Applications of nanomaterials to remove emerging contaminants in water

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VIRGINIA TECH

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Flow of talk

How can small science help us protect such a big beautiful world?

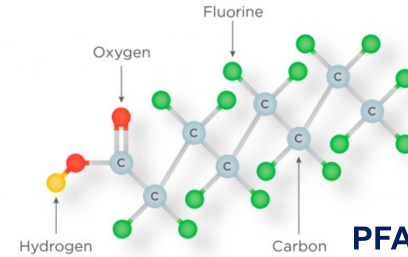
Emerging contaminants

Applications of nanomaterials

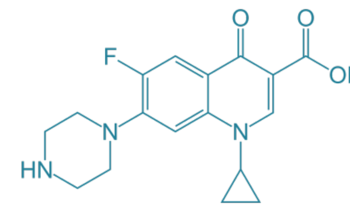
Implications of nanomaterials

Emerging Contaminants

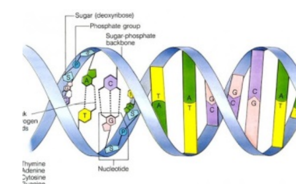
- Synthetic or naturally occurring chemicals or any microorganisms, not commonly monitored
- Potential to enter the environment and cause known or suspected adverse ecological and/or human health effects
- Either do not have federal regulatory standards based on peer reviewed science (Type 1 EC)
- Or the regulatory standards are evolving due to new sciences, detection capabilities, or pathways (Type 2 EC)



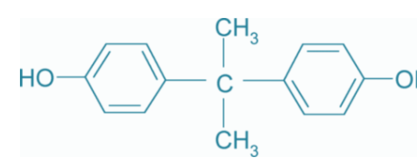
PFAS



Ciprofloxacin



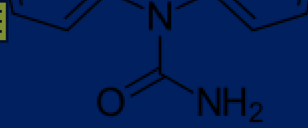
Antibiotic Resistance Gene



Bisphenol A

Microplastics

https://www.epa.gov/fedfac/emerging-contaminants-and-federal-facility-contaminants-concern

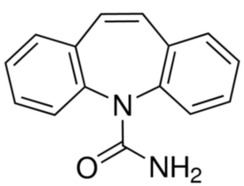


Drugs in water

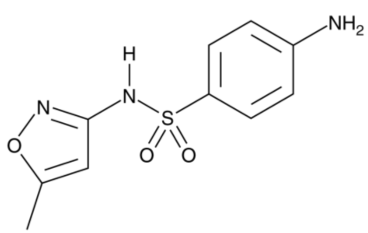
Drug

Chemical substance

Create specific biological response

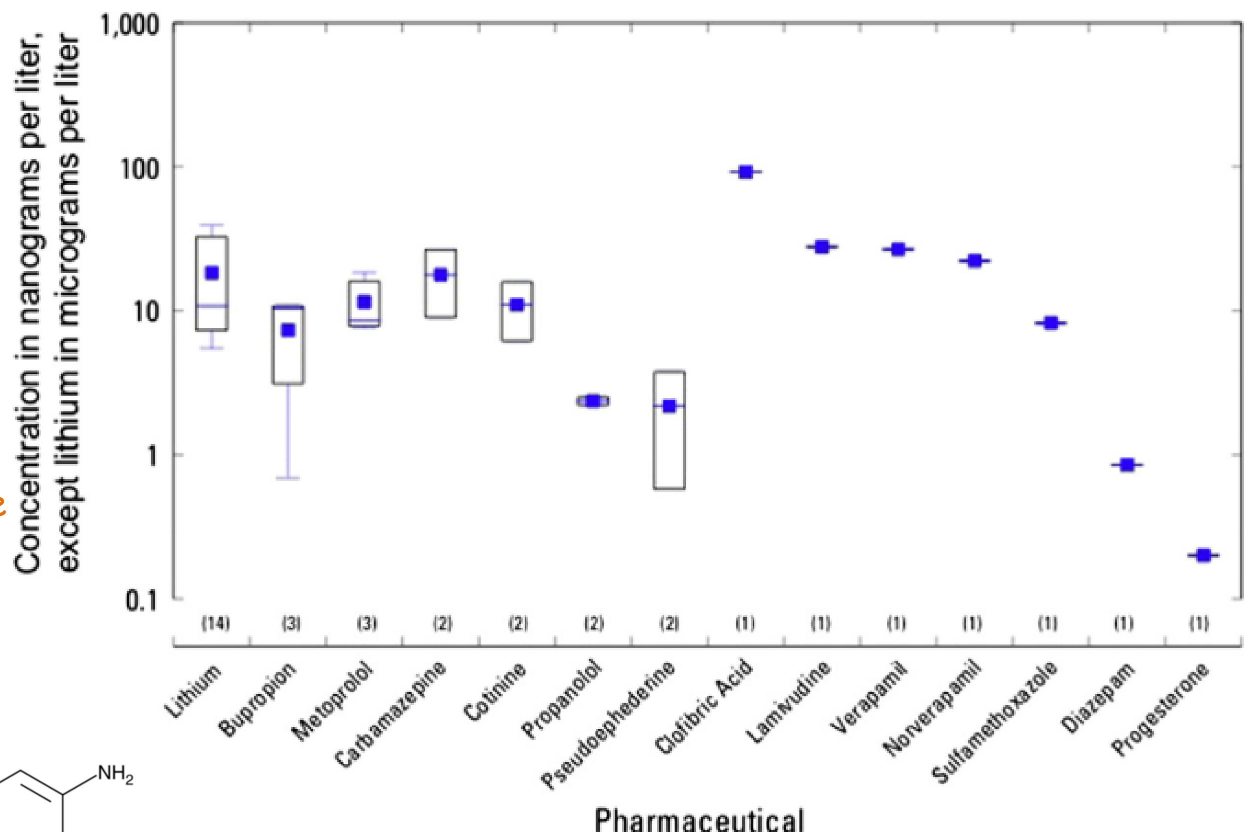


Carbamazepine



Sulfamethoxazole

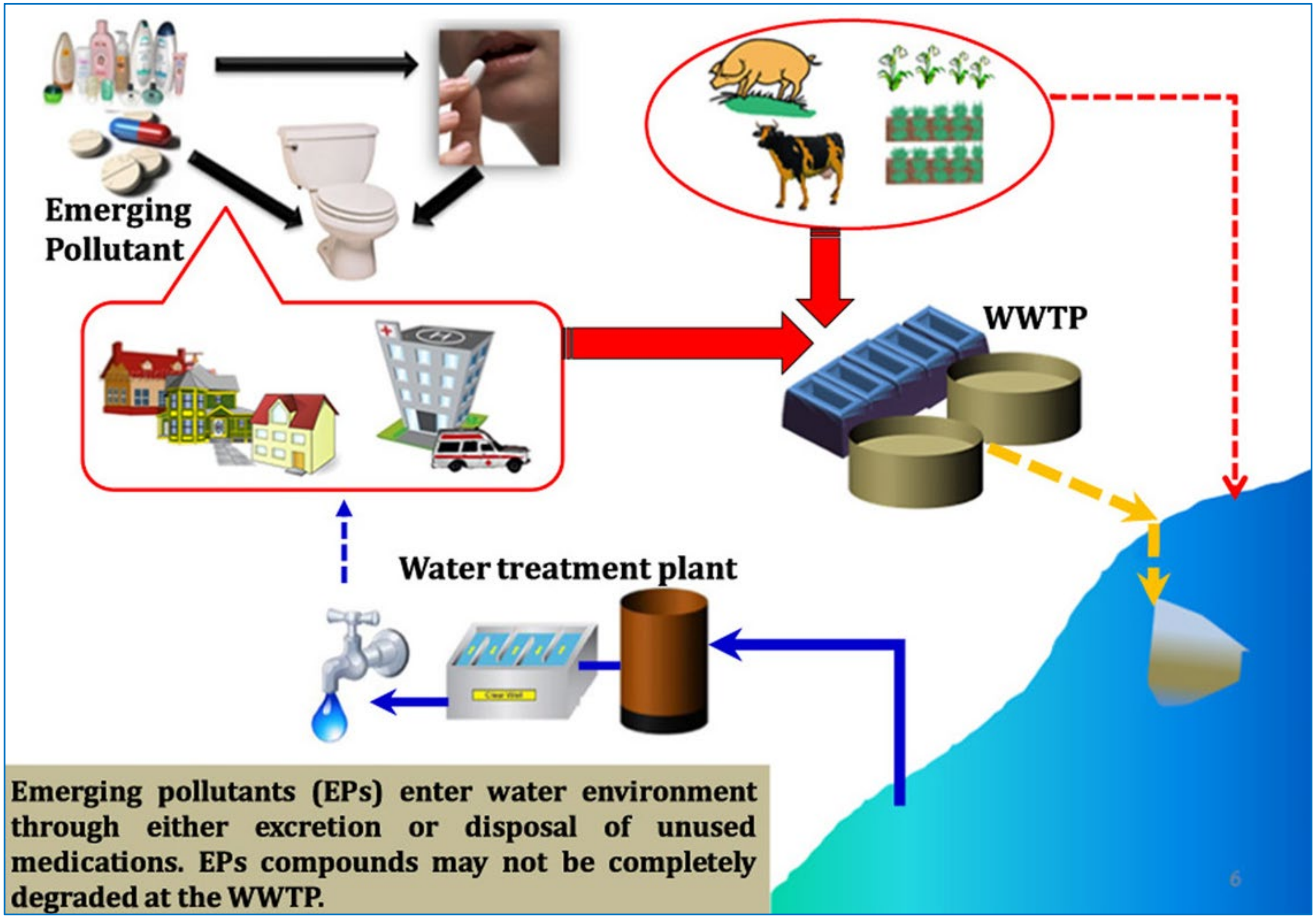
Detection of pharmaceuticals in treated water samples from 25 drinking water treatment plants in USA



Science of the Total Environment (2017), 579, 1629-1642

How do they reach water sources

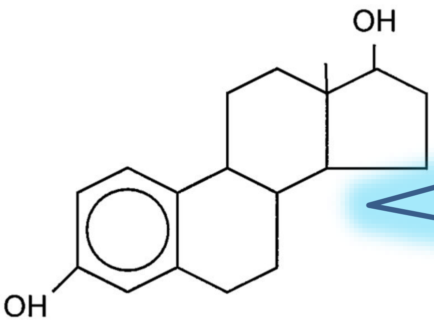
Origins of emerging pollutants and routes to the environment



Groundwater for Sustainable Development, 2018 (6), 169-180

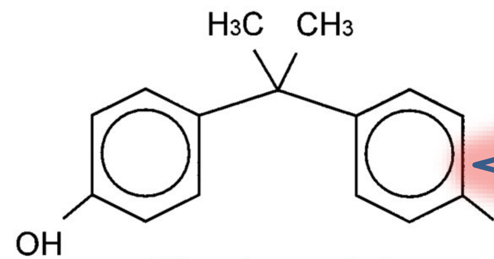
Endocrine disrupting compounds

Mimic hormones can alter normal hormone function in cells



β–Estradiol

Estrogen steroid hormone and the major female sex hormone

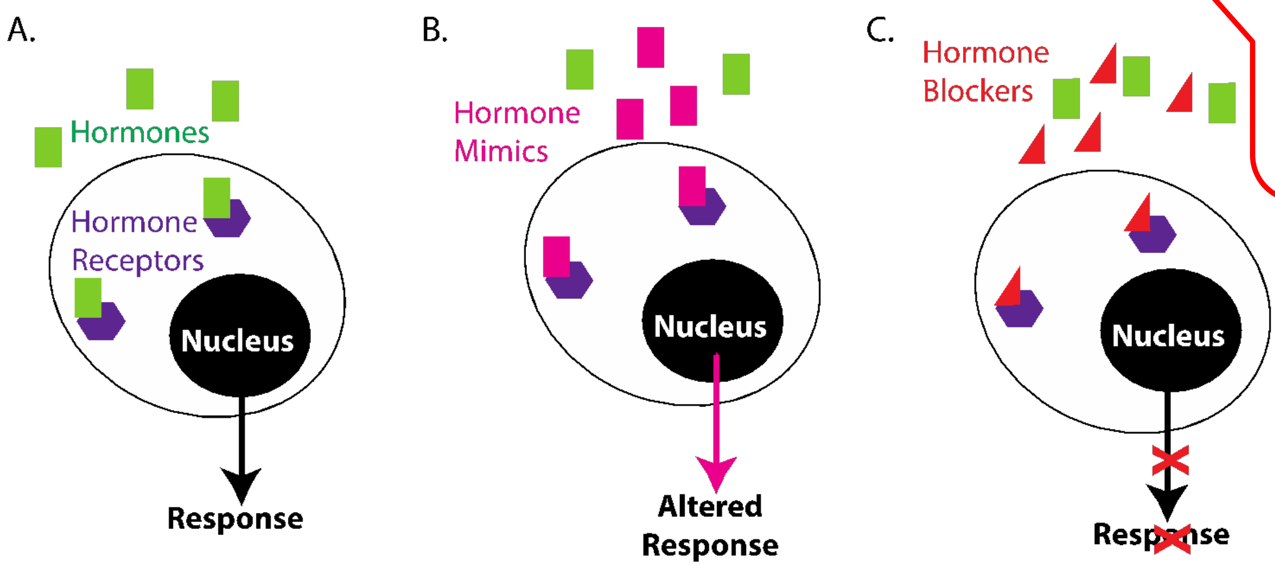


Bisphenol A

Production of polycarbonate plastics and epoxy resins

Bisphenol-A mimics estrogen hormone, could potentially alter the function of reproductive system

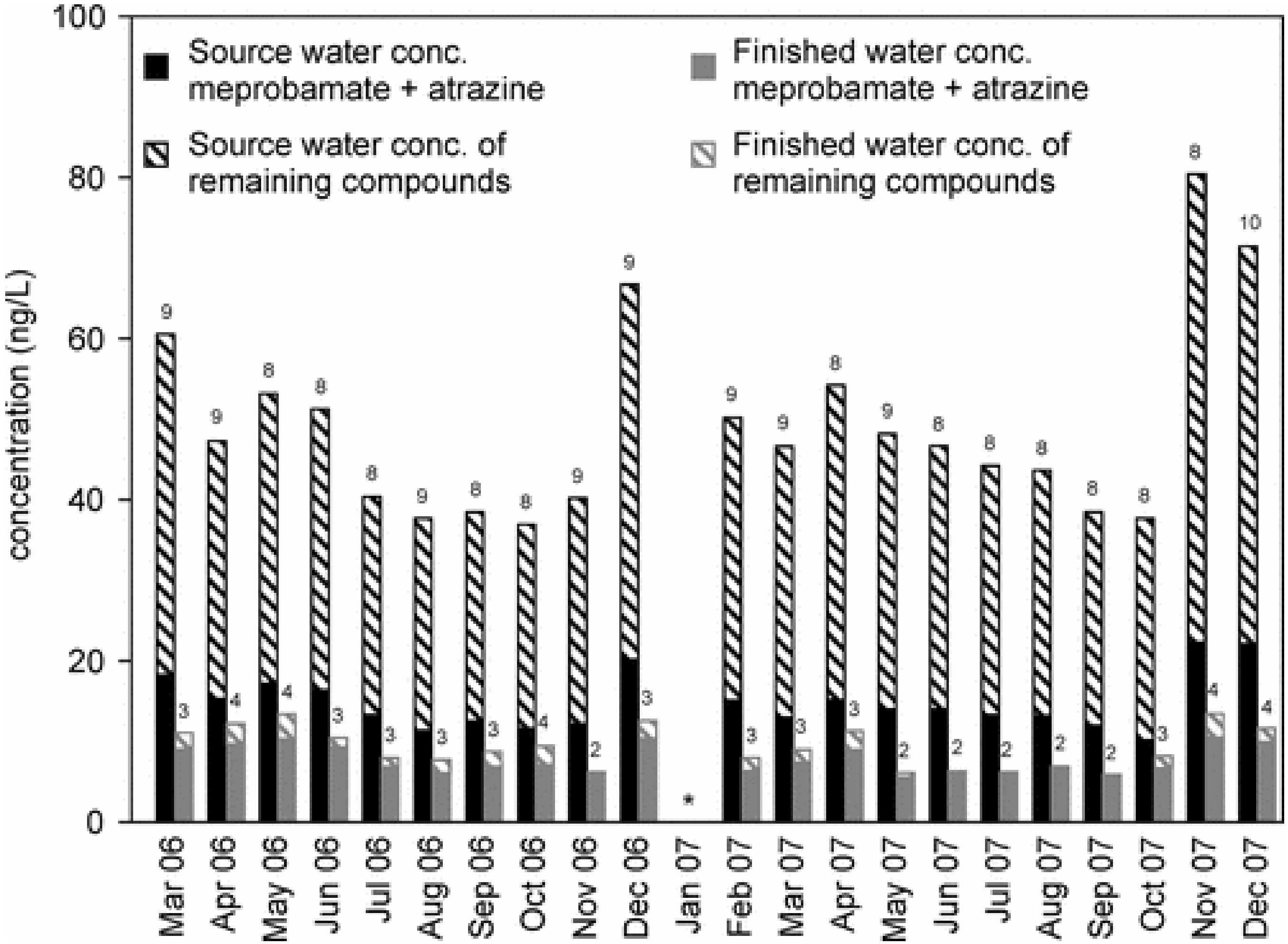
- Fertility problems
- Male impotence
- Heart disease
- Other conditions



http://thatslifesci.com/To-BPA-Or-To-Not-BPA-Regulating-Endocrine-Disruptors-TZintel/

Pharmaceuticals and endocrine disrupting compounds

47 pharmaceuticals and EDCs detected in source and finished water at DWTP-6 over a 22 month period



Environ. Sci. Technol. 2009, 43, 3, 597-603

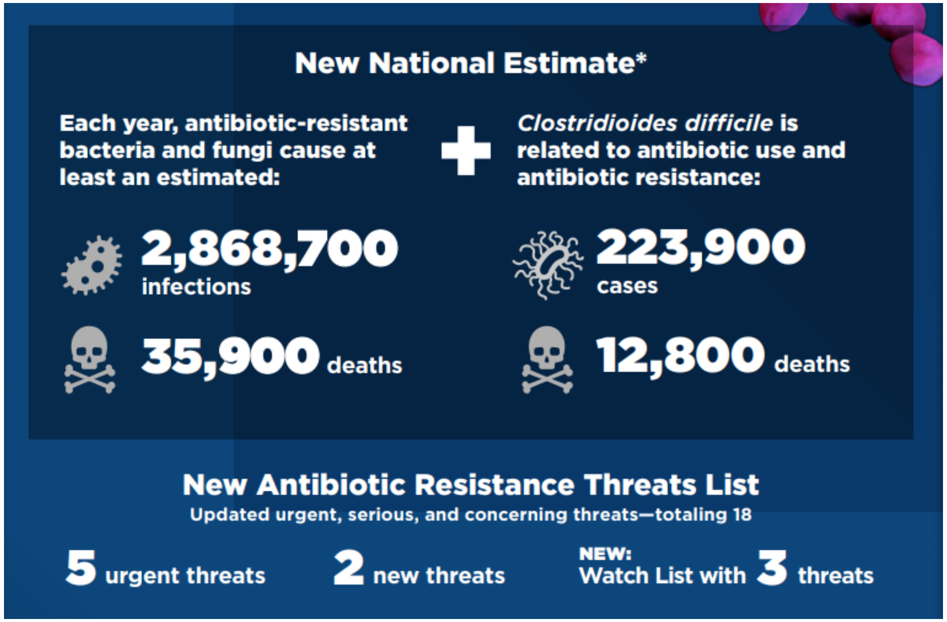
Antibiotic Resistance

"What does not kill you makes you stronger"

-Friedrich Nietzsche

Bacteria, not humans or animals, become antibiotic-resistant!

Super buds!



Economic burden continues to rise due to

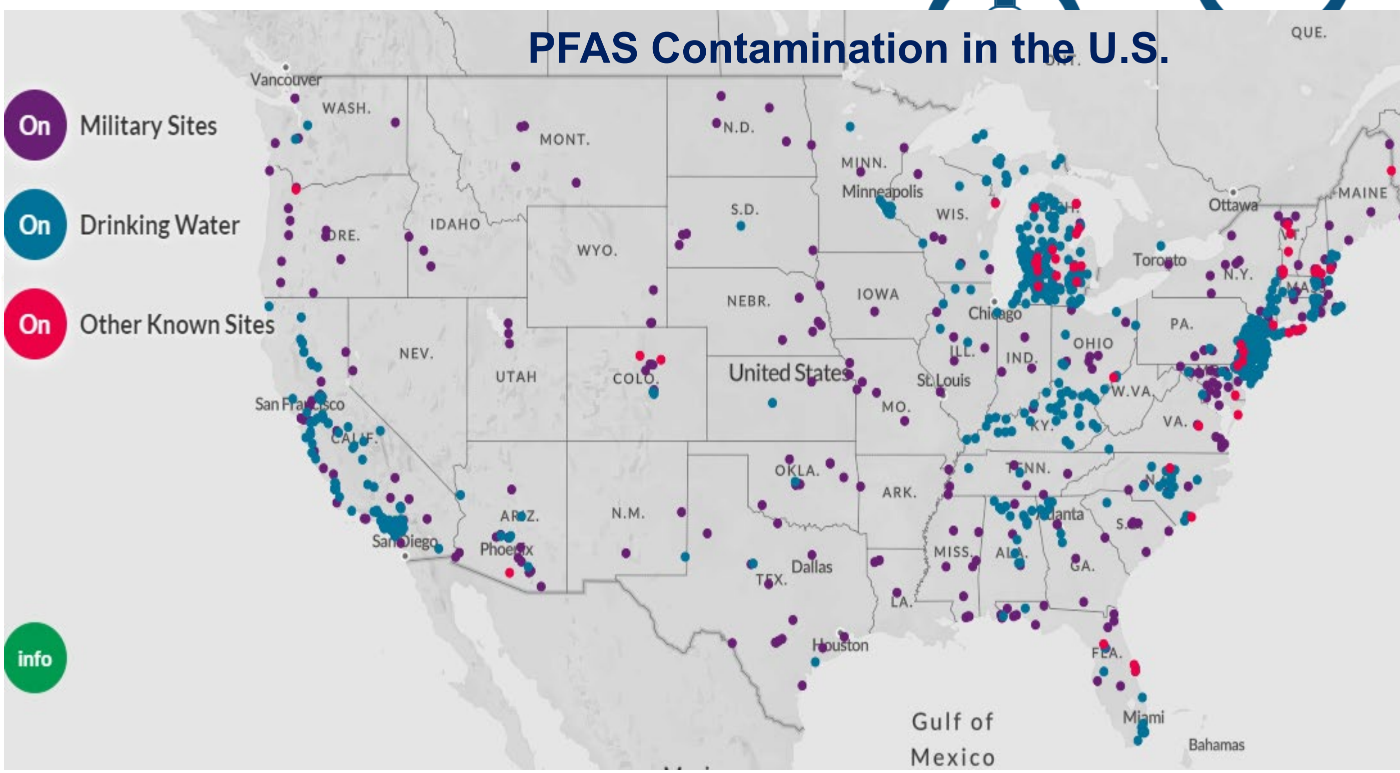
- increase of number of resistant infections
- increase of microbial resistant towards the number of drugs

https://www.cdc.gov/drugresistance/biggest-threats.html

Per- and polyfluoroalkyl substances (PFAS) – ‘forever chemicals’

Up to 110 million Americans could have PFAS - contaminated drinking water

- Characteristics – heat, stain, and water resistance that are desired by industry
- Consumer products – cookware, food packaging, and stain repellants
- Two of the most prevalent PFAS: Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS)
- Health effects – cancer, thyroid disease, weakened immunity

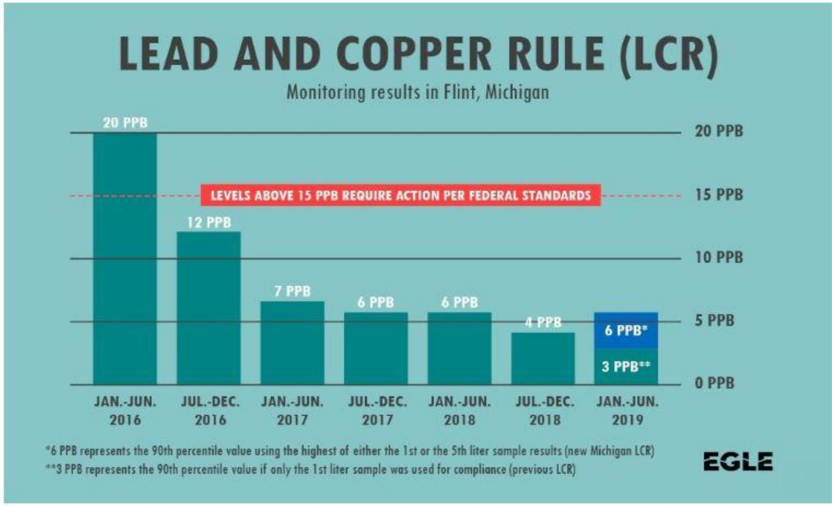


STATE	Minimum number of water utilities with PFOA or PFOS contamination exceeding 5 ppt, but below EPA UCMR (70 ppt) reporting levels
Massachusetts	36
New Jersey	31
Alabama	28
California	21
South Carolina	19
Tennessee	19
Kentucky	18
Pennsylvania	14
Florida	11
Indiana	10
Texas	10
North Carolina	9
Georgia	5
Arizona	4
New York	2
Kansas	1
Virginia	1
West Virginia	1
Oregon	1
Nevada	1

https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/

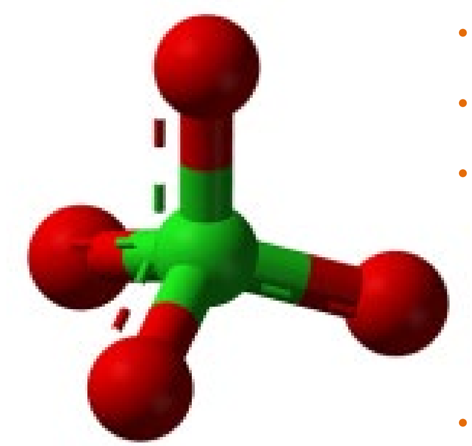
Flint water crisis

- Flint water crisis - public health crisis (2014)
  - April 2014, Flint changed its water source from treated Detroit Water and Sewerage Department water (sourced from Lake Huron and the Detroit River) to the Flint River.
  - No corrosion inhibitors to the water resulted the leaching of lead from aging pipes
  - extremely elevated levels of lead (neurotoxin) and over 100,000 residents affected
- Environmental Protection Agency (EPA) and Virginia Tech reported hazardous levels of lead in the water at residents' homes in 2015
  - Lead level was as high as 13,200 ppb; 5,000 ppb of lead is hazardous waste (EPA)
- Health effects:
  - affects heart, kidneys and nerves.
  - In children - impaired cognition, behavioral disorders, hearing problems and delayed puberty



https://www.cnn.com/2016/03/04/us/flint-water-crisis-fast-facts/index.html

Perchlorate



- Use: solid fuel for missiles and rockets
- Occurrence: Can be found naturally in the environment, most of it is man-made.
- Reason:
    - Since the 1950s, over 870 million pounds manufactured in USA.
    - Due to over production, use, and improper disposal contaminated soil, drinking water, and irrigation water
- Health effects: lower the thyroid activity (hypothyroidism), leads to have adverse effect on Skin, Cardiovascular system, Pulmonary system, Kidneys, Nervous system etc.

Estimated total exposure (USFDA)

- Food in infants (aged 6–11 months) and children (aged 2 years)

  - 0.26 to 0.39 μg/kg body weight per day.
- Baby food contributed (in infants) - 49%
- Dairy products contributed (in 2-year-olds) - 51%
- Vegetables contributed (in adults) - 26% to 38%

J Expo Sci Environ Epidemiol. 18(6):571-80

https://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/perchlorate-background-jan17.pdf?ua=1

Why do we need the new treatment? Where do we place it?

Our convectional treatment process is designed to remove the basic water quality parameters; not the emerging pollutants.

We need to remove the emerging contaminants too!

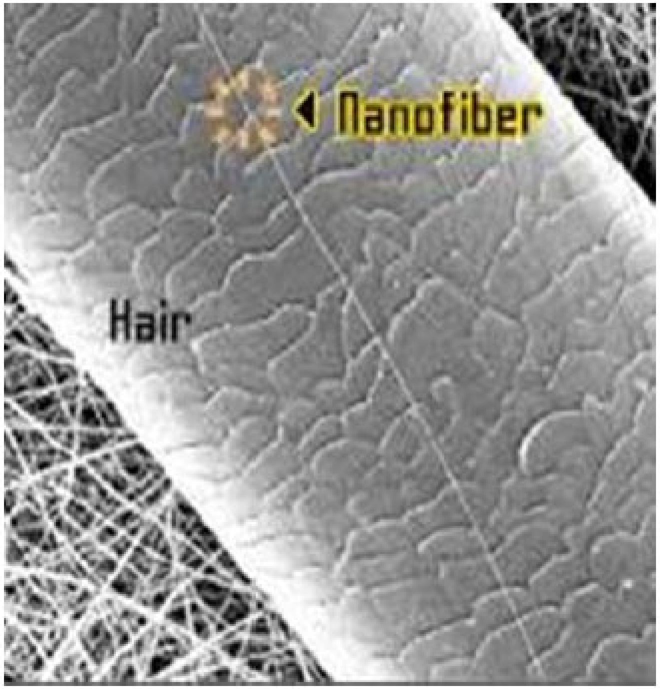
1. Need to purify the water at the point of use
   - Filters at household tap water
2. Where there are time/place/situation, we do not have access to the convectional treatment process
   - Places where people consume groundwater which are polluted with natural or man made chemicals
   - Emergency situations, Army camps etc.

Nanomaterials for Water treatment

Nano

Nano means “**Dwarf**” **(Greek) = 10^{-9}**

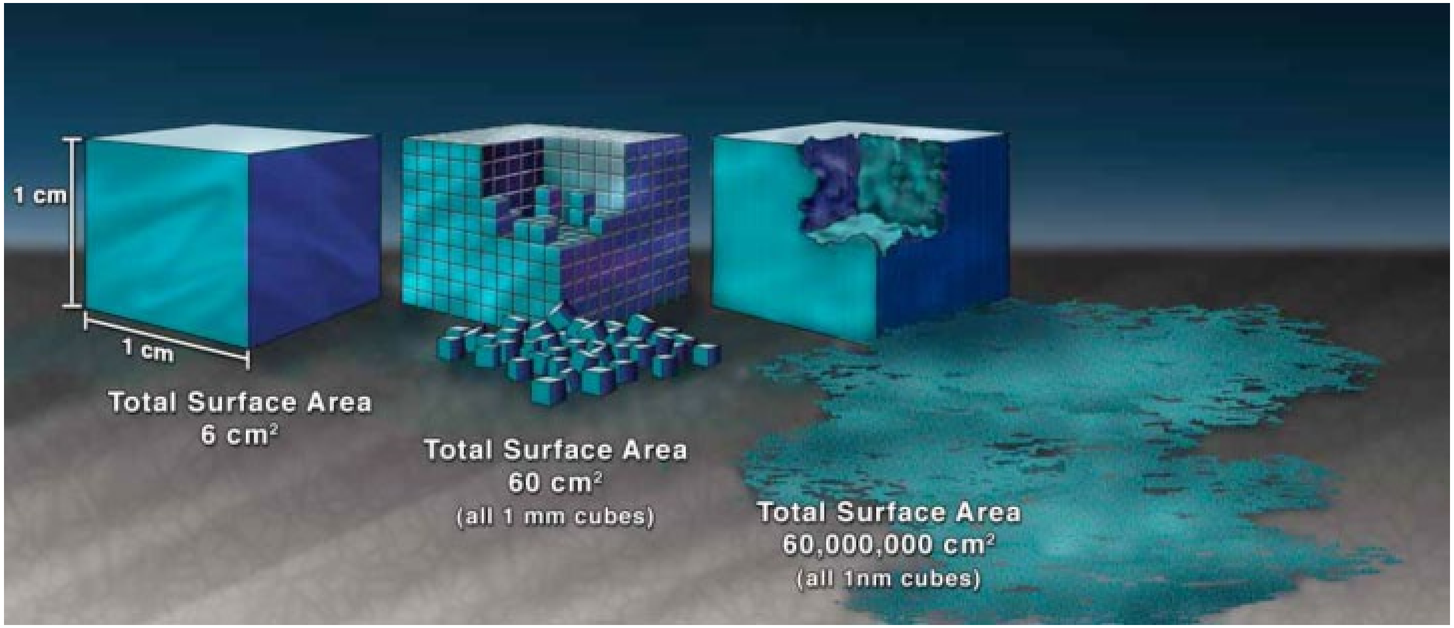
- Nanoparticles = 1 - 100 nm
- Width of one strand of human hair = ~50 to 100 μm = 50000 nm to 100000 nm
- **Nanoparticles** are usually 500 - 100000 times 'thinner' than a **human hair width**!



Pedro J.J. Alvarez, 2015

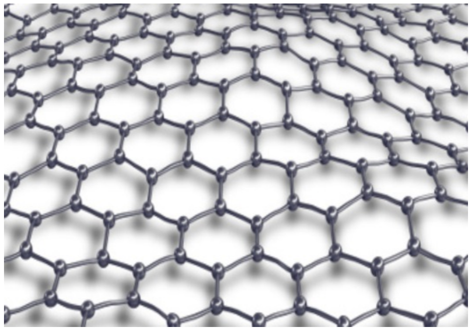
What's So Special about the Nanoscale?

- High surface area to Volume ratio
- One benefit of greater surface area—improve reactivity
- Helps “functionalization” of nanoscale material surfaces (adding particles for specific purposes)
- Ideal candidates for water treatment and desalination

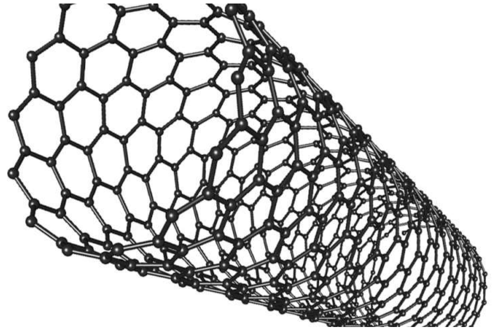


https://www.nano.gov/nanotech-101/special

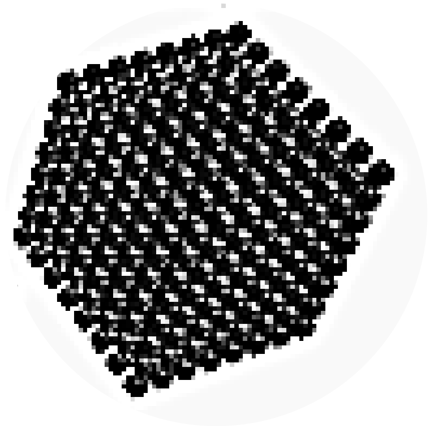
Nanomaterials



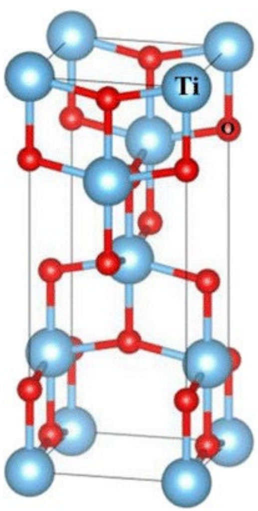
Graphene



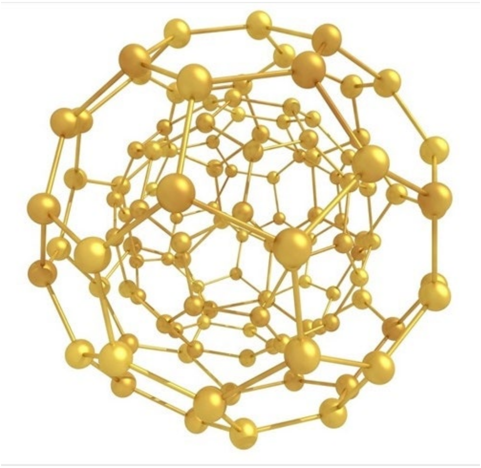
Carbon nanotube



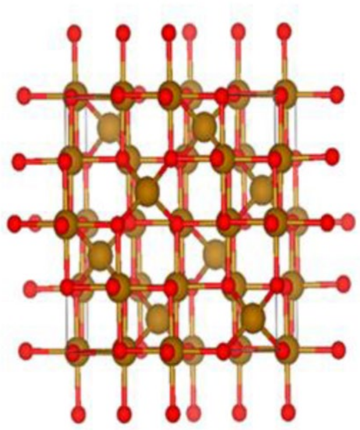
Zero-Valent Iron



Titanium dioxide



Gold nanoparticles

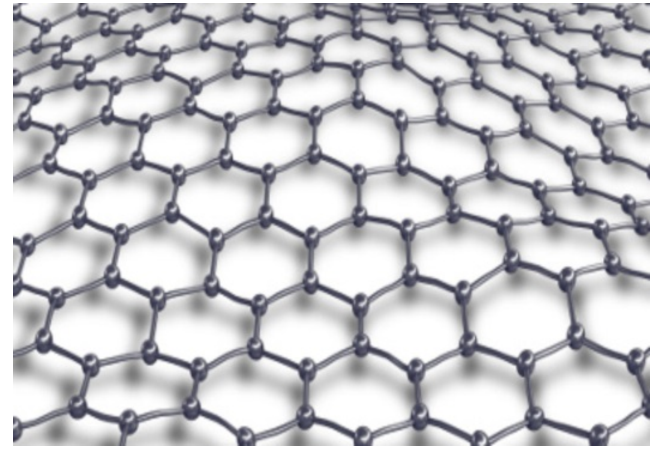


Magnetite


GRAPHENE

Graphene

Andre Geim (left) and Konstantin Novoselov won the Nobel Prize in Physics, 2010

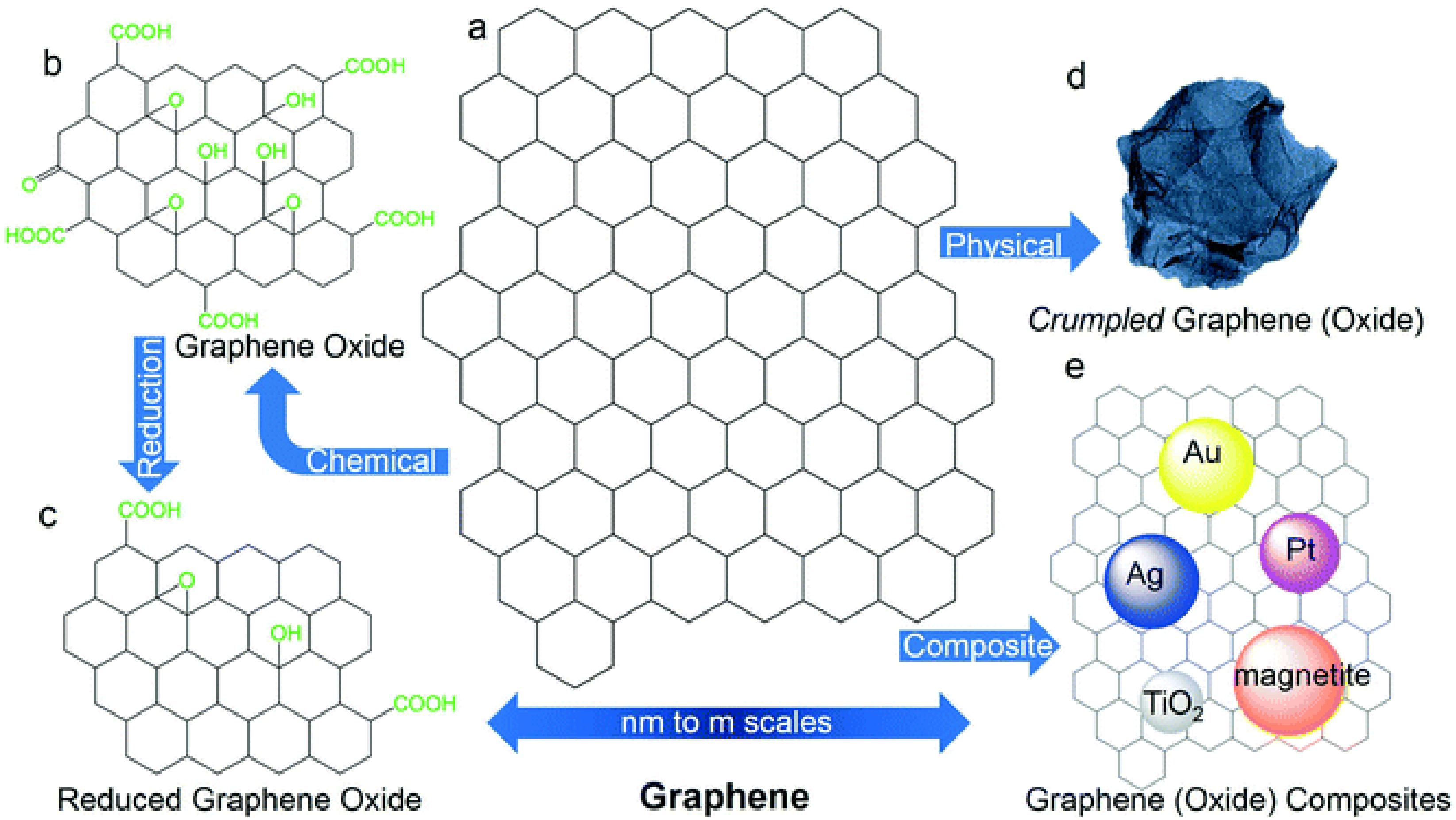


- Graphene is a form of carbon that exists as a sheet, one atom thick
- Atoms are arranged into a two-dimensional honeycomb structure
- About 100 times stronger than steel and conducts electricity better than copper
- About 1% of graphene mixed into plastics could turn them into electrical conductors

https://www.bbc.com/news/science-environment-11478645

https://www.npr.org/templates/story/story.php?storyId=130353581

Graphene-based materials

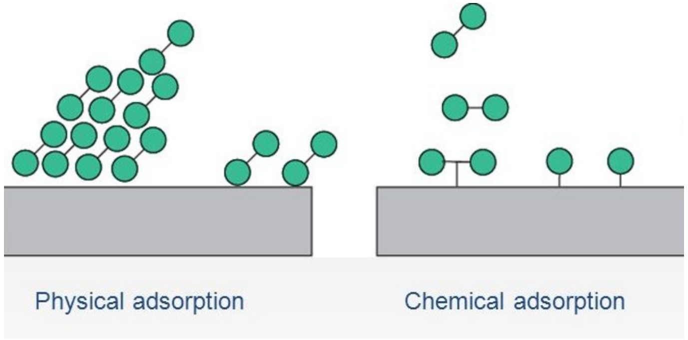


Environ. Sci.: Water Res. Technol., 2016, 2, 915-922

Graphene-based materials to contaminants

1. Organic contaminants
2. Heavy metal
3. Disinfection
4. ARG removal
5. Desalination
6. Thermal distillation

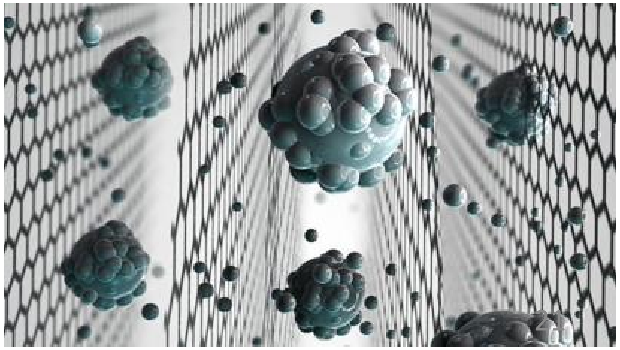
How it removes the contaminants



1. Adsorption

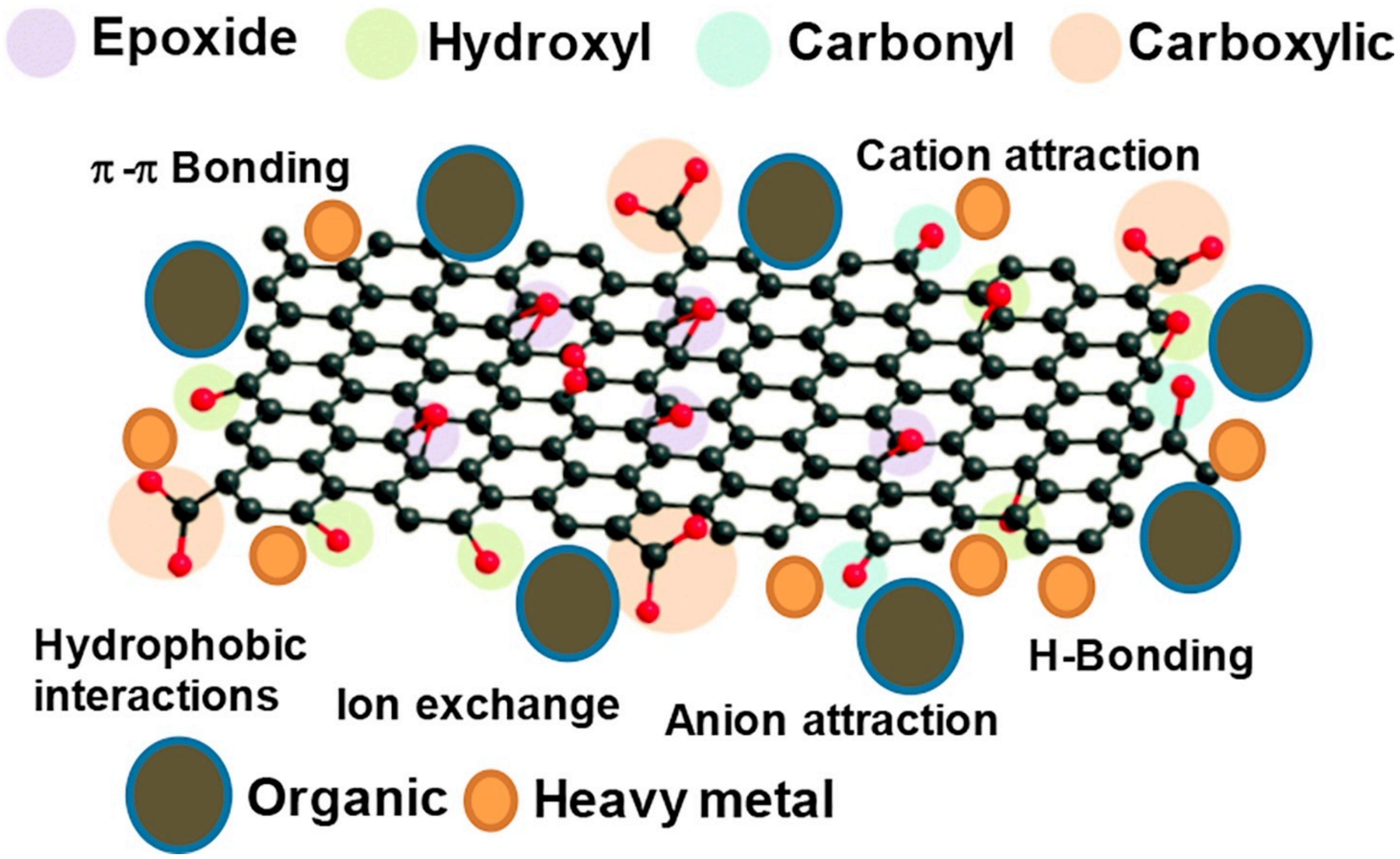
Contaminant degradation

2. Oxidation or Reduction reaction



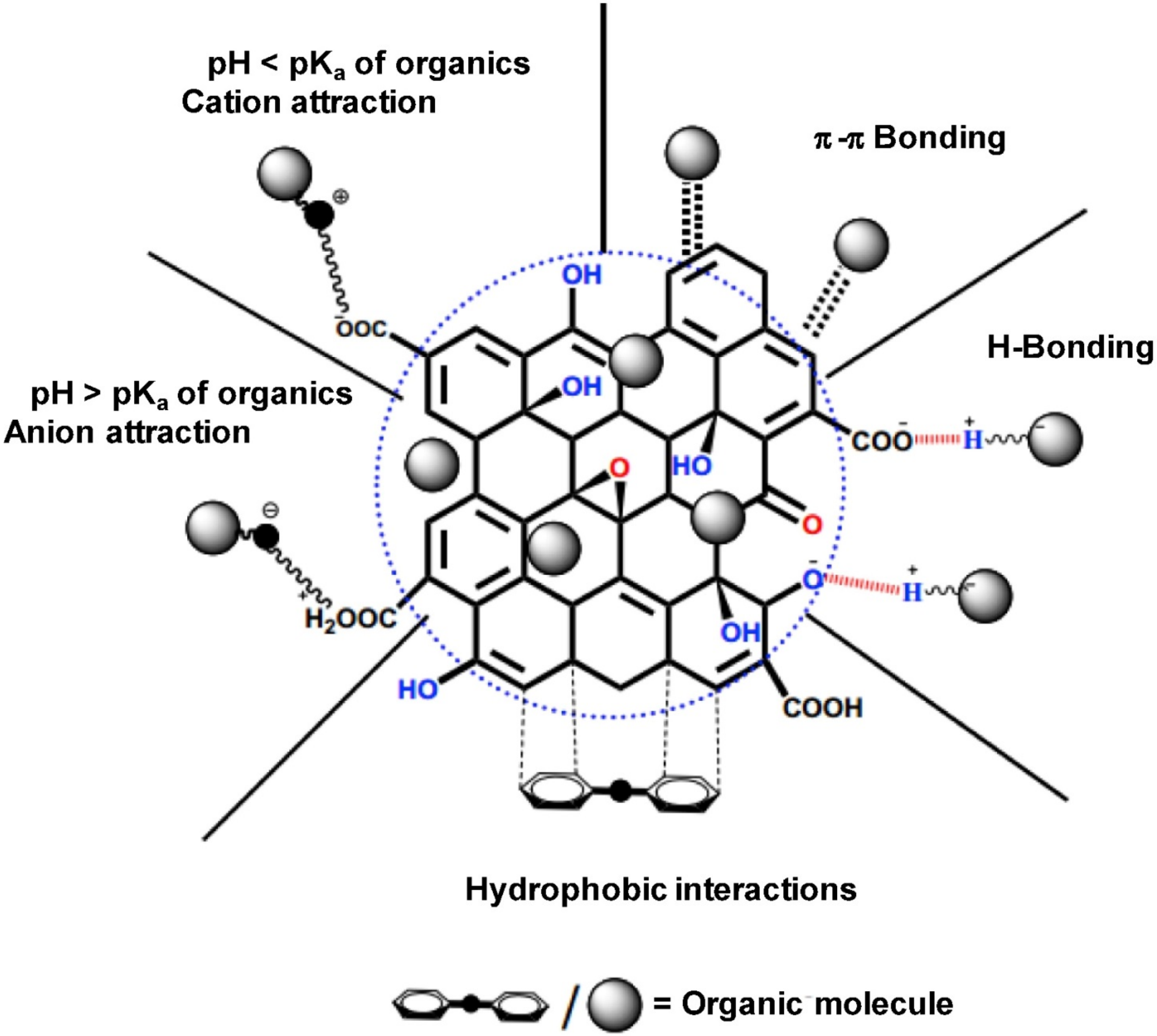
3. Membrane process

Adsorption



Chemosphere, 2018, 212, 1104-1124

Adsorption of organic contaminants



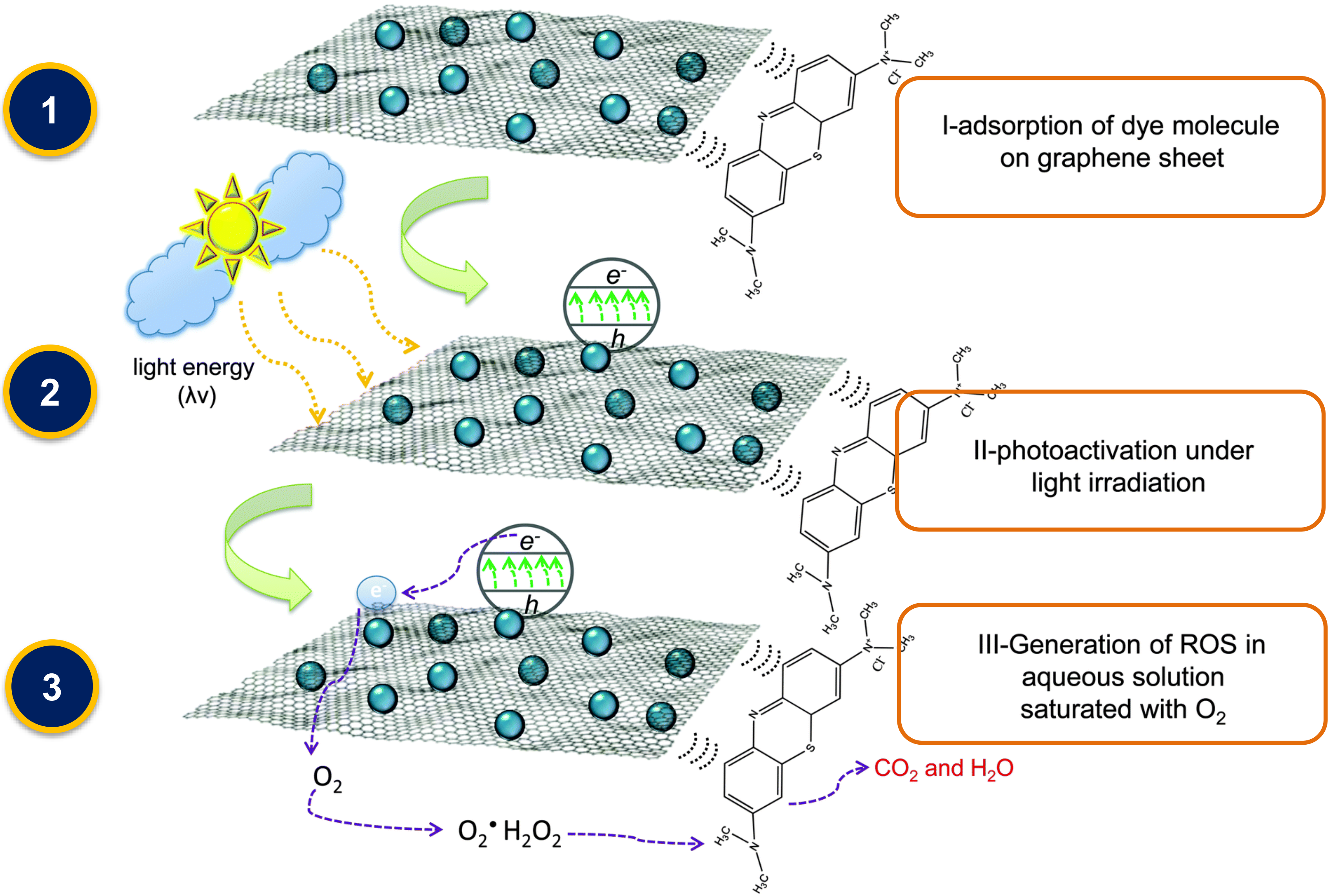
Chemosphere, 2018, 212, 1104-1124

Adsorption of organic contaminants

Nanomaterials	Pollutants	Maxmium adsorption (q_m, mg/g)	Treatment conditions	References
Graphene oxide	Levofloxacin	q_m 256.6	T 25 °C	Dong et al., 2016
Graphene oxide	Acetaminophen	q_m 704	T 25 °C; pH 8	Moussavi et al., 2016
Graphene oxide	metformin	k_F 47.1	T 30 °C; pH 6	S. Zhu et al., 2017
Graphene oxide	Anti-inflammatory nimesulide	q_m 82.41	T 25 °C	Jauris et al., 2017
Graphene oxide	17-α-ethinylestradiol	q_m 45	T 25 °C	Sun et al., 2017
	17-β-estradiol	q_m 48	T 25 °C	
CNTs-Graphene oxide	17-β-estradiol	q_m 144.4	T 25 °C	Kumar et al., 2017
	ciprofloxacin	q_m 1368	T 25 °C	

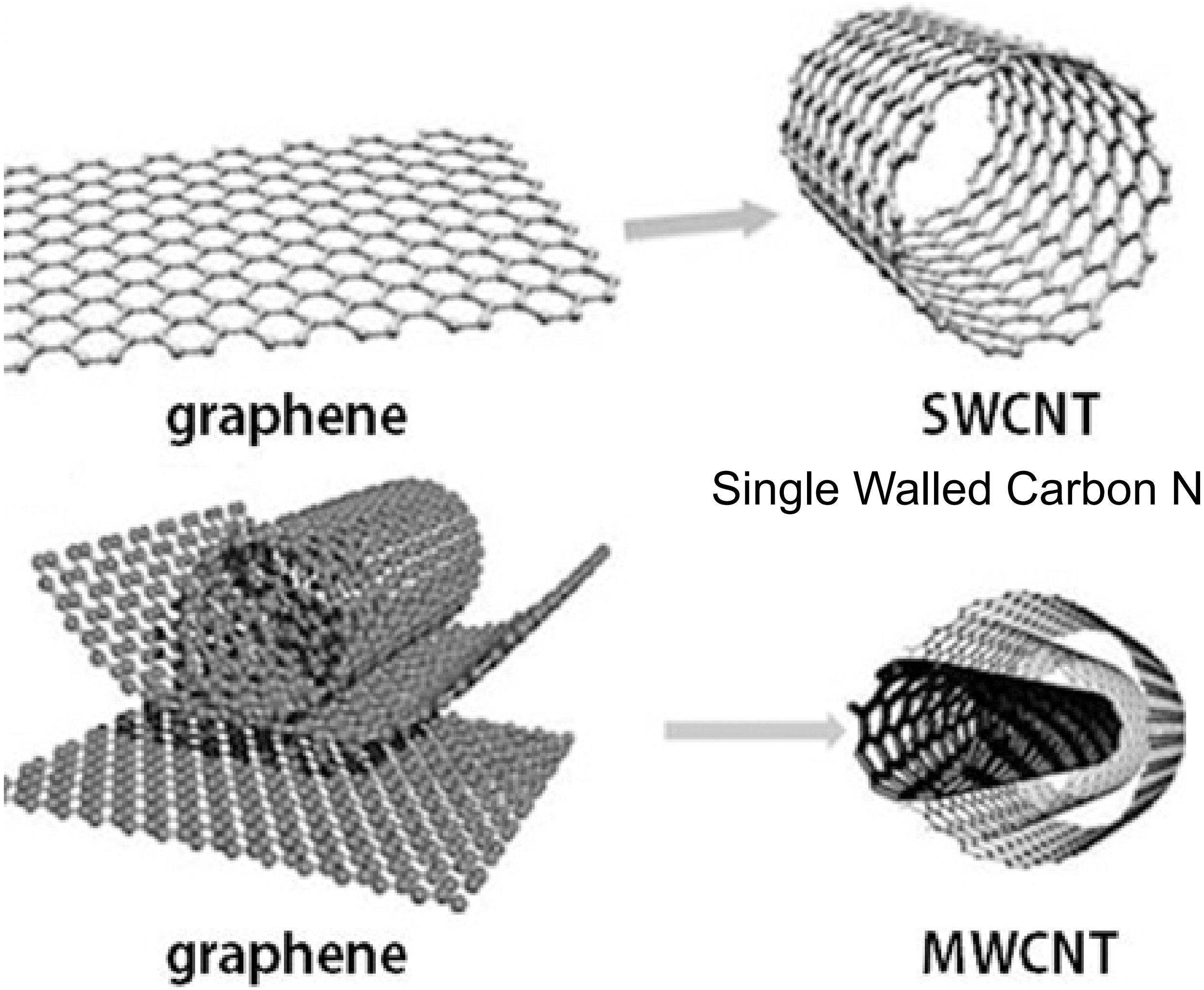
Science of The Total Environment, 2018, 627, 1253-1263

Graphene-based materials to remove organic contaminants



Chem. Soc. Rev., 2015, **44**, 5861-5896

CNTs for adsorption



Single Walled Carbon Nanotubes

Multi Walled Carbon Nanotubes

Front. Syst. Neurosci., 2014 ,8 (91), 1-24

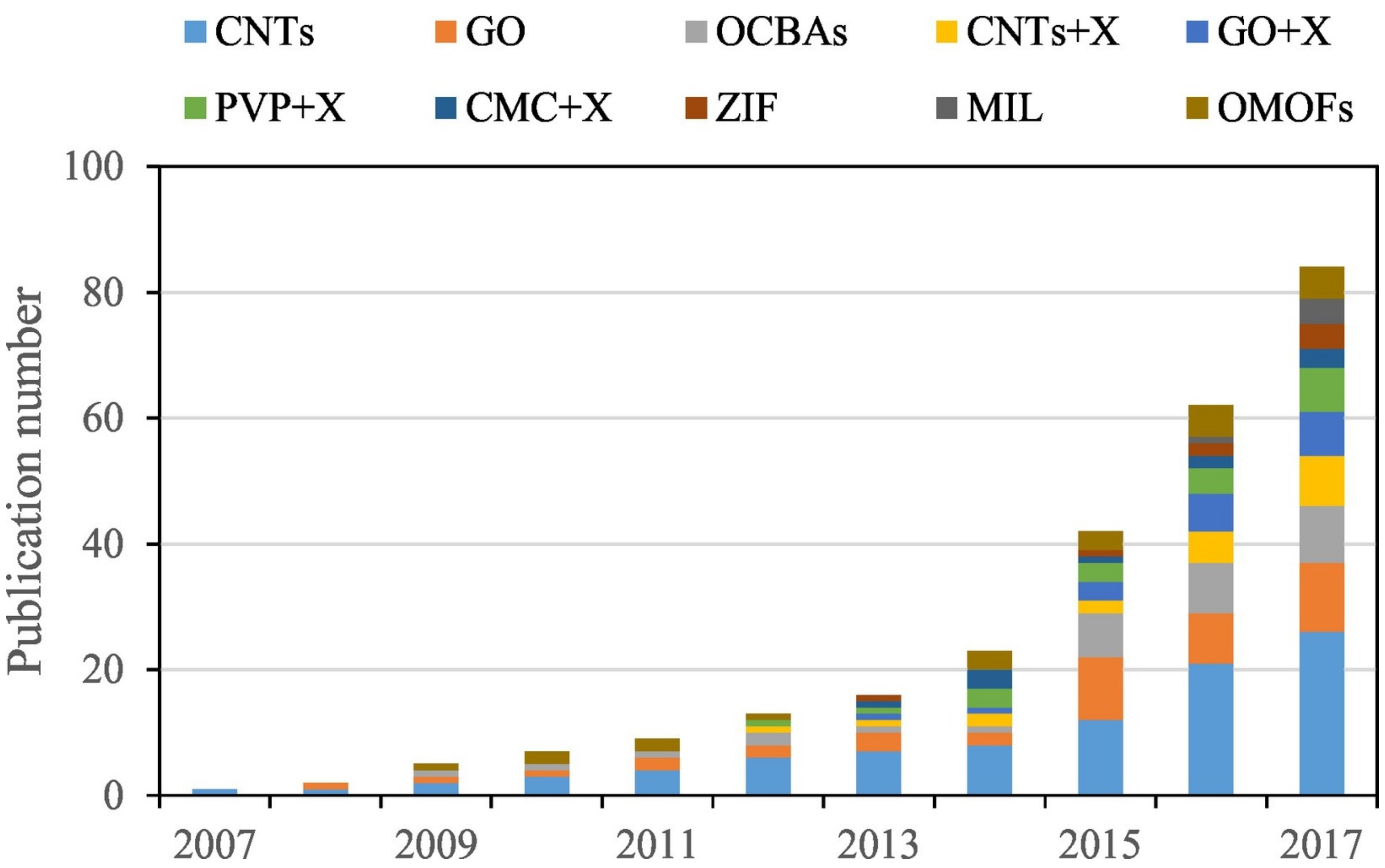
Adsorption of organic contaminants

Nanomaterials	Pollutants	Maxmium adsorption (q_m, mg/g)	Treatment conditions	References
MWCNT	Triclosan	q_m 157.7	T 25 °C; pH 7	Zhou et al., 2013
MWCNT	Norfloxacin	q_m 88.5	T 30 °C; pH 7	Yang et al., 2012
MWCNT	Sulfamethoxazole	k_F 201	T 20 °C	Kim et al., 2014
MWCNT	Lincomycin	k_F 287	T 20 °C	Kim et al., 2014
MWCNT	Sulfamethoxazole	q_m 45.8	pH 7	Tian et al., 2013
MWCNT	Sulfapyridine	q_m 86.1	pH 7	Tian et al., 2013
MWCNT	Sulfapyridine	k_F 350	pH 6.2	Ji et al., 2009
MWCNT	Sulfamethoxazole	k_F 510	pH 6.2	Ji et al., 2009
MWCNT	Ciprofloxacin	q_m 135	T 25 °C; pH 5	Carabineiro et al., 2012
MWCNT	Tetracycline	k_F 240	pH 5	Ji et al., 2010a, Ji et al., 2010b
MWCNT	Tetracycline	q_m 269.5	T 20 °C	Zhang et al., 2011
MWCNT	Sulfonamides	k_F 353–2814	T 25 °C	Zhao et al., 2016
MWCNT	Chloramphenicols	k_F 571–618	T 25 °C	Zhao et al., 2016
MWCNT	Non-antibiotic pharmaceuticals	k_F 317–1522	T 25 °C	Zhao et al., 2016

Science of The Total Environment, 2018, 627, 1253-1263

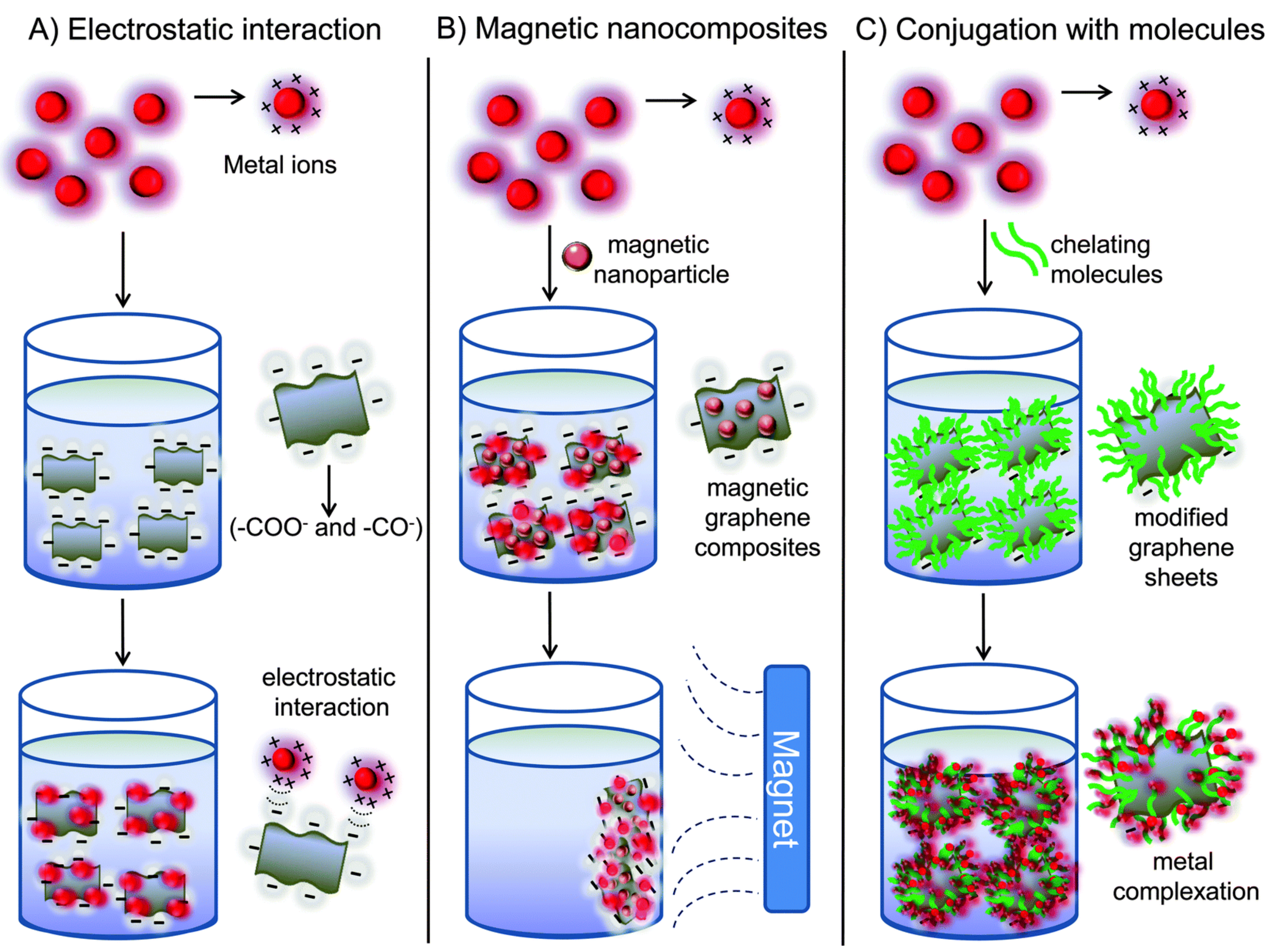
Removal of emerging contaminants by nanoadsorption

Trend of studies on emerging contaminant removal using nanoadsorption during 2007–2017



Science of The Total Environment, 2018, 627, 1253-1263

Graphene-based materials as adsorbents to remove metal ions



Chem. Soc. Rev., 2015, **44**, 5861-5896

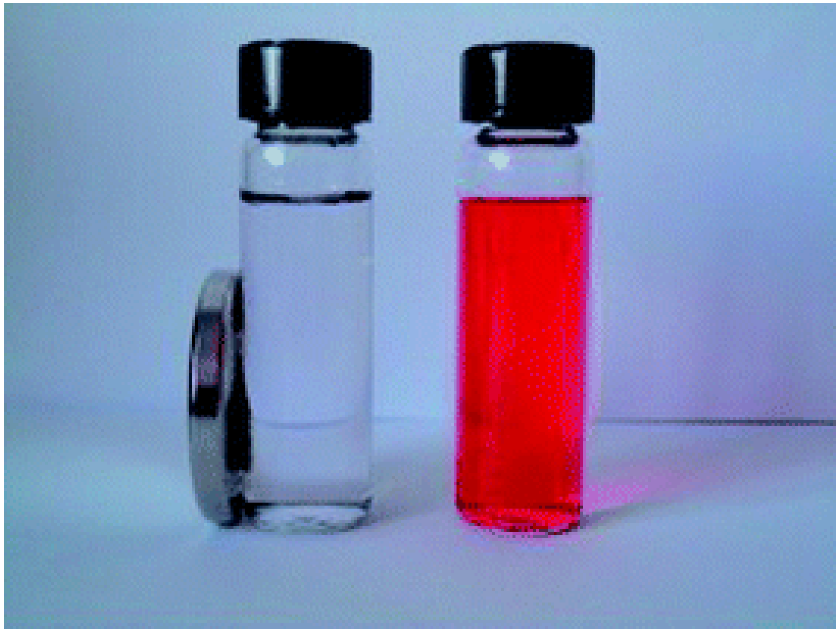
Graphene-based materials as adsorbents to remove metal ions

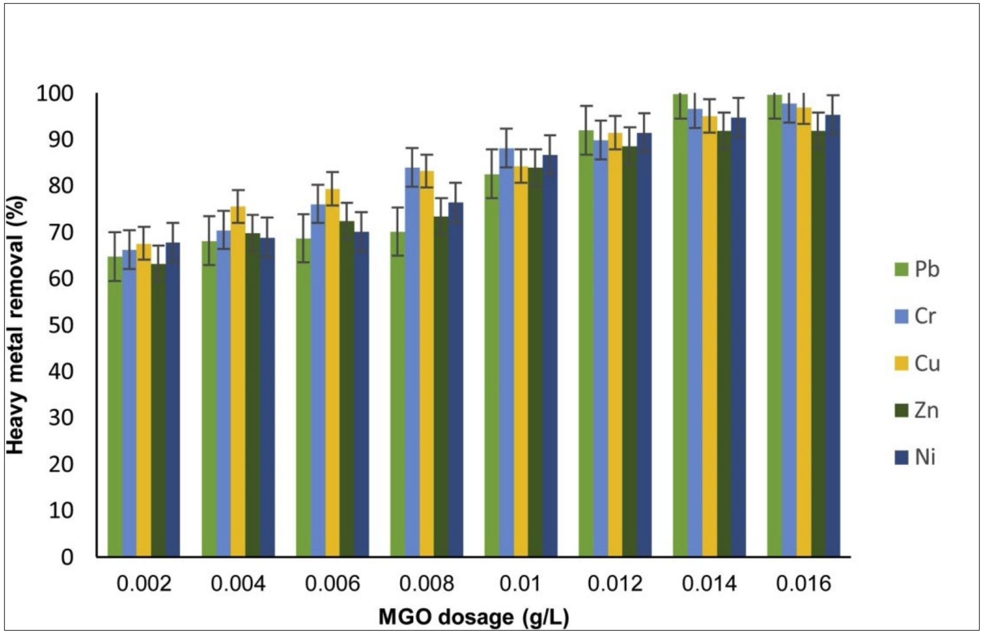
Adsorbent	Adsorbate	Environmental conditions				Maximum adsorption capacity (mg/g)	Interaction mechanism	Ref.
		m/V (g/L)	C0 (mg/L)	pH	T (K)			
GO/chitosan	Au(III)	0.2	80	4.0	298	1077	Ionic interaction	Liu et al. (2012b)
RGO/Fe_3O_4/MnO_2	As(III)	0.5	5	7.0	298.5	14		Luo et al. (2012)
RGO/Fe_3O_4/MnO_2	As(IV)	0.5	5	7.0	298.5	12		Luo et al. (2012)
GO	Co(II)	0.1	30	6.0	303	68	Electrostatic interaction	Zhang et al., 2011b
GO/Fe_3O_4	Co(II)	0.4	10	6.8	303	13	Inner-sphere surface complexation	Liu et al. (2011)
GO	Cd(II)	0.1	20	6.0	303	106	Electrostatic interaction	Zhang et al., 2011b
GO		0.1	1	6.0	298	530	Surface complexation	Sitko et al. (2013)
GO/Fe_3O_4/β-CD	Cr(VI)	1	100	3.0		120	Surface complexation	Fan et al., 2012b
GO		0.5	3.2	5.0	298	47	Coordination and electrostatic interaction	Yang et al. (2010)
GO	Cu(II)	0.1	1	5.0	298	294	Surface complexation	Sitko et al. (2013)
GO/Fe_3O_4		0.4	10	5.3	298	18	Electrostatic interaction, complexation	Li et al. (2012b)
RGO/$CoFe_2O_4$	Hg(II)	0.14	5	4.6	298	158		Zhang et al. (2014)
GO	Pb(II)	0.1	1	3–7	298	1119	Surface complexation	Sitko et al. (2013)
GO	U(VI)	0.06	98	5.0	293	98	Inner sphere surface complexation	Zhao et al. (2012b)

Science of The Total Environment, 2018, 627, 1253-1263

Graphene/Magnetite composite

- Graphene adsorbent – to adsorbs organic compounds and heavy metals
- Graphene/Magnetite composite – easy separation of graphene from water using magnetic property
- Regenerate the adsorbent and reuse it for further water treatment





Chemical Engineering Journal, 2011, **173** (1), 92-97

Journal of Water Process Engineering, 2020, 33, 101044

Graphene – Antibacterial property

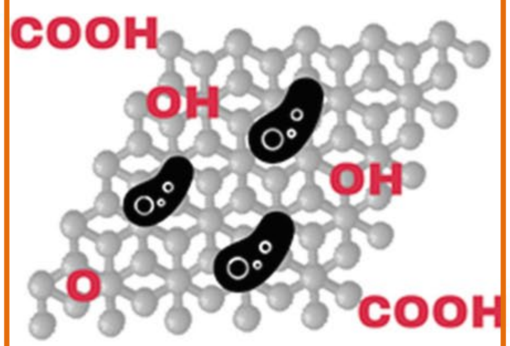
1. Nano-blade effect

membrane cutting and leacking of intracellular components

2. Oxidative stress induction

membrane damage via generation of reactive oxigen species

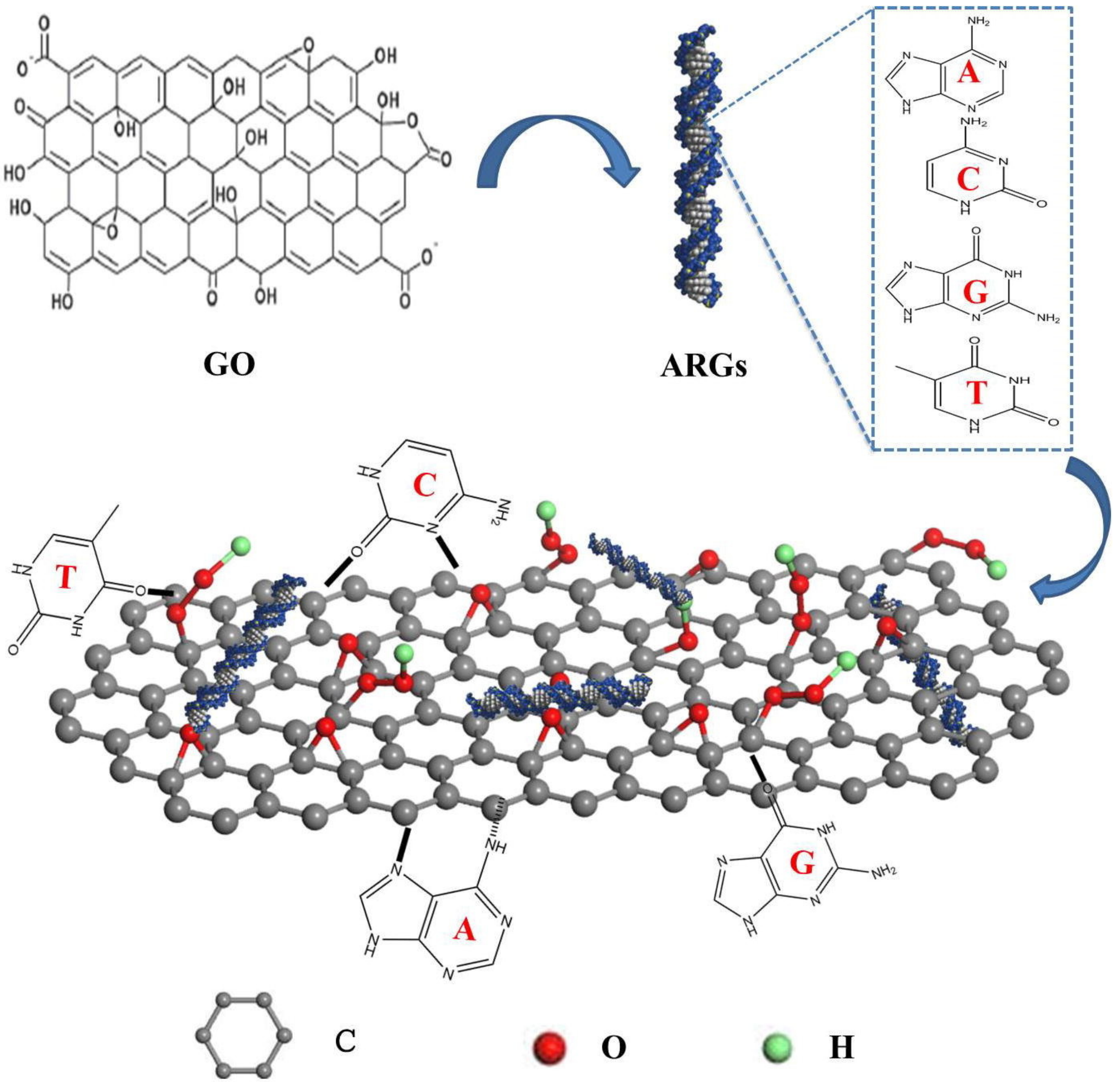
3. Wrapping



bacteria wrapped by GO nano-sheets

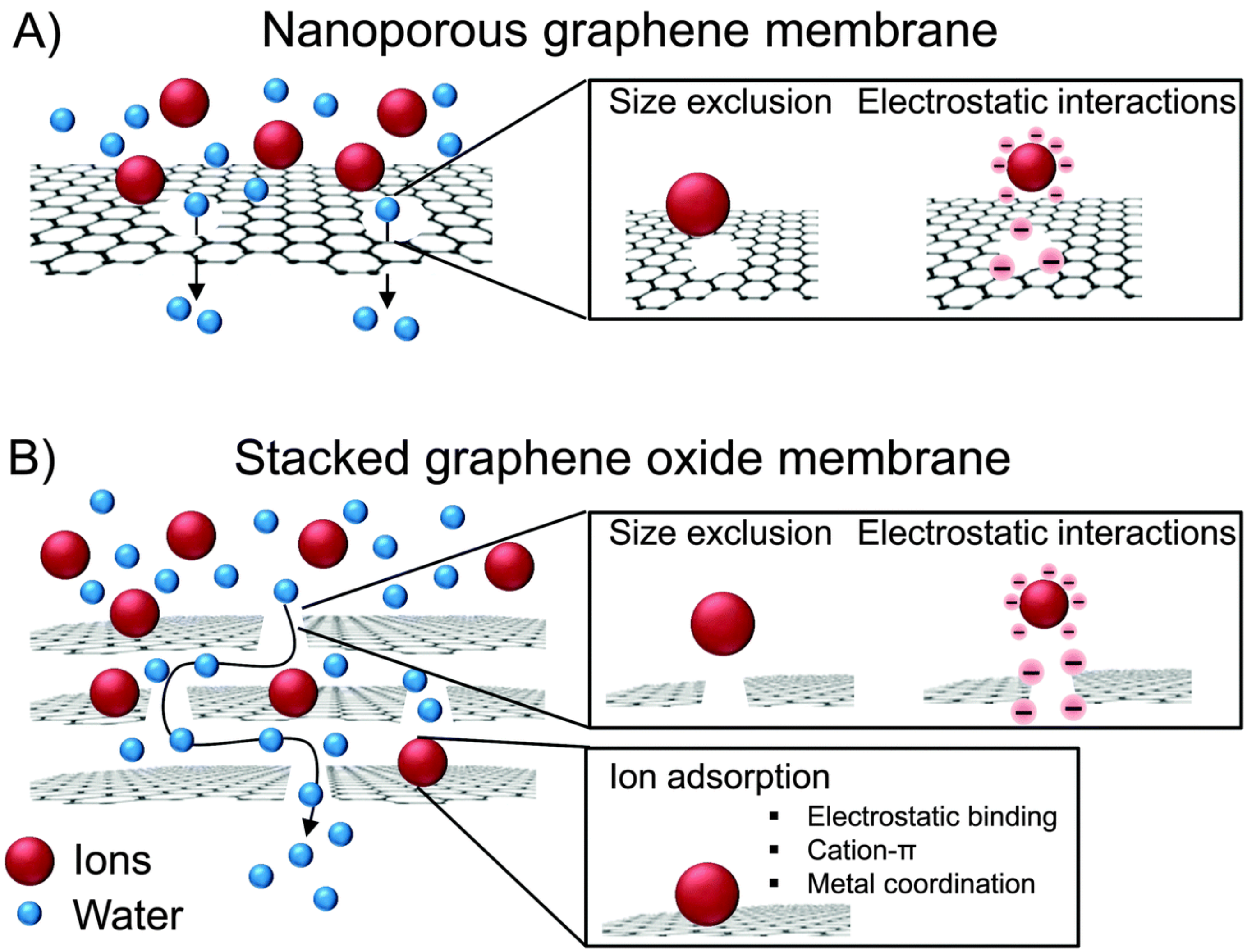
Advances in Experimental Medicine and Biology, (2019), Springer, New York, NY, 1-15

Graphene – Removal of ARGs



Chemical Engineering Journal 313 (2017) 836–846

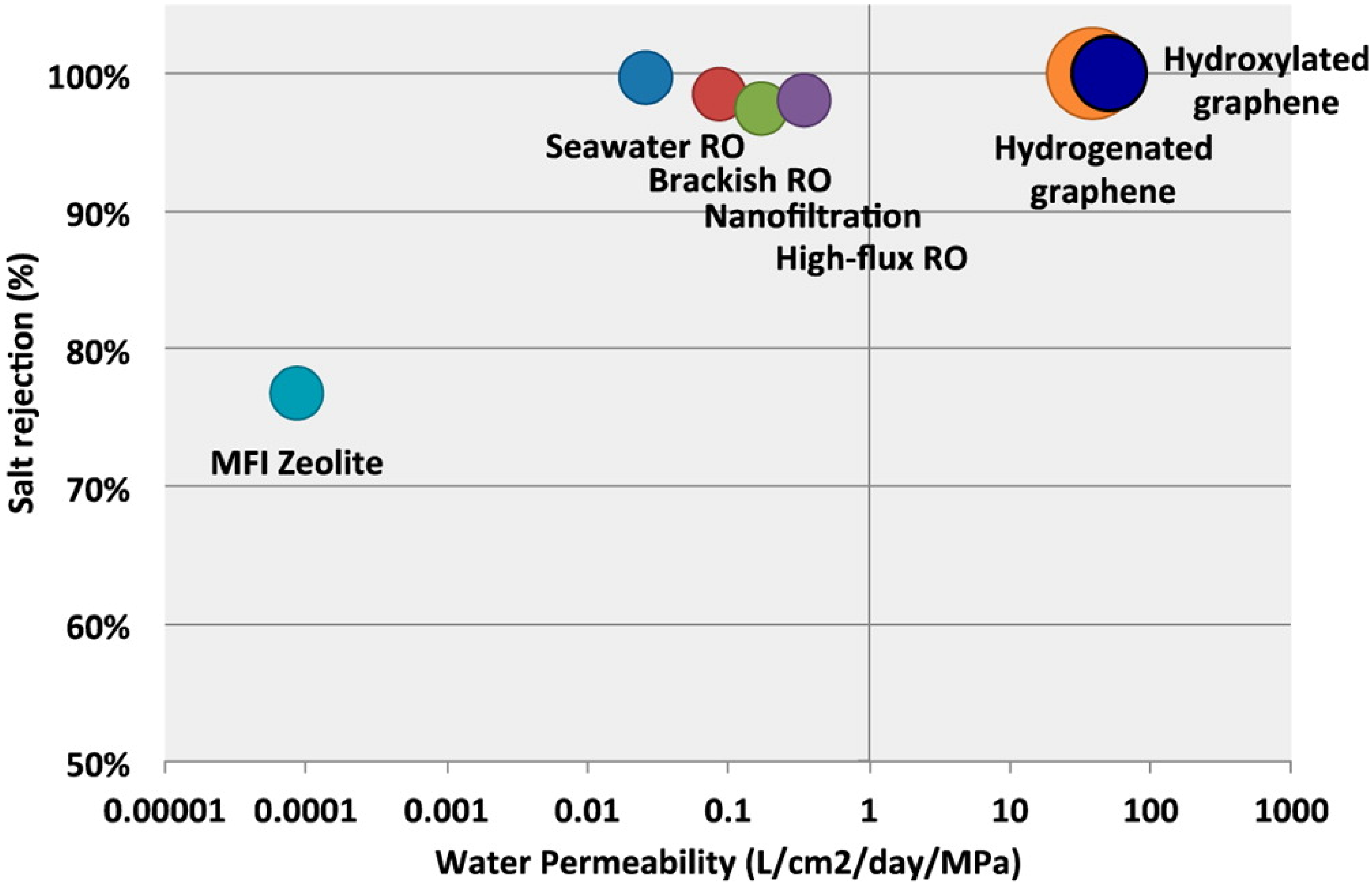
Desalination



Chem. Soc. Rev., 2015, **44**, 5861-5896

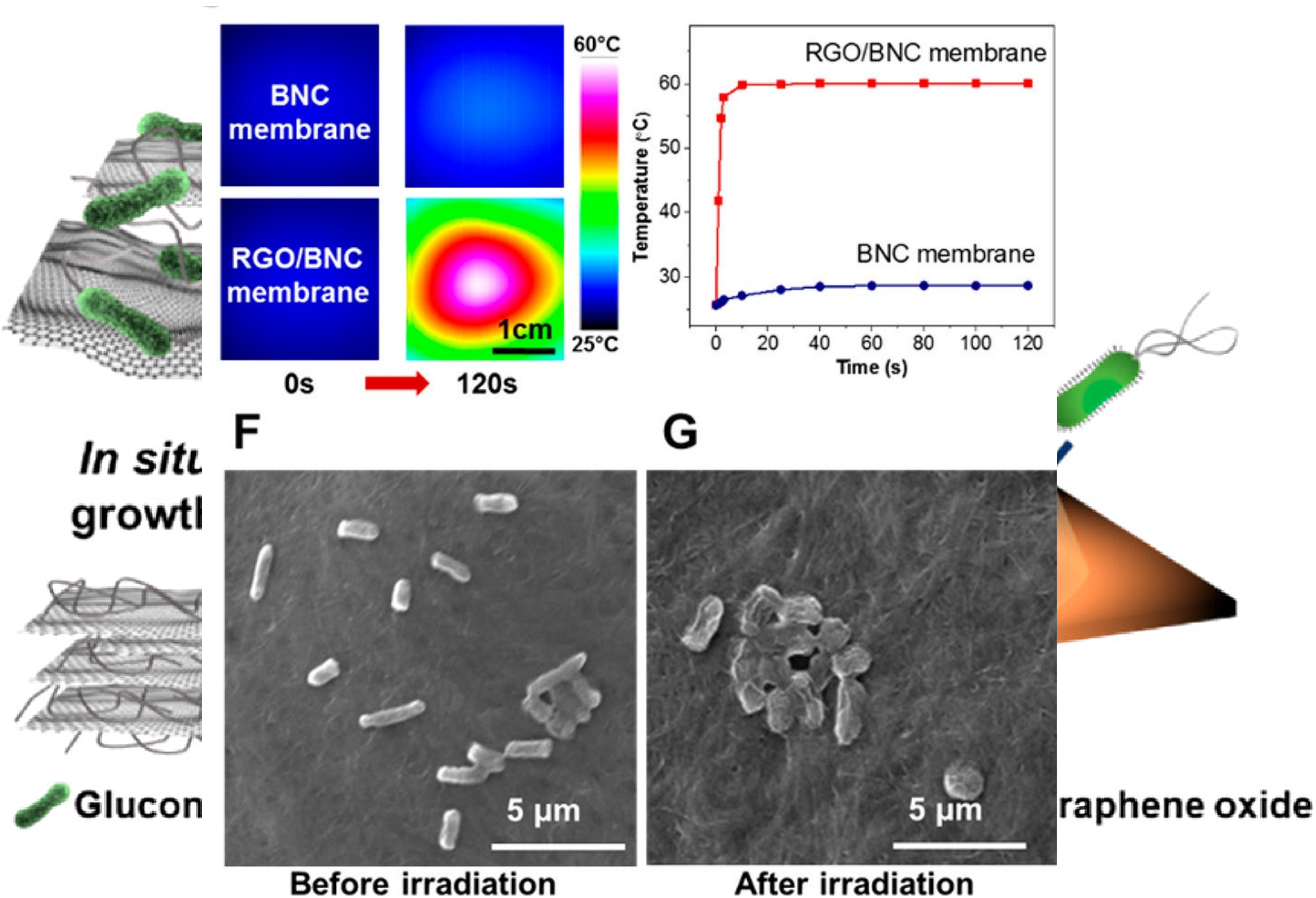
Desalination

OH-groups can hydrogen-bond with water and offer a smoother entropic landscape for water molecules to traverse, thus allowing for faster overall water flow



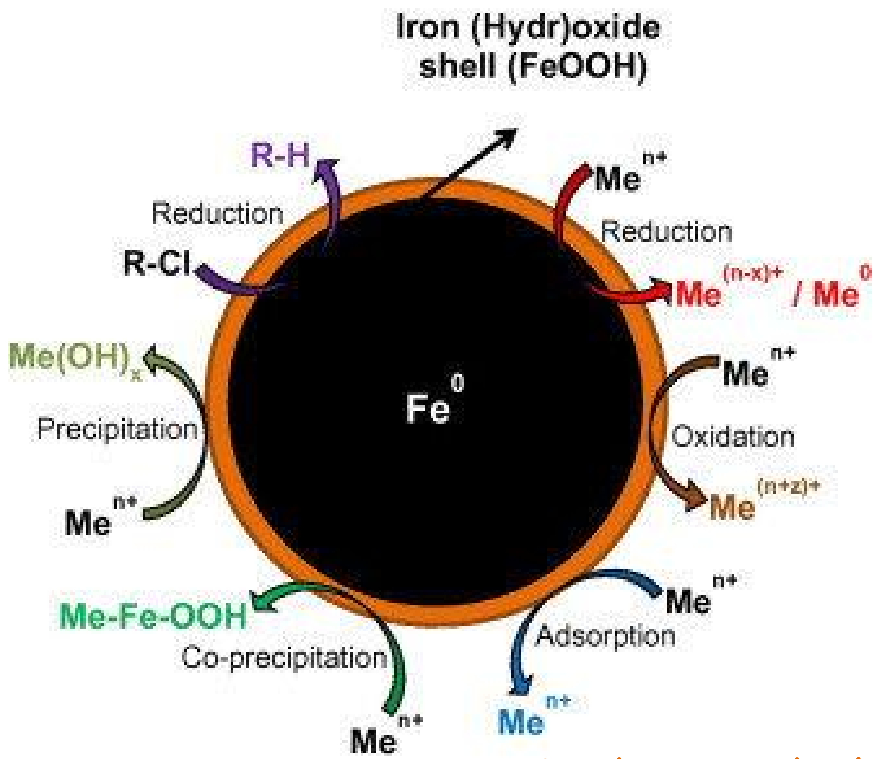
Nano Lett. 2012, 12, 7, 3602-3608

Photothermal membrane for disinfection



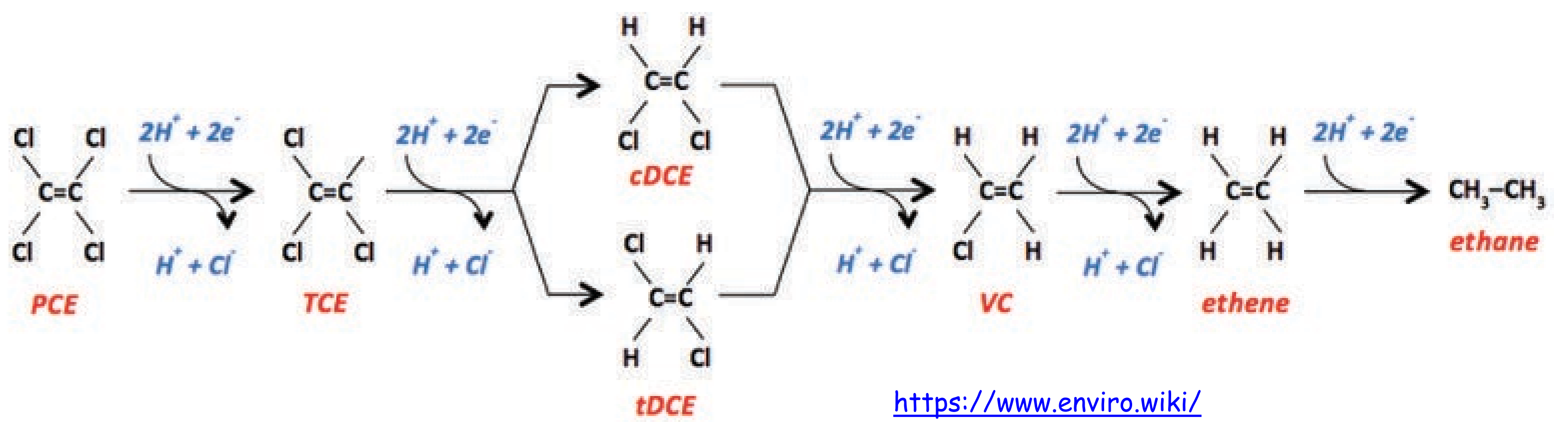
Environ. Sci. Technol. 2019, 53, 1, 412-421

Zerovalent Iron (ZVI)



- Core shell type structure
- core - consists of zero-valent or metallic iron
- Shell - mixed valent (i.e. Fe^{2+} and Fe^{3+}) oxide as a result of oxidation of metallic iron
- More surface area and more no. of reactive sites
- Exhibit dual properties of reduction and absorption

Reductive dechlorination

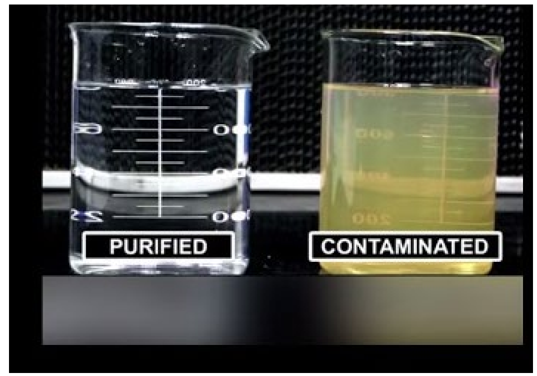


https://www.enviro.wiki/

Remediation of contaminated sites

Treatment of Arsenic contaminated ground water

- About 239 million people across 153 districts in 21 states of India contain an unacceptably high level of arsenic in water



Adsorbent

- Iron oxyhydroxide - selectively remove arsenic
- Gold – Disinfect bacteria

Removal efficiency

- arsenic concentration reduced from 250 to 300 ppb to 2 ppb

Cost

- 6 cents per 1000 liter

Installation

- 900 locations in India serving about 600,000 people

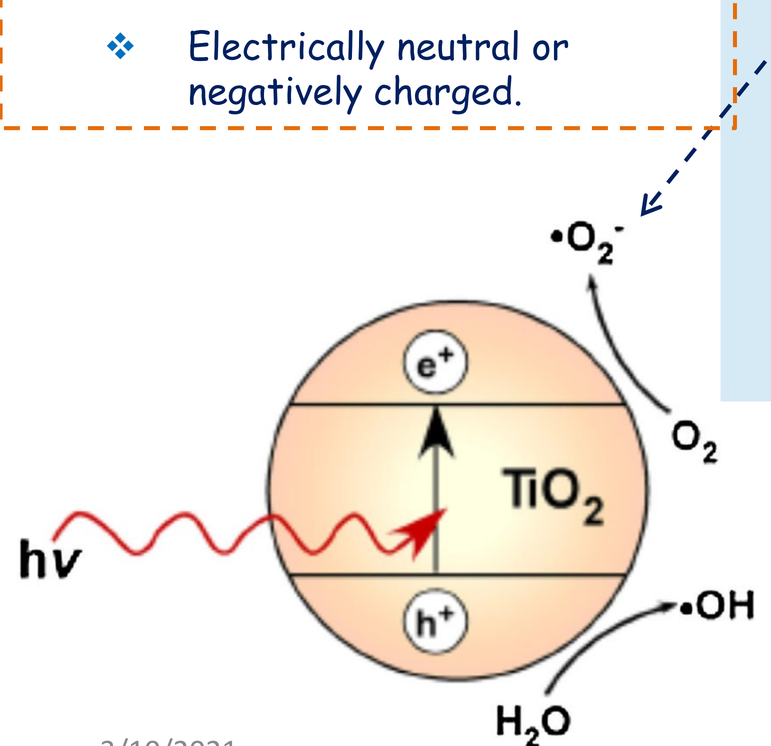
https://dst.gov.in/

https://www.thebetterindia.com/40227/water-purifier-developed-by-iit-madras/

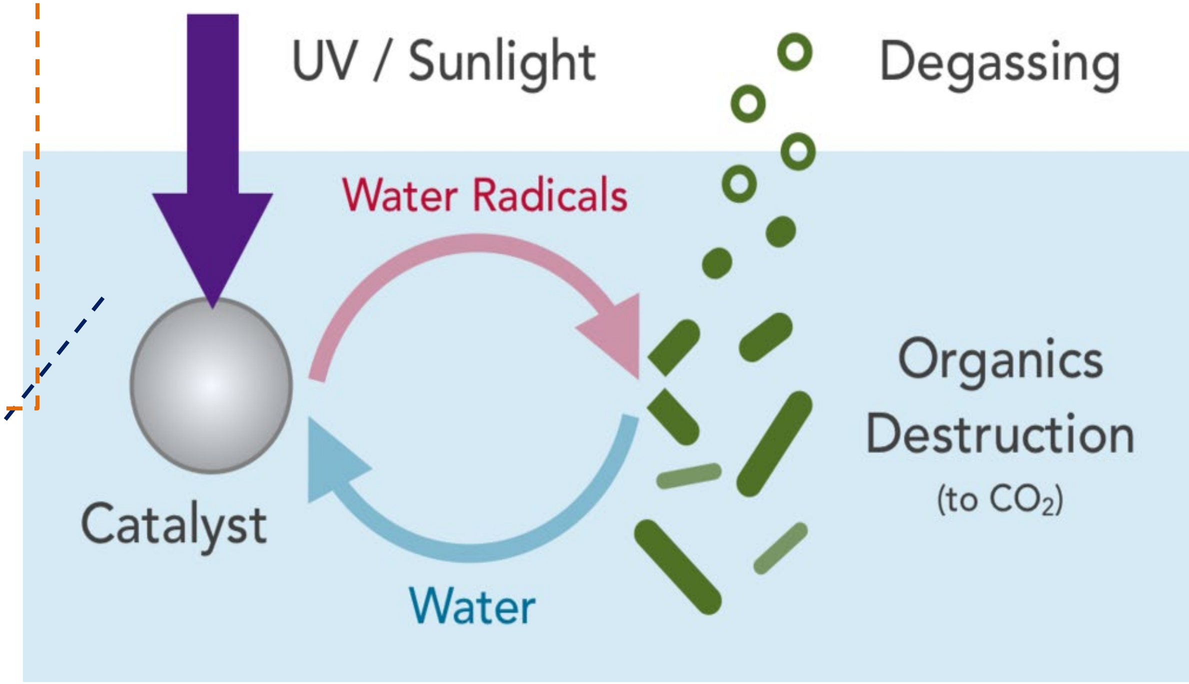
Photocatalysis

Advanced oxidation process generate free radicals ($OH^{\cdot}$, $O_2^{\cdot -}$, $HO_2^{\cdot}$)

- Small, Diffusible, Highly reactive & Short-lived
- Higher Oxidation potential 2.8 eV
- Electrically neutral or negatively charged.

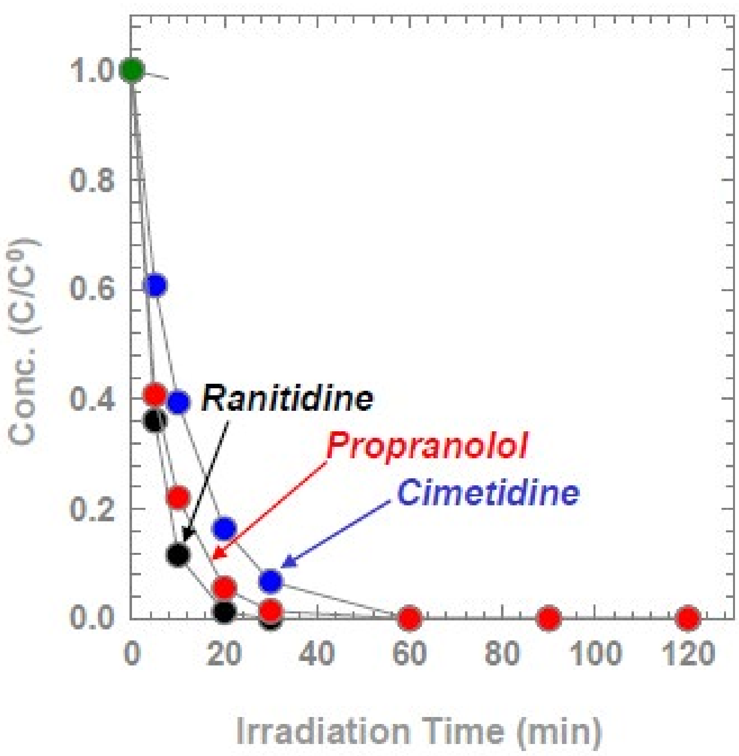


Titanium Dioxide (TiO_2)



Photocatalysis

Treatment of emerging contaminants (Pharmaceuticals, endocrine disruptors)

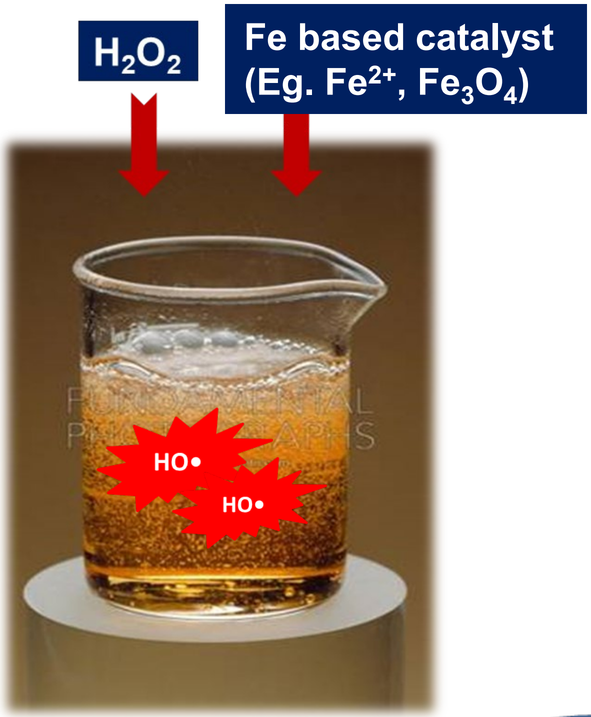


Environ. Sci. Technol. *45*: 10598-10604

Fenton Reaction

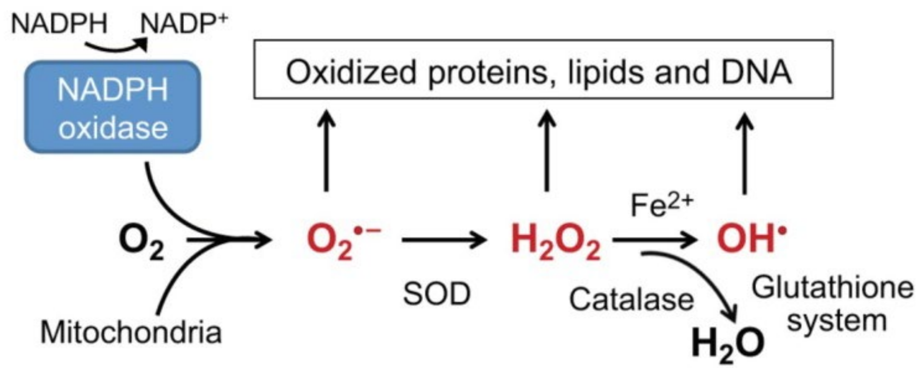
Works the same way how our body generates radicals!

Modified Fenton Process

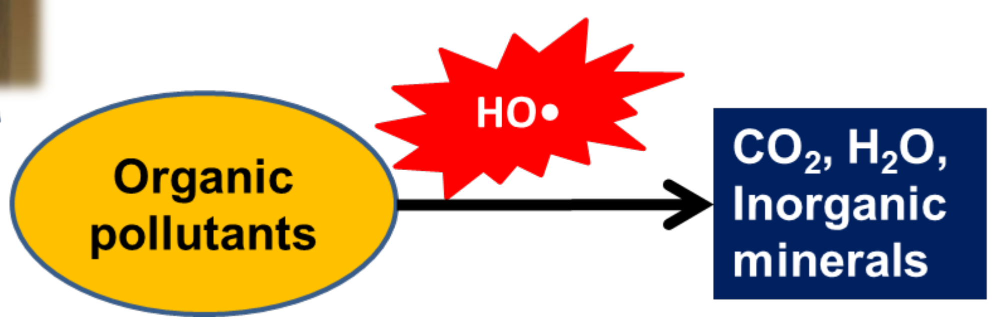


fphoto.photoshelter.com

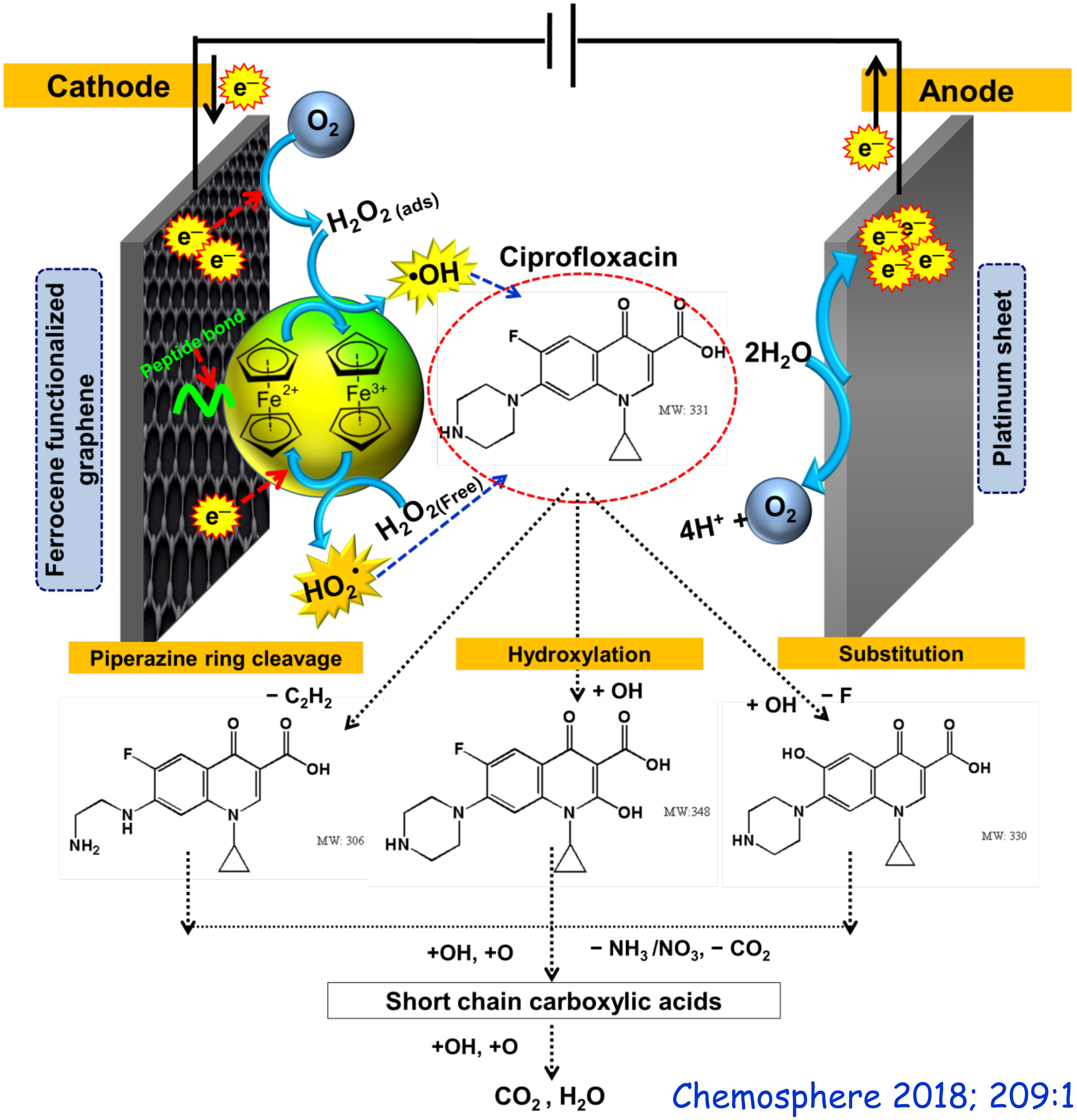
Radical generation mechanism in body



Development, 2014 (141), 4206-4218



Electro-Fenton reaction

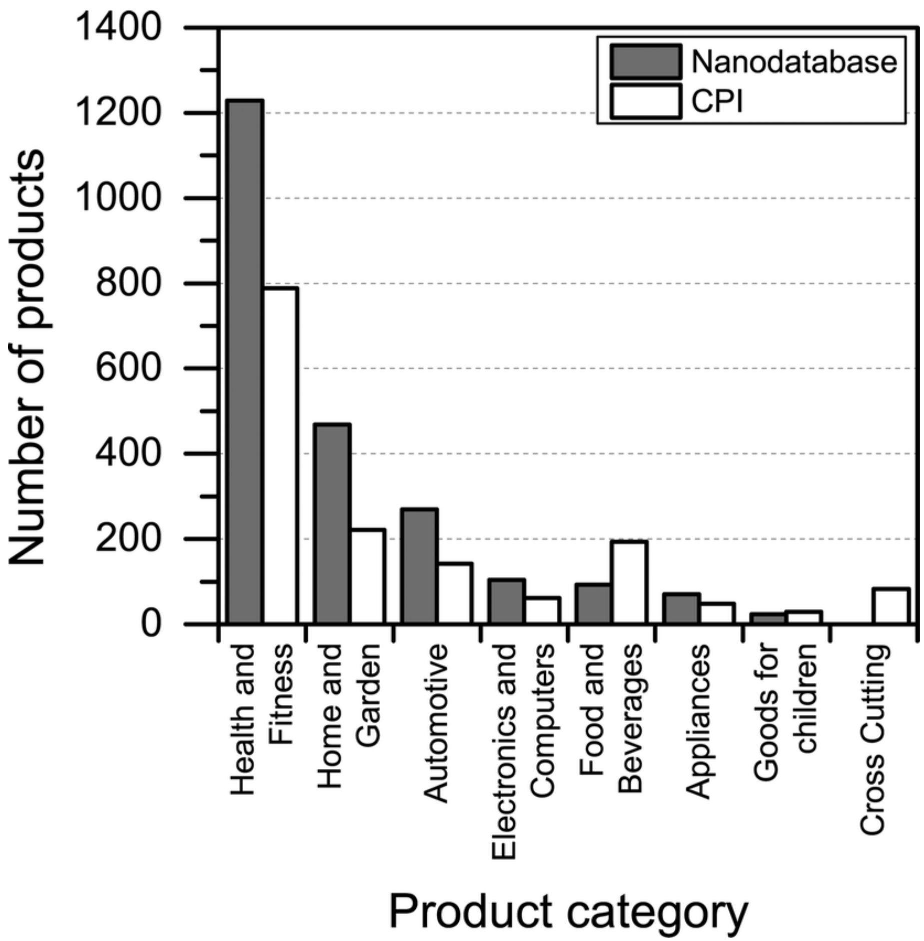


Chemosphere 2018; 209:113-123.

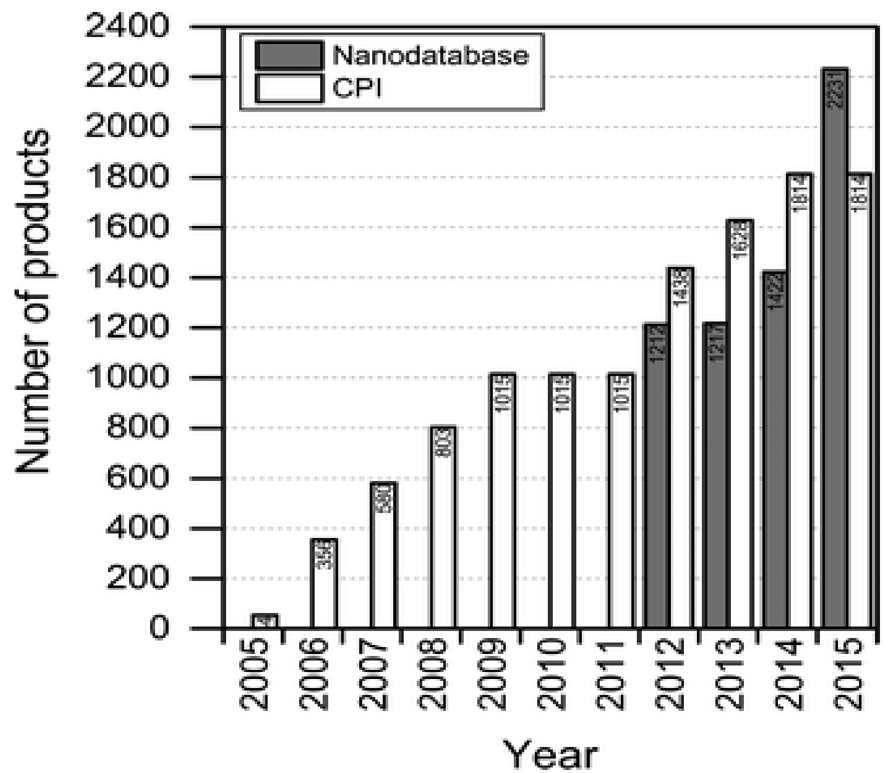
Implications of Nanomaterials

Nanomaterials In Consumer Products

Distribution of nano based products into product categories



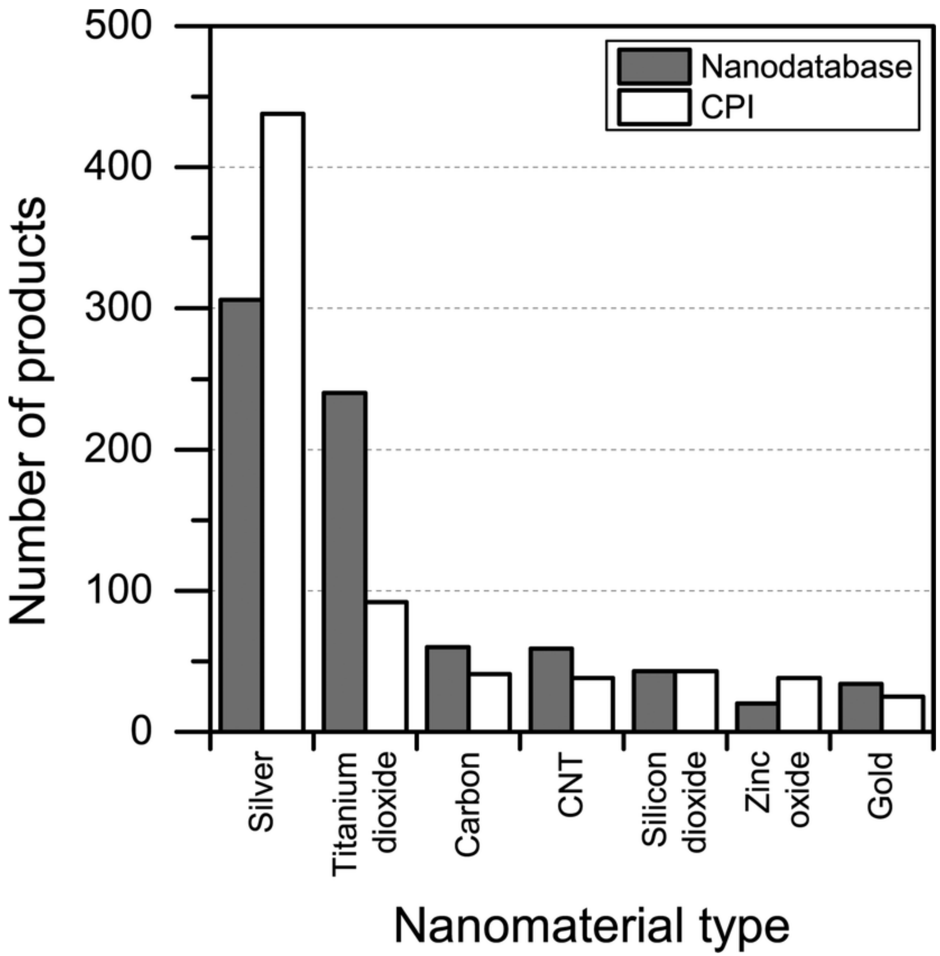
Increasing Trend in number of products



Environ. Sci.: Nano, 2016, **3**, 169-180

Nanomaterials In Commercial Products

Widely Used Nanomaterials In Commercial Products



Environ. Sci.: Nano, 2016, **3**, 169-180

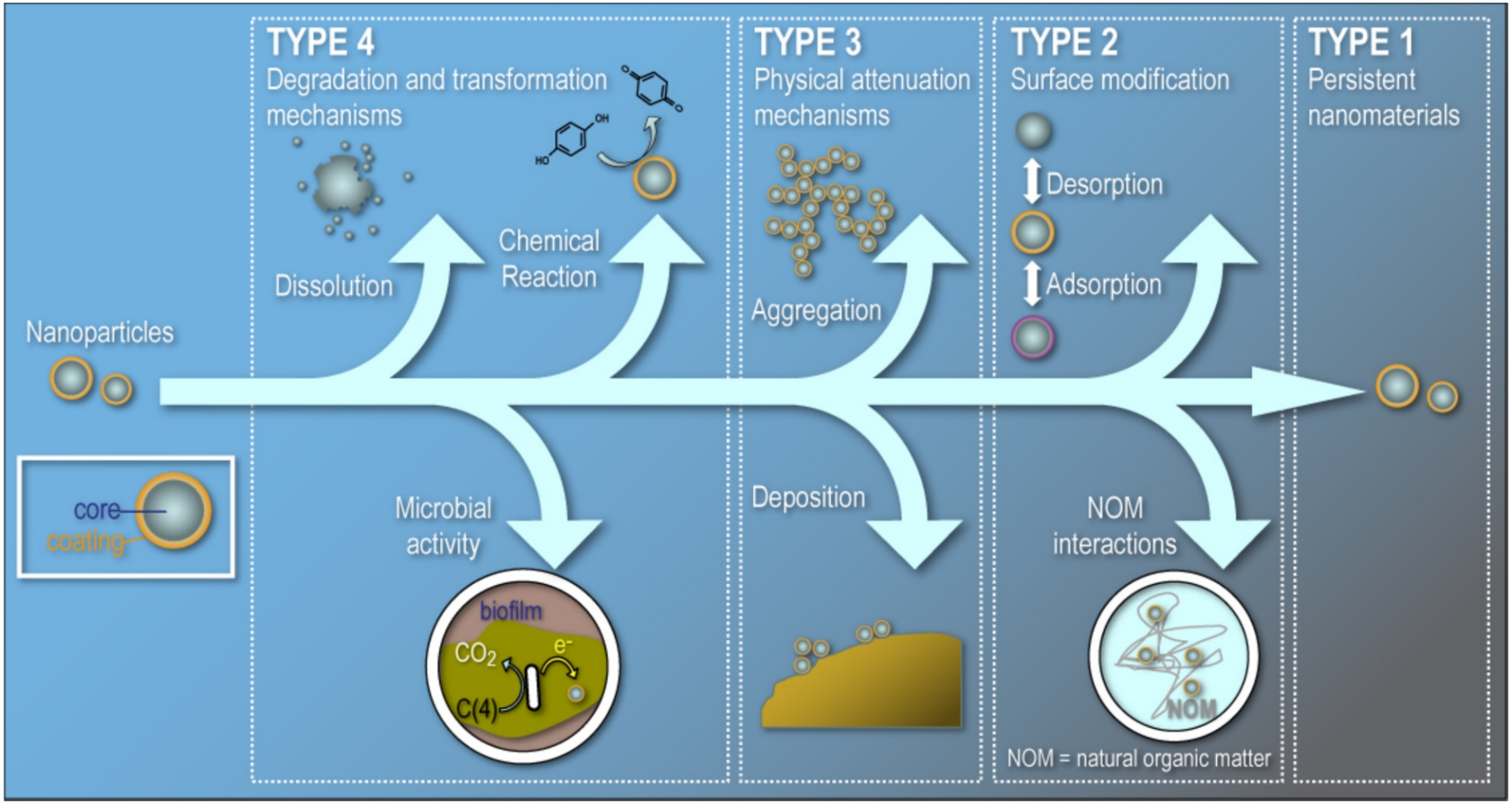
Nano-silver in Bandages & socks

Fullerene in "revitalizing" night creams

Nano ZnO "transparent" sunscreen

Implications of Nanomaterials

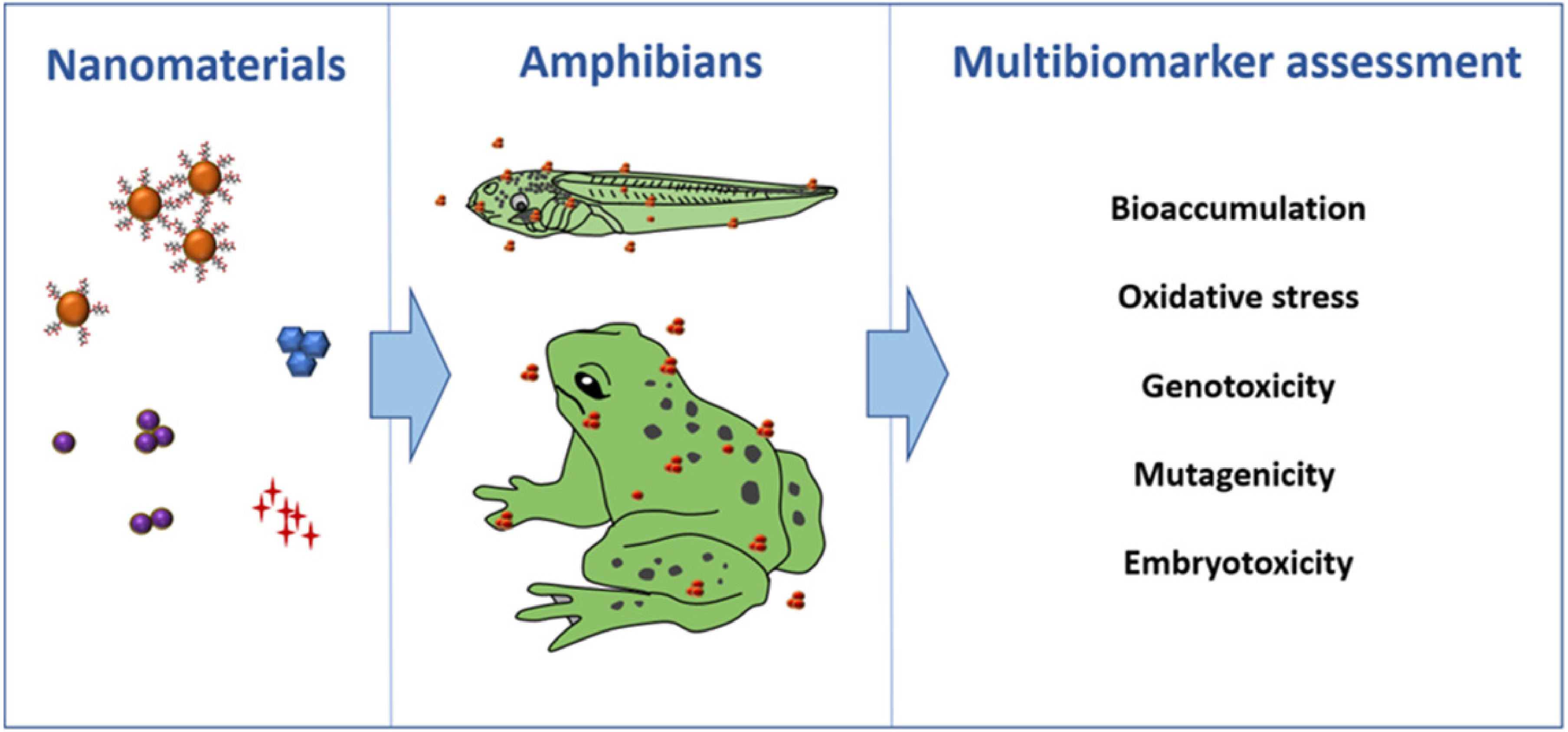
Possible nanoparticle modifications in the environment



ACS Nano 3(7): 1616-1619

Implications of Nanomaterials

Amphibians as a model system in ecotoxicological studies



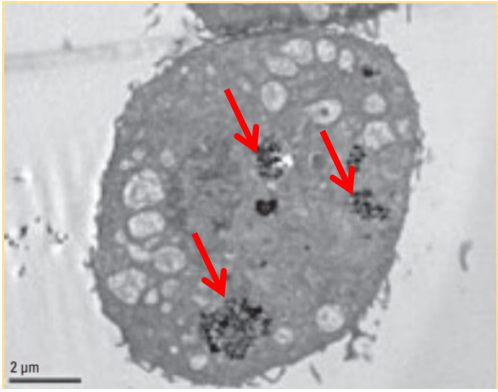
Science of the Total Environment, 686 (2019) 332-344

Implications of Nanomaterials

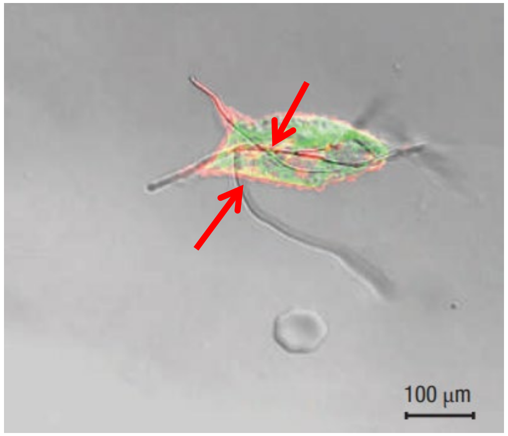
Cytotoxicity studies of selected nanomaterials

Nanomaterial	Effects observed
Fullerene	
C_{60} water suspension	Antibacterial; cytotoxic to human cell lines; taken up by human keratinocytes; stabilizes proteins
C_{60} encapsulated in poly(vinyl-pyrrolidone), cyclodextrins, or poly(ethylene glycol)	Damages eukaryotic cell lines; antibacterial
Hydroxylated fullerene	Oxidative eukaryotic cell damage
Carboxyfullerene (malonic acid derivatives)	Bactericidal for Gram-positive bacteria; cytotoxic to human cell lines
Fullerene derivatives with pyrrolidine groups	Antibacterial; inhibits cancer cell proliferation; cleave plasmid DNA
Other alkane derivatives of C_{60}	Antimutagenic; cytotoxic; induces DNA damage in plasmids; inhibits protein folding; antibacterial; accumulates in rats' livers
Metallofullerene	Accumulates in rats' livers
Inorganic	
Silicon dioxide (SiO_2)	Pulmonary inflammation in rats
Anatase (TiO_2)	Antibacterial; pulmonary inflammation in rodents
Zinc oxide (ZnO)	Antibacterial (micrometer scale); pulmonary effects in animals and humans

Nanoiron into microalgea cell



Rat lung cell ingesting Carbon nanotubes

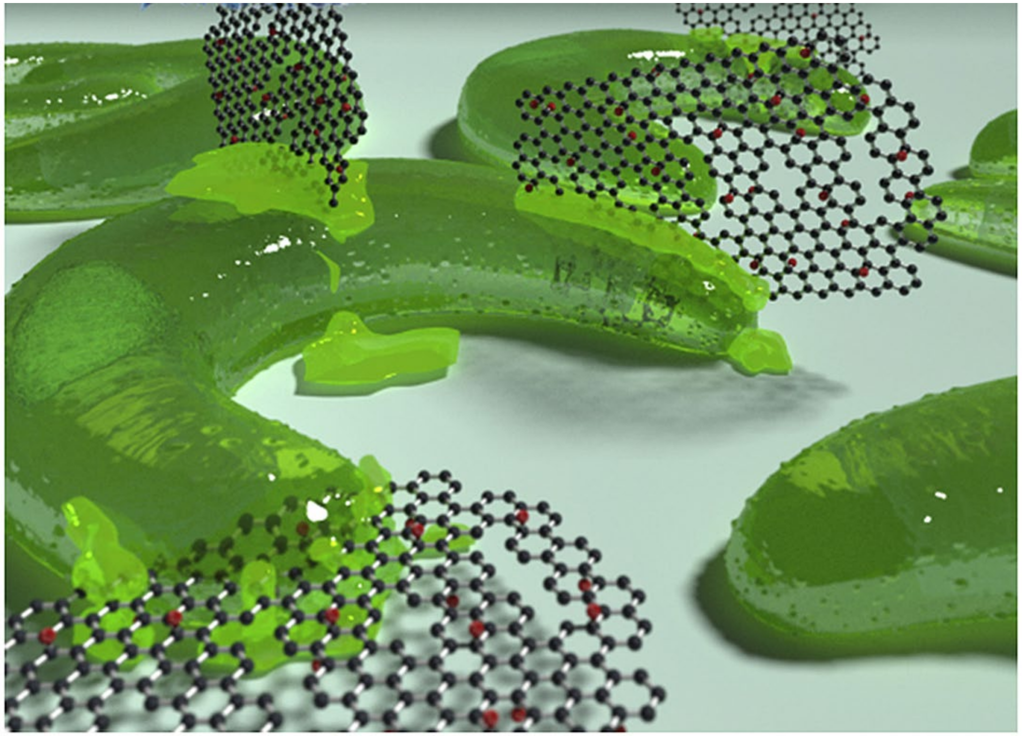


Environ. Sci. Technol. 2006, 40, 14, 4336-4345

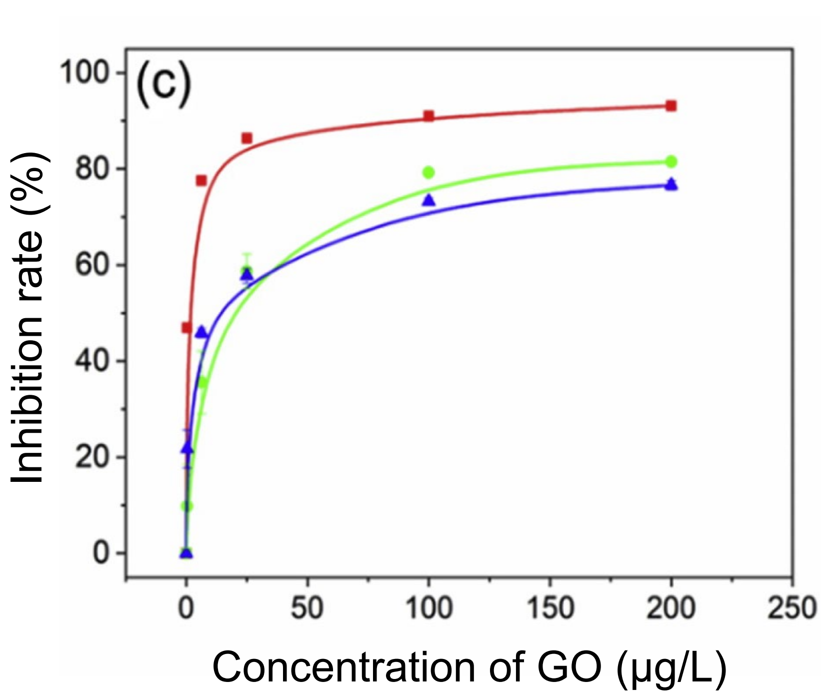
Nature nanotechnology, 2006, 1(1), 23-24

Implications of Nanomaterials

GO can act as a "nano-blade" that causes mechanical damage to algal cells



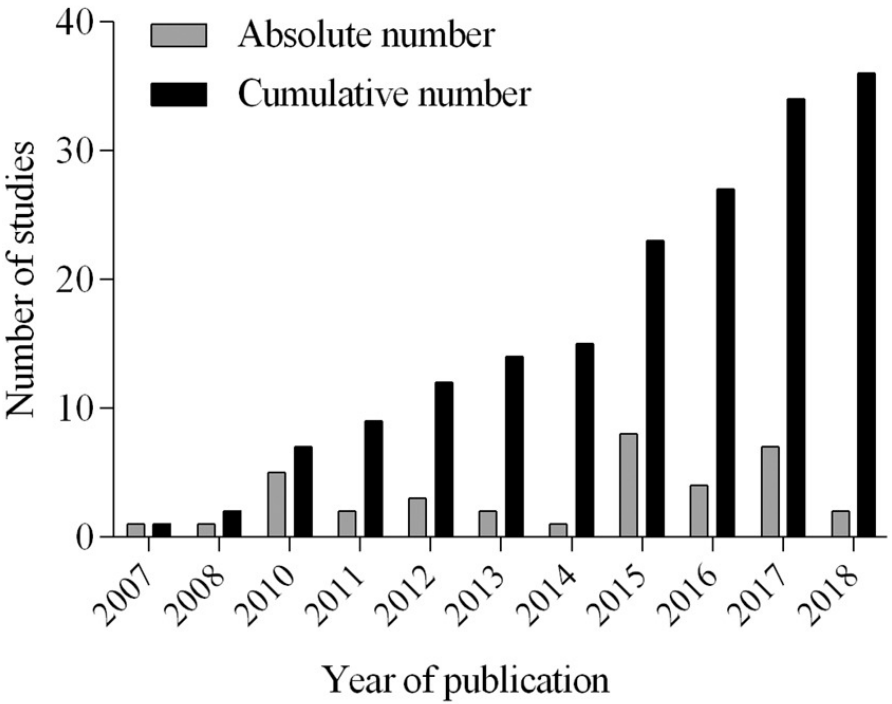
alga *"R. subcapitata"*

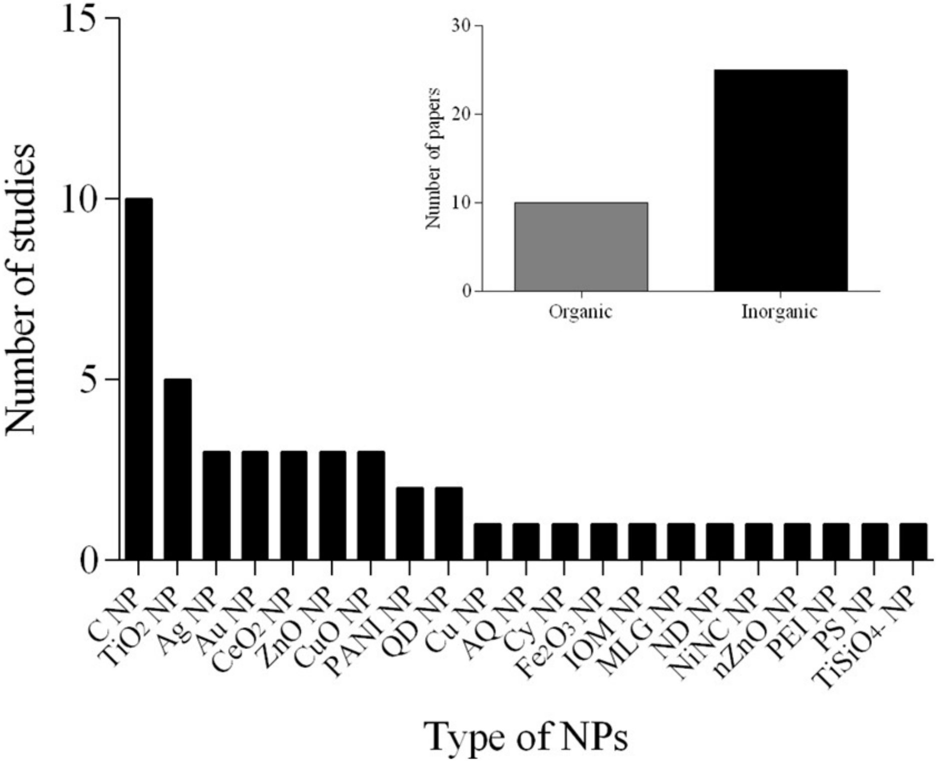


Carbon 155 (2019) 386-396

Implications of Nanomaterials

Absolute and cumulative and number of NM-induced toxicity studies on amphibians

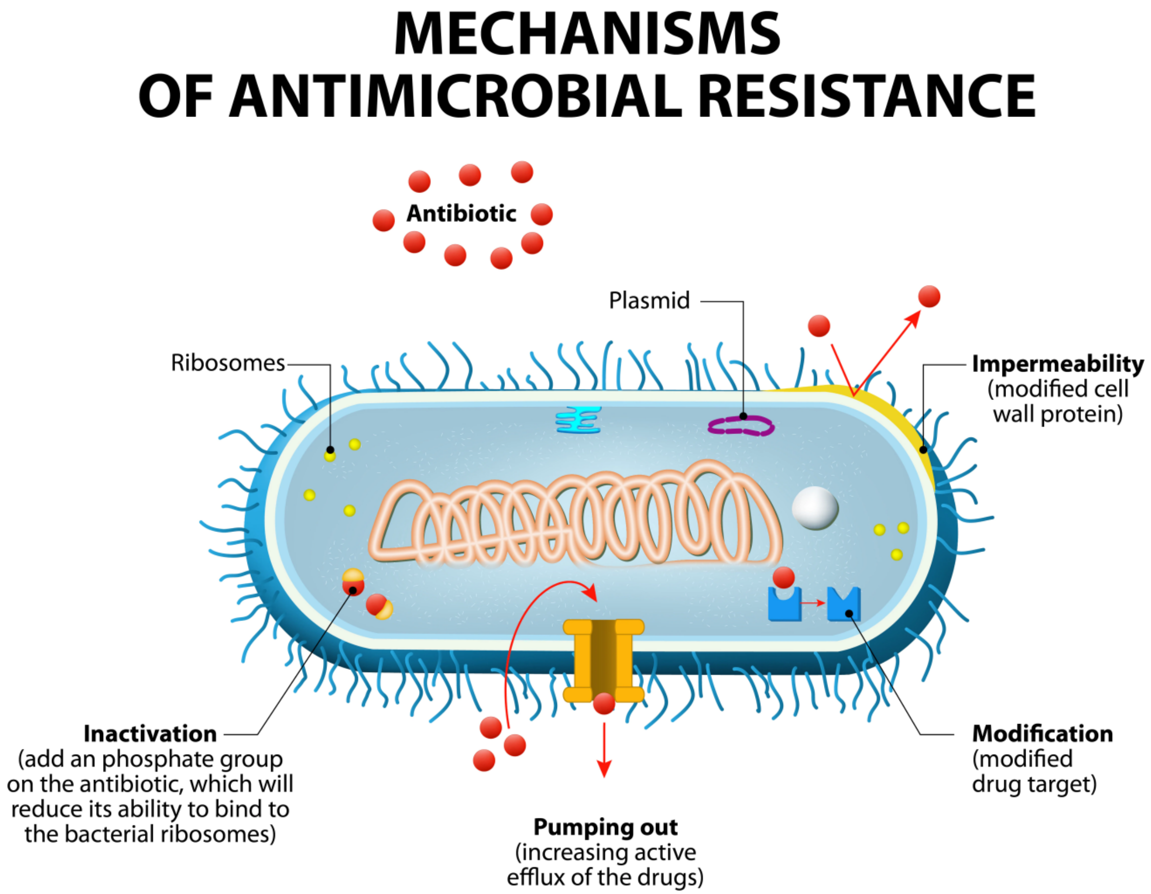




Science of the Total Environment, 686 (2019) 332–344

Thank you!

How do microorganisms gain resistance to drugs?



Methods of Resistance

- Impermeability of the drug
- Alteration in the drug's target
- Enzymatic drug modifications
- Efflux of the drug

Methods of Resistance Acquisition

- Chromosomal mutations
- Genetic transfer (ex: plasmids)

https://www.thermofisher.com/blog