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Using Solar Photocatalytic Composites to Remove Microcystin-LR in Water

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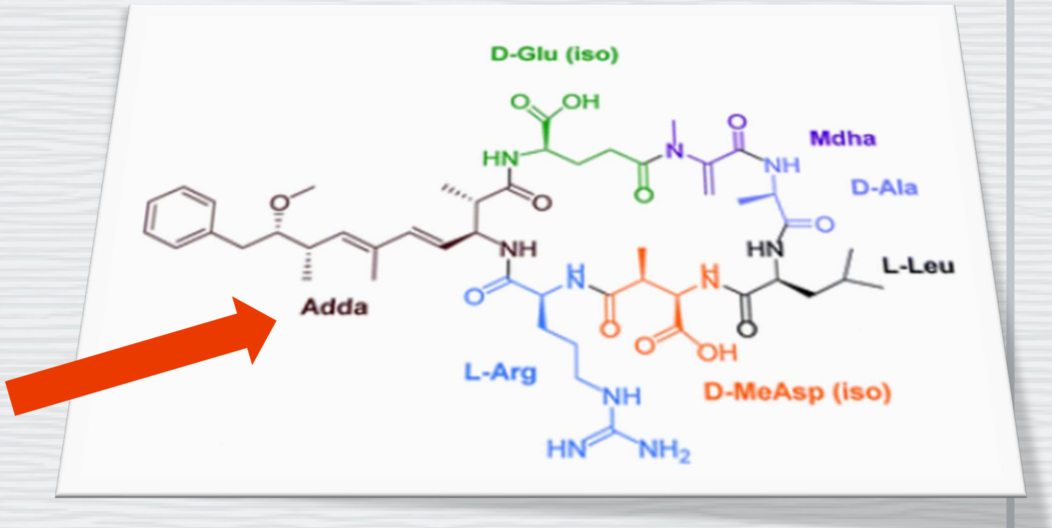
Introduction

- Frequent occurrence of intense algal bloom in surface water especially Lake Erie is a serious problem in Ohio.
- Most common toxins produced by cyanobacterial algal bloom are microcystins (MCs).
- It is (MC-LR) one of the toxic compounds, a possible carcinogen to human.

- MC-LR is composed of a cyclic heptapeptide containing seven 7 amino acids.
- Among the 7 amino acids, 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-decadienoic acid (Adda) shows the toxicity by conjugated diene on the (Adda) side chain.
- Degradation product containing (Adda) functional groups have been reported to have biological toxicity.



- Adsorption and filtration could isolate MC-LR, but the toxicity remain due to its structural complexity. Titanium dioxide (TiO_2) can be used to degrade MC-LR due to its strong oxidizing capacity, stability, low cost, and non-toxicity towards both human and environment.

- However, TiO_2 photocatalytic oxidation can't be used efficiently in large water systems unless it has a support to float and contact with sunlight.

How does TiO_2 work?

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UV (< 380 nm / Sunlight)

↓ $h\nu > E_{bg}$

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^-_{cb}/h^+_{vb}) \rightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

$$h^+_{vb} + OH^-\left((H_2O)^{Surface}\right) \rightarrow {}^\circ OH + (H^+) \qquad (2)$$

$$e^-_{cb} + O_2 \rightarrow {}^\circ O_2^{\circ -} + H^+ \rightarrow {}^\circ OOH \qquad (3)$$

$${}^\circ OH + \text{Organic pollutants} \rightarrow \uparrow CO_2 + H_2O + \text{mineralized products} \qquad (4)$$

Objectives

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Our goal was to devise a TiO_2-based solar photocatalytic system in conjunction with zinc-activated charcoal (ZAC), clay, and sodium silicate to degrade and remove microcystin-LR (MC-LR) in water.

Specific objectives were to:

Develop a lab-scale TiO_2-based solar photoreactor integrated with zinc-activated charcoal (ZAC), clay, and sodium silicate.

Evaluate the effectiveness of lab-scale photoreactor to degrade and remove MC-LR in water under simulated and natural solar radiations.

Develop a field prototype using natural solar radiation to degrade and remove MC-LR in water.

Materials and methods

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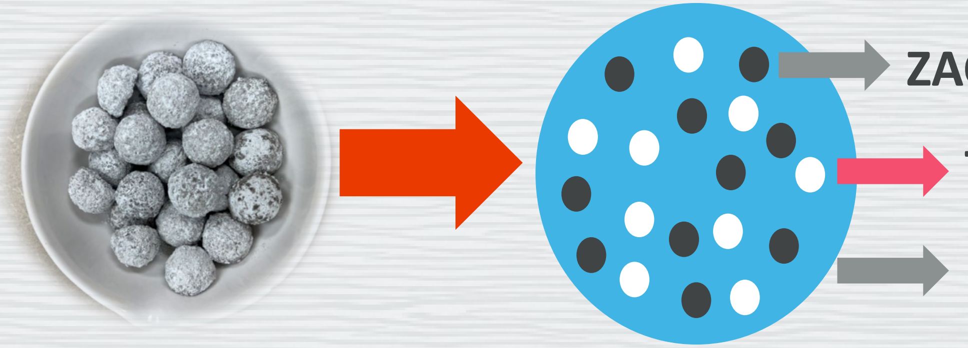
What is the TiO_2/ZAC/Soil composite?



ZAC: Zinc activated charcoal (~100 um, 14%)

TiO_2 powder (anatase, 230 nm): 21%

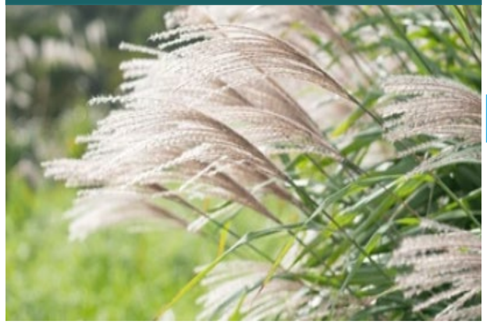
Soil (43%) and Na_2SiO_3 glue (21%)

Sintering temp: 500 °C (4 hr.)

- **Advantages of using composite**
- Adsorption of MC-LR by ZAC
- TiO_2 acts efficiently as a photocatalyst to degrade MC-LR
- TiO_2 does not mix with water
- A network of balls along with a floater will give a broader application.

Preparation of Zinc-activated carbon (ZAC)

Miscanthus



Sun dried

Grinder

Powder

$H_2SO_4 + ZnCl_2$

Filtration/H_2O wash

ZAC

Preparation of TiO_2/ZAC/Soil composite

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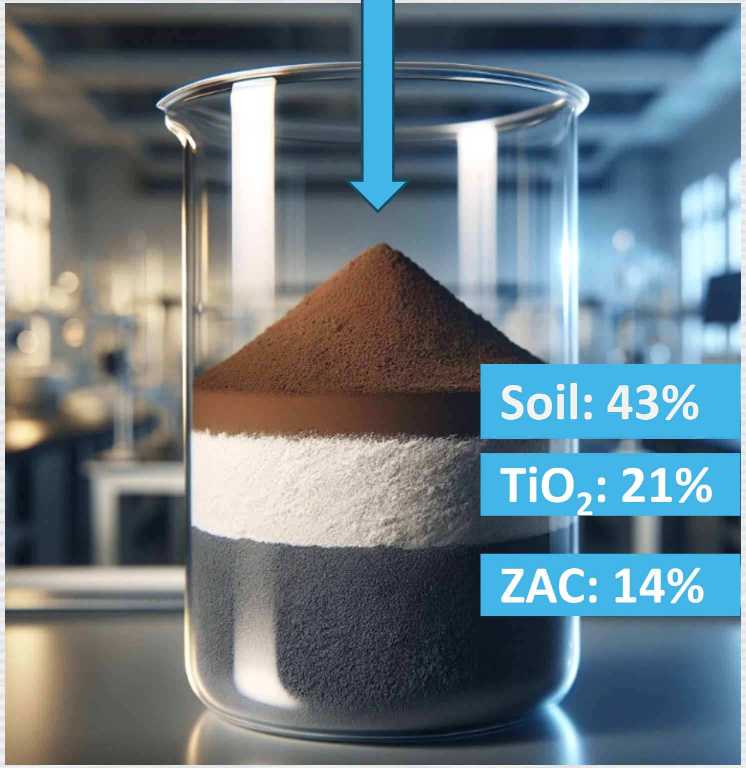
Agricultural waste materials

Chemical Activation ($ZnCl_2$)

$ZnCl_2$-Activated carbon (ZAC)

H_2O + Na_2SiO_3 (Glue) and mixing

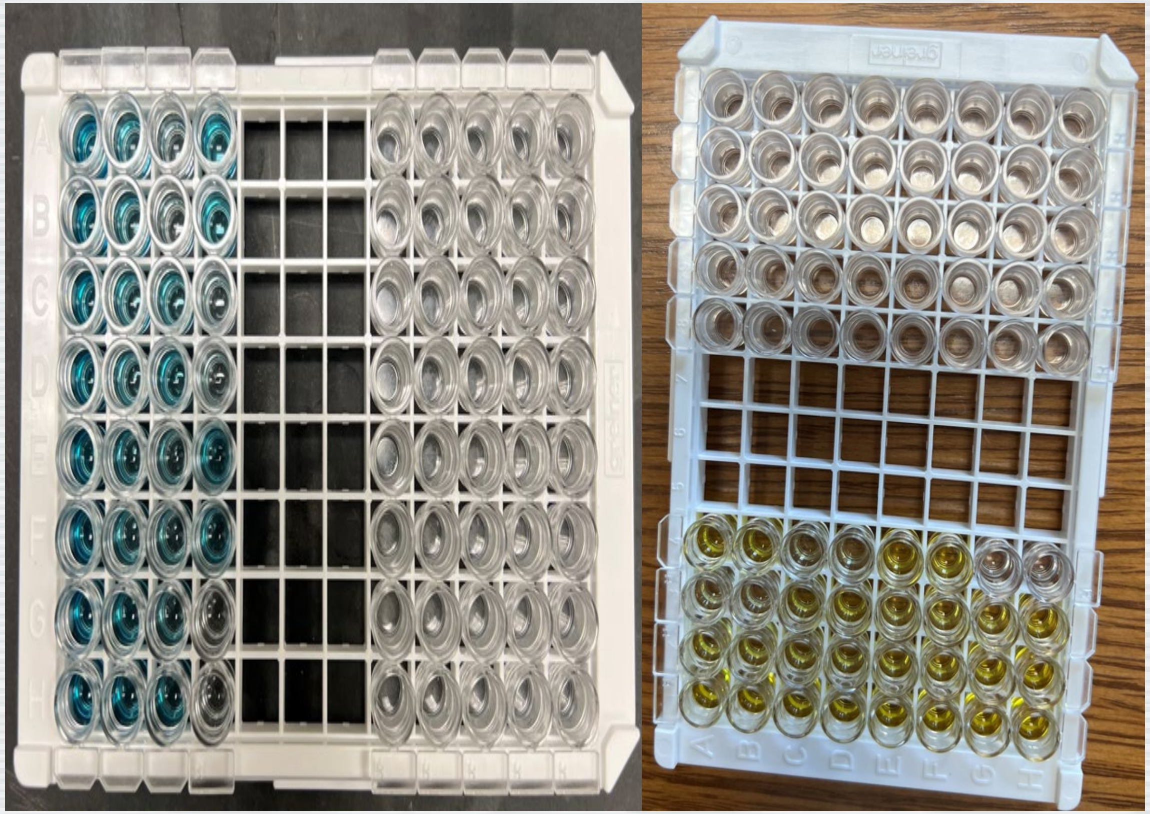


Handmade Balls

Sintering in furnace at 500 °C temp

Microcystin-LR analysis

- ELISA Test method was used to analyze MC-LR
- MC-LR was procured from…………



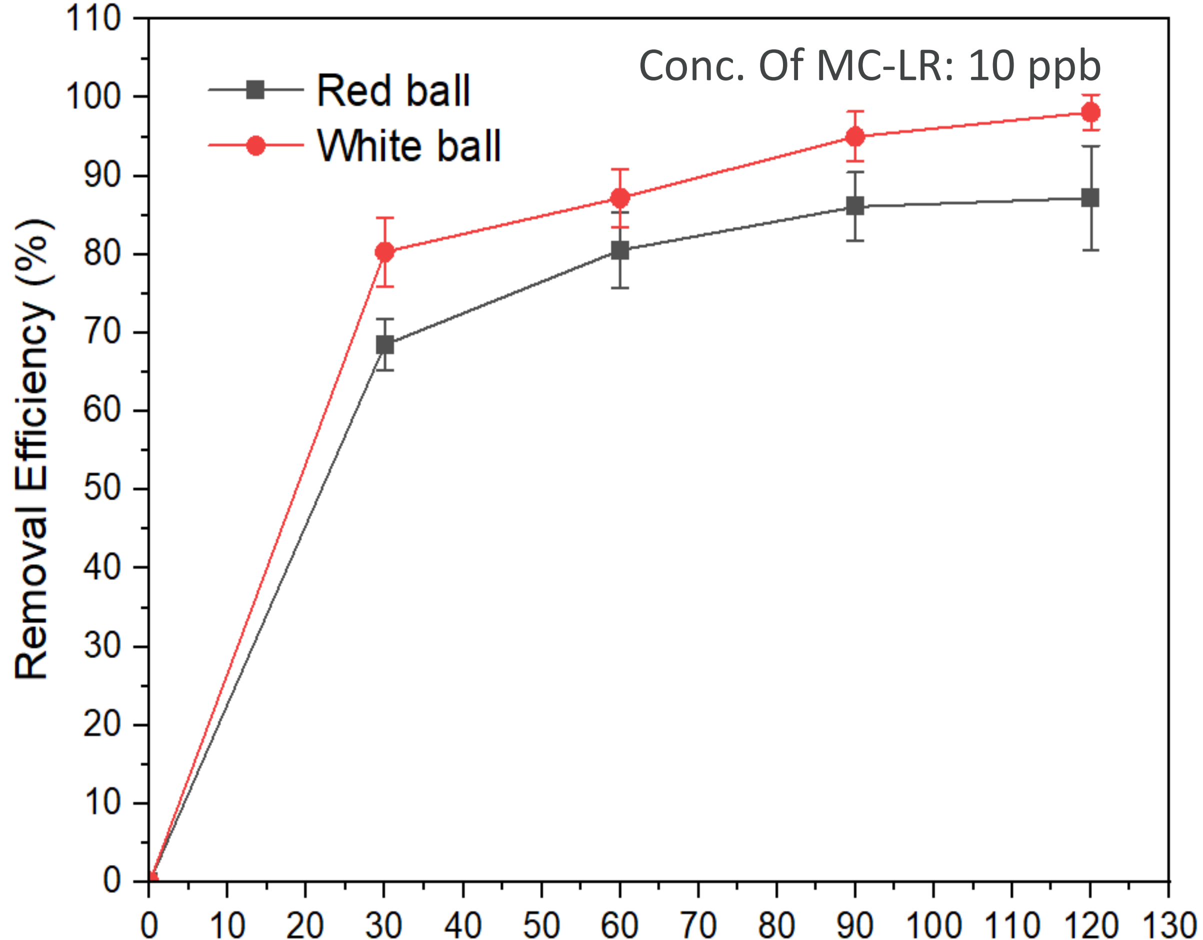
Experiment with artificial solar simulator

Sol 500 UV lamp filtered with H2 filter glass, solar simulator, wavelength ~ 350 nm.

Results

Optimization of Composite composition

Removal of Microcystin-LR from water



Hard and stable

Removal Efficiency: 82%

Red ball Composition

40% soil + 40% TiO_2 + 20% Na_2SiO_3

Soft and mixed with H_2O

Removal Efficiency: 96%

Very unstable.

White ball Composition

40% ZAC+ 40% TiO_2 + 20% Na_2SiO_3

Optimization of Composite composition

Ash colored ball Composition
21% TiO_2 + 14% ZAC+ Soil 43%+ 21% Na_2SiO_3

Not mixed with H_2O
Removal Efficiency: 96%
Very stable

Optimization (exposure time)

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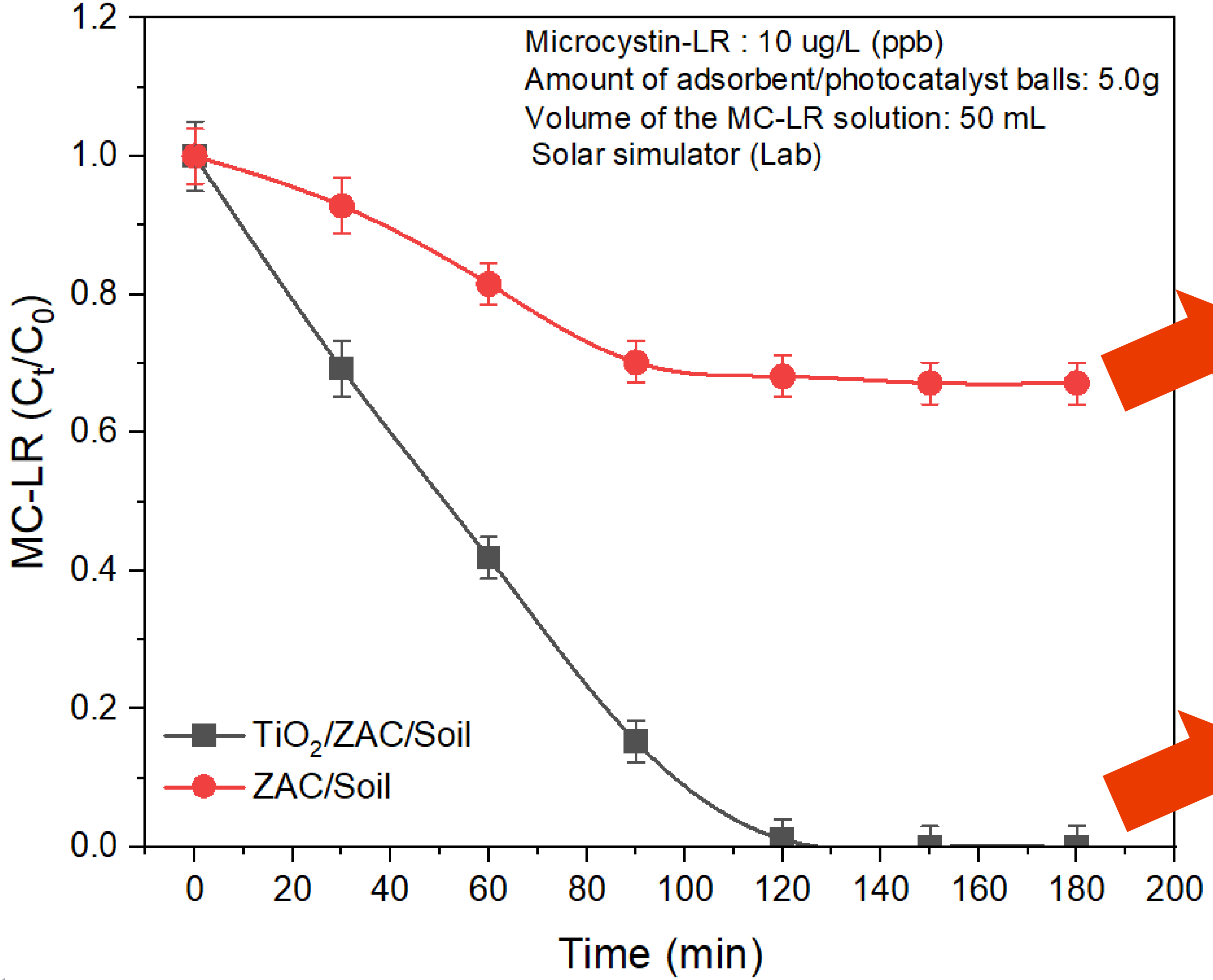


ZAC/Soil balls

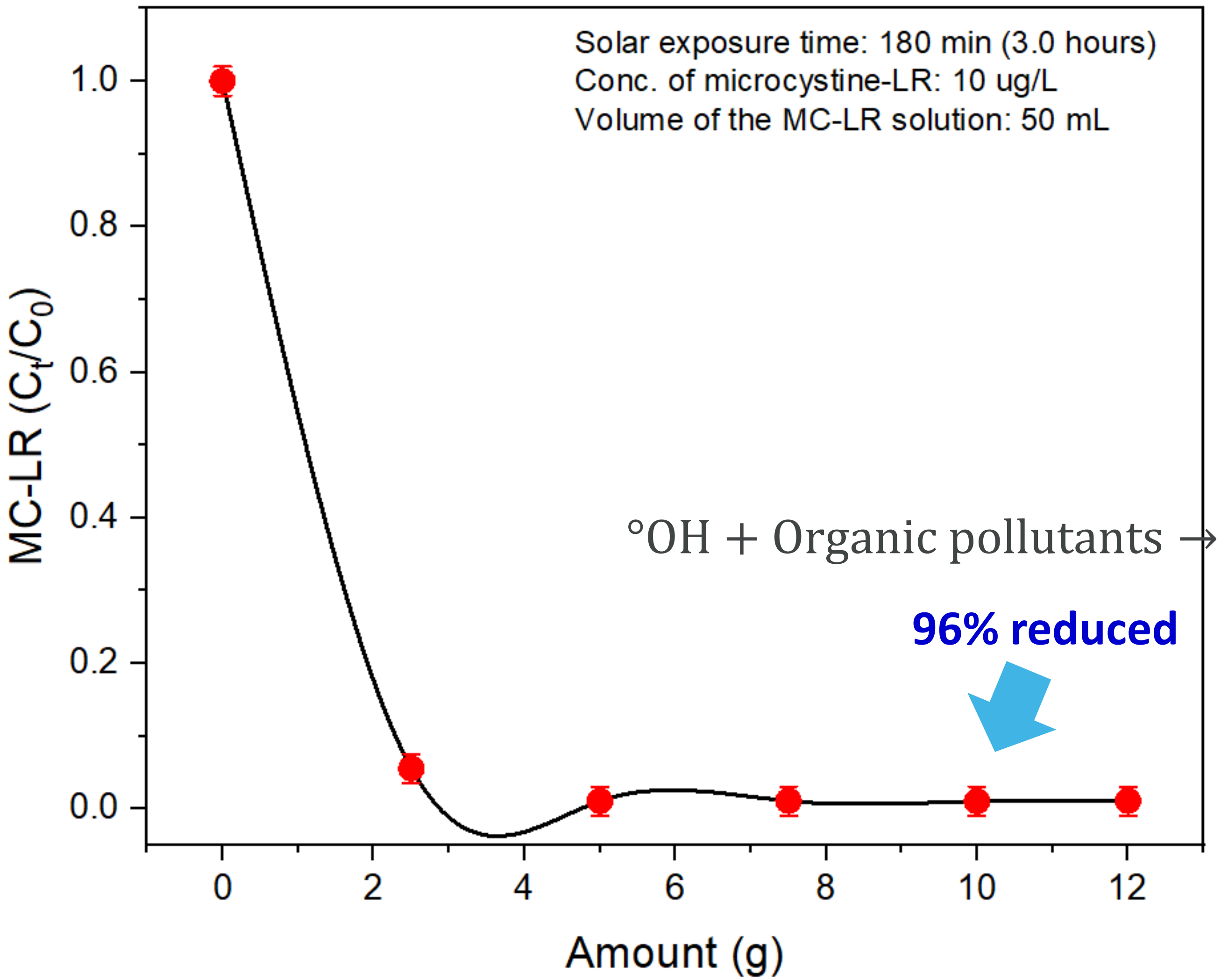
MC-LR Adsorption → 30% removal

TiO_2/ZAC/Soil balls

MC-LR Adsorption → 96% removal

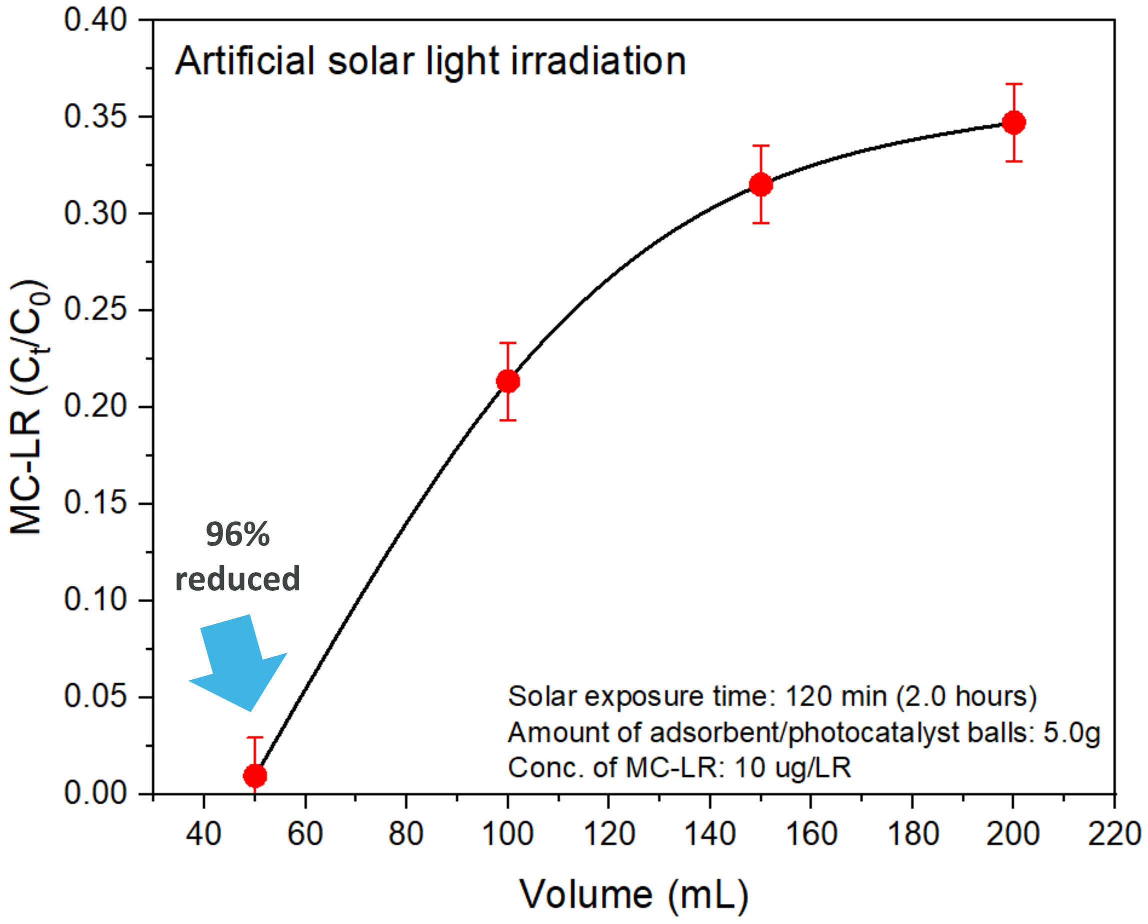
Photodegradation

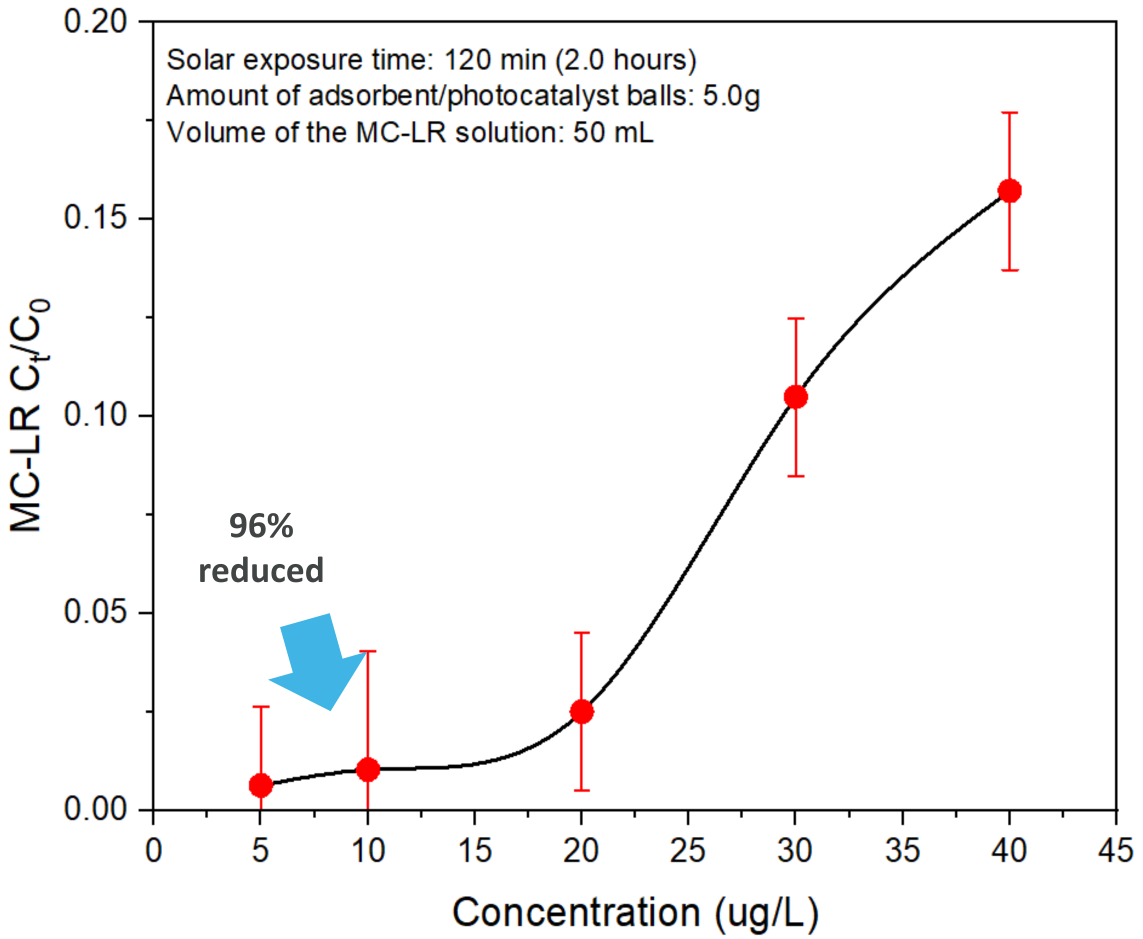
Optimization of amount of adsorbent



$$^{\circ}OH + \text{Organic pollutants} \rightarrow \uparrow CO_2 + H_2O + \text{mineralized products}$$

Optimization (volume and conc.)





Optimization (pH)

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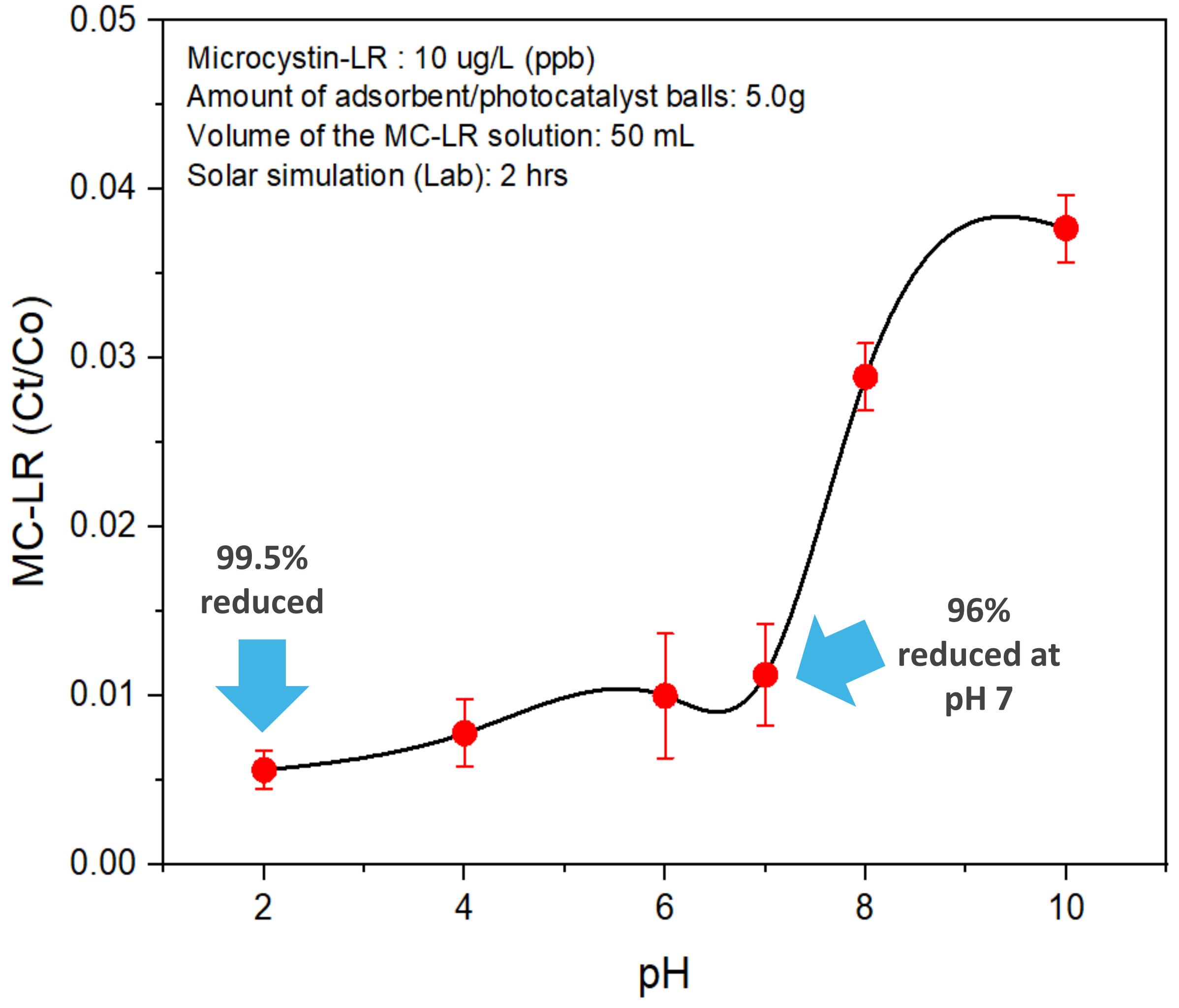

- **MC-LR is negatively charged molecule from pH 2 to 12.**
- At acidic pH (2-6), the TiO_2 surface becomes positively charged (TiO_2-H^+) and bind negatively charged MC-LR molecular adsorption.
- At pH>7, TiO_2 surface becomes negatively charged (TiO_2 $(OH)^-$) and repulse negatively charged MC-LR molecule.

Optimization (pH)

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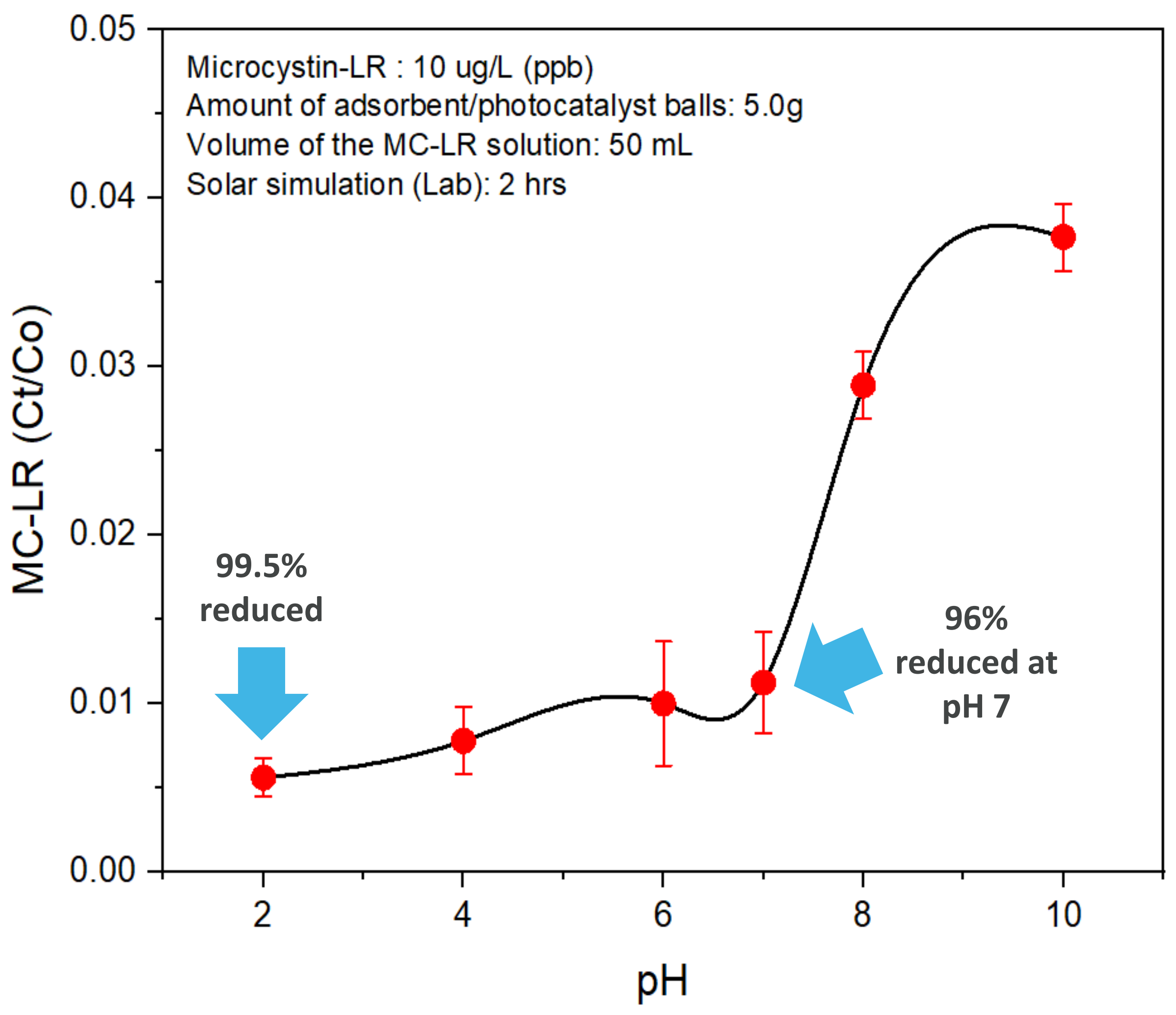

- **MC-LR is negatively charged molecule from pH 2 to 12.**
- In acidic condition, more OH radicals might be produced, while in alkaline condition, other ROS like superoxide anions ($O_2 \bullet^-$) might be more prevalent.
- Therefore, acidic pH showed higher degradation efficiency of MC-LR.
- Under natural condition, the water pH would be close to slightly acidic to neutral, the pH 7 will be preferable pH.

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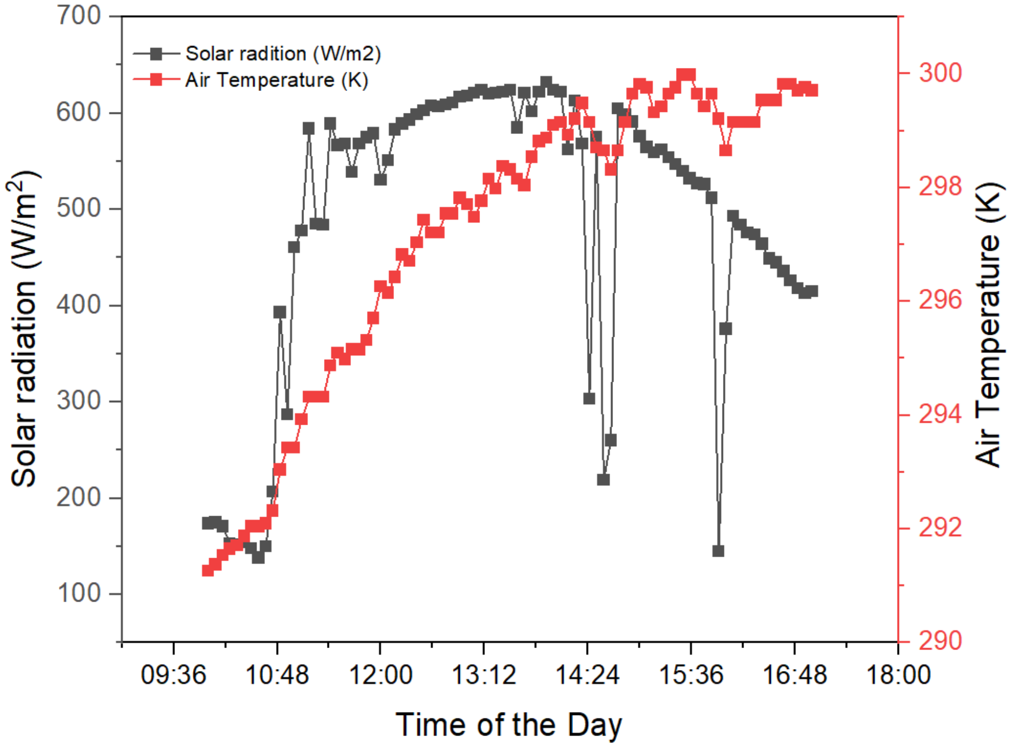
MC-LR degradation under natural sunlight

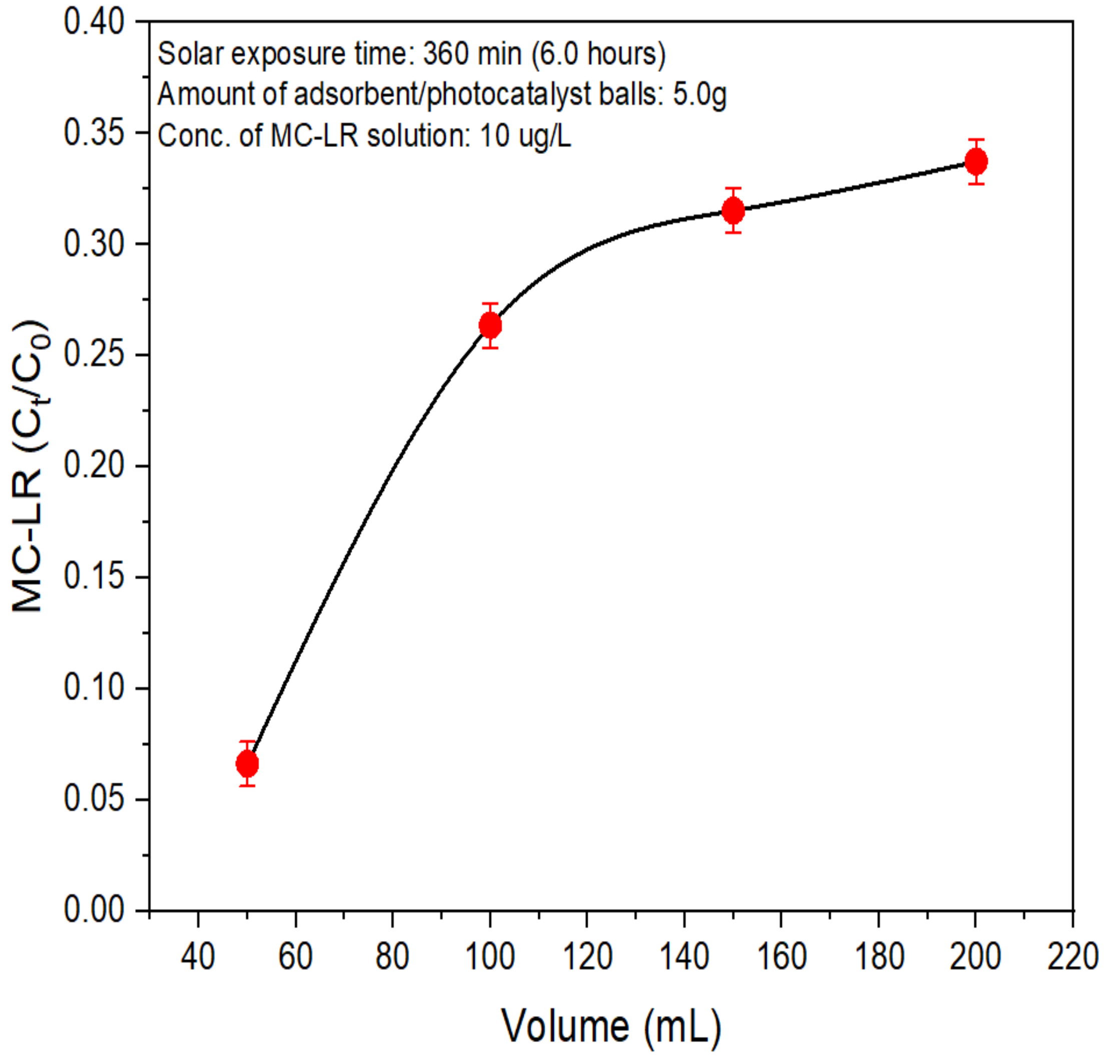
Sunlight exposure: 6 hr.
Volume of solution: 50 mL

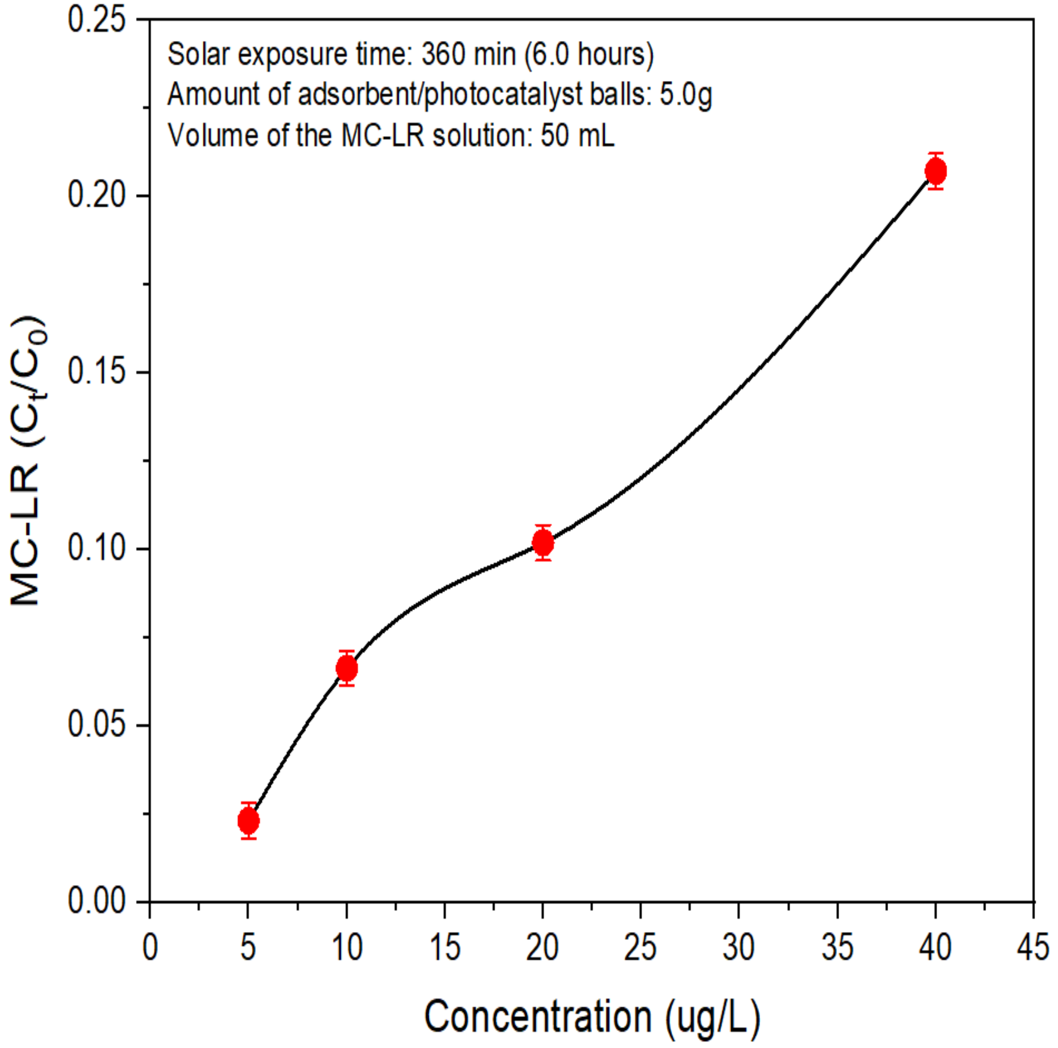
Amount of adsorbent: 5.0 g
Conc. Of MC-LR: 10 ug/L



Average solar radiation: 487 (W/m^2)

Optimization (volume and conc.





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Optimization of amount of adsorbent

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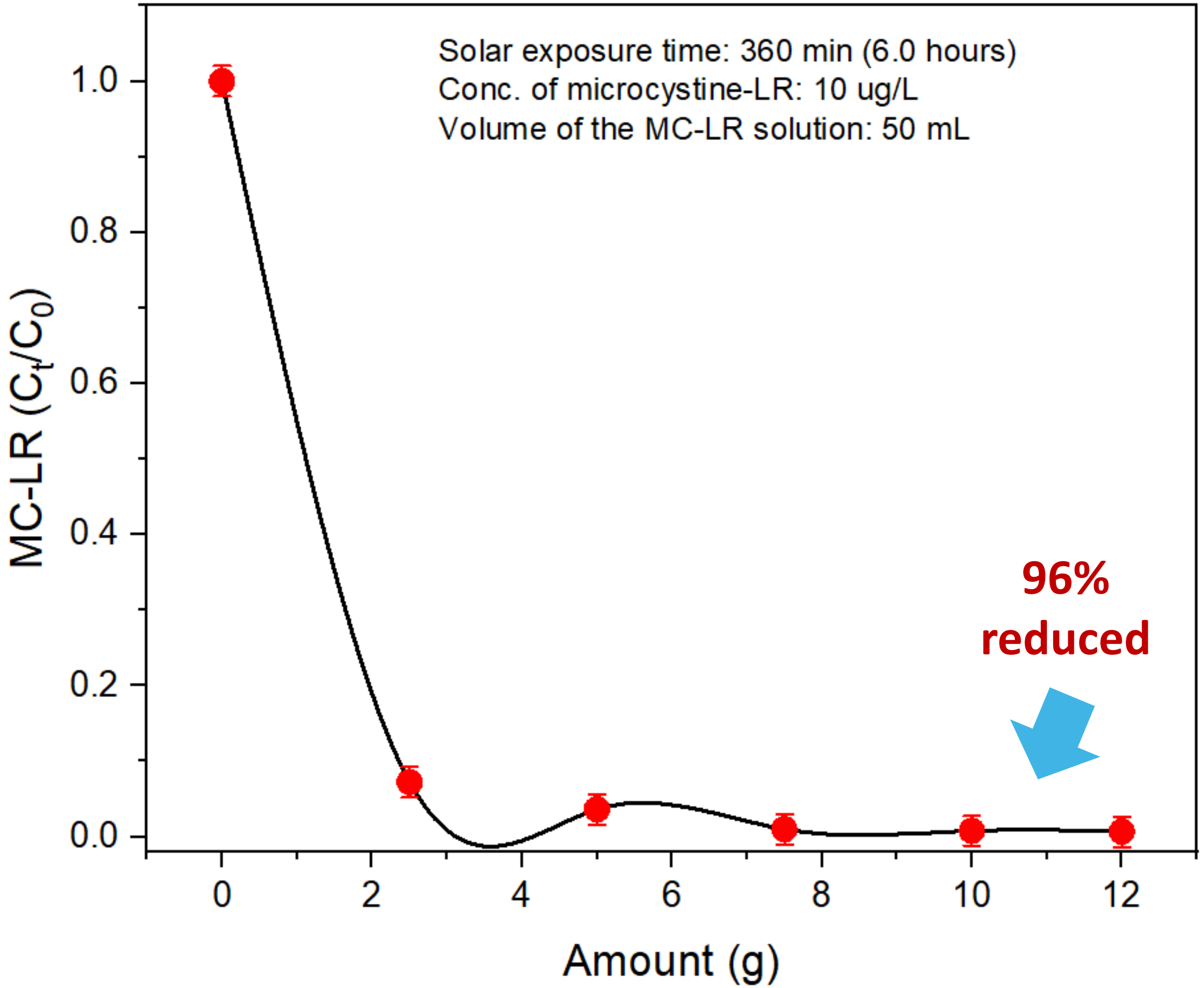

- For photocatalysis activity of TiO_2 , approx. 3.2 eV energy, corresponding to the **387 nm** wavelength is required.
- During summer, the solar spectrum includes a range of wavelengths from ultraviolet to visible and infrared light.
- The UV portion of sunlight, which includes 320-400 nm, 280-320 nm, and <280 nm, is mostly responsible for activating TiO_2.

Optimization (pH)

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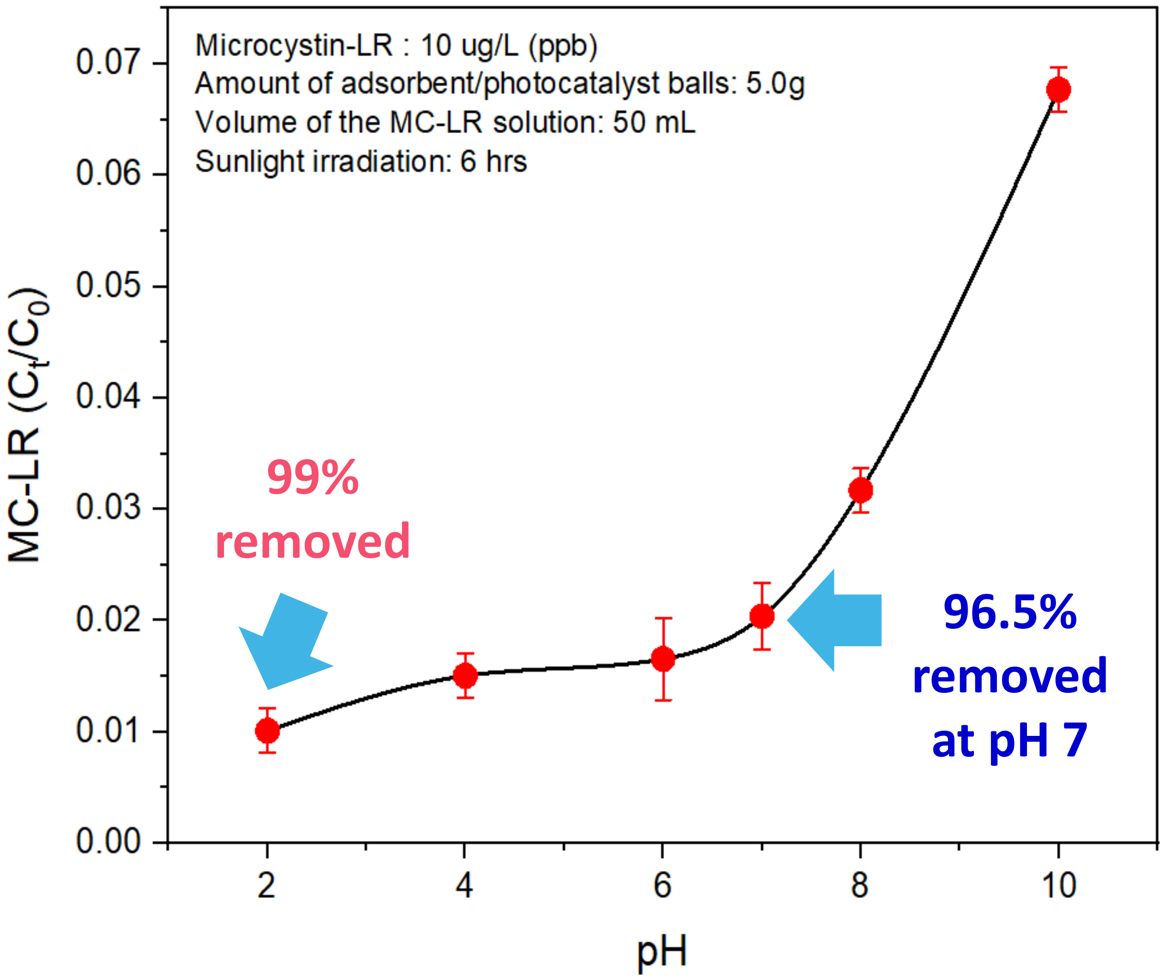
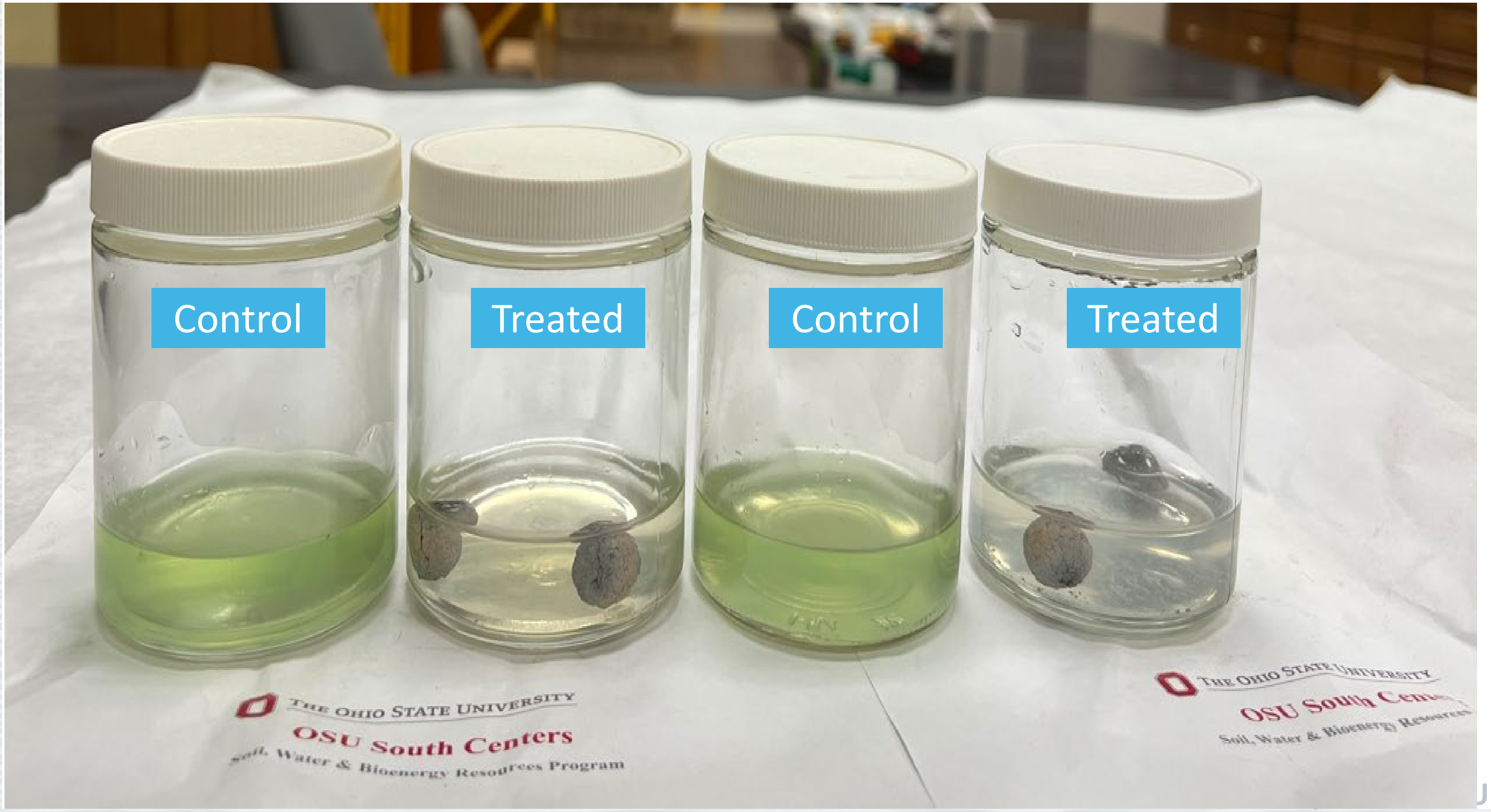


- Degradation of MC-LR under sunlight irradiation is slower compared to the direct UV-light in the lab.
- Intensity of UV-light from the sun is much lower compared to that from the artificial UV sources.
- This lower intensity results in a slower rate of electron-hole pair generation in TiO_2, which in turn leads to slower generation of reactive O_2 species (ROS) essential for MC-LR degradation.

Effect of Algae containing microcystin-LR

Degradation of algae with our composite material under sunlight (3 hr.)

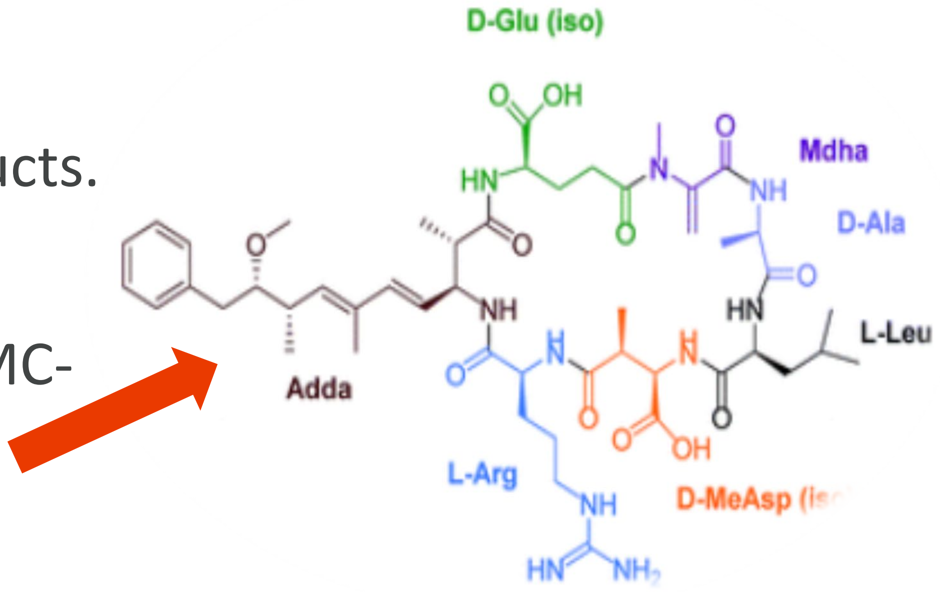


Toxicity of degraded products

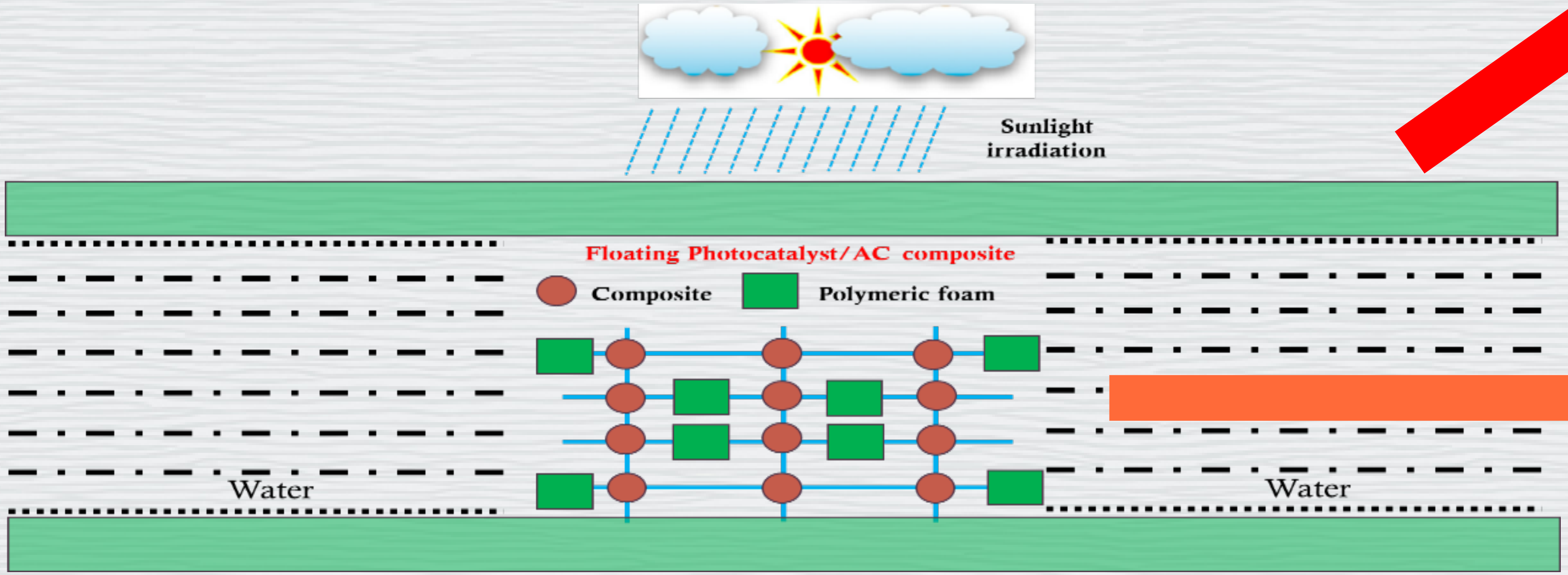
At what stage of treatment does the water become detoxified?

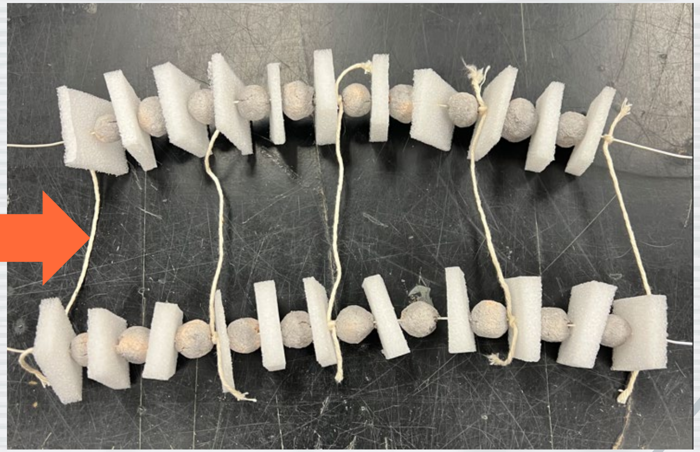
- MC-LR loses its toxicity as soon as the molecule is transformed to oxidized products.

- The first oxidation of Adda amino acid of MC-LR results in loss of toxic activity.



Prototype using natural solar radiation to degrade MC-LR in water at OSU South Centers





Degraded products of MC-LR using TiO_2 with solar light

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No.	Molecular weight and formula	Possible structure
1	$C_{49}H_7N_{10}O_{12}$ (994.5)	MC-LR: Cyclo[-Adda-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
2	$C_{15}H_{28}N_6O_6$ (388.2)	H-Arg-NHCH(OH)CH(CH_3)CO-Glu-H
3	$C_{17}H_{32}N_6O_6$ (416.2)	OH-Arg-MeAsp-Leu-H H-MeAsp-Leu-Mdha (OH)-H
4	$C_{17}H_{30}N_6O_6$ Na (414.2)	[H-Arg-NHCH(CHO)CH(CH_3)CO-Glu-CH_3]$^-$$Na^+$
5	$C_{21}H_{37}N_7O_8$ (515.3)	Arg-MeAsp-Leu-Ala-COOH
6	$C_{23}H_{41}N_7O_8$, (543.3)	Arg-MeAsp-Leu-Ala-COCHOHCH3
7	$C_{34}H_{56}N_{10}O_{11}$, (780.4)	Cyclo[-NHCH(CH_3)CH(CH_3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
8	$C_{33}H_{54}N_{10}O_{12}$, (782.4)	Cyclo[-NHCHOHCH(CH_3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
9	$C_{34}H_{54}N_{10}O_{12}$, (794.4)	Cyclo[-NHCH(CHO)CH(CH_3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
10	$C_{34}H_{54}N_{10}O_{13}$, (810.4)	Cyclo[-NHCH(COOH)CH(CH_3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
11	$C_{37}H_{58}N_{10}O_{12}$, (834.4)	Cyclo[-NHCH(CHCHCOCH3)CH(CH3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
12	$C_{36}H_{56}N_{10}O_{13}$, (836.4)	Cyclo[-NHCH(CHCHCOOH)CH(CH3)CO-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
13	$C_{48}H_{72}N_{10}O_{11}$, (964.5)	Cyclo[-Adda(−Methoxy)-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
14	$C_{48}H_{74}N_{10}O_{13}$, (998.5)	Cyclo[-Adda-Glu(−Carboxy)-Mdha-Ala-Leu-MeAsp-Arg-]
15	$C_{49}H_{72}N_{10}O_{13}$, (1008.5)	Cyclo[-DmAdda-Glu-Mdha-Ala-Leu-MeAsp-Arg-]
16	$C_{48}H_{74}N_{10}O_{14}$, (1014.5)	(CO)Ala-Leu-MeAsp-Arg-Adda-Glu($NCOCH_3$)
17	$C_{49}H_{74}N_{10}O_{14}$, (1026.5)	$(OH)_2$-Cyclo[-Adda-Glu-Mdha-Ala-Leu-MeAsp-Arg-]

Conclusions

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- ❑ TiO_2/ZAC/soil composite was efficient (96%) to eliminate MC-LR compounds under lab and natural sunlight irradiation.
- ❑ After the reaction, the electron and hole recombine, and the TiO_2 returns to its original state, ready to be activated again by sunlight. This makes TiO_2 a reusable catalyst.
- ❑ Both TiO_2 and degraded products leaving no harmful residues or toxins, making it an environmentally compatible treatment option for the degradation and removal of harmful MC-LR toxin in water.
- ❑ We expected to use the composite in a prototype under natural solar radiation.

Thank you

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