PHOTOLYTIC DEGRADATION OF *N*-NITROSAMINES

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INTRODUCTION

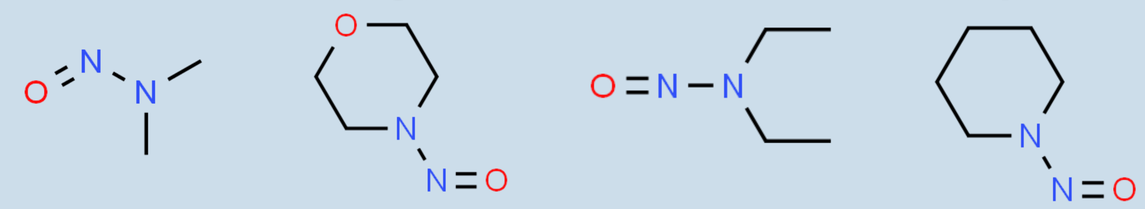
Numerous disinfection by-products (DBP) are formed from reactions between disinfectants and organic/inorganic substances during water disinfection. Many DBPs have been confirmed to be harmful to human health, including nitrogen-containing DBPs, such as nitrosamines. Therefore, it is necessary to develop effective processes for the removal of DBPs from water, such as advanced oxidation and membrane processes. In this work, the photolytic degradation of *N*-nitrosamines in ultrapure, pool and brackish water and in the retentate after the RO/NF process using a UV-LED photoreactor was investigated.

LED SPECIFICATION	VALUES	
	UV-A	UV-C
EMISSION ANGLE	120°	120°
LED SPACING	8.3 mm	16.6 mm
WAVELENGTH	365 nm	272 nm
LED SOURCES PER STRIP	15	8

MATERIALS AND METHODS

N-nitrosamines solution => 5 mg/L in MilliQ water, brackish water, and 4 mg/L in simulated pool water

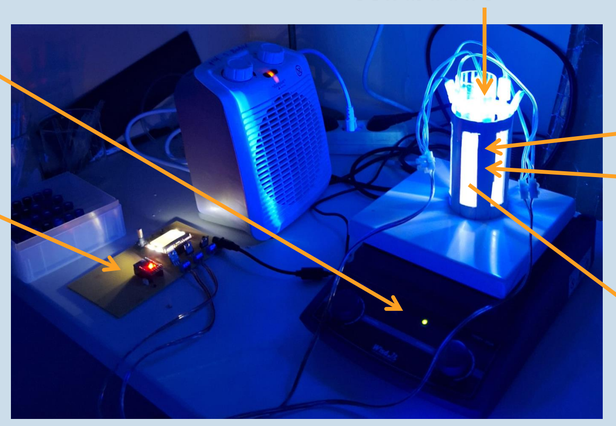
NDMA **NMOR** **NDEA** **NPIP**

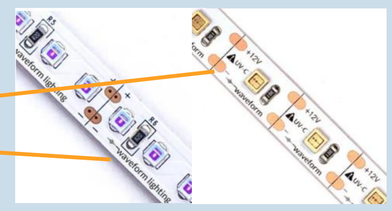


Magnetic stirrer

Arduino control board

Reactor





UV-A LED UV-C LED

HPLC analysis

A cylindrical quartz lab-scale reaction vessel with an inner diameter of 37 mm, length of 150 mm and wall thickness of 1.5 mm was used. Sections of the UV-LED strip were attached as vertical columns on cylindrical supports with a diameter of 60 mm so that the distance of the radiation source from the reactor wall was 10 mm.

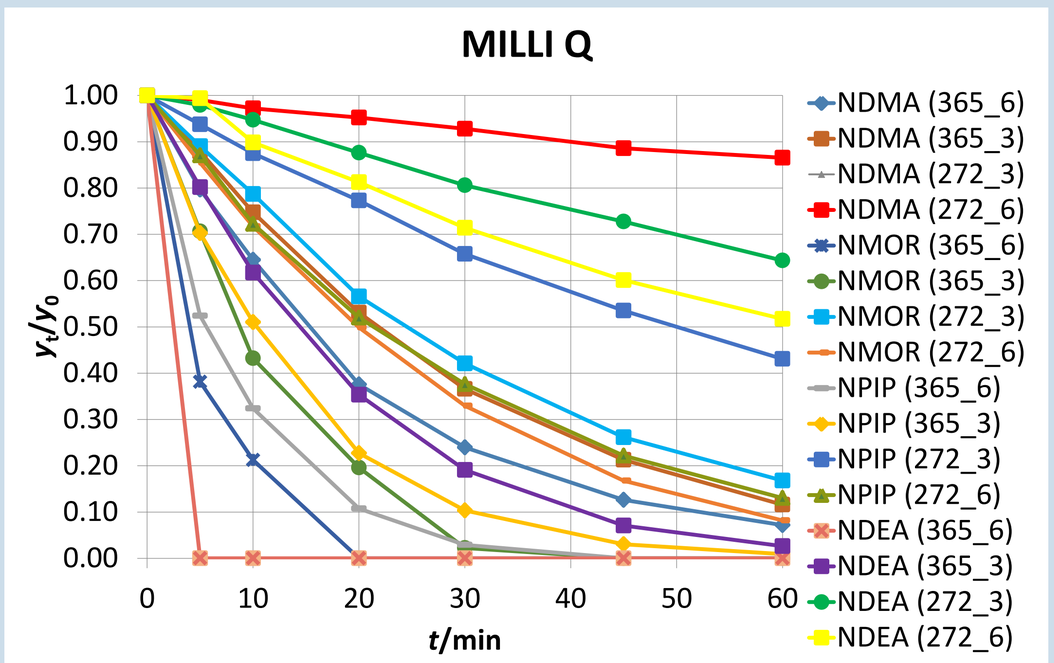
Four different cylindrical LED supports were used:

1) 6 columns and UV-A LEDs,
2) 6 columns and UV-C LEDs,
3) 3 columns and UV-A LEDs,
4) 3 columns and UV-C LEDs.

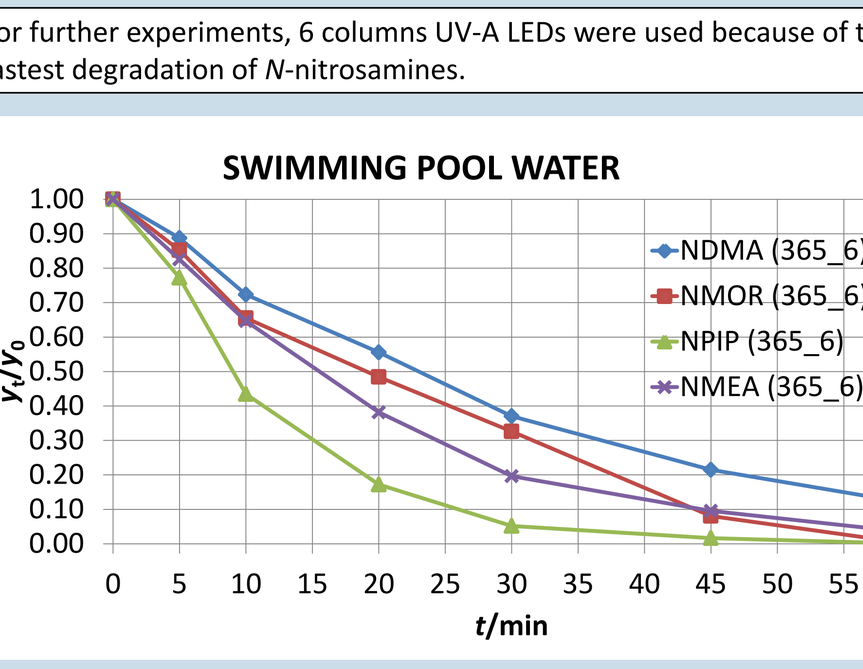
Aliquots of irradiated *N*-nitrosamines solution were analysed by HPLC-DAD on Kinetex C18 (Phenomenex, 150 mm x 4.6 mm, 5 mm, 100 Å) chromatographic column. The mobile phase was composed of MilliQ water (A) and acetonitrile (B). The flow rate was 0.5 mL/min. The column temperature was 20 °C. The injection volume for each sample was 20 µL.

RESULTS

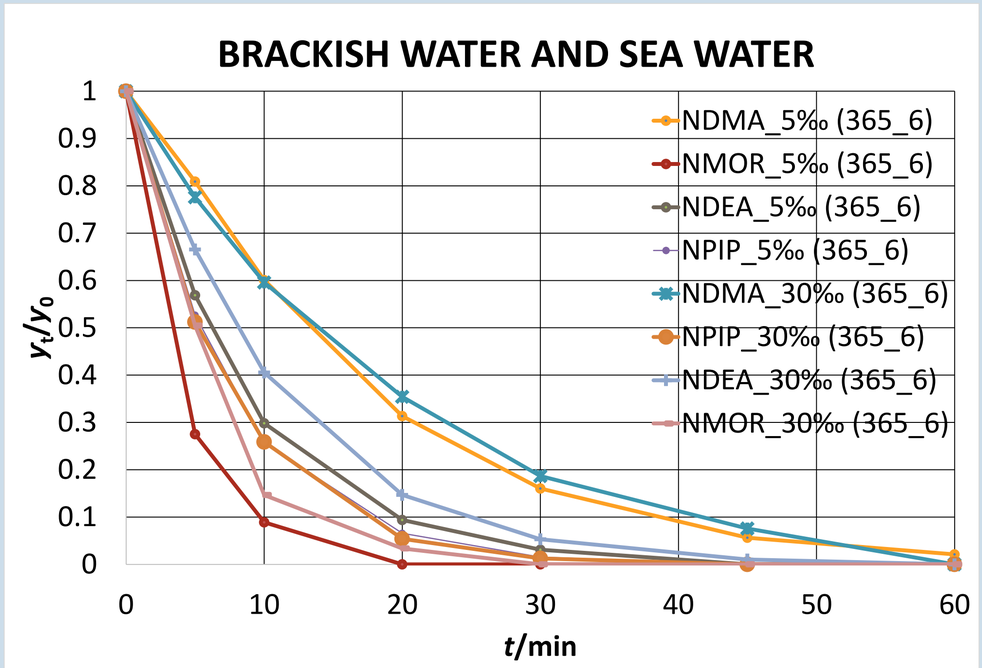
For further experiments, 6 columns UV-A LEDs were used because of the fastest degradation of *N*-nitrosamines.



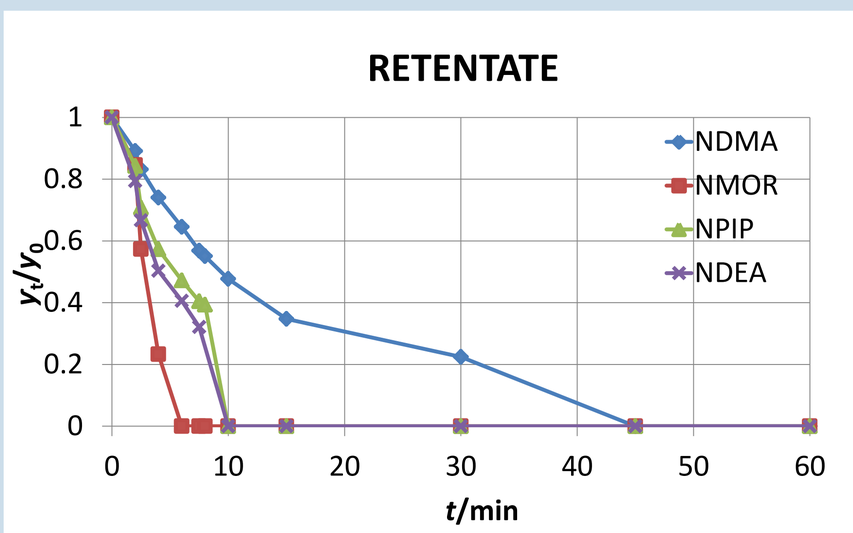
	k_{app} (min^{-1})	$t_{1/2}$ (min)
λ_N	NDMA	
365_6	0.0446	15.54
365_3	0.0361	19.20
272_3	0.0025	277.26
272_6	0.0045	154.03
λ_N	NMOR	
365_6	0.9805	0.71
365_3	0.1219	5.69
272_3	0.0302	22.95
272_6	0.0417	16.62
λ_N	NPIP	
365_6	0.116	5.98
365_3	0.0788	8.80
272_3	0.0141	49.16
272_6	0.0340	20.39
λ_N	NDEA	
365_6	0.0965	7.18
365_3	0.0612	11.33
272_3	0.0073	94.95
272_6	0.0118	58.74



k_{app} (min^{-1})	$t_{1/2}$ (min)
NDMA	
0.0358	19.36
NMOR	
0.0529	13.10
NPIP	
0.0955	7.26
NMEA	
0.0569	12.18



5 ‰ NaCl		30 ‰ NaCl	
k_{app} (min^{-1})	$t_{1/2}$ (min)	k_{app} (min^{-1})	$t_{1/2}$ (min)
NDMA		NDMA	
0.0655	10.58	0.0575	12.05
NMOR		NMOR	
0.2421	2.86	0.1735	4.00
NPIP		NPIP	
0.1394	4.97	0.1205	5.75
NDEA		NDEA	
0.1165	5.95	0.1540	4.50



k_{app} (min^{-1})	$t_{1/2}$ (min)
NDMA	
0.0510	13.59
NMOR	
0.6345	1.09
NPIP	
0.1205	5.75
NDEA	
0.1540	4.50

CONCLUSION

1) By reducing the distance of the LEDs from the reactor and using UV-A LEDs, faster degradation of *N*-nitrosamines is obtained.
2) Matrix affects the photodegradation of *N*-nitrosamines. The photolytic degradation of *N*-nitrosamines in pool water was slower than degradation in brackish water.
3) Degradation in brackish water with 5 ‰ salinity was slightly faster than degradation of *N*-nitrosamines in sea water with 30 ‰ salinity.
4) The concentration of *N*-nitrosamines affects the rate of photodegradation. Complete degradation of *N*-nitrosamine in the retentate (0.1 mg/L) was achieved in only 10 minutes, except for NDMA (45 min).

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