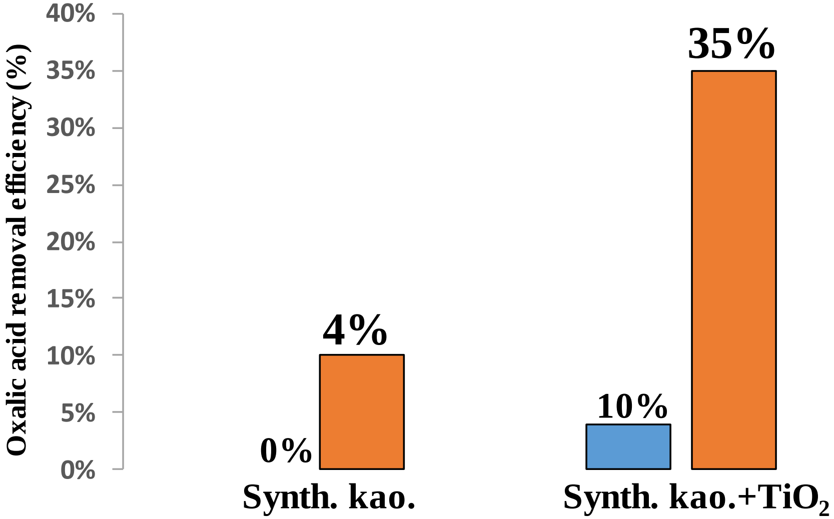
XRD



FTIR-ATR



Photocatalytic activity



Synthesis via $Ti(OH)_4$ formation.

TiO_2 polymorph in synthetic kaolinite-TiO_2 composite is anatase.

Photocatalytic activity of the composite increased significantly.

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Acknowledgments

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