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New approaches to determination of the quantum yield of hydroxyl radical generation and its reactivity with emerging contaminants

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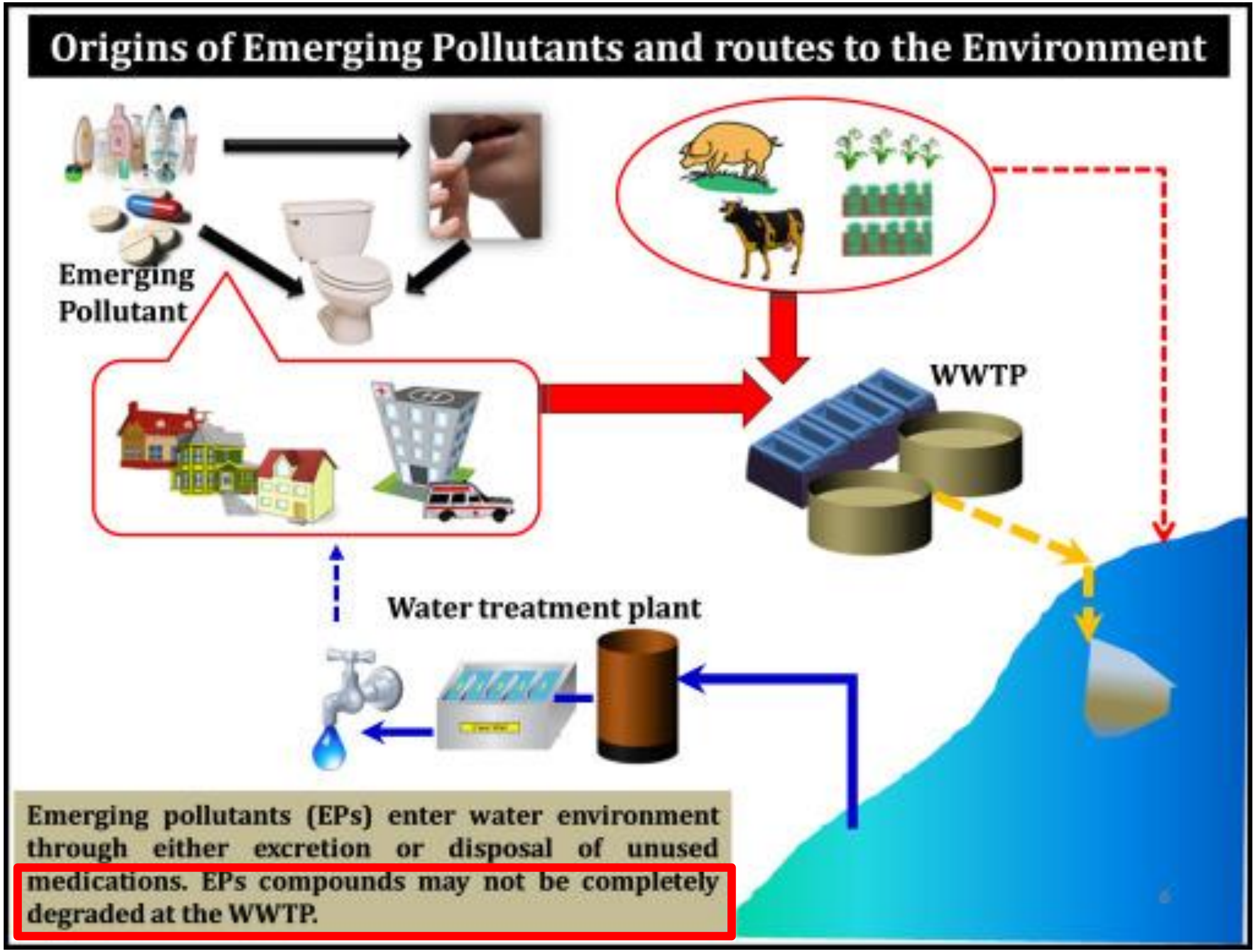
Emerging Pollutants (EPs) and Advanced Oxidation Processes (AOPs)



Origins of Emerging Pollutants and routes to the Environment

Emerging pollutants (EPs) enter water environment through either excretion or disposal of unused medications. EPs compounds may not be completely degraded at the WWTP.

Task:

destruction and mineralization of Eps

Problem:

Bio stability

Chemical stability

Solvation – AOPs:

(photo)catalysis

photolysis

Ozonation

Chlorination

Key intermediates:

h^+

$^{\bullet}$OH radical

$Cl^{\bullet}$ radical

$SO_4^{\bullet -}$ radical

Fe(III) species in Environmental Photochemistry and AOPs

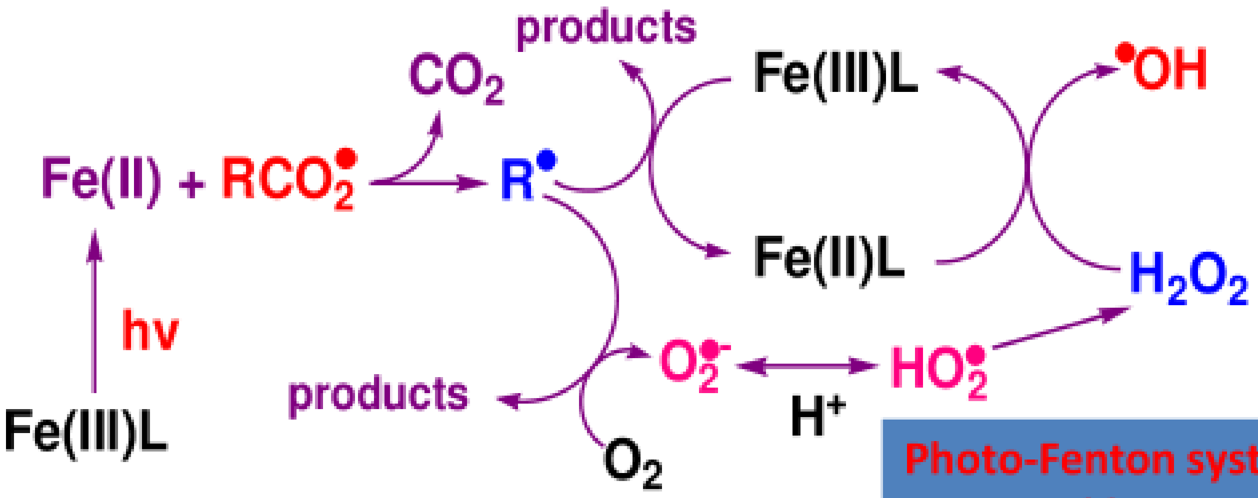
Generation of ROS (${}^\bullet OH$, $HO_2{}^\bullet$ and H_2O_2) capable to effective mineralization of organic substances

$$FeOH^{2+} + h\nu \longrightarrow Fe(II) + {}^\bullet OH$$

$$Fe(II) + H_2O_2 = Fe(III) + {}^\bullet OH + OH^-$$

Fenton system, pH 3

(pH 3, model system, $\phi({}^\bullet OH$, 300-370 nm) = 0.2 – 0.07)



Fe(III)L $\xrightarrow{h\nu}$ Fe(II) + $RCO_2^\bullet$ → $R^\bullet$ + CO_2

$R^\bullet$ + Fe(III)L → products + Fe(II)L

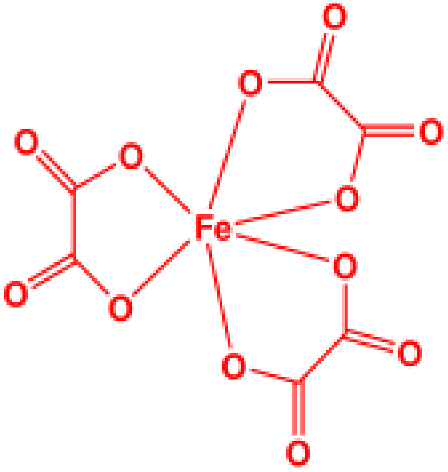
Fe(II)L + H_2O_2 → Fe(III)L + ${}^\bullet OH$

$R^\bullet$ + O_2 → products + $O_2^{\bullet -}$

$O_2^{\bullet -}$ ⟷ (H^+) $HO_2^\bullet$ → H_2O_2

Photo-Fenton systems

Fenton-like systems



Ferrioxalate

L – aliphatic acid (oxalate, tartrate, citrate..), neutral pH

$\phi({}^\bullet OH$, 308 nm) = 0.25 (oxalate)

Application of Fe(III) carboxylates in AOPs:
What we know and have to know

1) Charge transfer absorption bands in the region of UV sunlight

2) Photooxidation of wide range of emerging contaminants:

   - *Herbicides*
   - *Phenols and Bisphenols*
   - *Pharmaceutical and personal care products (PPCP)*
   - *Dyes, etc.*

3) pH working range from 3 to 7 **(depends on stability constants)**

4) Main oxidative agent – $^{\bullet}OH$ radical **(spin traps, product analysis)**

5) Reactivity of $^{\bullet}OH$ radical with target compounds **(rate constant k_{OH}; important to estimate efficiency of photooxidation in real conditions)**

6) Quantum yield (ϕ_{OH}) of $^{\bullet}OH$ radical generation **(efficiency of a photosystem, possibility of its practical application)**

Goals:

- Simple and affordable approach to the determination of ϕ_{OH} values during UV photolysis of natural Fe(III) carboxylate complexes
- Reliable method for direct determination of rate constants of hydroxyl radical (k_{OH}) reactions with target compounds

Methods:

- Nanosecond laser flash photolysis
  - Nd:YAG laser, λ_{ex} = 355 nm, λ_{reg} = 320 - 760 nm, $\tau \approx$ 6 ns

- Steady-state photolysis
  - Exilamp XeCl, λ_{ex} = 308 nm, $I_0 \approx$ 0.15 J/min
  - Hg lamp DRSh-500, λ_{ex} = 365 nm, $I_0 \approx$ 1.2 J/min
- High performance liquid chromatography (HPLC) **Agilent LC 1200**

Determination of ϕ_{OH} upon UV photolysis of natural Fe(III) carboxylate complexes: idea

- **Reliable reference system**

$[\mathrm{FeOH}]^{2+} - h\nu \rightarrow \mathrm{Fe(II)} + OH^{\bullet}$ $\phi(^{\bullet}OH, 308\ nm) = 0.2$; $\phi(^{\bullet}OH, 365\ nm) = 0.074$

- **Simple, cheap and accessible analytical method**

  High performance liquid chromatography (HPLC)

- **Selective trap for hydroxyl radical**

  benzene does not react with other ROS, except for the $^{\bullet}OH$

  $OH^{\bullet} + C_6H_6 \rightarrow C_6H_6(OH^{\bullet})$, $k_{OH} = 7.8 \times 10^{9}\ M^{-1}s^{-1}$

  $C_6H_6(OH^{\bullet}) \rightarrow phenol\ (270\ nm)$, $= 53\%$

- **simple calculations, possibility to avoid source intensity calibration**

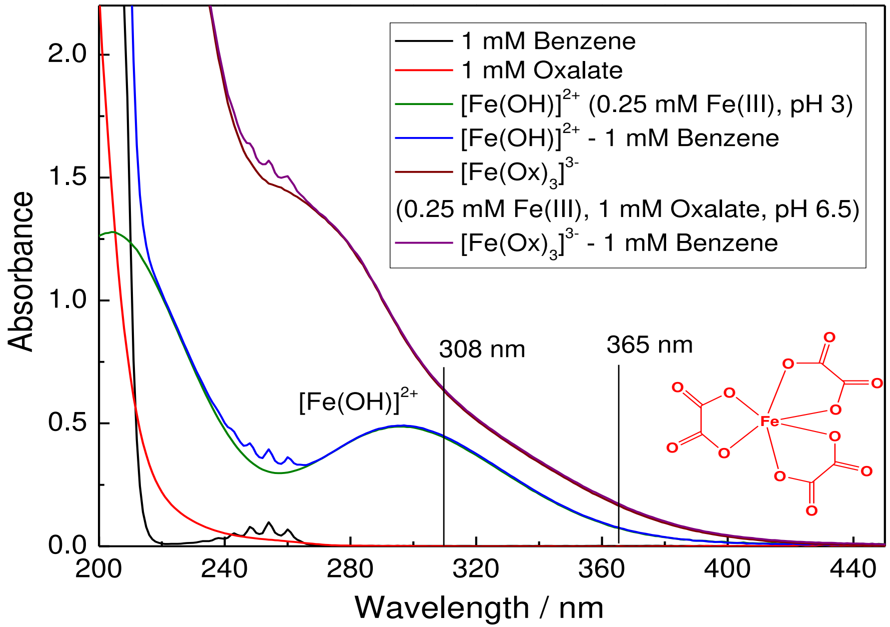
$$\varphi_{OH} = \varphi_{OH}([FeOH]^{2+}) \frac{k_{obs}(Fe-Ox) I_{abs}([FeOH]^{2+})}{k_{obs}([FeOH]^{2+}) I_{abs}(Fe-Ox)}$$

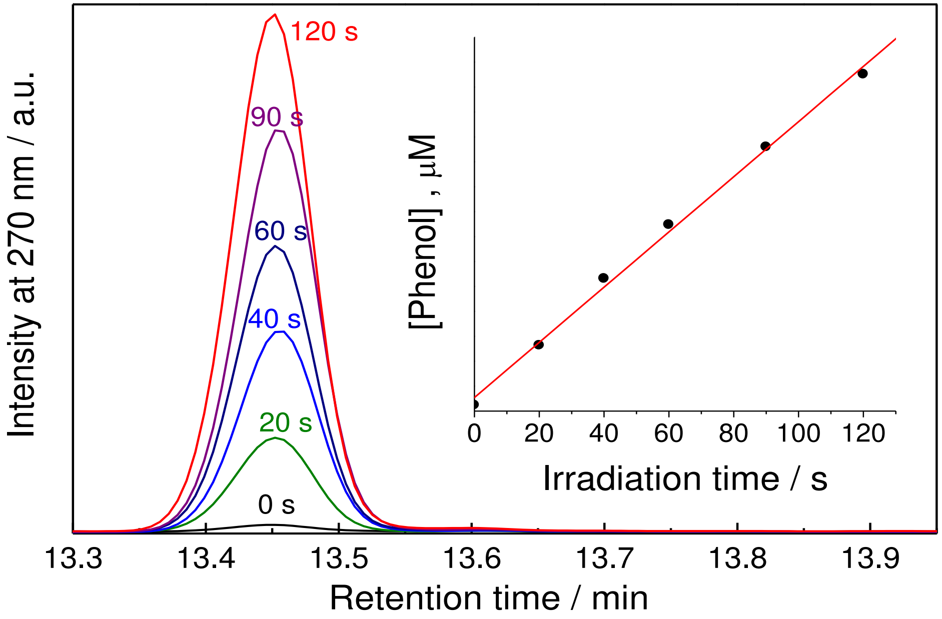
Determination of ϕ_{OH} upon UV photolysis of natural Fe(III) carboxylate complexes: methodology

$OH^{\bullet} + C_6H_6 \rightarrow C_6H_6(OH^{\bullet})$

$C_6H_6(OH^{\bullet}) \rightarrow phenol,\ \eta = 53\%$

$$\varphi_{OH} = \varphi_{OH}([FeOH]^{2+}) \frac{k_{obs}(Fe - Ox) I_{abs}([FeOH]^{2+})}{k_{obs}([FeOH]^{2+}) I_{abs}(Fe - Ox)}$$



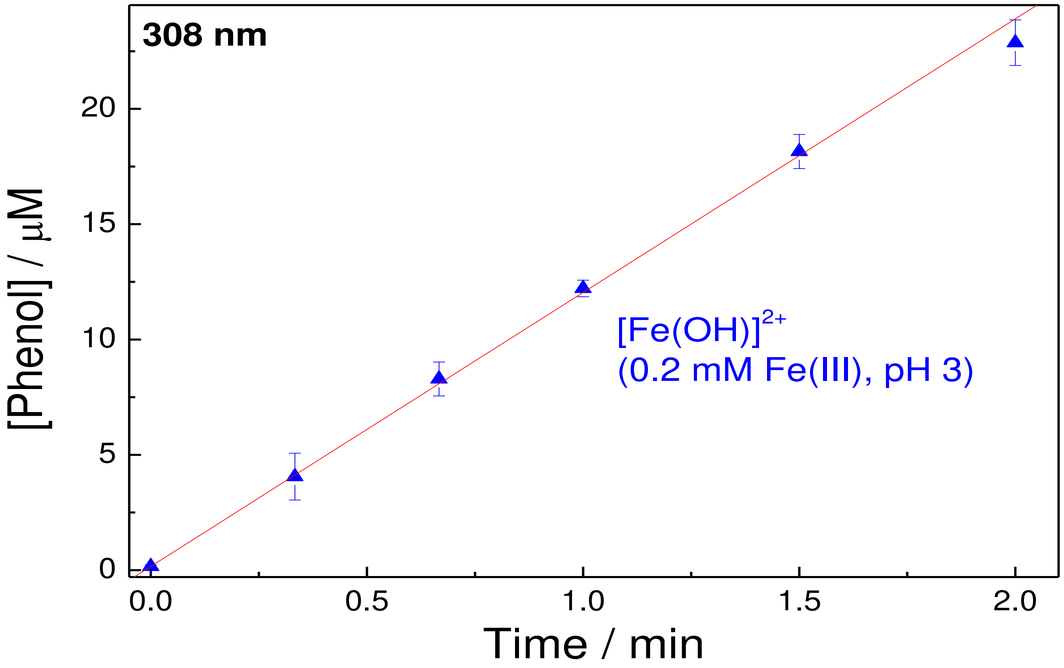


% of excitation light absorbed (I_{abs}) in reference and studied systems

$$k_{obs} = \frac{\Delta[PhOH]}{\Delta t}$$

Phenol generation rate in both systems

Checking the applicability of the method for determining ϕ_{OH} on reference system



Independent definition of the •OH radical quantum yield in the [Fe(OH)]$^{2+}$ system

$$\varphi_{OH} = \frac{k_{obs}}{\eta I_{abs}}$$

This work:

ϕ(•OH, 308 nm) = 0.23 ± 0.04

ϕ(•OH, 365 nm) = 0.09 ± 0.01

Literature:

ϕ(•OH, 308 nm) = 0.2 ± 0.03

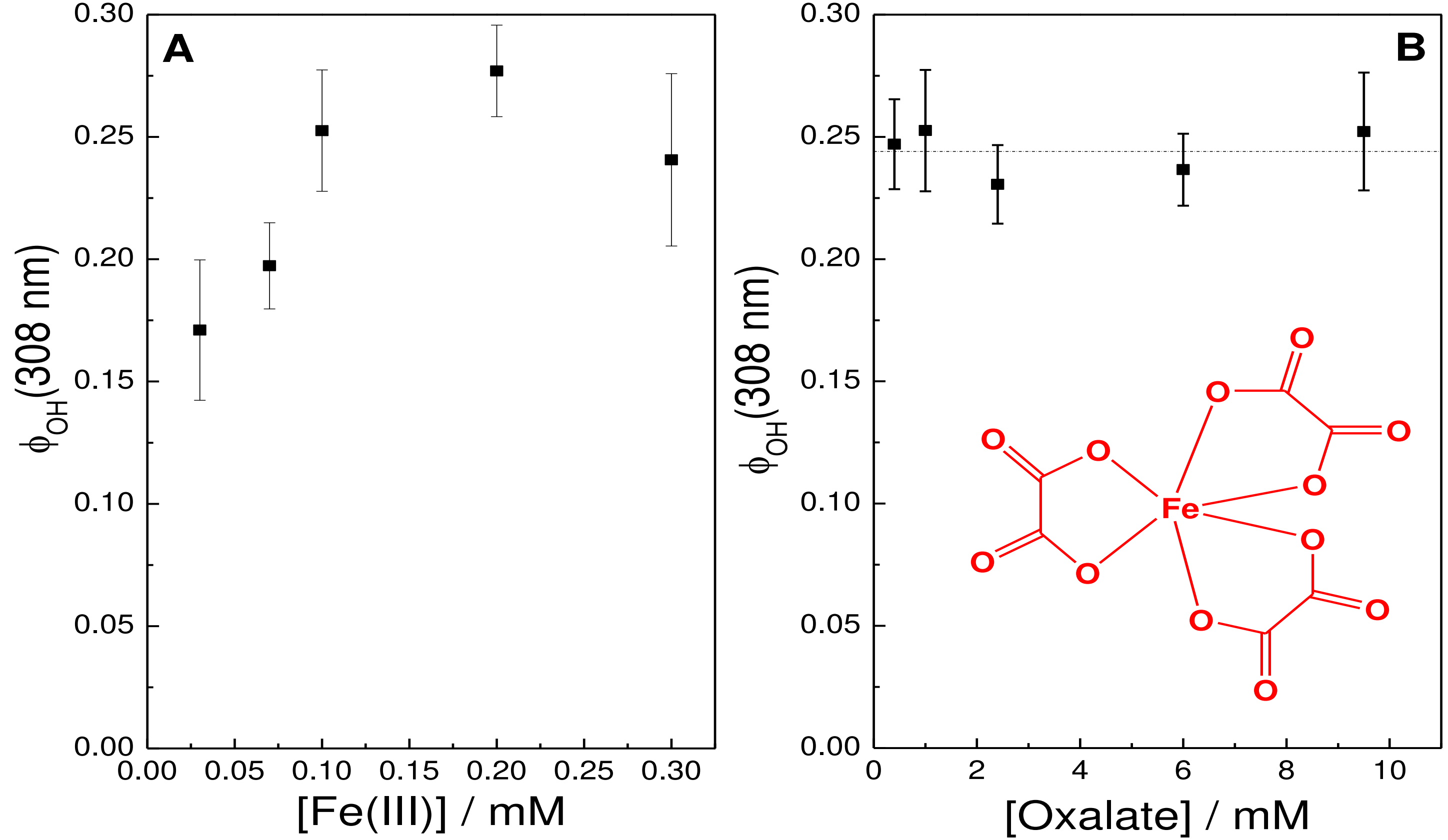
ϕ(•OH, 365 nm) = 0.074 ± 0.015

- **Good agreement between independent measurements with literature data**
- **The 15-20% difference may be due to:**

Higher % conversion of benzene to phenol

$$C_6H_6(OH^\bullet) + Fe(III) \rightarrow phenol + Fe(II) + H^+$$

ϕ_{OH}(308 nm, pH 6.5): influence of [Fe(III)] and [Oxalate]

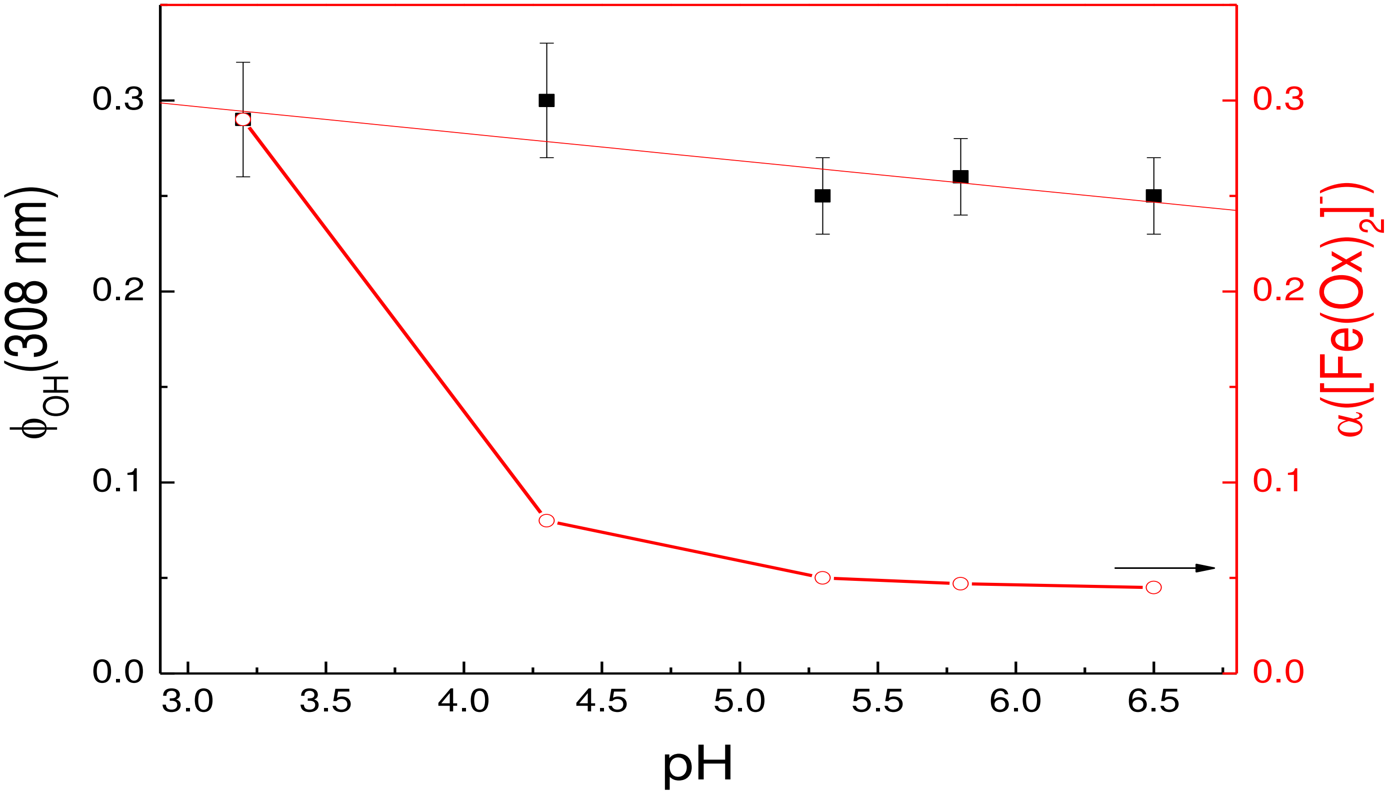


$Fe(II) + O_2^{-\bullet} + 2H_2O \longrightarrow H_2O_2 + Fe(III) + 2OH^-$ $k = 7.2\times10^8\ M^{-1}s^{-1}$

$Fe(III) + O_2^{-\bullet} \longrightarrow O_2 + Fe(II)$ $k = 1.5\times10^8\ M^{-1}s^{-1}$

$Fe(II) + H_2O_2 \longrightarrow {}^{\bullet}OH + Fe(III) + OH^-$ $k = 63\ M^{-1}s^{-1}$

ϕ_{OH}(308 nm): influence of pH



Quantum yield increases about 20% with decreasing of pH from 6.5 to 3.2

- **Equilibrium between $HO_2^{\bullet}$ and $O_2^{-\bullet}$ radicals (pK_a = 4.8)**
- **Shift of equilibrium from $Fe(Ox)_3^{3-}$ to more photoactive form $Fe(Ox)_2^{-}$**

ϕ_{OH}(308 nm): influence of irradiation wavelength

λ, nm	254	282	308	365
φ_{OH}	0.28 ± 0.04	0.22 ± 0.04	0.25 ± 0.03	0.22 ± 0.03

- φ_{OH} only slightly decreased with increasing of excitation wavelength

- quantum yield of Fe(III)-oxalate photolysis is also practically independent on the excitation wavelength in the range of 270 – 430 nm and increases by less than 15% (from 1.24 to 1.4) at lower wavelengths

Determination of rate constants of •OH radical reaction (k_{OH}) with target compounds

Literature approaches:

Steady-state photolysis (competitive method with HPLC detection)

$S + {}^\bullet OH \longrightarrow \quad k_{OH}^{S}$; $\quad X + {}^\bullet OH \longrightarrow \quad k_{OH}^{X}$

«+» simple realization, accessible analytical method

«-» relative method (k_{OH}^{X}/k_{OH}^{S});

X and S doesn't absorb excitation light

Absence of reactions between primary species and X/S

Pulse radiolysis or flash photolysis (intermediate absorption)

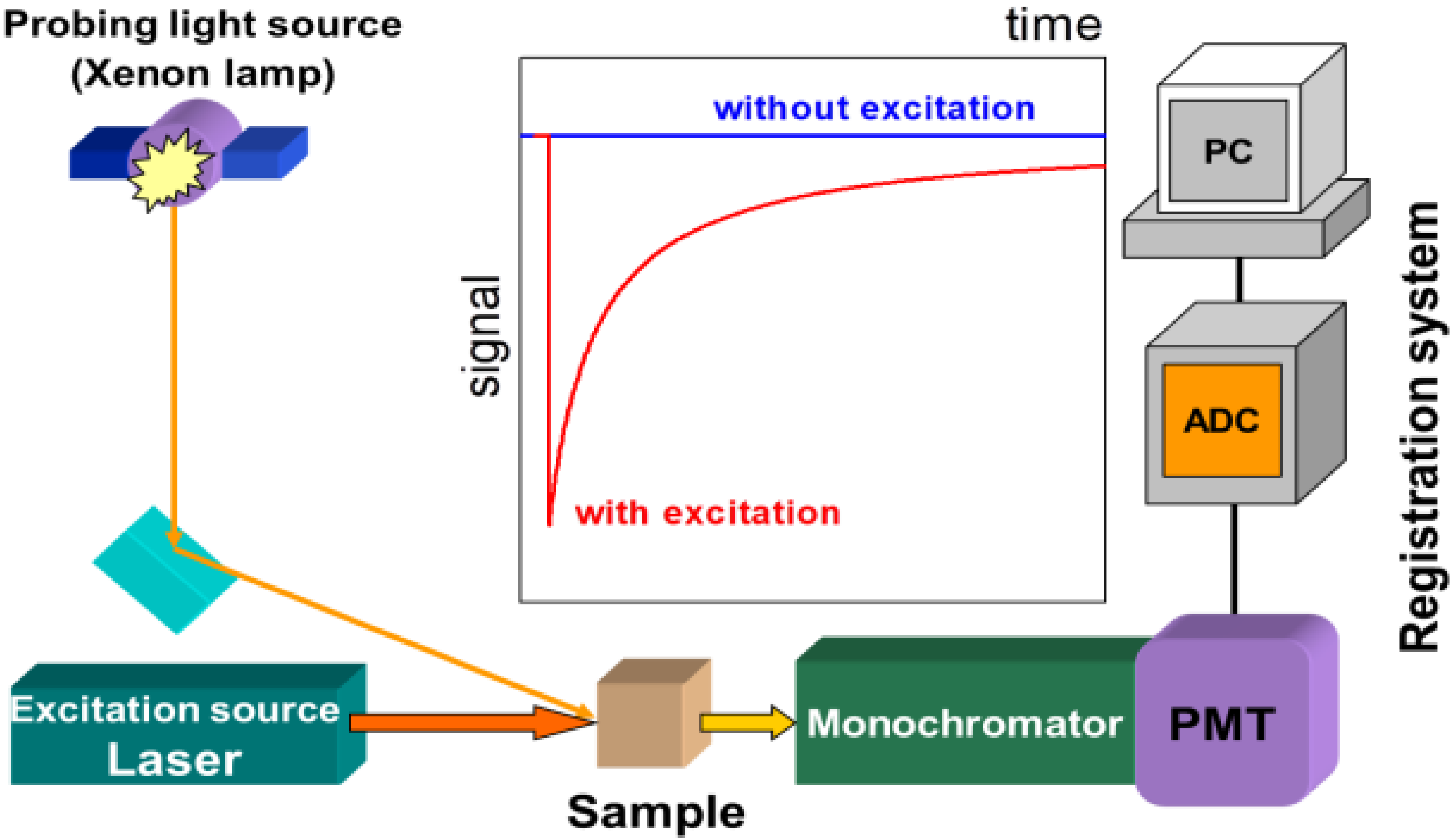
«+» direct detection of •OH radical reaction with X

«-» rather sophisticated and rare methods

In the case of FP high •OH quantum yield and absence of photochemical activity of X are important requirements

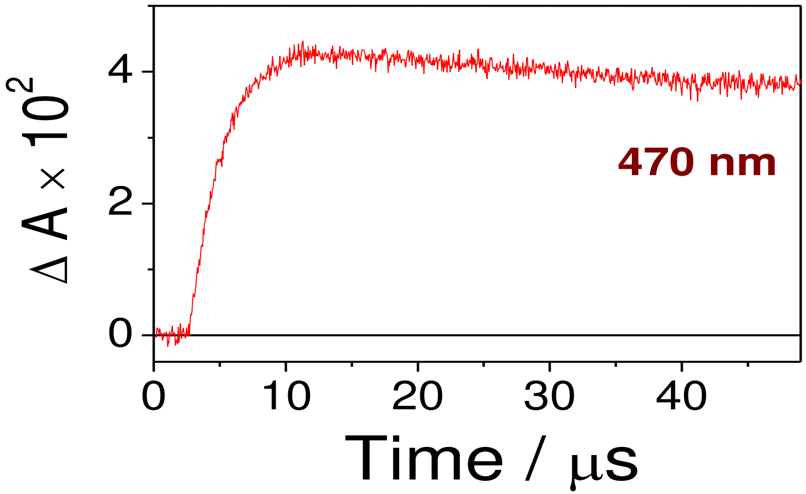
Intermediate X-•OH have to absorb in proper range of wavelengths

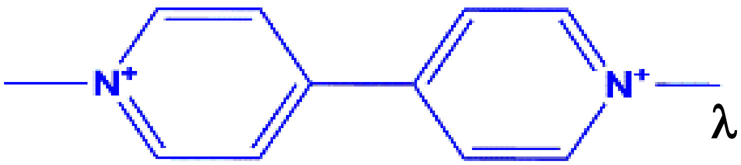
Nanosecond laser flash photolysis technique



Recorded signal – change in sample absorption at a selected wavelength (ΔA)

Methylviologen dication as prospective •OH radical trap in time-resolved experiments





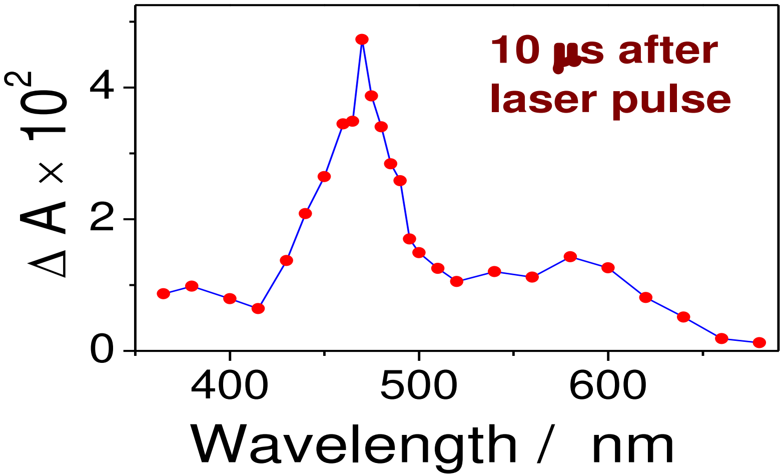
MV^{2+}

λ < 300 nm

$Fe(OH)^{2+}_{aq} \xrightarrow{h\nu} Fe^{2+}_{aq} + {}^{\bullet}OH$

$MV^{2+} + {}^{\bullet}OH \longrightarrow MV({}^{\bullet}OH)^{2+}$

$k = (2.5 \pm 0.2) \times 10^8\ M^{-1}s^{-1}$

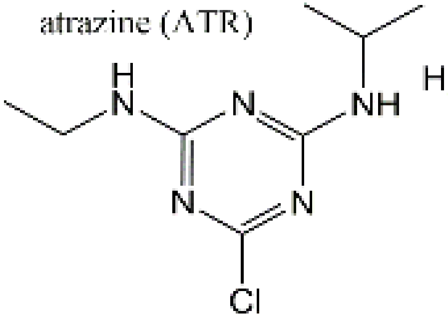


Properties of $MV({}^{\bullet}OH)^{2+}$

- **λ_{max} = 470 nm**
- **ε_{max} = 16000 $M^{-1}cm^{-1}$**

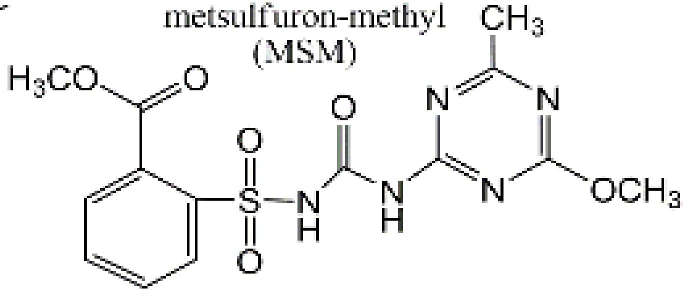
S. Solar, W. Solar, N. Getoff, J. Holcman, K. Sehested: J. Chem. Soc., Faraday Trans. 1, 81, 1101 (1985)

Organic herbicides as model target contaminants to check reactivity of •OH radical



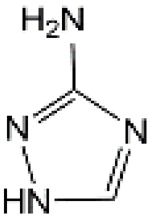
atrazine (ATR)

1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine

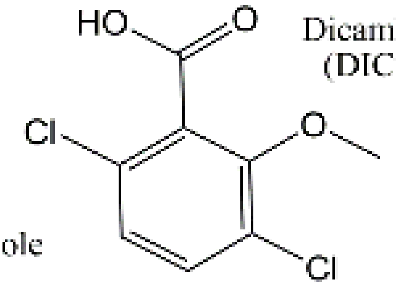


metsulfuron-methyl (MSM)

methyl 2-(*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)sulfamoyl)benzoate

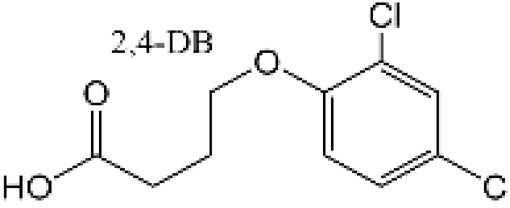


3-amino-1,2,4-triazole (AMT)



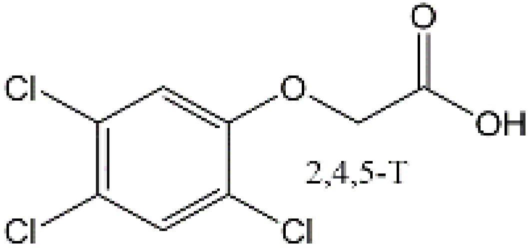
Dicamba (DIC)

3,6-Dichloro-2-methoxybenzoic acid



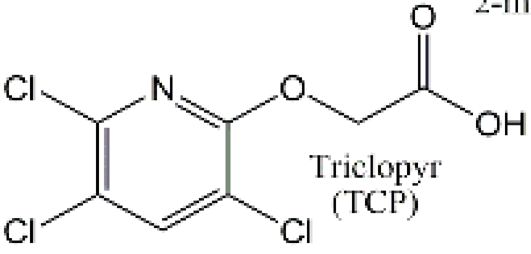
2,4-DB

4-(2,4-dichlorophenoxy)butyric acid



2,4,5-T

2,4,5-Trichlorophenoxyacetic acid



Triclopyr (TCP)

[(3,5,6-Trichloro-2-pyridinyl)oxy]acetic acid

- **No own absorption at 355 nm**
- **Stable in the presence of Fe(III), no complexation with Fe(III) ions**
- **X(•OH) adducts have no absorption at 470 nm**

Kinetics of MV(•OH) formation in presence of X

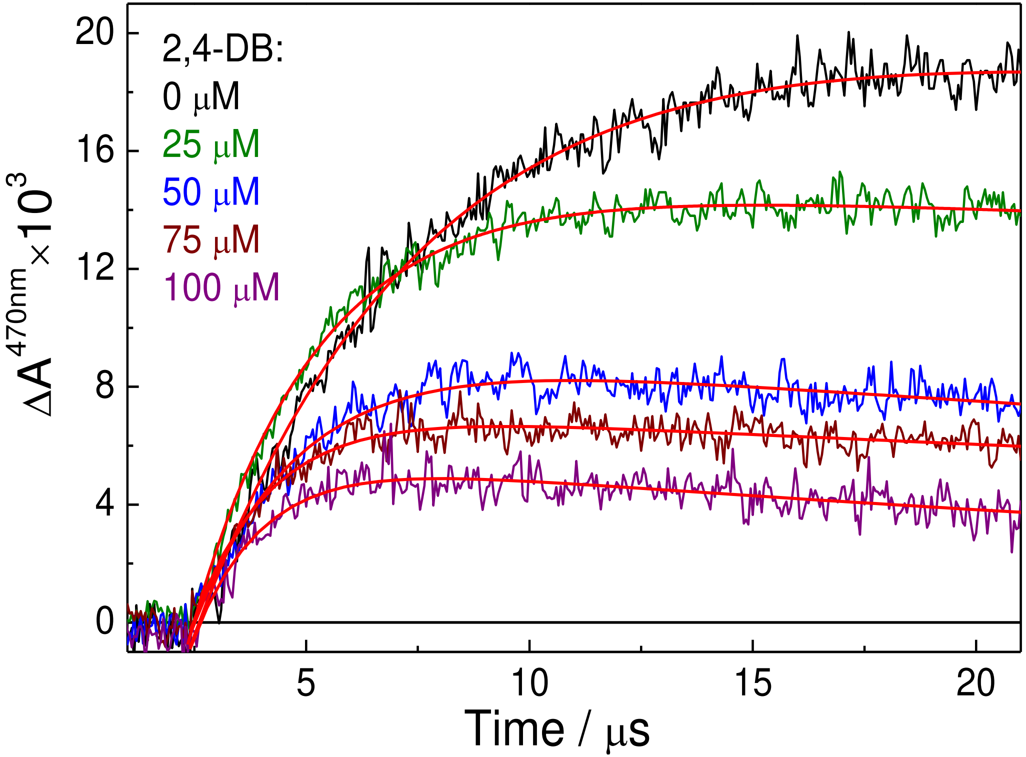
$$\Delta A^{470nm}(t) = \mathbf{A}\left[e^{(-k_d t)} - e^{(-k_{obs} t)}\right]$$

$$k_{obs} = k_{OH}^{MV}[MV^{2+}]_0 + k_{OH}^{X}[X]_0$$

$$OH^\bullet + X \xrightarrow{k_{OH}^{X}} X(OH^\bullet)$$

$$OH^\bullet + MV^{2+} \xrightarrow{k_{OH}^{MV}} MV(OH^\bullet)^{2+}$$

$$MV(OH^\bullet)^{2+} \xrightarrow{k_d}$$

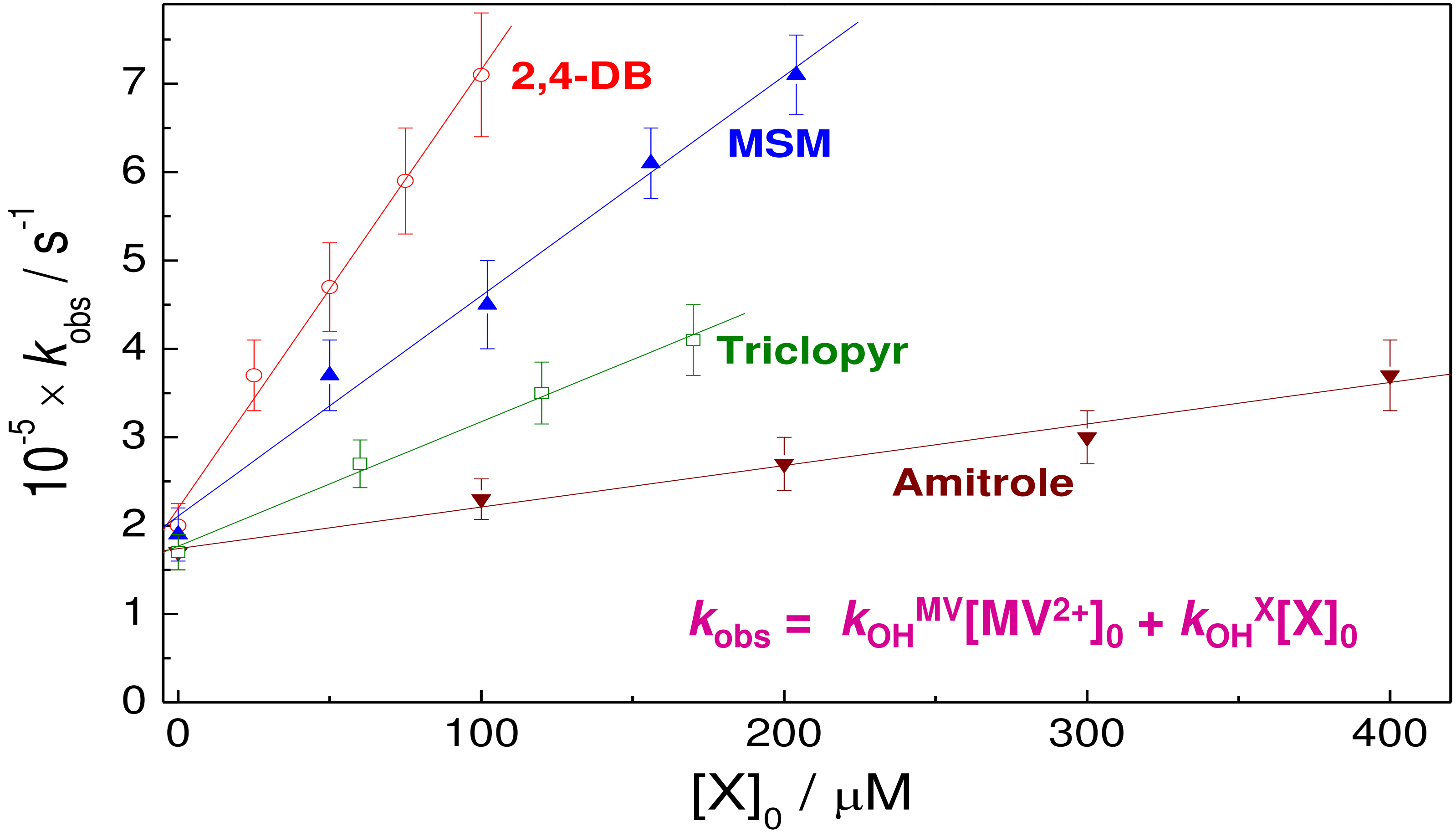


$$\frac{d[OH^\bullet]}{dt} = -(k_{OH}^{X}[X]_0 + k_{OH}^{MV}[MV^{2+}]_0)[OH^\bullet]$$

$[OH]_0 << [X]_0, [MV^{2+}]_0$

$$\frac{\mathrm{d}[MV(OH^\bullet)^{2+}]}{\mathrm{dt}} = k_{OH}^{MV}[MV^{2+}][\mathrm{OH}^\bullet] - k_\mathrm{d}\,[MV(OH^\bullet)^{2+}]$$

Determination of k_{OH} values with target compounds



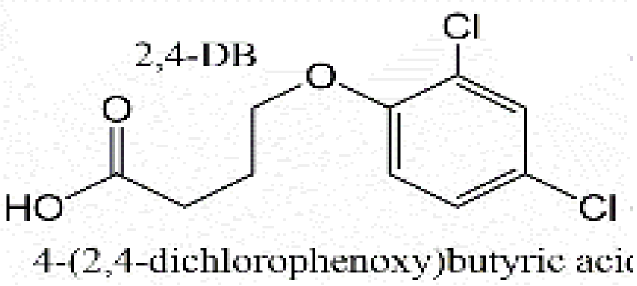
- Good linear dependence k_{obs} from initial herbicide concentration
- Good precision (10-15%) of k_{OH} determination for target compounds

Comparison of k_{OH} values with literature results

	Amitrol	Atrazine	2,4-DB	MSM	2,4,5-T	Triclopyr
pKa	4.14	1.6	2.6	3.75	2.7	2.7
pH	**2.9** 3, 7	**2.9**, 3.0, 3.6	**2.9** 2.5, 9.0	**2.9**, 3.4	**2.9**, 8.5	**2.9**, 7.0
$k_{OH}^{X} \times 10^{-9}$	**0.47**	**3.5**	**5.0**	**2.5**	**6.3**	**1.4**
$k_{OH}^{X} \times 10^{-9}$ (lit)	0.36; 0.57	2.9, 2.6	5.2; 6.6	3.5	6.4	1.7
Method	SSP, SSP	SSP, SSP	PR, PR	LFP	PR	ozonation

SSP – steady-state photolysis, LFP – laser flash photolysis, PR – pulse radiolysis

- **Good agreement with literature values**
- **Results at pH 3 should be carefully extrapolated to higher pH values**



Conclusions

- Simple and reliable method for the determination of ϕ_{OH} values during the photolysis of natural iron carboxylate complexes is proposed.
- It is shown that the most popular Fe(III) – oxalate system demonstrates high values of ϕ_{OH}, which are practically constant in a wide range of pH, excitation wavelengths and initial concentrations of iron and oxalate ions.
- An express method for determining the rate constants of the reaction of •OH with organic pollutants is proposed:

"+" One-wavelength technique, good for "optically silent" X(•OH)

"+" good precision of k_{OH}^{X} values due to high sensitivity

"-" doesn't work for X(•OH) with absorption at 470 nm

"-" results at pH 3 can be inappropriate at higher pH values

RSF-NSFC

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Фотодеградация органических гербицидов в системе Fe(III) – оксалат

$10^2\times\varphi_{OH}([FeOH]^{2+}) = 20$; $10^2\times\varphi_{OH}([Fe\text{-}Ox) = 25$; $\varphi_{OH}([Fe\text{-}Ox)/\varphi_{OH}([FeOH]^{2+}) = 1.25$

Соединение	$10^2\times\phi_{degr}$ $([FeOH]^{2+})$	$10^2\times\phi_{degr}$ (Fe-Ox)	ϕ_{degr}(Fe-Ox) / $\phi_{degr}([FeOH]^{2+})$
2,4-DB	12 ± 2	16 ± 3	1.33 ± 0.1
2,4,5-T	13 ± 2	17 ± 3	1.31 ± 0.1
Triclopyr	16 ± 3	17 ± 3	1.06 ± 0.06
Dicamba	14 ± 3	18 ± 4	1.29 ± 0.1
Atrazine	9.5 ± 2	10 ± 2	1.05 ± 0.04

- **Концентрации гербицидов (≤ 0.1 мМ) не хватает для полного перехвата гидроксильных радикалов**
- **В ходе фотолиза происходит 20-30% конверсия гербицидов в фотопродукты, конкурирующие за OH радикал**
- **Влияние других АФК на фотодеградацию гербицидов незначительно**

Системы генерации •ОН радикала при нейтральном pH

$$H_2O_2 - h\nu \rightarrow 2\ OH^{\bullet};\ \varphi(OH^{\bullet},\ 308\ \text{nm}) = 0.8 \qquad (1)$$

$$S_2O_8^{2-} - h\nu \rightarrow 2\ SO_4^{-\bullet};\ \varphi\ (SO_4^{-\bullet}, 308\ \text{nm}) = 0.55 \qquad (2)$$

$$SO_4^{-\bullet} + OH^- \longrightarrow OH^{\bullet} + SO_4^{2-}\ (\text{pH} > 9)$$

$$NO_2^- + H_2O - h\nu \rightarrow OH^- + OH^{\bullet} + NO;\ \varphi(OH^{\bullet},\ 308\ \text{nm}) = 0.07\ (3)$$

$$NO_3^- - h\nu \rightarrow OH^{\bullet} + NO_2;\ \varphi(OH^{\bullet},\ 302\ \text{nm}) = 0.014 \qquad (4)$$

Ограничения существующих систем:

- Слабое поглощение/отсутствие поглощения в ближнем УФ (1-4)
- Генерация других активных радикалов (1, 3)
- Генерация ОН радикала только в щелочной среде (2)
- Низкие квантовые выходы фотолиза (3, 4)

Образование АФК при фотолизе комплекса $[Fe(Ox)_3]^{3-}$

$[Fe(Ox)]_3^{3-} \xrightarrow{hv} [Fe(II)(Ox)]_2^{2-} + Ox^{\bullet-}$ $\phi = 0.6$ (1)

$Ox^{-\bullet} \longrightarrow CO_2 + CO_2^{-\bullet}$ $k_2 = 2\times10^6\ s^{-1}$ (2)

$CO_2^{-\bullet} + O_2 \longrightarrow CO_2 + O_2^{-\bullet}$ $k_3 = 2.4\times10^9\ M^{-1}s^{-1}$ (3)

$CO_2^{-\bullet} + [Fe(Ox)]_3^{3-} \rightarrow CO_2 + [Fe(II)(Ox)]_2^{2-} + Ox^{2-}$ $k_4 \approx 8\times10^9\ M^{-1}s^{-1}$ (4)

$Fe(II) + O_2^{-\bullet} + 2H^+ \longrightarrow H_2O_2 + Fe(III)$ $k_5 = 10^7\ M^{-1}s^{-1}$ (5)

$Fe(II) + H_2O_2 \longrightarrow {}^{\bullet}OH + Fe(III) + {}^{-}OH$ $k_6 = 63\ M^{-1}s^{-1}$ (6)

$Fe(II) + {}^{\bullet}OH \longrightarrow Fe(III) + {}^{-}OH$ $k_7 = 4.3\times10^8\ M^{-1}s^{-1}$ (7)

${}^{\bullet}OH + Ox^{2-} \longrightarrow Ox^{-\bullet} + {}^{-}OH$ $k_8 = 7.7\times10^6\ M^{-1}s^{-1}$ (8)

В ходе фотолиза происходит постоянная регенерация ионов Fe(III), окисление лиганда и образование АФК