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Degradation of pesticide atrazine with UV/H_2O_2 process

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NETCHEM Remote Access Laboratory Guide

Degradation of pesticide atrazine with UV/H_2O_2 process

In this exercise, you will:

- Perform one of advance oxidation water treatment
- Measure concentration of organic pollutant before and after treatment
- Gain experience in HPLC-DAD usage

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Background

Advance oxidation processes

- AOPs rely on in-situ production of highly reactive hydroxyl radicals ($^{\bullet}OH$).
- These reactive species are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed.
- Consequently, $^{\bullet}OH$ reacts unselectively once formed and contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules.
- Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide).

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Background

Advance oxidation processes

- In general, when applied in properly tuned conditions, AOPs can reduce the concentration of contaminants from several-hundreds ppm to less than 5 ppb and therefore significantly bring COD and TOC down.
- Chemistry in AOPs could be essentially divided into three parts:
  - Formation of $^{\bullet}OH$;
  - Initial attacks on target molecules by $^{\bullet}OH$ and their breakdown to fragments;
  - Subsequent attacks by $^{\bullet}OH$ until ultimate mineralization.
- The mechanism of $^{\bullet}OH$ production highly depends on the type of AOP technique that is used
- In UV/H_2O_2 process two $^{\bullet}OH$ radicals are formed by homolytic O-O bond cleavage of H_2O_2

$$H_2O_2 + UV \rightarrow 2^{\bullet}OH$$

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Background

Advance oxidation processes

- AOPs have several advantages in the field of water treatment:
  - can effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase
  - Due to the remarkable reactivity of $^{\bullet}OH$, it virtually reacts with almost every aqueous pollutant without discriminating. AOPs are therefore applicable in many, if not all, scenarios where many organic contaminants must be removed at the same time
  - Some heavy metals can also be removed in forms of precipitated M(OH)x
  - In some AOPs designs, disinfection can also be achieved, which makes these AOPs an integrated solution to some water quality problems
  - Since the complete reduction product of $^{\bullet}OH$ is H_2O, AOPs theoretically do not introduce any new hazardous substances into the water

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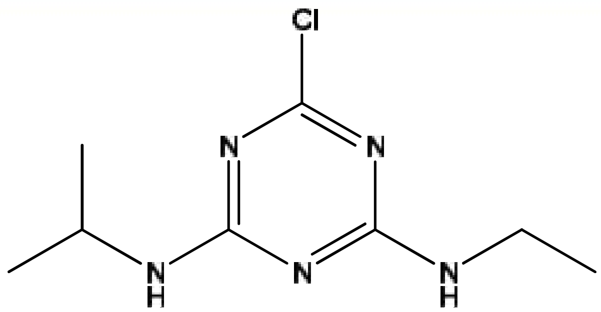
Background



Atrazine

- an herbicide that is used to stop pre- and postemergence broadleaf and grassy weeds in crops such as sorghum, maize, sugarcane, lupins, pine, and eucalypt plantations, and triazine-tolerant canola
- In the United States as of 2014, atrazine was the second-most widely used herbicide after glyphosate, with 76 million pounds of it applied each year.
- one of the most widely used herbicides in Australian agriculture.
- Its use was banned in the European Union in 2004, because of its persistent groundwater contamination.
- As of 2001, Atrazine was the most commonly detected pesticide in US drinking water

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Background

HPLC instrumentation

- technique in analytical chemistry used to separate, identify, and quantify each component in a mixture.
- It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material.
- Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out the column.

Figure 1. Dionex UltiMate 3000 (Thermo Scientific)

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Experimental

For this lab exercise, you will need the following laboratory equipment and chemicals:

- analytical balance,
- 0.005-0.05 , 0.1-1 and 1-10 mL micropipette,
- 100 mL volumetric flask,
- 100 mL beaker,
- Petri dish,
- Atrazine (analytical standard, Sigma-Aldrich, USA)
- H_2O_2 (30%, Sigma-Aldrich, USA)
- Acetonitrile (HPLC grade, Sigma-Aldrich, USA)
- deionized water
- UV-C photoreactor (254 nm)
- HPLC/DAD instrument (Dionex UltiMate 3000 ,Thermo Scientific)
- 0.45 µm regenerated cellulose membrane filters.

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Procedure

I. Prepare a stock solution of atrazine with concentration of 12 mg/dm^3

II. Calibration standards: Prepare a set of atrazine solutions with concentrations of 1, 4, 8 and 10 mg/dm^3 by appropriate dilution of stock solution with deionized water

III. Perform calibration on HPLC instrument

IV. HPLC conditions: mobile phase A is acetonitrile, mobile phase B is deionized water; gradient elution from 95% of deionized to 5% with 20 min; flow rate 0.3 ml/min; column Hypercarb (100x2.1 mm, 3 µm); injection volume 5 µl; column temperature 40 °C; UV detection 215 nm.

V. Prepare 100 mL of working solution which contains 10 mg/dm^3 of atrazine and 10 mM of H_2O_2.

VI. Perform UV/H_2O_2 treatment in a batch UV-C photoreactor (Fig. 2).

VII. After 0, 2, 4, 6, 10 and 20 min take sample aliquot (2 cm^3), filter through the 0.45 µm regenerated cellulose membrane filter and perform quantification on HPLC instrument

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Procedure

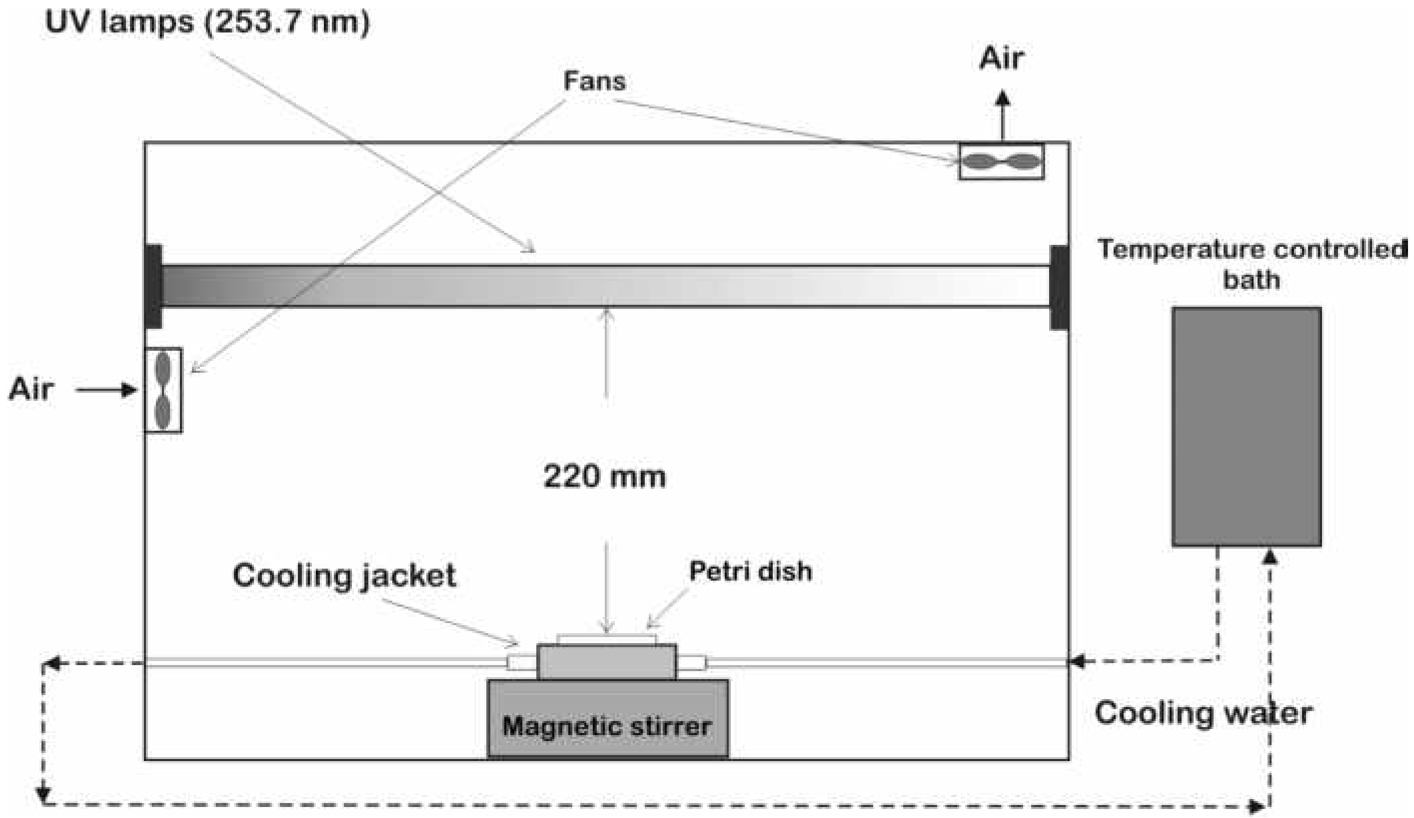

Figure 2. Scheme of the batch photoreactor

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Results

- Obtained atrazine concentrations from the calibration curve insert in Table 1.
- Calculate removal efficiency, according to the equation 1, and present the results on the graph as a removal efficiency (RE) in function of time (Figure 3.)

$$\mathrm{RE}\ (\%) = \frac{c\ \ - c}{c} \times 100 \quad \mathrm{eq}(1)$$

where c is the concentration of atrazine after treatment time t, and c_0 is the initial atrazine concentration (mg/L).

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Results

Table 1. Concentration of atrazine in function of time during the UV/H_2O_2 treatment

Time (min)	Concentration (mg/dm^3)
0	
2	
4	
6	
10	
20	

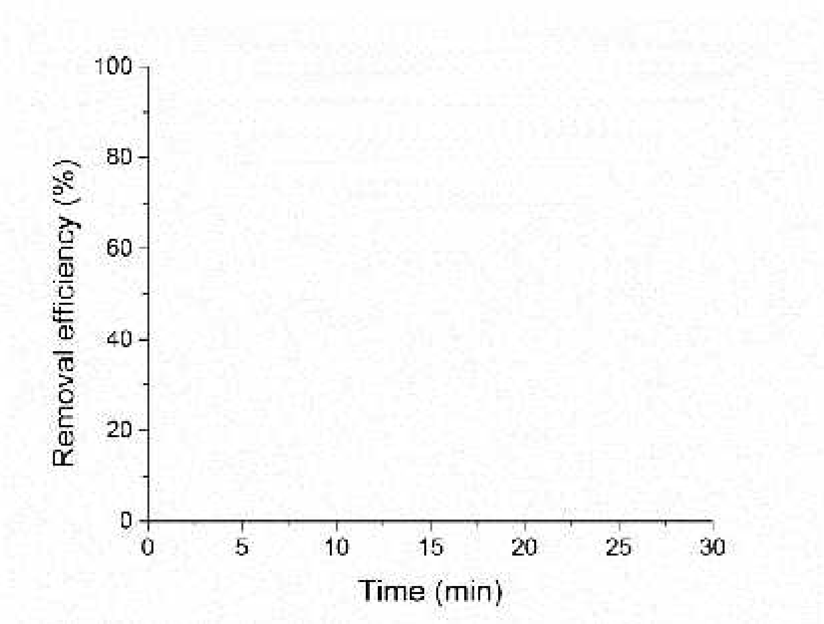

Figure 3. Removal efficiency in function of time

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Further reading

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DESCRIPTION OF REMOTE ACCESS		
1. NETCHEM COMMUNICATION SIDES (NOTE: NETCHEM Communication is defined as event that involves all kinds of internet interactions (in real time and not in real time) between participants via devices (PCs, laptops, tablets andmobilephones))		
host side (NOTE: Host side of NETCHEM Communication is defined as PC who invites other users to join the session)	**participant's PC in classroom**	
guest side (NOTE: Guest side of NETCHEM Communication is defined as PC who joins the invitation to session)	**participant's PC in laboratory**	
2. COMMUNICATION SOFWARE		
Team Viewer	Meeting: No	
	Remote control: No	
	Meeting and Remote control simultaneously: No	
Skype	Call 1:1: No	
	Conference Call: Yes	
3. COMUNICATION HARDWARE		
on host side	**1 PC for each participant**	
on guest side	**1 PC, 1 headsets with microphone, camera**	
4. INFORMATION EXCHANGE TYPE		
Educational (one side is dominantly receptive)	**Yes**	
	Place of Educator participant: guest side	
	Number of educator(s): 1	
	Place of student participant: **host side**	
	Number of student participant(s): **15**	
Consultative (two sides are equal in giving-receiving information)		
	Number of host side participant(s): **No**	
	Number of guest side participant(s): **No**	

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Remote Access Connection Instructions

What makes these labs different and unique from other classroom experiments is that we have incorporated a section in each activity to remotely characterize your samples from your classroom.

Request a remote lab session specifying information such as: the day, the time, and the instrument you are interested in using by visiting our web site:

http://netchem.ac.rs/remote-access

You will see the list of partners with the instruments provided to chose from.

You will be contacted by a Remote Access staff member to set up a test run to ensure you are set up properly and have the required infrastructure.

Send samples or verify the in-house sample you would like us to prepare and load for characterization.

Send your samples to the Remote Access center that you chose on your request.

There are two communications soft-ware packages, that will allow us to communicate instructions and answer questions during the session.

- TeamViewer: You can obtain a free download at: https://www.teamviewer.com/en/index.aspx
- Skype

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Remote Access Connection Instructions

You will need:

a) Computer with administrator access to install plug-ins and software

b) An internet connection

c) Speakers

d) Microphone

e) Projector connected to the same computer

f) Web browser (Firefox preferred)

During the test run you can refer to this guide to perform the following steps, but it's very important that you only proceed with these steps during your scheduled times. You may interfere with other remote sessions and potentially damage equipment if you log in at other times.

a) Open and logon to your Zoom / Team-viewer account. You will be given the access code to enter at the time of your test and then again during the remote session.

- If you are using the Zoom software, Remote Access staff will give you the access code.
- If you are using the Team-viewer software, Remote Access staff will give you the ID & password.

b) You should soon see the Remote Access desktop and at this point you can interact with the icons on the screen as if it were your desktop.

c) Switch to full screen mode by selecting the maximize screen option in the top right corner of the screen.

d) Upon completion of the session, move your mouse to the top right corner of the screen, and click on the X to disconnect the remote session. It will ask if you want to end the remote session. Click Yes.

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Author, Editor and Referee References

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Contributors to this material were: Jelena Mitrovic

Refereeing of this material was done by: ______________________

Editing into NETCHEM Format and onto NETCHEM platform was completed by: _______________

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References and Supplemental Material

The NETCHEM platform was established at the University of Nis in 2016-2019 through the Erasmus Programme.

Please contact a NETCHEM representatives at your institution or visit our website for an expanded contact list.

The work included had been led by the NETCHEM staff at your institution.

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