Part 3. The Terrestrial Environment

Additional Chapter 3.
The Terrestrial Pollution Solutions
(Hot topics)

Additional Chapter 3. The Terrestrial Pollution Solutions

Contents

Additional Chapter 3. The Terrestrial Pollution Solutions

3.1 The Terrestrial Pollution : Dioxin

Die

DIOXIN

Chemical stability

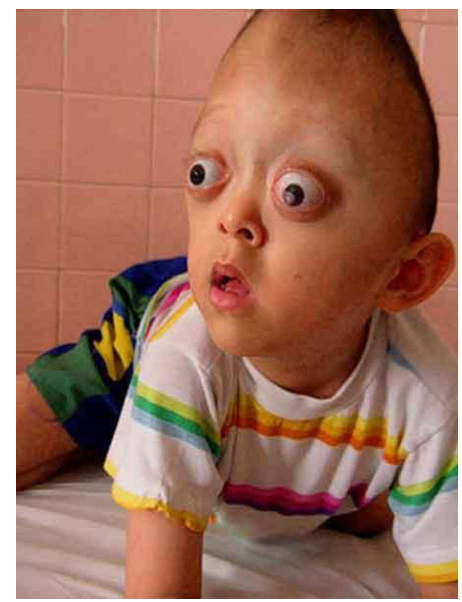
Colorless, ordorless
Absorption at far

BEFORE AFTER

Yushchenko endured dioxin poisoning, likely by political foes, which, along with nearly killing him, left his skin severely disfigured. WILLisms.com

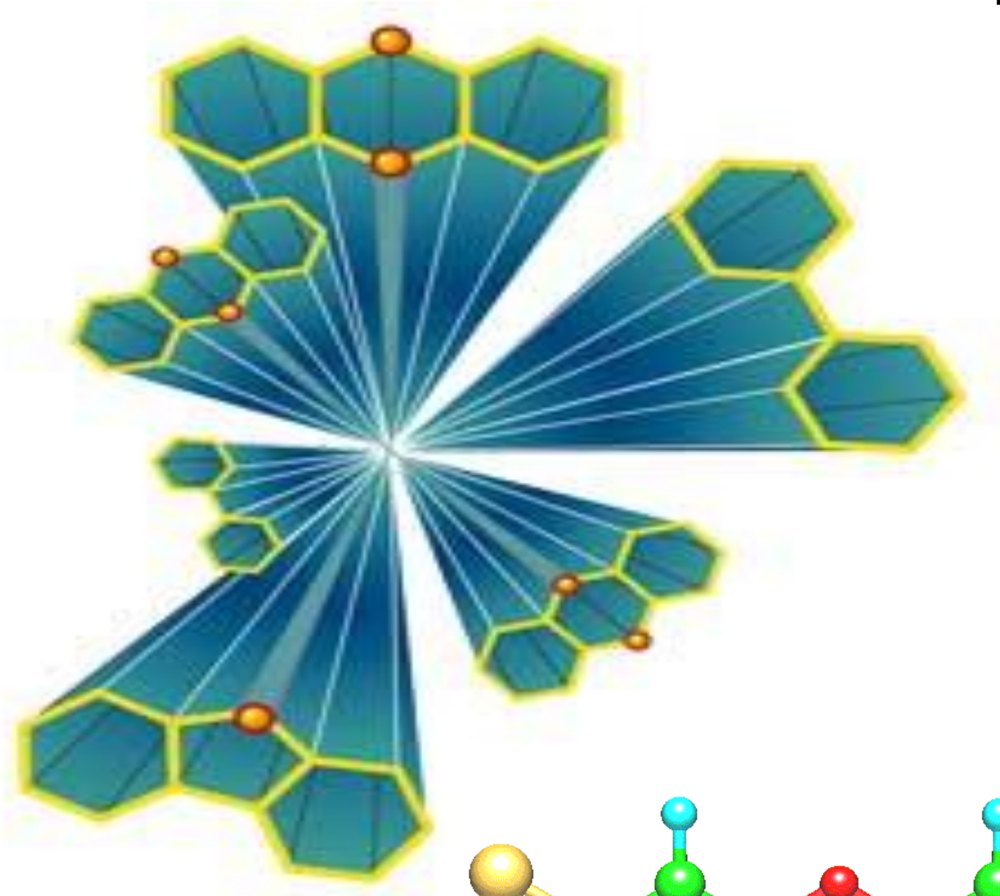
Toxic

- Cancer hazard
- Immune system
- Hormonal systems.
- Diabetes
- Endometriotis
- Thyroid disorder

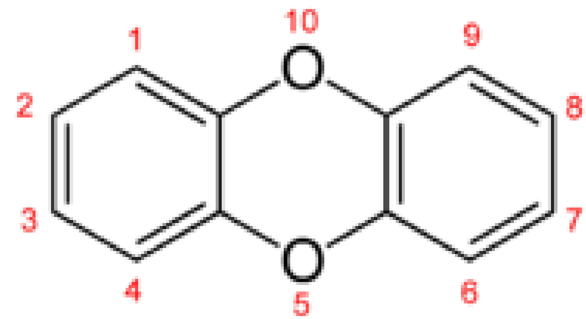


Additional Chapter 3. The Terrestrial Pollution Solutions

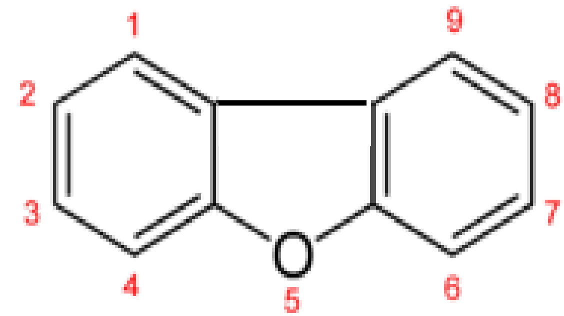
3.1 The Terrestrial Pollution : Dioxin

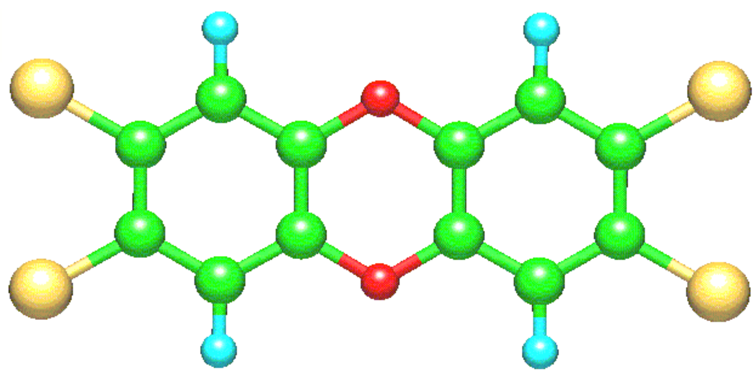


PCDDs : Polychlorinated dibenzo-p-dioxins
(75 congeners)



PCDFs : Polychlorinated dibenzofurans
(135 congeners)

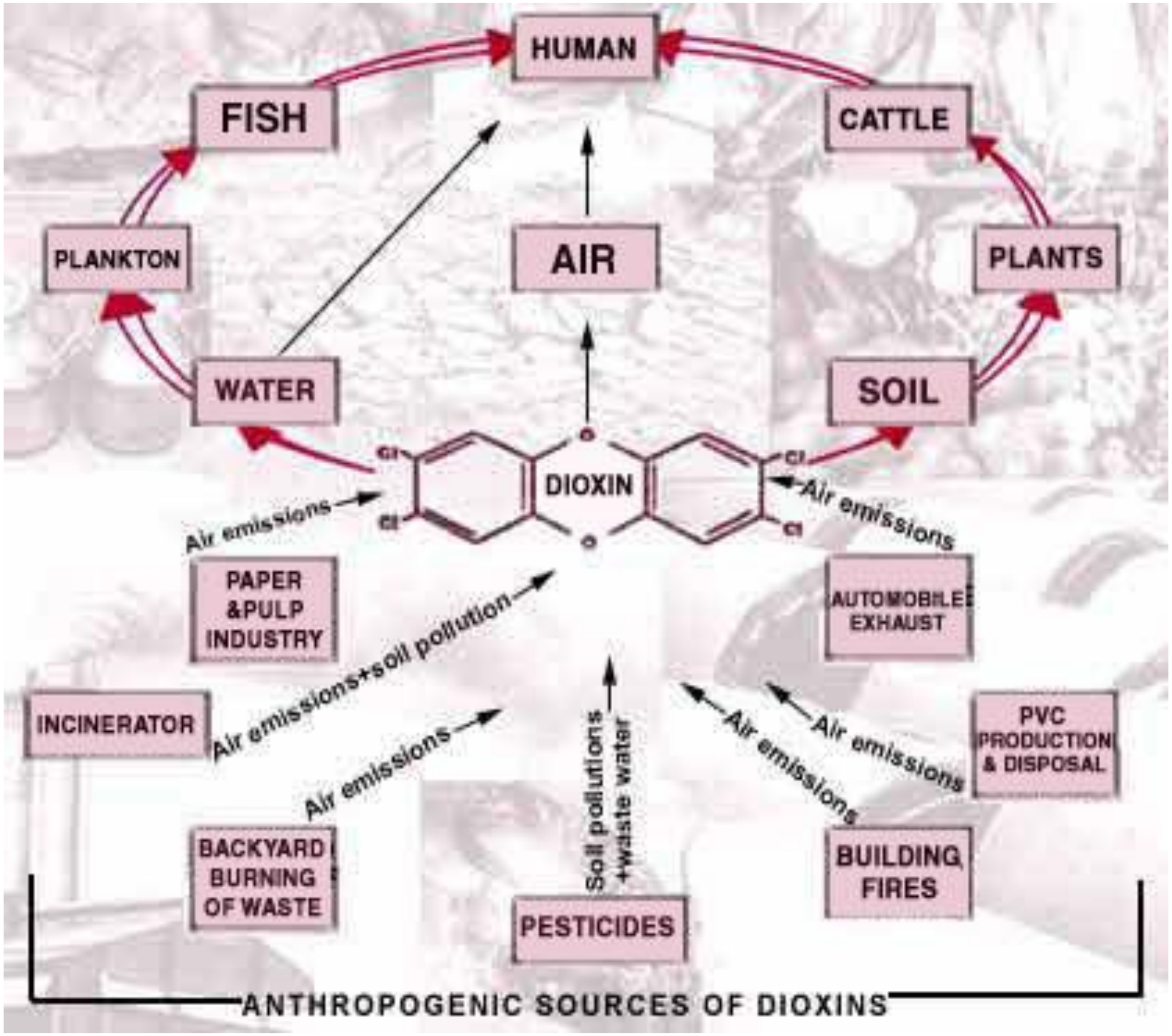




2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

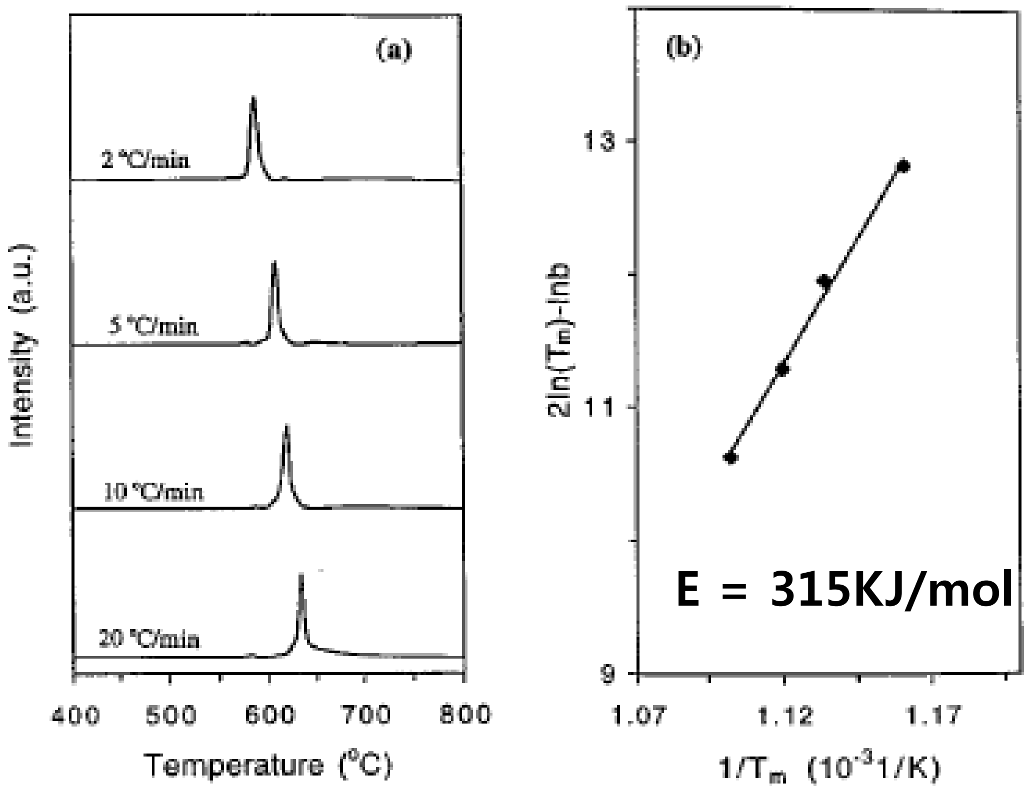
Additional Chapter 3. The Terrestrial Pollution Solutions

3.1 The Terrestrial Pollution : Dioxin formation



Additional Chapter 3. The Terrestrial Pollution Solutions

3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)



(a) TPD profiles of dioxin on carbon nanotubes at heating rates of 2, 5, 10, and 20 °C/min.
(b) Relationship between the maximum desorption temperature (T_m*) and the heating rate (b) for dioxin on carbon* nanotubes.

J. Am. Chem. Soc. 2001, **123**, 2058

3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)

$$2 \ln T_m - \ln b = \frac{E}{RT_m} + \ln ZA$$

T_m - the peak desorption temperature
b - heating rate
E - activation energy for desorption
R - the gas constant
Z – constant
(depends on the desorption kinetics)

$$\theta = \frac{q}{q_m} = \frac{BP}{1 + BP}$$

θ- fractional surface coverage
q - the amount adsorbed at absolute temperature T and vapor pressure P
qm – the monolayer amount
B - the Langmuir constant

sorbent	peak desorption temp. (°C) at different heating rates				desorption activation energy (kJ/mol)	Langmuir constant B at 25 °C (1/atm)	ref
	2 °C/min	5 °C/min	10 °C/min	20 °C/min			
carbon nanotubes	588	609	620	634	315	2.7×10^{52}	this work
ZX-4 carbon (Mitsubishi)	481	517	543	?	119	1.3×10^{18}	3
γ-Al_2O_3	306	353	394	?	47.9	4.5×10^{5}	3

Ind. Eng. Chem. Res. 1999, **38**, 2726
J. Am. Chem. Soc. 2001, **123**, 2058

3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)

Encapsulation of MWCNTs in Ba^{2+}-alginate to form coated micro-beads

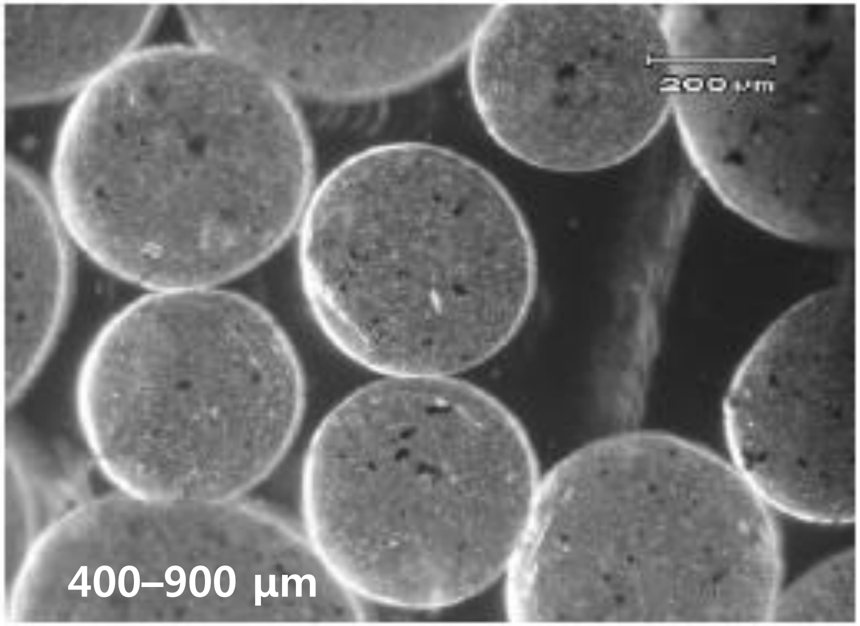
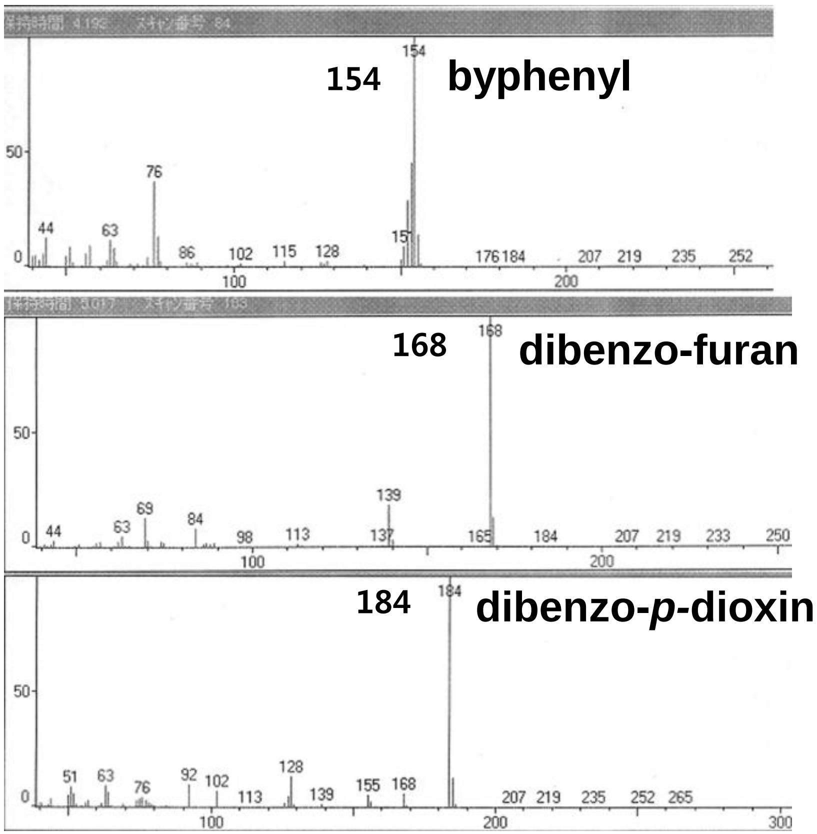


Photo of microscopic observation of MWCNTs/Ba2+-ALG composite beads. Beads having diameters between 400–900 mm were observed.

Analyst, 2004, **129**, 565

Additional Chapter 3. The Terrestrial Pollution Solutions

3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)



GC-MS determination/identification of the target compounds extracted from the MWCNTs/Ba2+-ALG composite micro-beads using hexane. Retention times for BP, DF and DD were 4.12 min, 5.02 min, and 5.29 min, respectively. Column: DB-5MS (length, 30 m; id, 0.25 mm; film, 0.25 mm). Flow rate of the carrier gas (He), 1.2 mL min21.

Amount of remained dioxin

	BP	DF	DD
Pre-conc	4.0	4.0	4.0
Ba^{2+} ALG	3.24	3.27	3.24
MWNTs/ Ba^{2+} ALG	0.04	0.06	0.15

-The hexagonal arrays of the carbon atoms in the graphene sheets of MWCNTs interact strongly with the aromatic bonds of the model compounds, due probably to van der Waals interactions.

- In addition, the MWCNTs/Ba2+alginate composite adsorbents could be reused by regenerating the beads with hexane, or methanol.

Analyst, 2004, **129**, 565

Additional Chapter 3. The Terrestrial Pollution Solutions

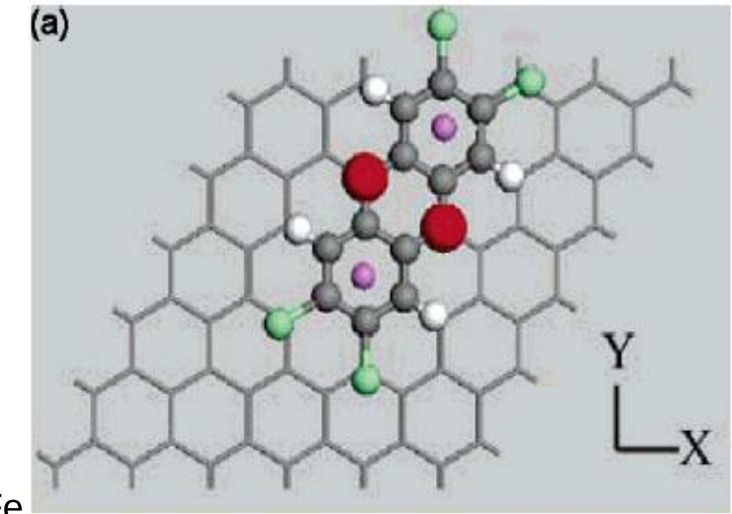
3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)

Theoretical Study of Binding of Metal-Doped Graphene Sheet and Carbon Nanotubes with Dioxin

π*-metal-*π interaction is much stronger than the directed *π*-*π* interaction.

Binding Energy

M	Li			Ca			Fe
X	Gr	CNT	Dx	Gr	CNT	Dx	CNT
2M + X → 2M−X	−2.10	−2.76	−0.48	−0.89	−1.51	−0.50	−2.02
2M−X + Dx → X−2M−Dx	−1.05	−0.58	−1.32	−2.31	−2.05	−1.98	−3.49



Gr – Graphite, M - Li, Ca or Fe

Binding Energy of Gr-M :
Li(-2.10eV) > Ca(-0.89eV)

Distance of Gr-M : **Li(1.74Å) < Ca(2.36Å)**

Binding Energy of Gr-M-Dx :
Gr-M : **Li(-1.05eV) < Ca(-2.31eV)**

Distance Gr-M-Dx :
Gr-Li(1.93Å), Li-Dx(1.95Å) > Li(1.774Å)
Gr-Ca(2.35Å), Ca-Dx(2.45Å)

Gr-Li-Dx < Gr-Ca-Dx

Geometry of the Ca complex is characterized by a deformation of Dx (Dioxin)

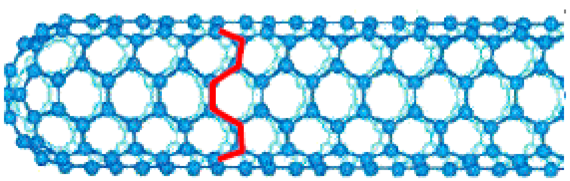
J. AM. CHEM. SOC. 2005, **127**, 9839

Additional Chapter 3. The Terrestrial Pollution Solutions

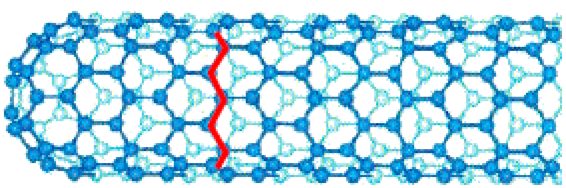
3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)

Theoretical Study of Binding of Metal-Doped Graphene Sheet and Carbon Nanotubes with Dioxin

Armchair nanotube



Zigzag nanotube

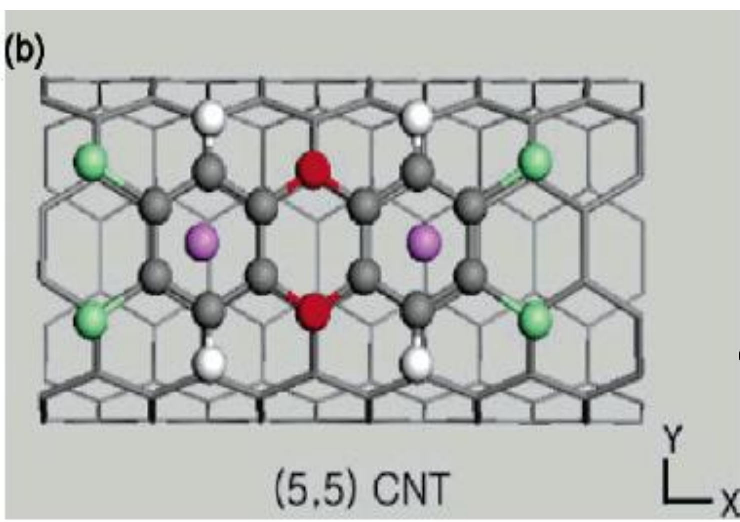


M	Li			Ca			Fe
X	Gr	CNT	Dx	Gr	CNT	Dx	CNT
2M + X → 2M−X	−2.10	−2.76	−0.48	−0.89	−1.51	−0.50	−2.02
2M−X + Dx → X−2M−Dx	−1.05	−0.58	−1.32	−2.31	−2.05	−1.98	−3.49

Armchair CNTs are better for the interaction than zigzag CNTs

CNT-Li-Dx < CNT-Ca-Dx

(twisted conformation of dioxin)



Fe-doping to CNT is the most efficient way of adsorbing dioxin

Binding energy : -3.49eV

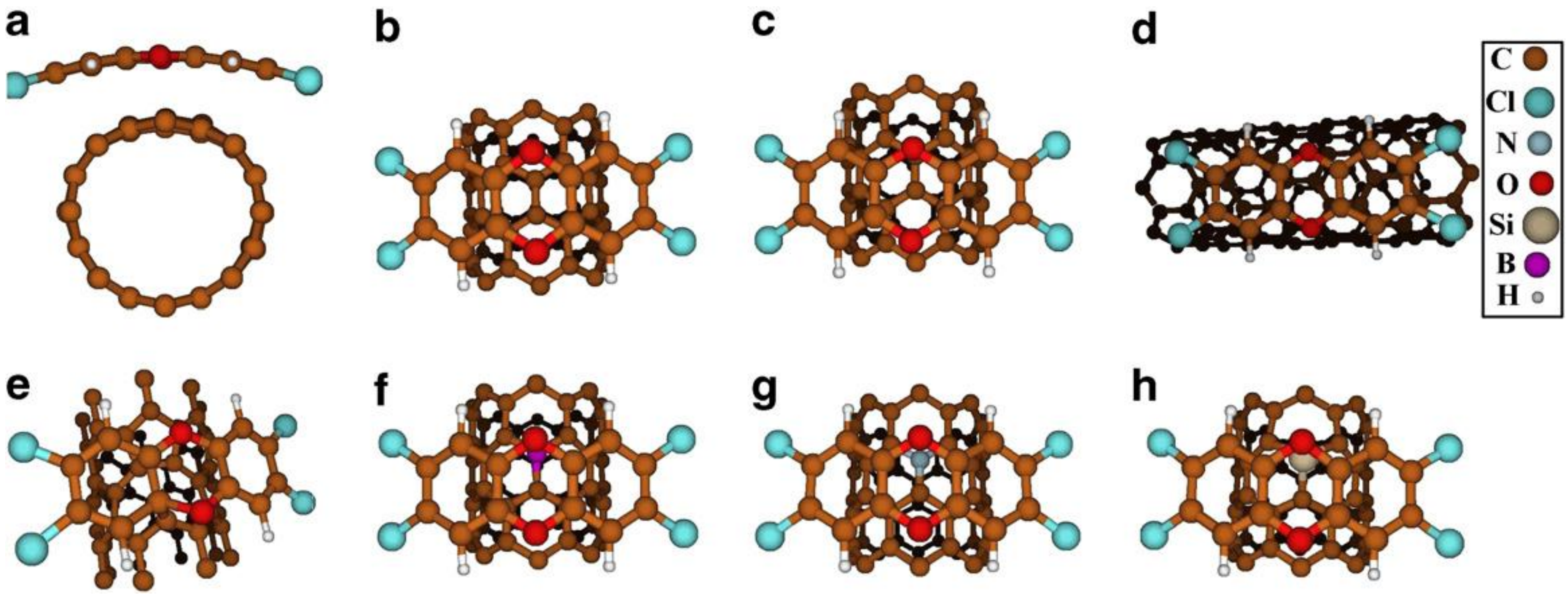
cf) direct benzene-benzene interaction is less than -0.12 eV

J. AM. CHEM. SOC. 2005, **127**, 9839

Additional Chapter 3. The Terrestrial Pollution Solutions

3.2 The Terrestrial Pollution Solution: Dioxin removal (CNT as a sorbent)

Ab initio study of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin adsorption on single wall carbon nanotubes



Schematic view of the most stable configurations SWNT/dioxin. (b–d) stand for pristine SWNT interacting dioxin in different configurations. In (a) we show a lateral view of SWNT/dioxin showed in (b). In panel (e), the SWNT has a vacancy. (f–h) panels show N-, B-, Si-doped SWNT interacting with dioxin, respectively.

Table 1
Calculated binding energy values for the SWNT/Dioxin configurations showed in Fig. 1

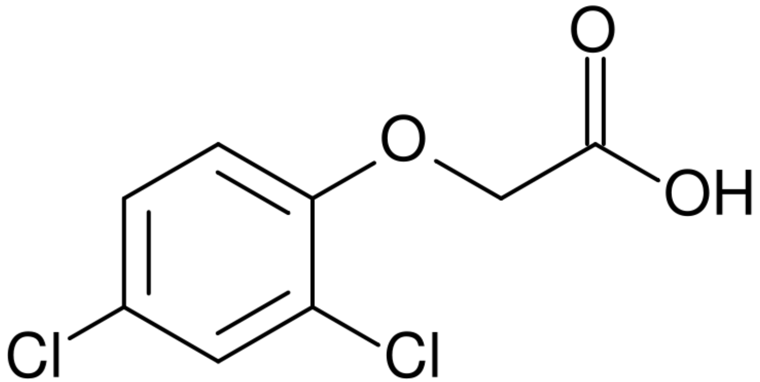
System	Binding energy (eV)
SWNT/dioxin (Fig. 1b)	−0.10
SWNT/dioxin (Fig. 1c)	−0.35
SWNT/dioxin (Fig. 1d)	−0.77
SWNT/vac_dioxin (Fig. 1e)	−1.21
SWNT/B_dioxin (Fig. 1f)	−0.43
SWNT/N_dioxin (Fig. 1g)	−0.45
SWNT/Si_dioxin (Fig. 1h)	−0.30

- The dioxin can adsorb on the carbon nanotube surface being stronger when the nanotube presents lattice defects.
- Doping carbon nanotubes with B, N and Si is not a promising route for improving the dioxin absorption.

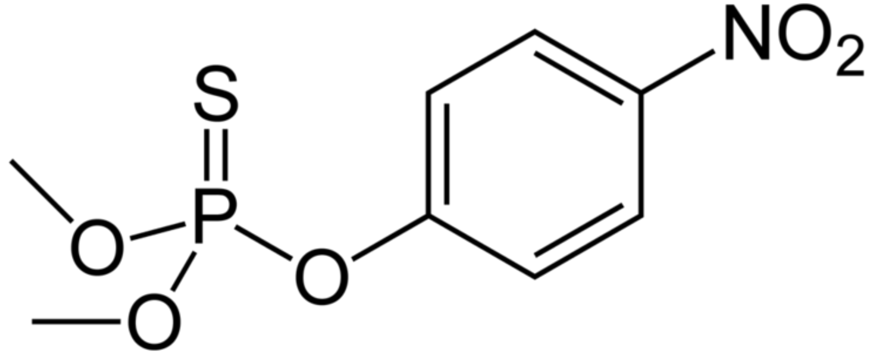
Chem. Phys. Lett. 2007, **437**, 79

3.3 The Terrestrial Pollution : Biocide

Herbicide : 2,4-Dichlorophenoxyacetic acid



Pesticide : Methyl parathion



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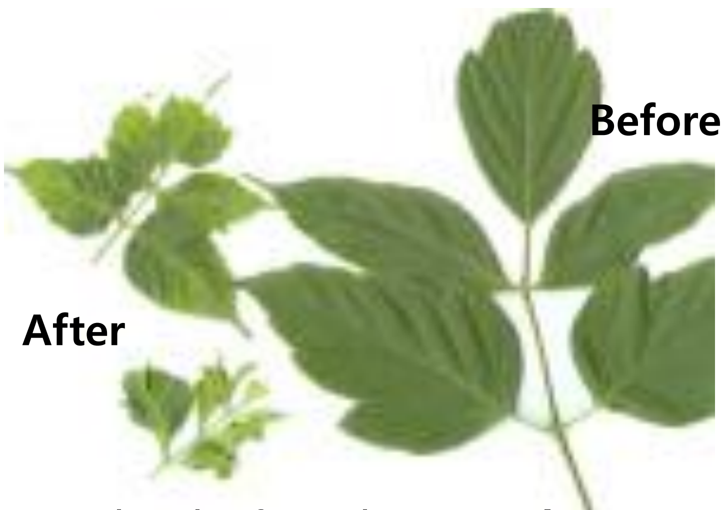
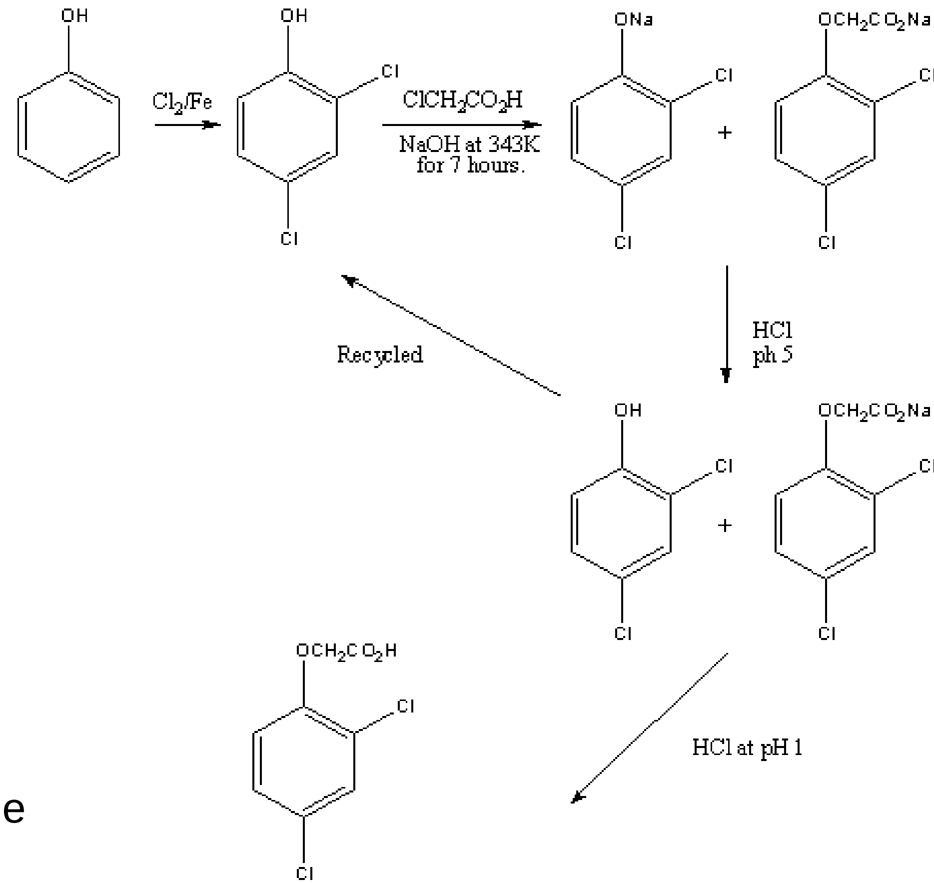
3.3 The Terrestrial Pollution : Biocide (Herbicide formation)

Herbicide : 2,4-Dichlorophenoxyacetic acid





2,4-D

Molecular formula: $\mathbf{C_8H_6Cl_2O_3}$
Relative molecular mass: 221.0
Melting point: 140-141 °C
Solubility in water: slightly soluble
Solubility in organic solvents: soluble

Acute toxicity

Cancer, Endocrine disruption, Reproductive toxicity, Neurotoxicity, Kidney/Liver damage, Toxicity to Dogs, Fish, Birds, Earthworms, and Beneficial insects

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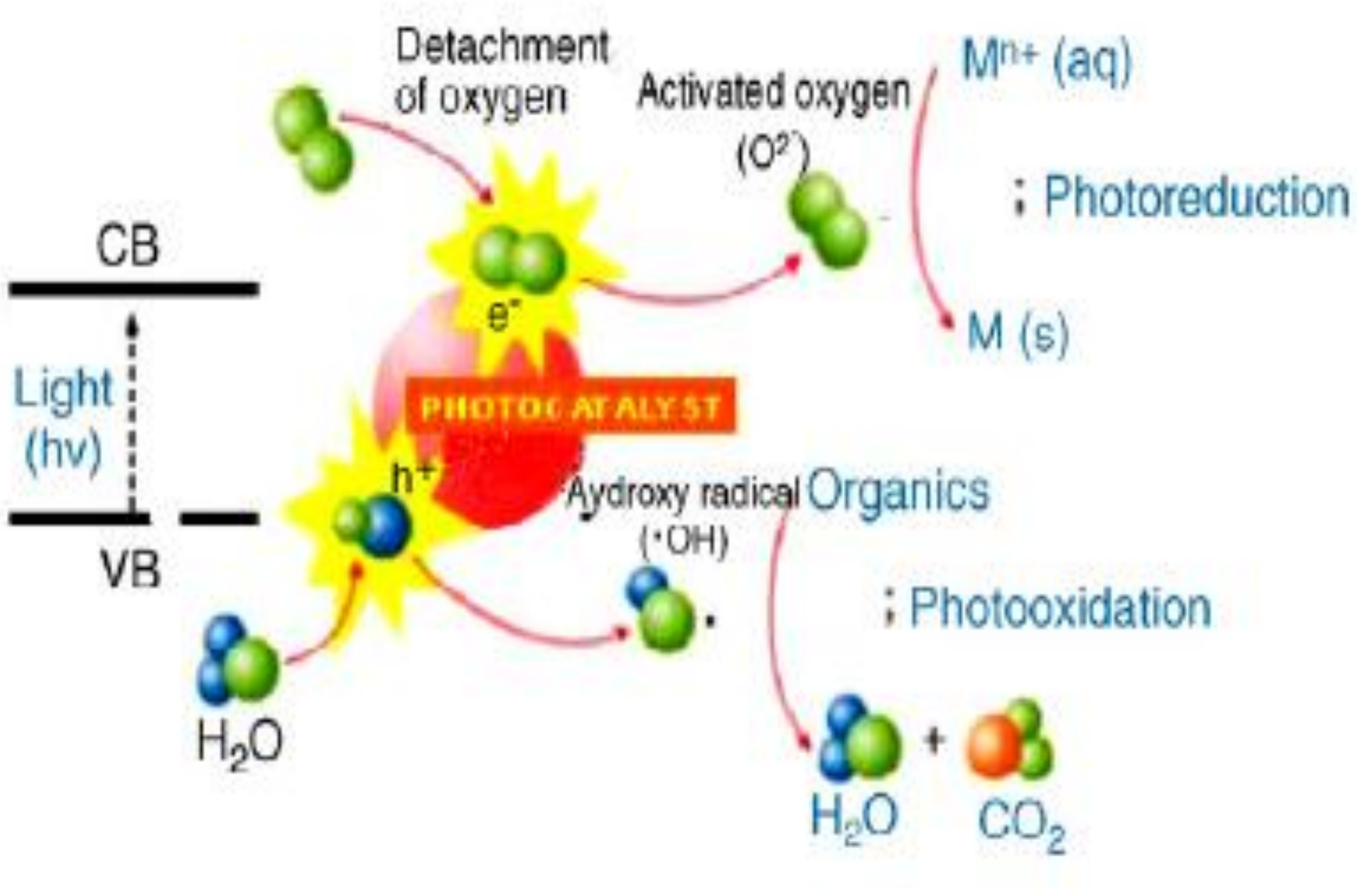
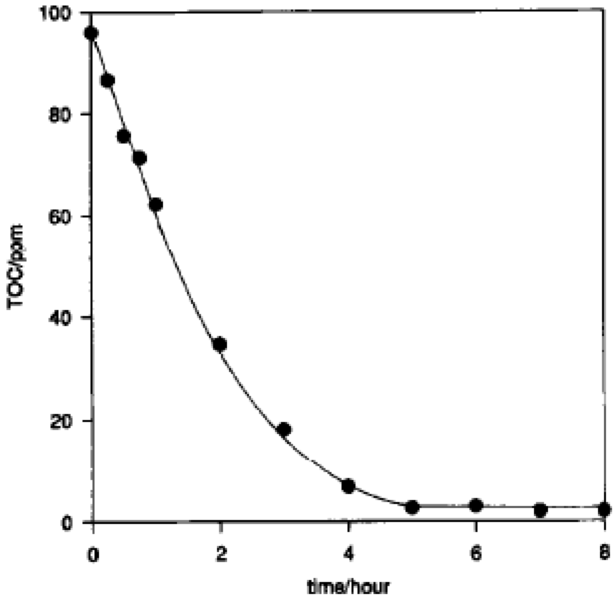
3.4 The Terrestrial Pollution Solutions: Biocide (Photocatalyst)



Additional Chapter 3. The Terrestrial Pollution Solutions

3.4 The Terrestrial Pollution Solutions: Biocide (Photocatalyst)

2,4-dichlorophenoxyacetic acid degradation by photocatalyst

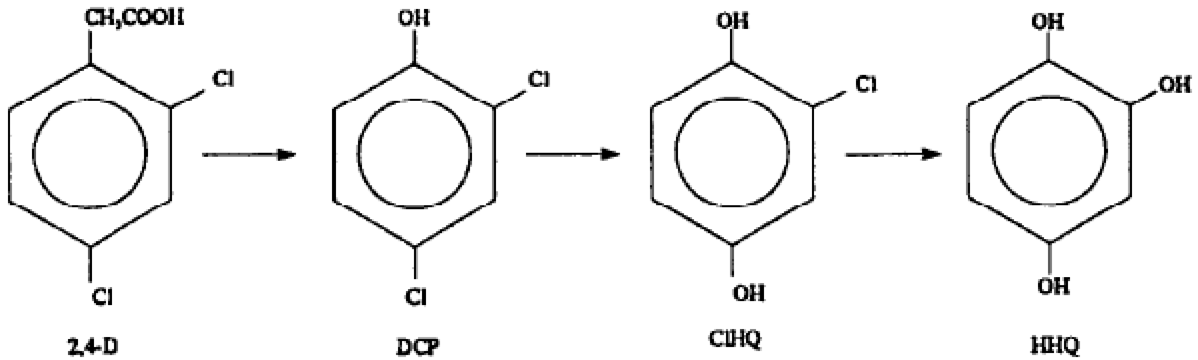


Time-course of TOC for a 2,4-D solution in the presence of ZnO.

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \tfrac{1}{2}O_2$$

$$2H^+ + O_2 + 2e^- \rightarrow H_2O_2$$

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+$$



Electrochimica Acta 1996, **41**, 1981

3.4 The Terrestrial Pollution Solutions: Biocide (Iron-mediated oxidation)

2,4-dichlorophenoxyacetic acid degradation by Fe^{3+}/H_2O_2 system

Ferrous ion (Fe^{2+})

To produce OH· from hydrogen peroxide (H_2O_2)
Large-scale iron sludge formation tends to occur

Fe^{3+}/H_2O_2 system

To use relatively low concentrations of ferric ion as a catalyst for H_2O_2 decomposition

Free radical mechanism

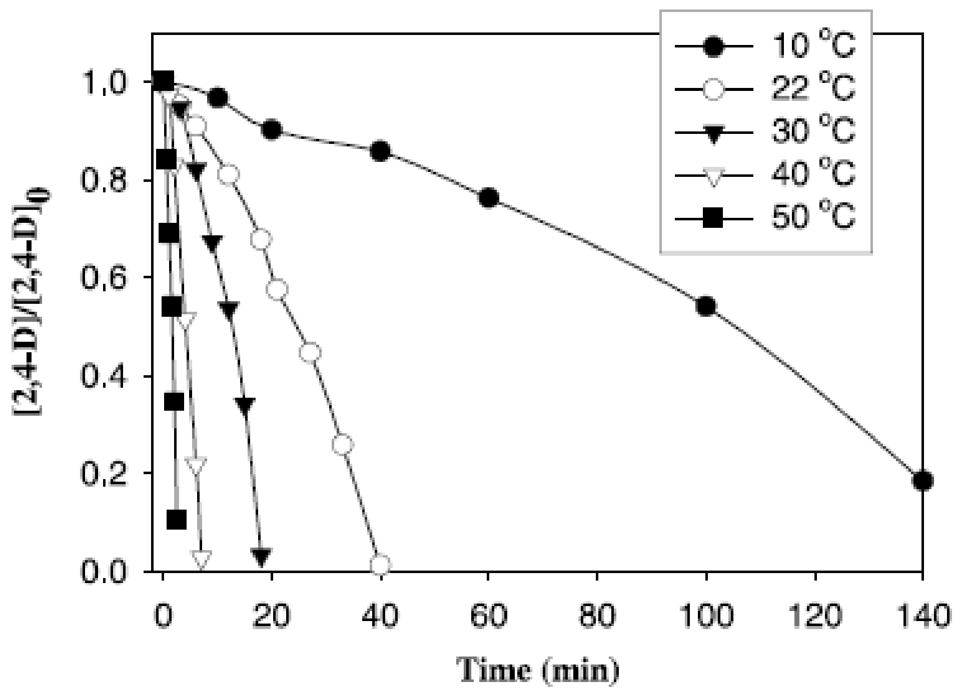
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$$

$$HO_2^{\cdot} + Fe^{3+} \rightarrow H^+ + Fe^{2+} + O_2$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$$



increased reaction temperature can enhance system reactivity

Chemosphere 2003, **51**, 963

3.4 The Terrestrial Pollution Solutions: Biocide (Photocatalyst)

Methyl parathion degradation by ZnO/TiO_2 photocatalysts

Complete degradation is achieved within 45 or 150 min TiO_2 or ZnO

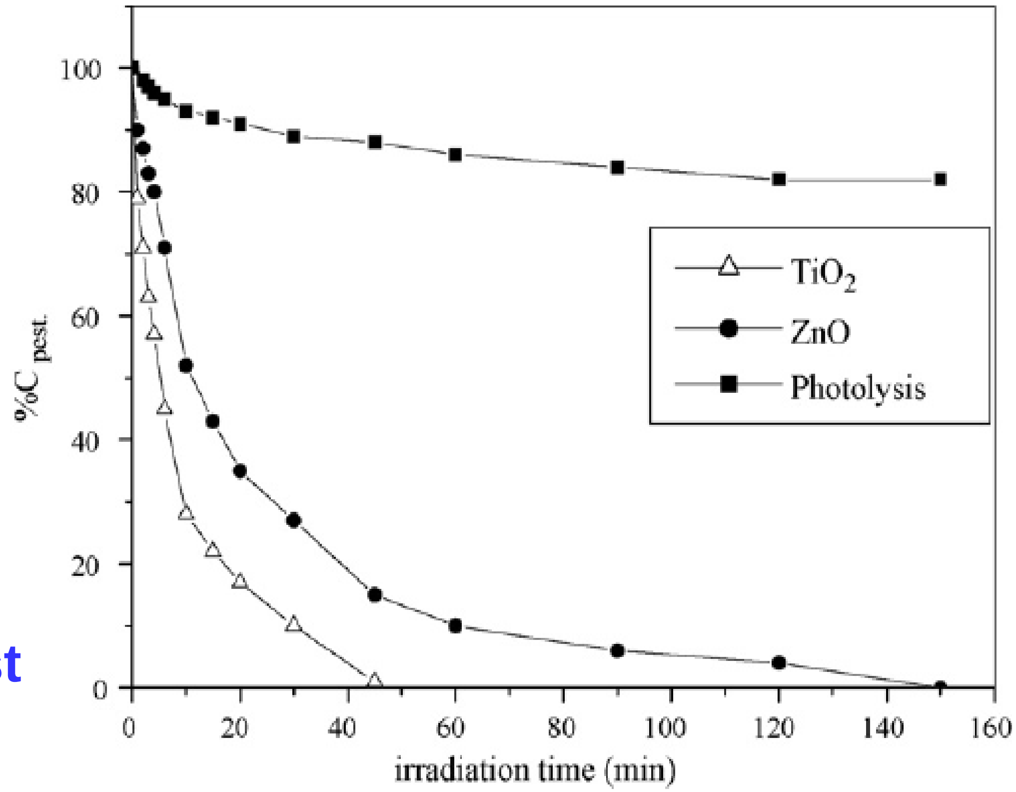
semiconductor

↓ $\hbar\nu$

electron–hole pairs

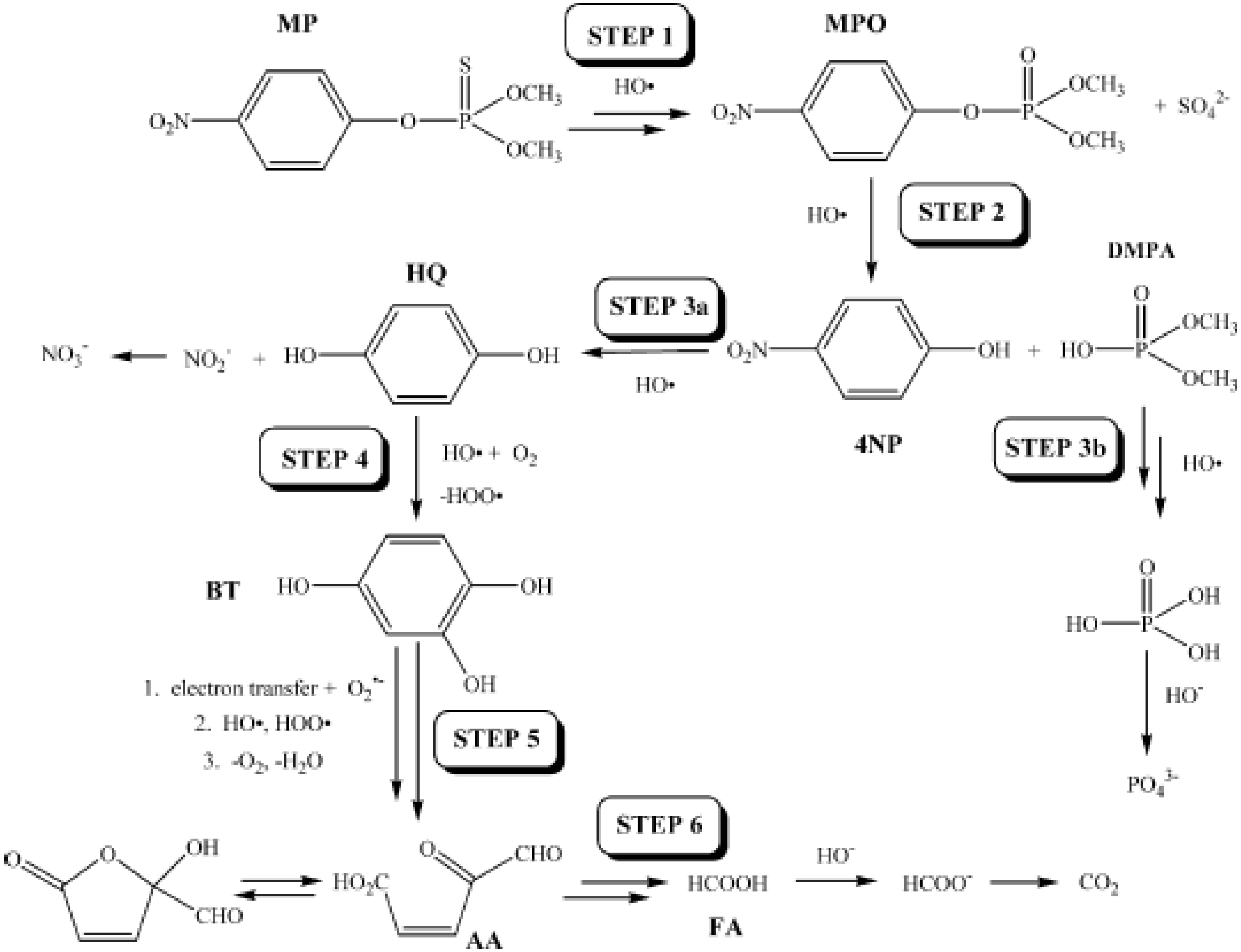
↓ ***migrate***

surface of the photocatalyst



3.4 The Terrestrial Pollution Solutions: Biocide (Photocatalyst)

Methyl parathion degradation by ZnO/TiO_2 photocatalysts



Overall reaction mechanism for the photocatalytic oxidation of methyl parathion

J. Photochem. Photobiol. A: Chem. 2007, **146**, 189

Catalysis Today 2007, **124**, 156

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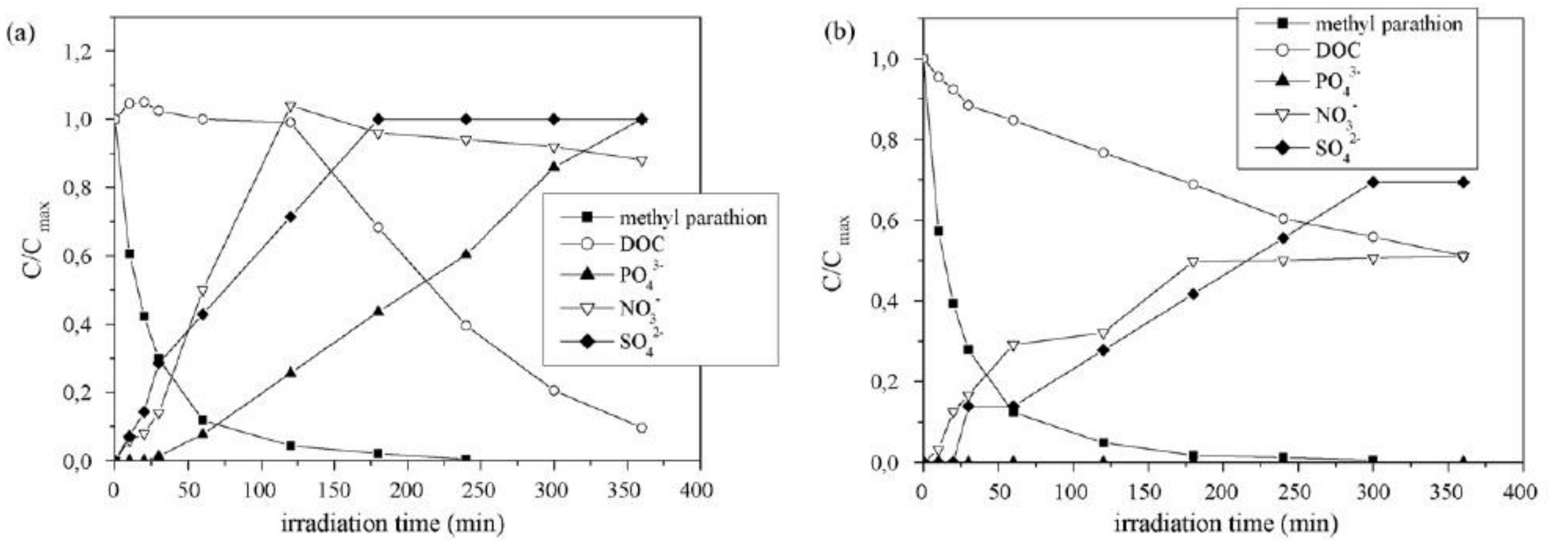
3.4 The Terrestrial Pollution Solutions: Biocide (Photocatalyst)

Methyl parathion degradation by ZnO/TiO_2 photocatalysts



Parathion/DOC reduction and $SO_4^{2-}/PO_4^{3-}/NO_3^{-}$/ release as a function of irradiation time, methyl parathion = 25 mg L^{-1} : (a) TiO_2 = 100 mg L^{-1} and (b) ZnO = 500 mg L^{-1}.

-Titanium dioxide proved to be more efficient photocatalyst since the oxidation and decomposition of the insecticide proceeded at higher reaction rates.

- Moreover, complete mineralization was achieved only in the presence of titanium dioxide

Catalysis Today 2007, **124**, 156