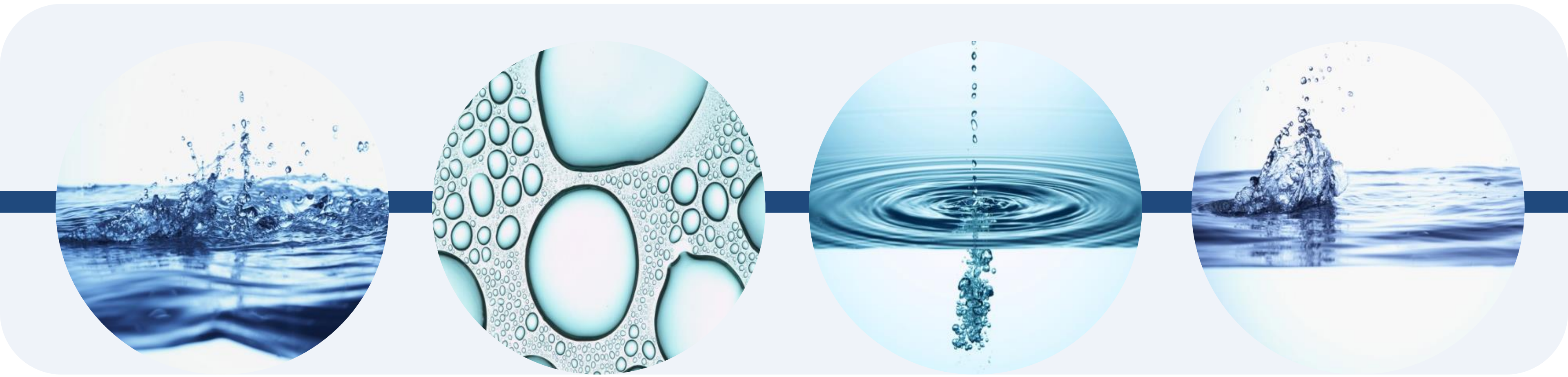

Novel Materials for Waste Water Treatment

Kieran Nolan, Dublin City University,

DCU

DCU
Ollscoil Chathair Bhaile Átha Cliath
Dublin City University

DCU Water Institute

Safe, Secure Water

Water Institute

http://dcuwater.ie

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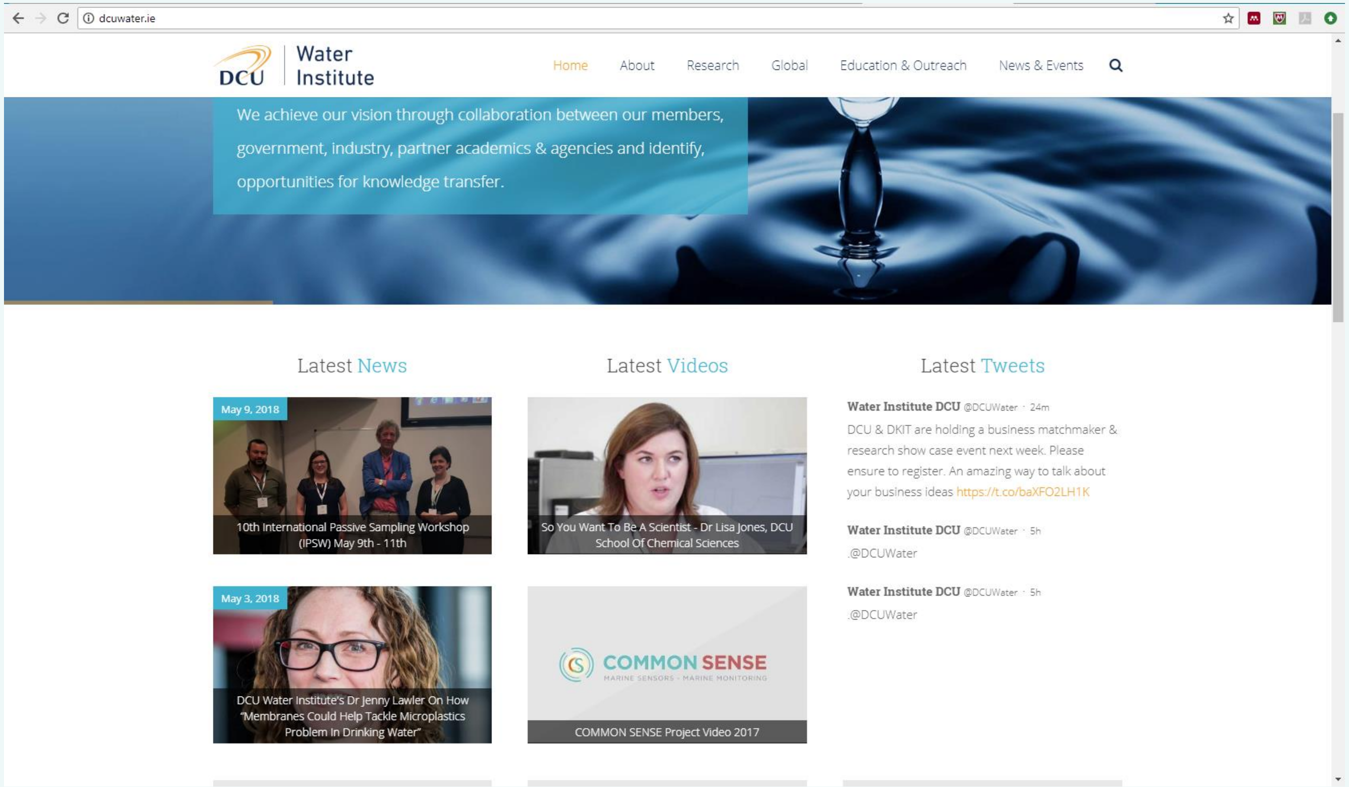
Engagement



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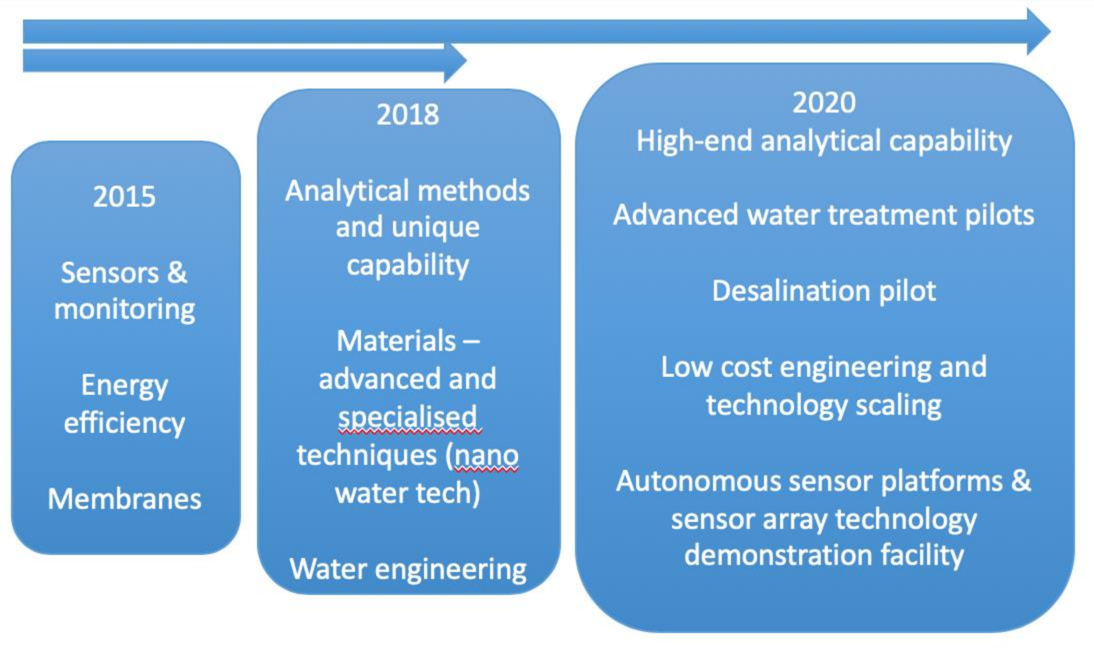
Growth of specialist technology areas

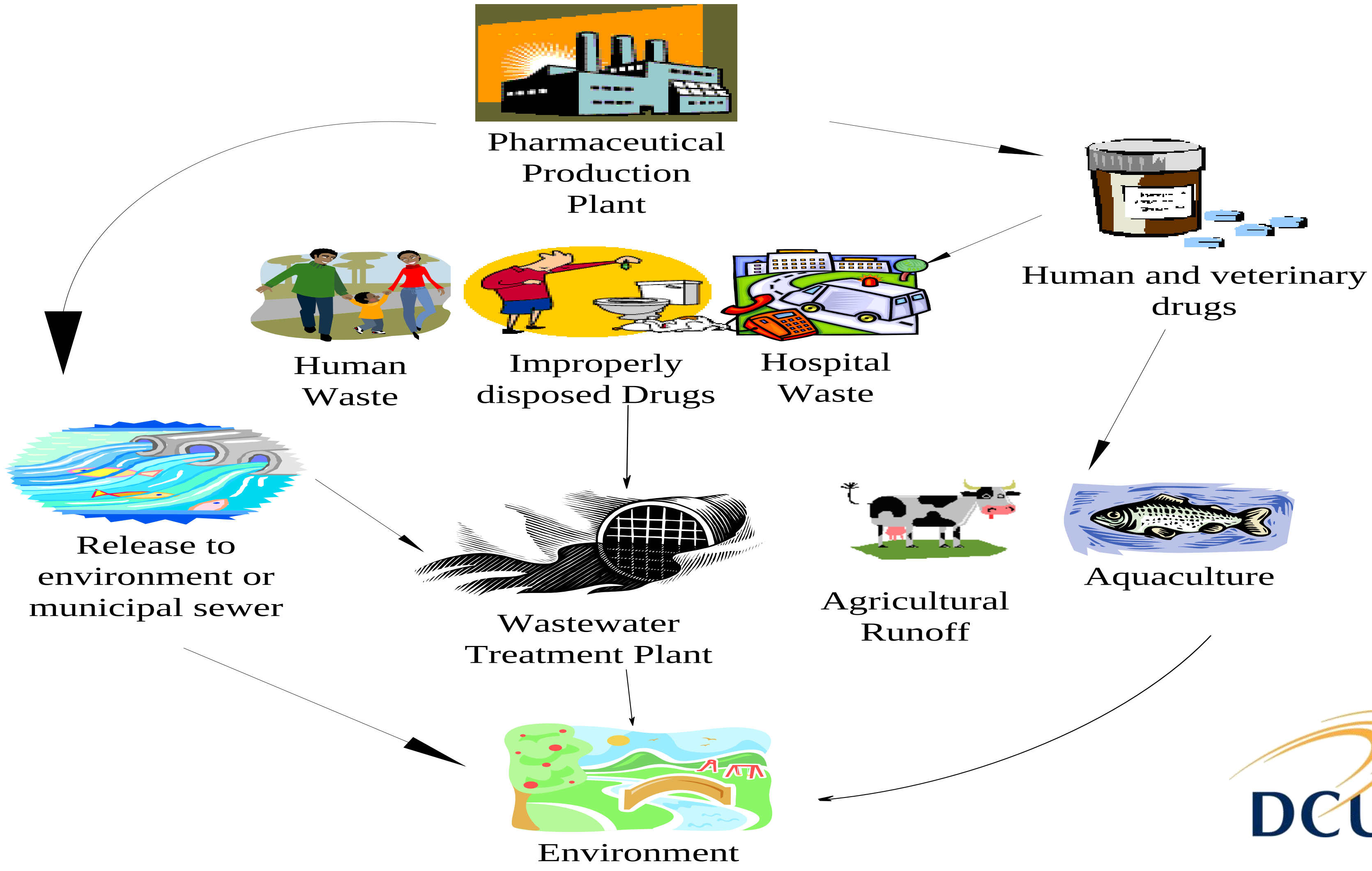


http://dcuwater.ie

Talk Overview

- Part 1 – Photocatalysis
- Part 2 – Graphene Composite Development for Photocatalysis
- Part 3 – Graphene Composite Development for Membrane Filtration

Sources of pharmaceuticals in the environment



Primary Treatment

- Primary treatment is the first stage of the MWW treatment process and is generally concerned with removal of larger settleable solids and grit from the raw influent wastewater stream
- The Biochemical Oxygen Demand (BOD) removal efficiency for primary treatment is on average 42.5%
- Typical primary processes are screening, grit removal and primary clarification

Secondary Treatment

- Secondary Treatment, by definition, is installed post primary treatment to provide for additional removal of mainly Biochemical Oxygen Demand (BOD) and Suspended Solids (SS) from the wastewater stream
- removal efficiencies of 85% for BOD and Suspended Solids
- Most secondary treatment processes are variants of activated sludge system

Tertiary Treatment

- In the past 30 years, treatment processes installed post-secondary clarification, have been colloquially referred to as Tertiary Treatment
- This implies a ‘third stage’ and is largely seen as a polishing stage
- “to enhance an effluent which is already of good quality.”

Solution: Advanced Tertiary Treatment

Photo AOPs

UV oxidation, UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, Photo-Fenton, Sonophotocatalysis, Vacuum UV, UV/Ultrasound. Microwave **Photocatalysis**

Non-Photo AOPs

Supercritical water oxidation, Ionizing radiation, Wet air oxidation. Pulsed plasma, O_3/H_2O_2, Fenton reagent, Ultrasound, Electrochemical oxidation, US/H_2O_2,US/O_3

Others

Ultrafiltration, nanofiltration, reverse osmosis, Ion Exchange, **Adsorption**

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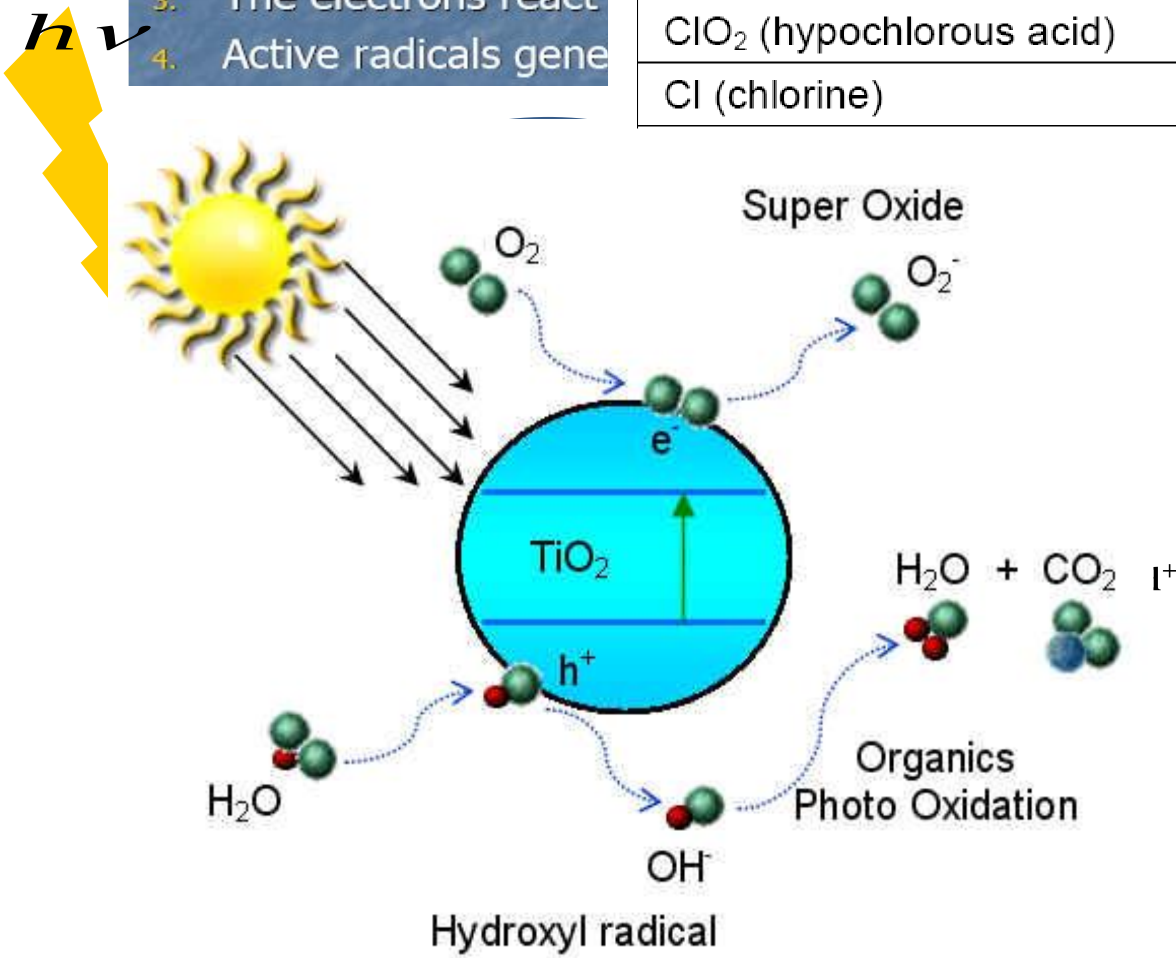
Photocatalysis

1. The photoexcited Ti
   to the TiO_2 surface.
2. The photogenerated
   the interface to proc
3. The electrons react
4. Active radicals gene

Oxidants	Oxidation potential (V)
• OH (hydroxy radical)	2.80
O_3 (ozone)	2.07
H_2O_2 (hydrogen peroxide)	1.77
ClO_2 (hypochlorous acid)	1.49
Cl (chlorine)	1.36



$$TiO_2 \xrightarrow{hv} e^- + h^+$$

$$h^+ + H_2O \rightarrow OH\bullet + H^+$$
$$e^- + O_2 \rightarrow O_2^-\bullet$$
$$O_2^-\bullet + H^+ \rightarrow HO_2\bullet$$

$TOC + Ox \rightarrow TOC$ (partially oxidized species) + $CO_2 + H_2O$

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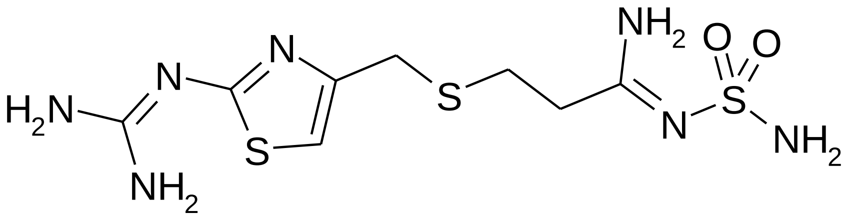
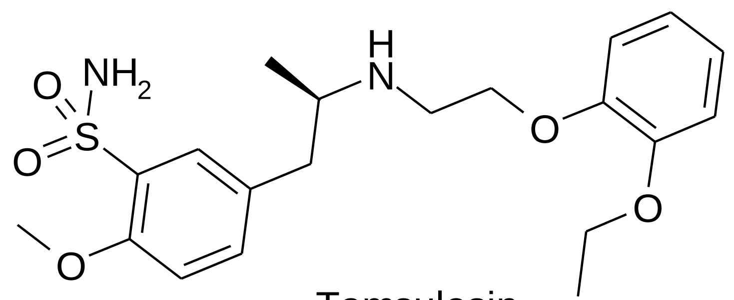
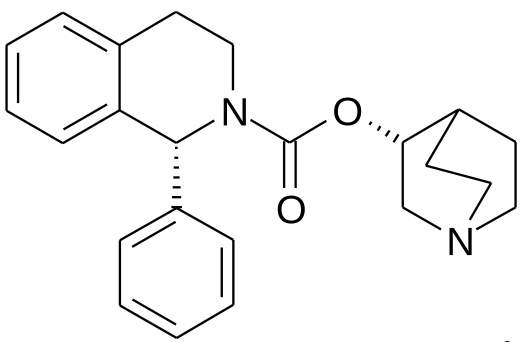
Target APIs – Industrial waste streams



Famotidine



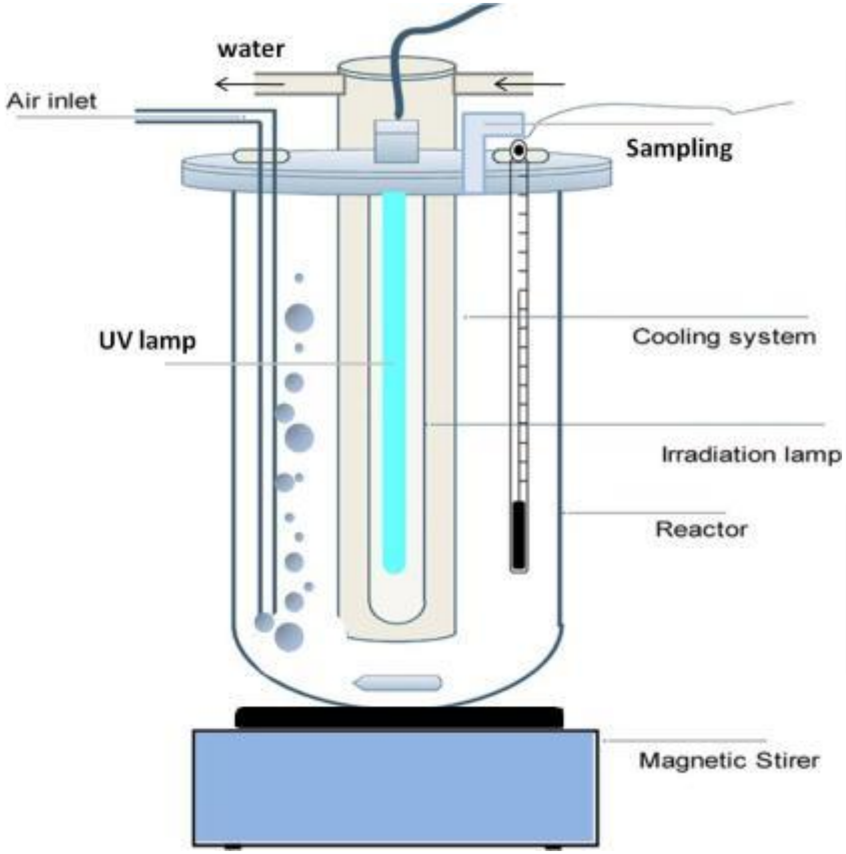
Tamsulosin



Solifenacin

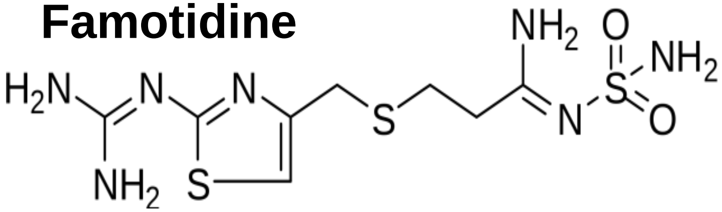
- **All manufactured Dublin.**
- **Range of therapeutic action.**

Standard Experimental Set-Up for UV Experiments



1. Famotidine 100 mg/liter as model
2. Adsorption 1 hour in dark
3. UV illumination and interval sampling

Famotidine



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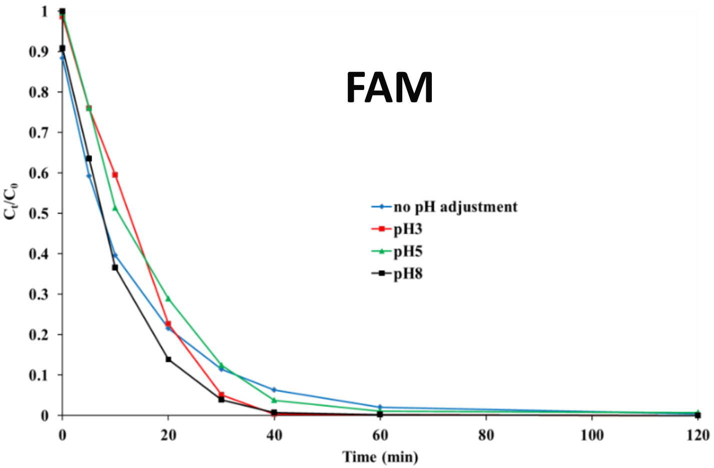
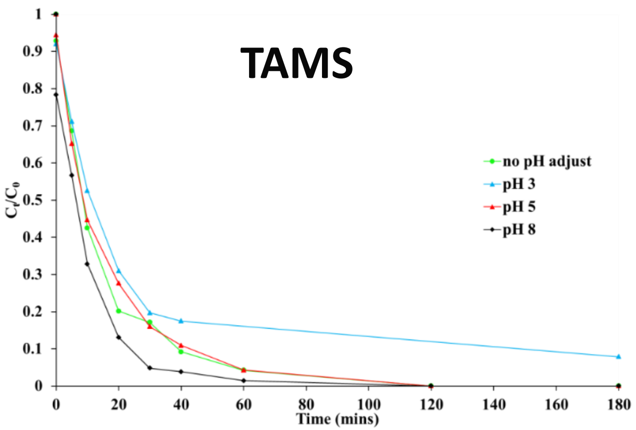
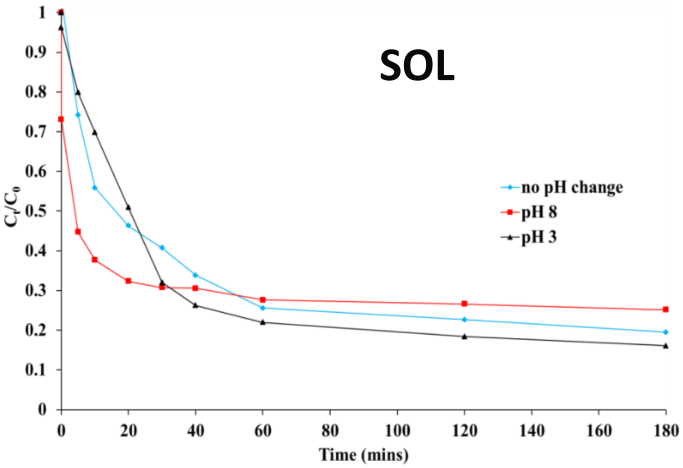
Photocatalytic Studies



- pH generally did not affect the photocatalytic degradation.
- With P-25 the optimum amount of TiO_2 was 0.1 or 0.2 g/320 mL
- Studies with Solifenacin indicated that although a large amount is adsorbed initially at pH 8, the complete elimination was less than that of pH 3 where there was much less initial adsorption.





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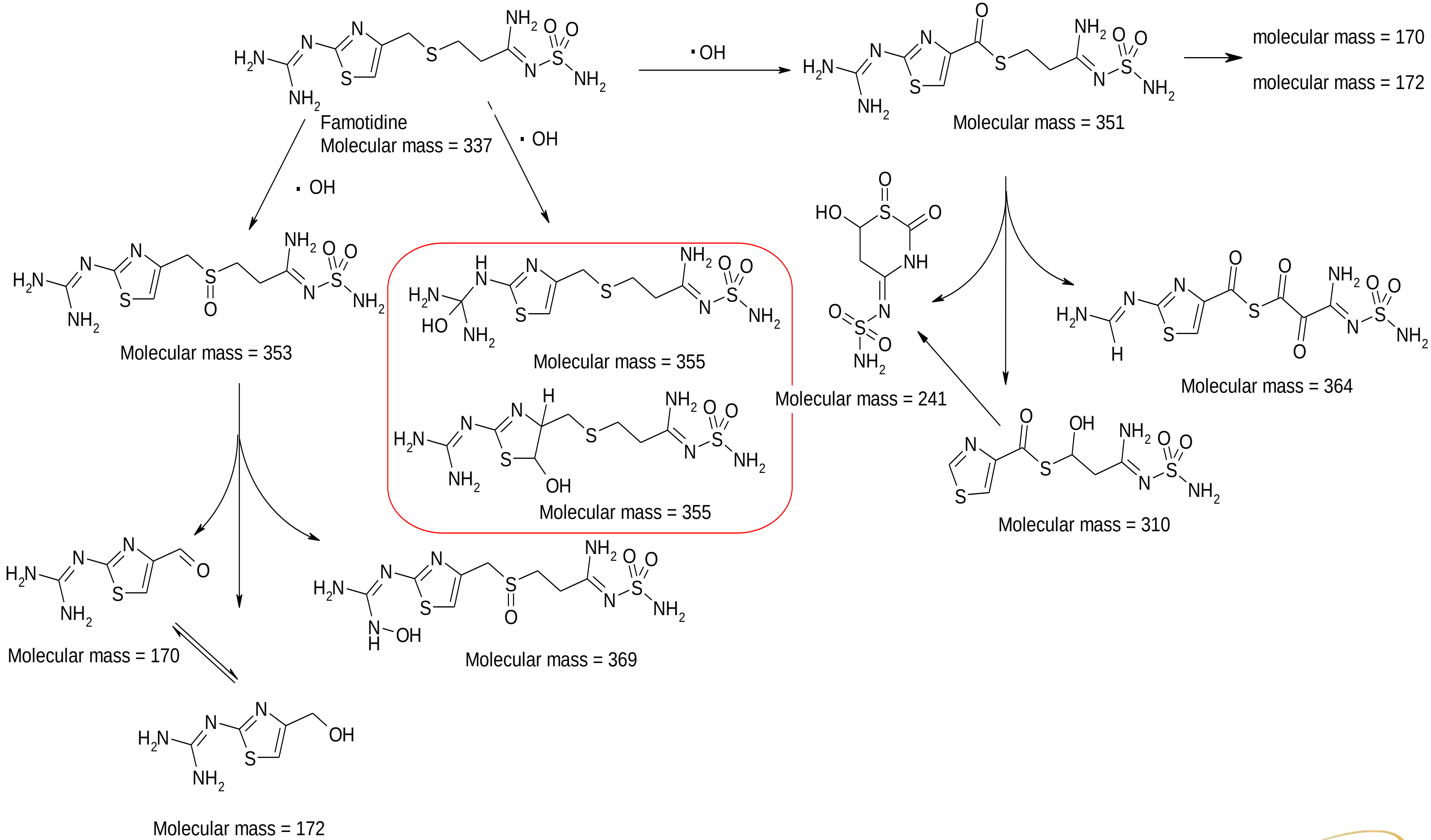
Pathway of Degradation: Famotidine

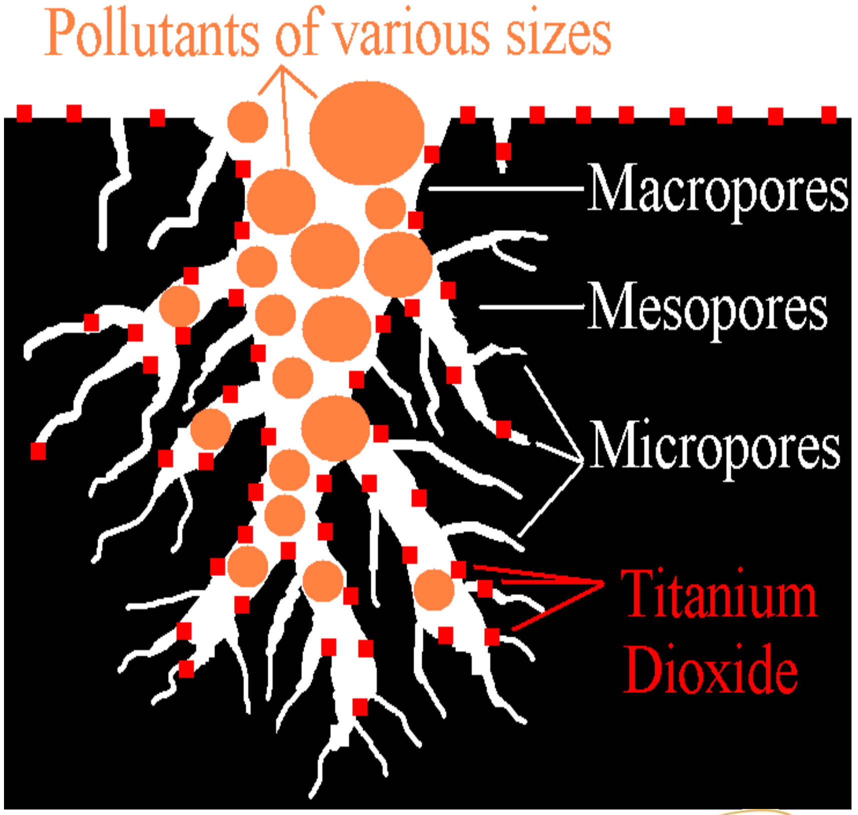


Problems with TiO_2

- TiO_2 are nanoparticles! Removal a major problem
- Cannot have TiO_2 nanoparticles leaching into the environment – major consequences
- Only UV region used

Why not develop an Integrated Photo Catalytic Adsorbent of TiO_2 and Activated Carbon ?

- Concentrate pollutant
- Improve photodegradation performance
- Immobilise intermediates
- Easy to separate
- Adsorption without light



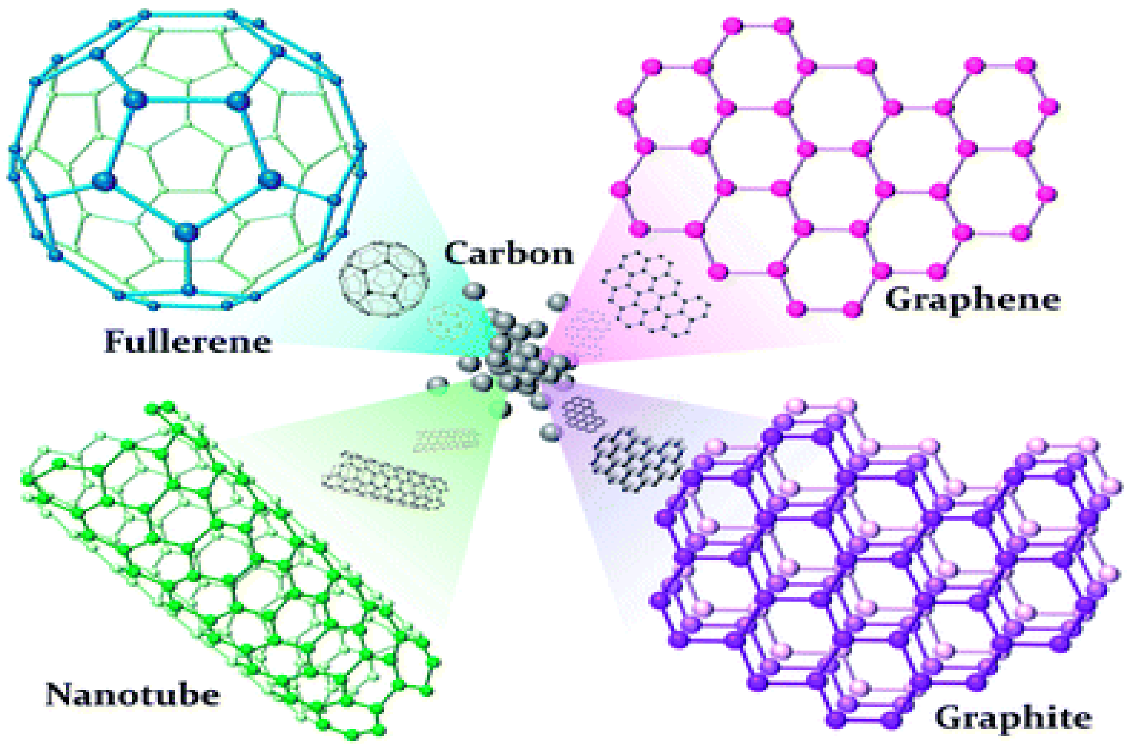
IPCA Evaluation

- The best performing IPCAs can adsorb and degrade >90% of the API in solution after 3 hours of UV illumination

- IPCAs can be regenerated and exhibit essentially unchanged photodegradation potential

- Adsorption capacity of IPCA is not significantly reduced compared to AC

Part II
Graphene Composite Development for Photocatalysis
Possible Visible Light Activity?


Carbon
Fullerene
Graphene
Nanotube
Graphite


(i) Ti (OCH(CH$_3$)$_2$)$_4$
and IPA mixture
(ii) Sol-gel reaction
at pH = 12, 60°C
for 12 h
: TiO$_2$
GO
GO-TiO$_2$ nanocomposite

Aim

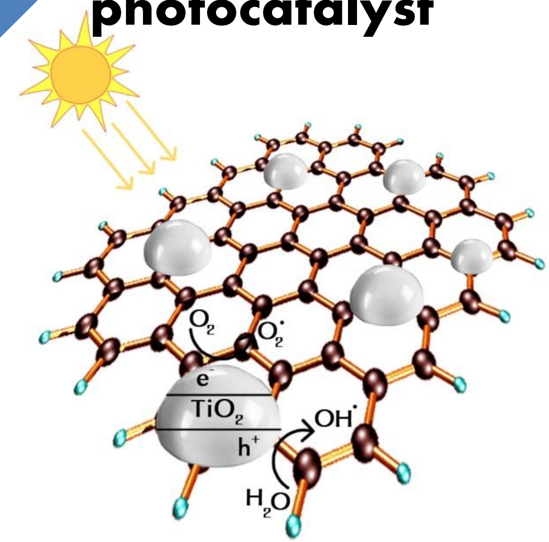
Designing a graphene base platform for TiO_2 integration

Synthesis of graphene

Studying adsorption properties

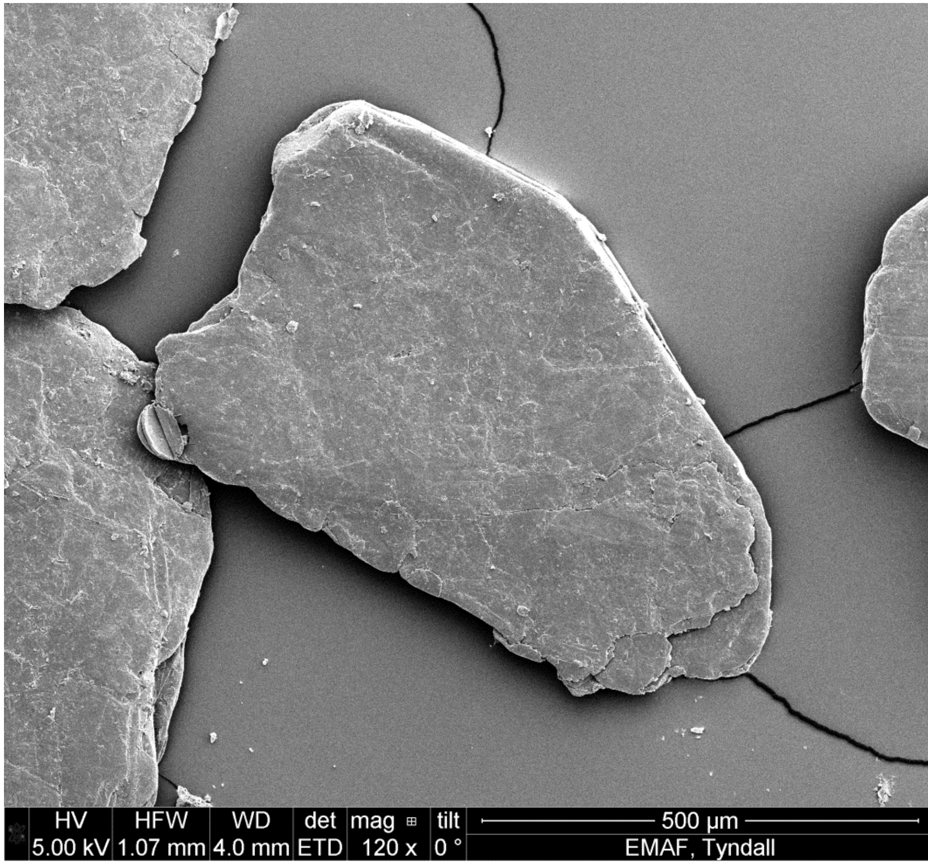
Integrating with TiO_2 & modification

An efficient visible light active photocatalyst

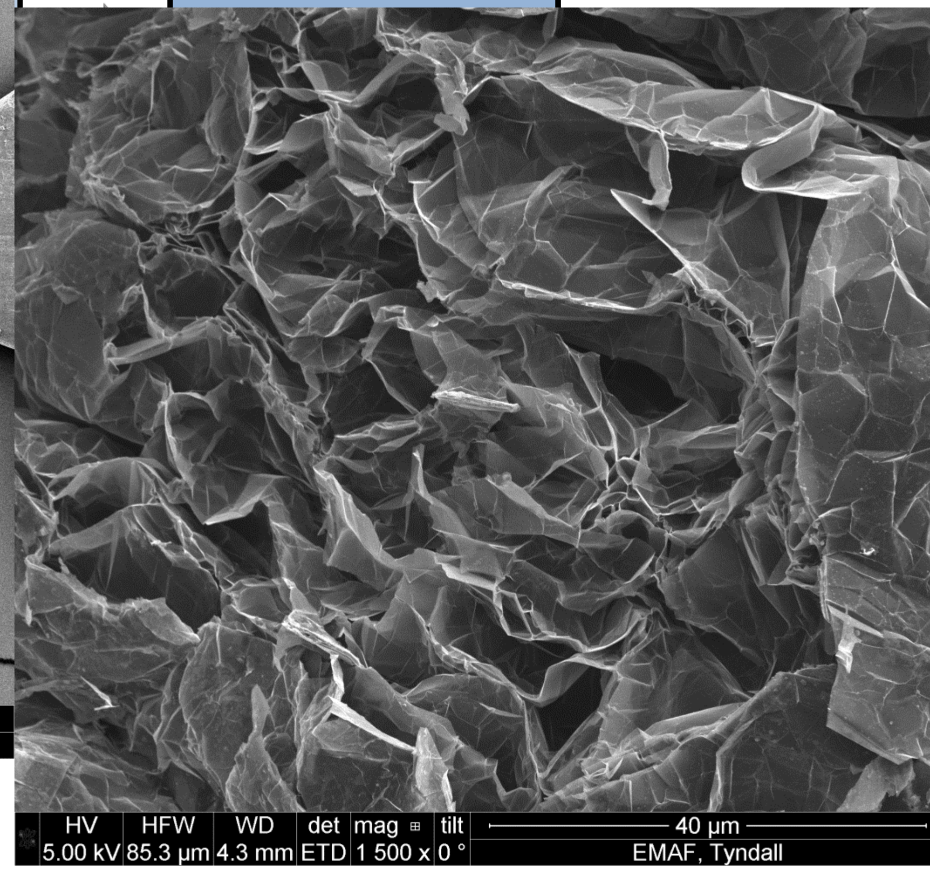


Organic Pollutant Oxidation

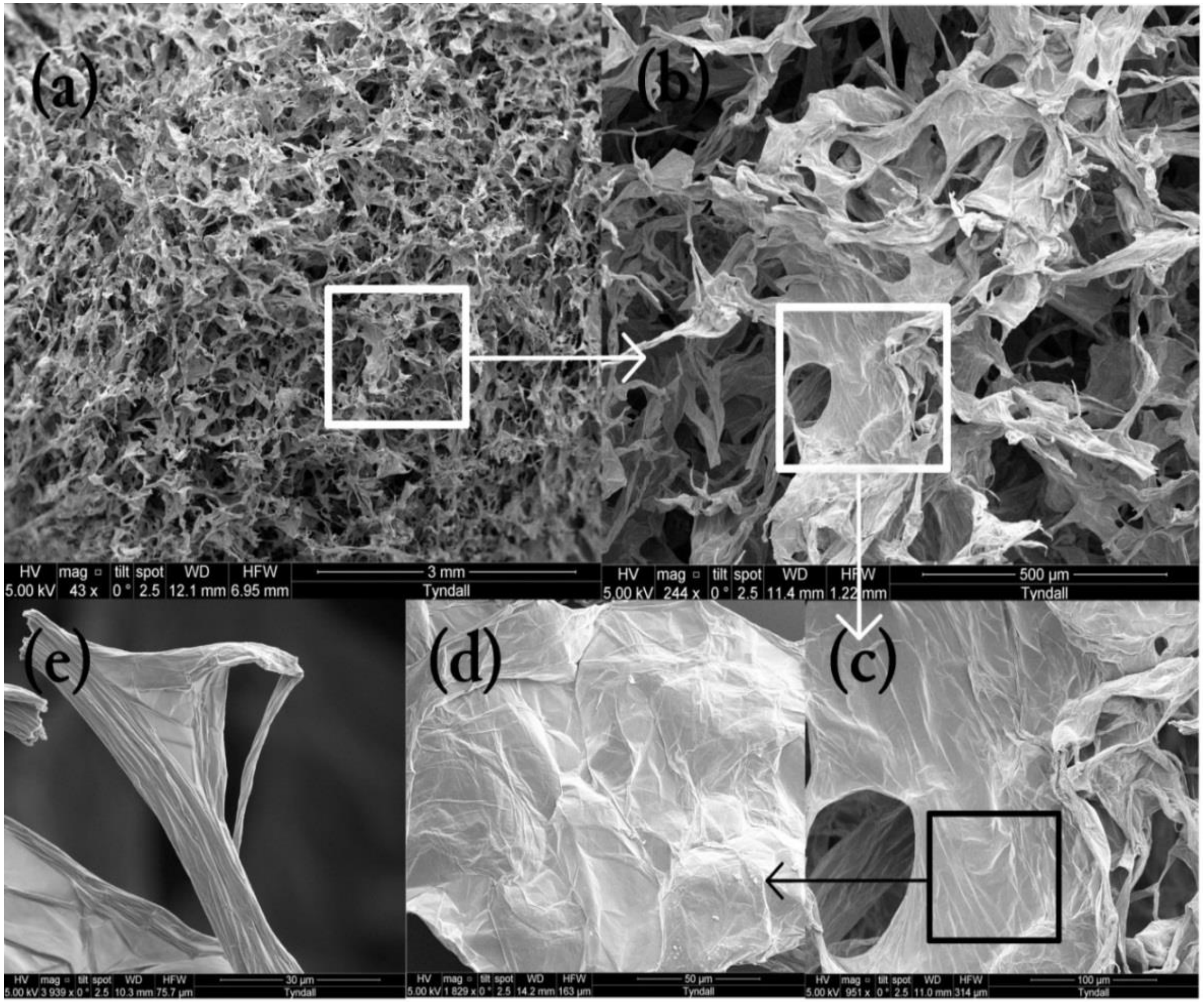
Graphene Oxide Synthesis



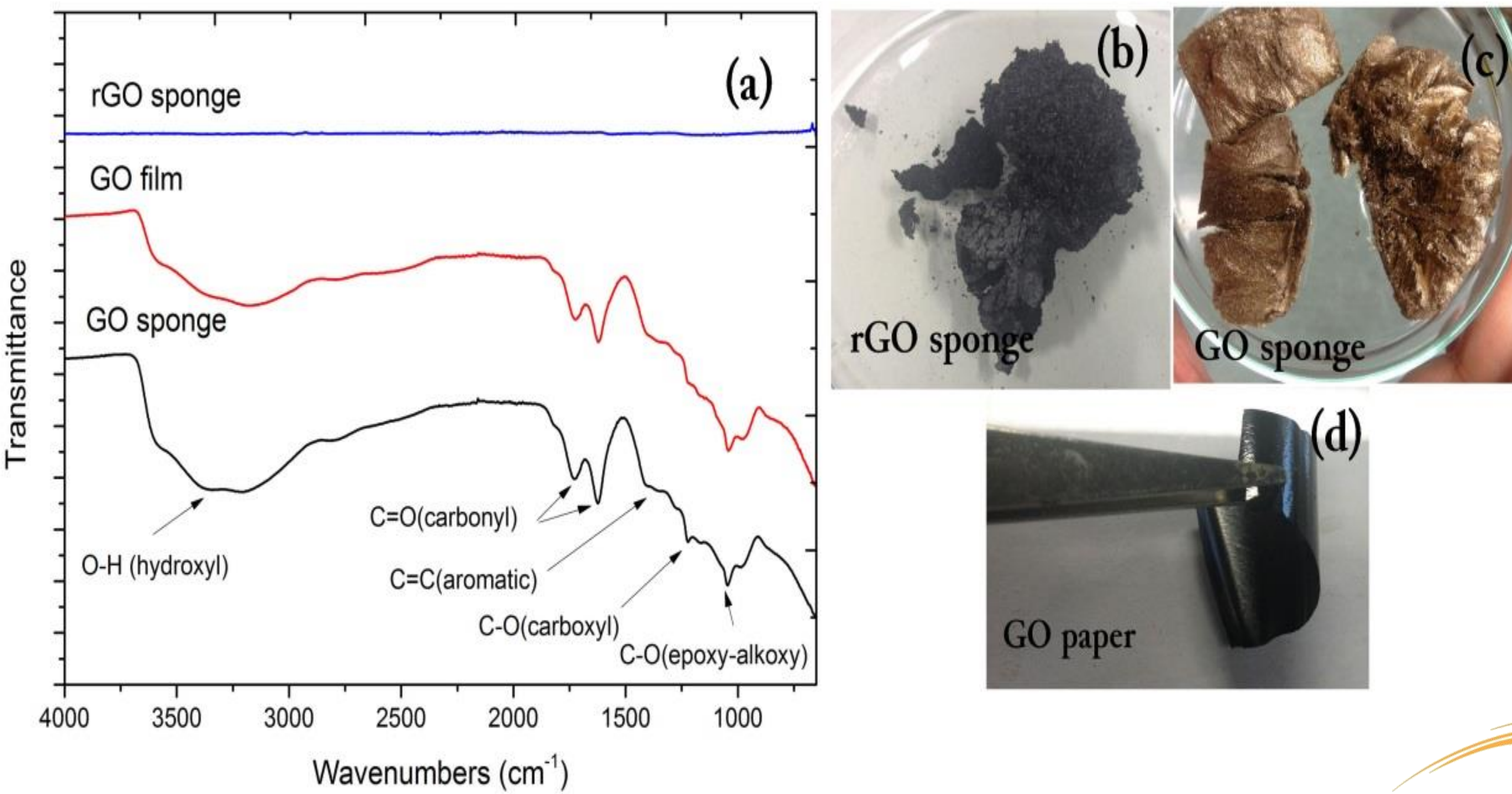
Chemical and



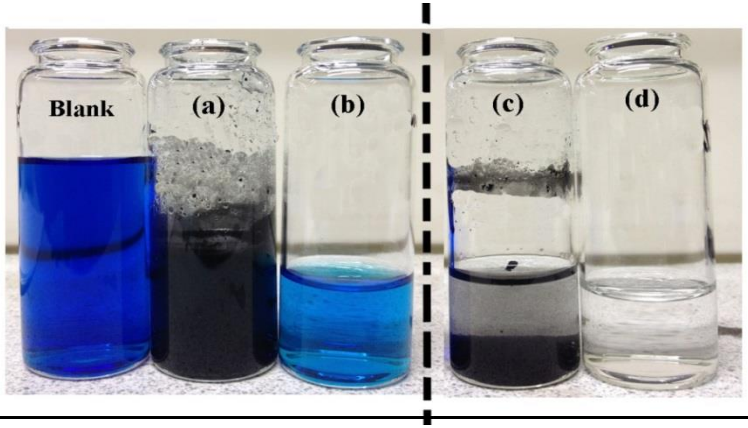
Graphene Oxide



Graphene Paper and Sponge



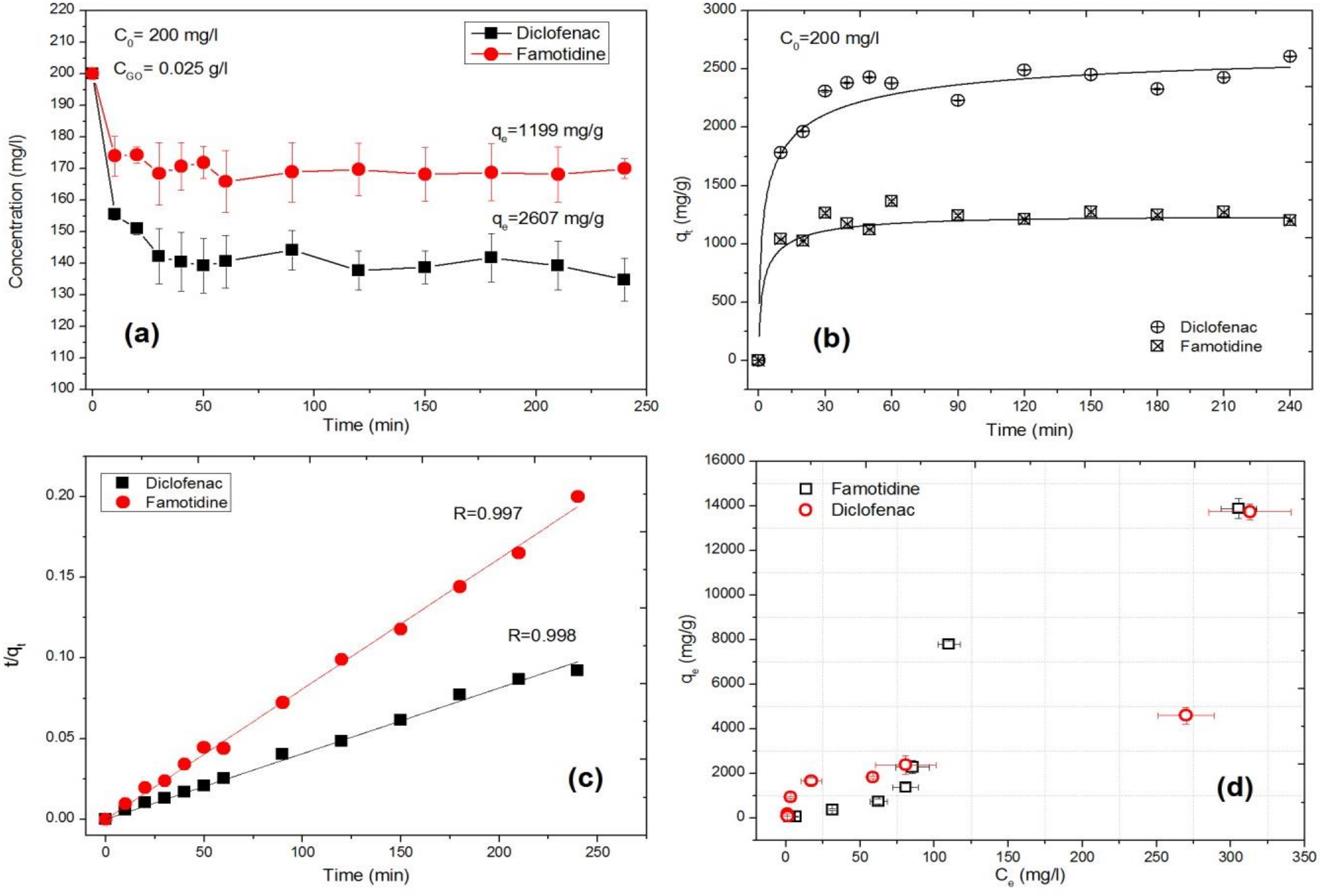
Adsorption



Properties	GO	HRGO
BET surface area (m^2/g)	547.37	345.92
Pore volume cc/g (size< 66nm)	2.366	1.7
Average pore radius nm	8.64	9.87
BJH desorption pore radius nm	1.89	2.039

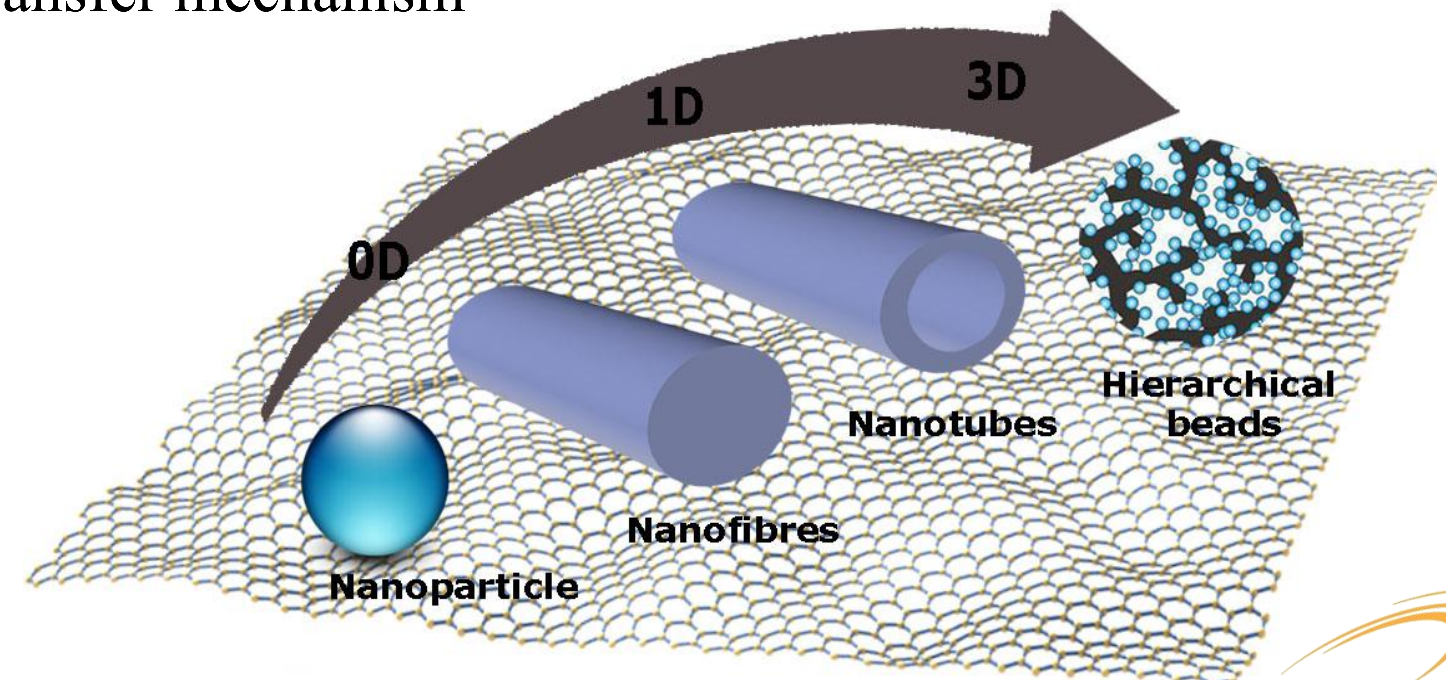
Sample	BET surface area (m^2/g)	MB surface area (m^2/g)
Graphene oxide	547.37	2605.5
Reduced graphene oxide	345.92	2210.2

Pharma Adsorption



Graphene – Photocatalysis - Nano particles vs Nano Rods???

- Dimensionality of TiO_2 nanostructure is an important factor factor on efficiency and mechanism of photocatalysis
- Surface area
- Synthesis method (sol-gel, hydrothermal, …)
- Electron transfer mechanism
- Pore size



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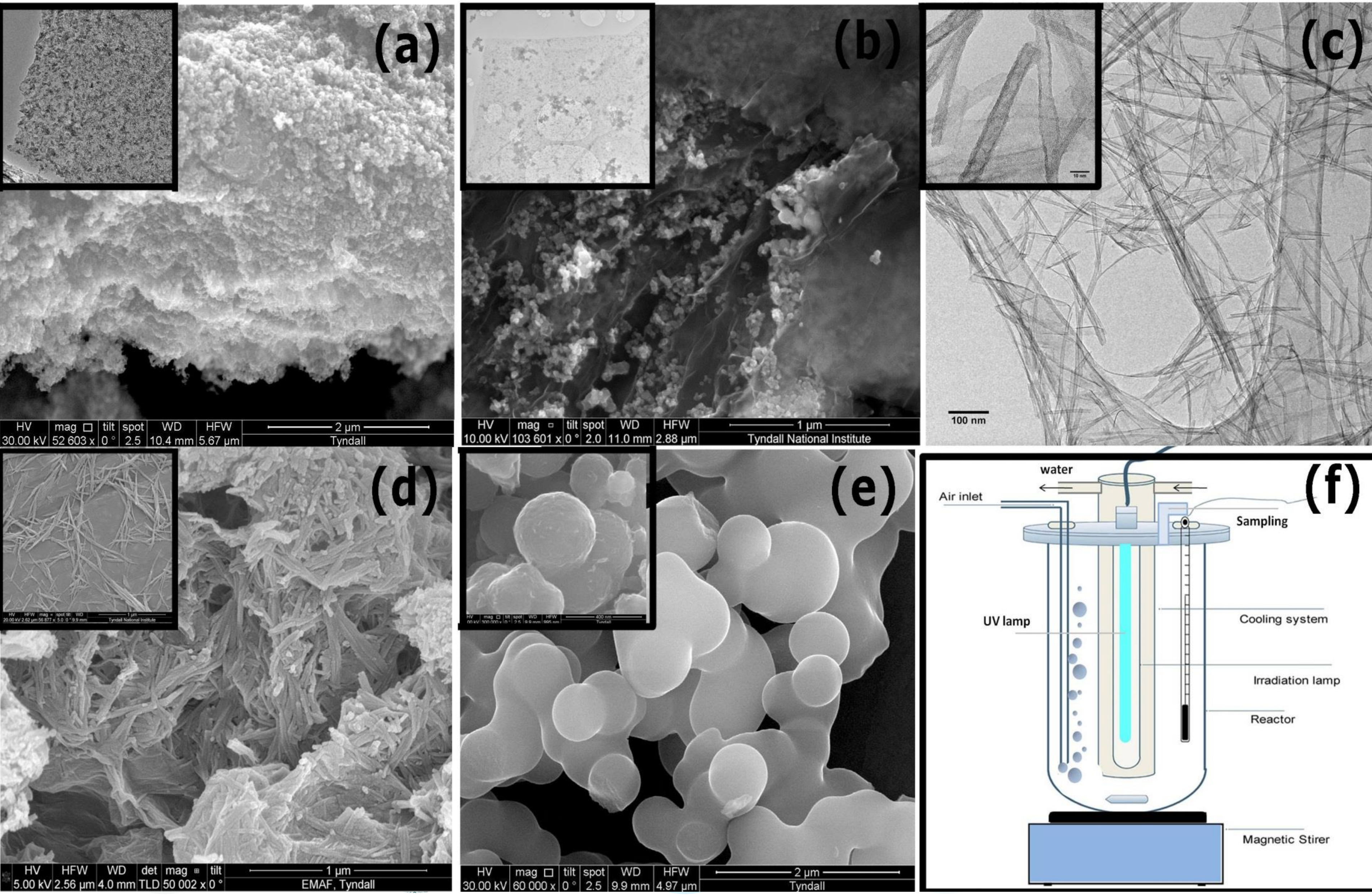
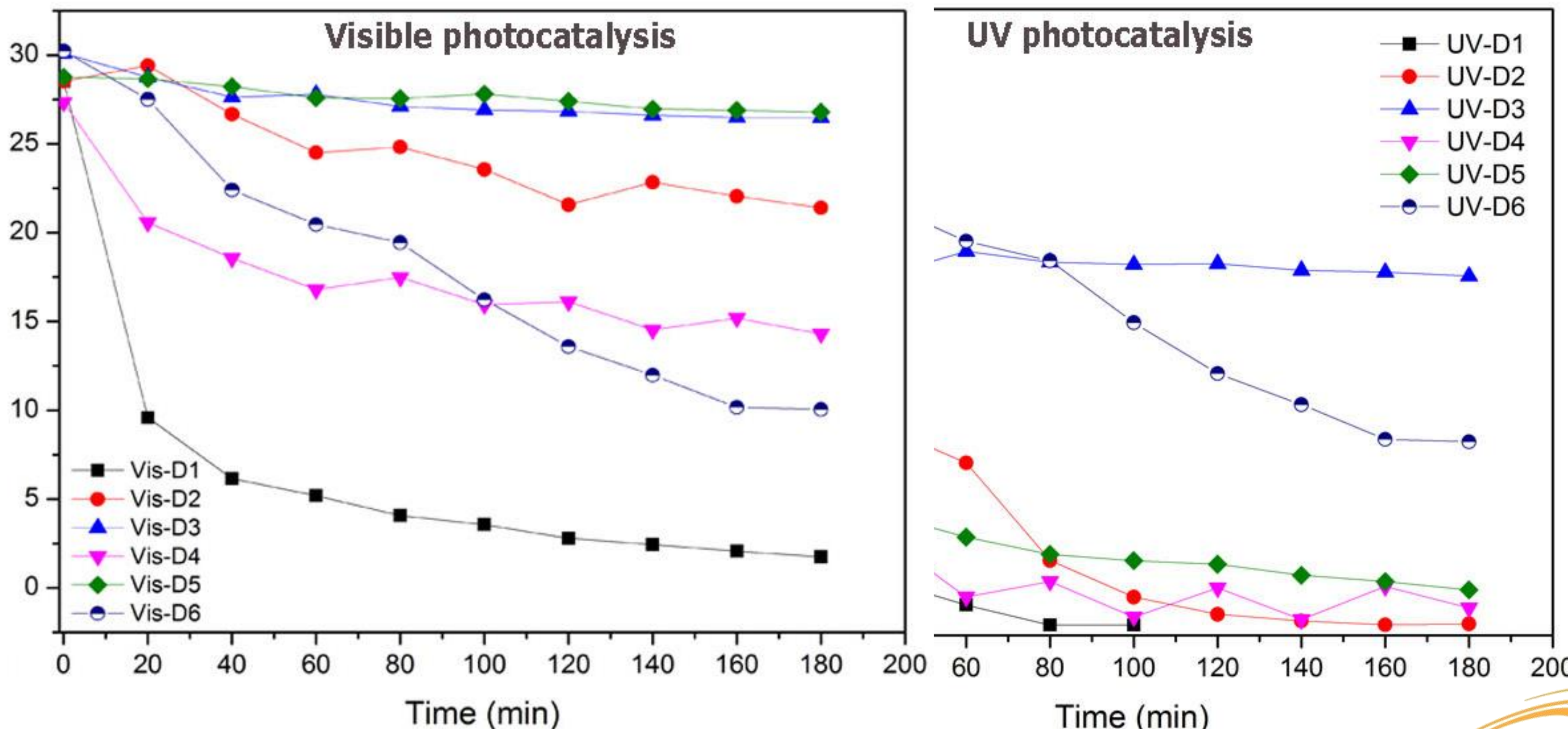
Results: Photocatalysis



Results: Photocatalysis

- In-situ hydrothermally synthesized TNTs on graphene oxide shows excellent photocatalytic activity towards famotidine degradation under UV and visible light (sample D1)



Results: Photocatalysis

Advantages of TiO_2/GO composites

- Easy post separation process
- Reusable
- Higher UV efficiency comparing activated carbon/TiO_2 composite
- UV re-generation capability
- High adsorption capacity for specific organic compounds
- TNT/GO Possesses Visible Light Activity
- TNT/GO Excellent in preventing membrane fouling

Part 3. Water Treatment using Filtration and Nanostructured Composites for the Removal of Biological and Emerging Pollutants

Graphene – Copper Composites

Goals of the Project

- The design and operation of filtration systems for private water schemes.
- Understanding the mechanism of action for anti-bacterial activity with Graphene and Graphene related materials.
- Develop novel graphene composites for removal of biological and emerging pollutants.
- To design a robust and easy to install barrier systems for small water supplies.
- To improve the processes for the removal of microbial pollution and emerging contaminants.

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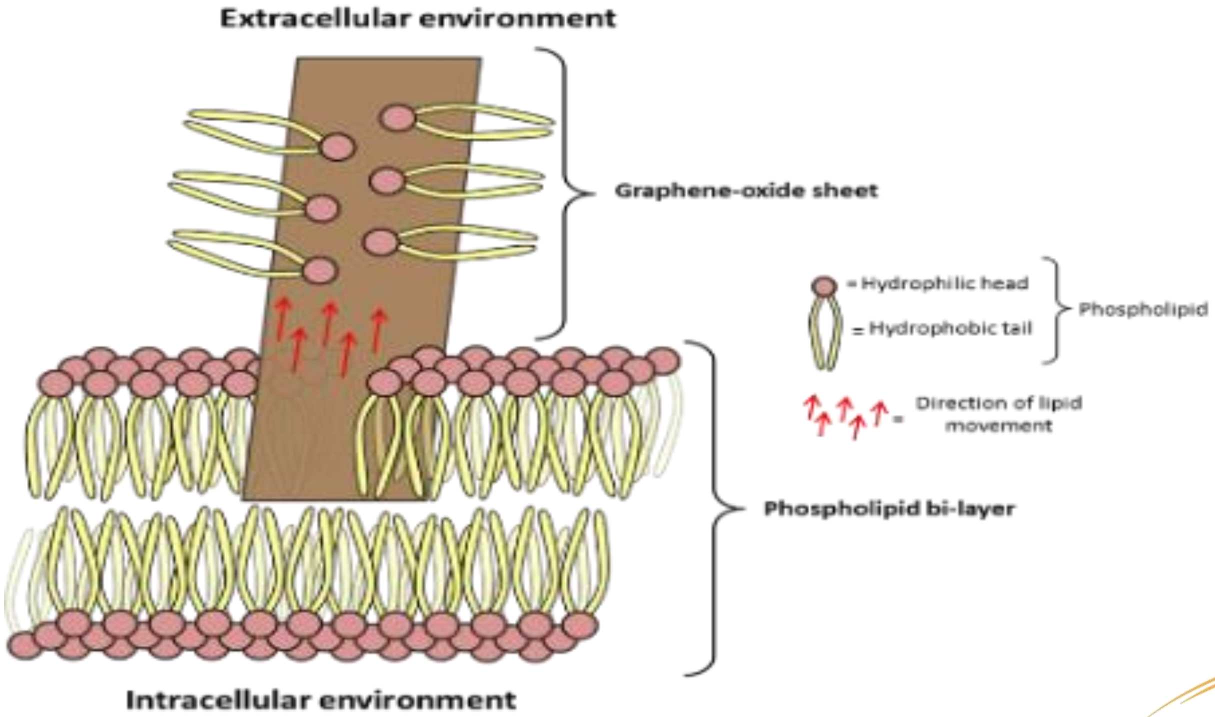
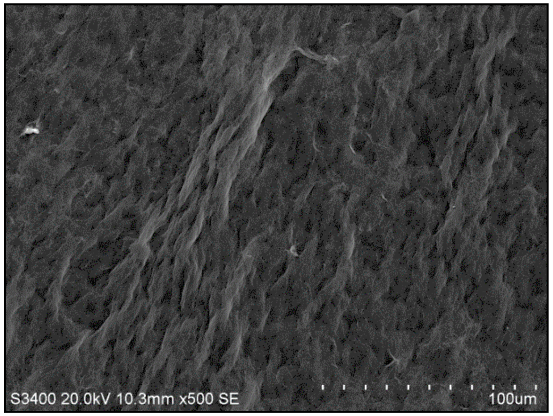
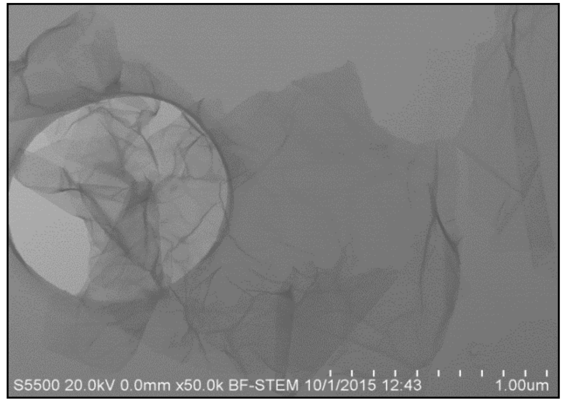
At the start of this project both GO and rG shown to have antibiotic activity

Proposed Mechanism for Antibacterial Activity of GO



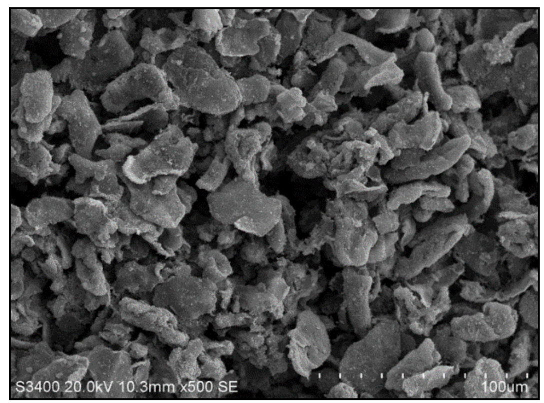


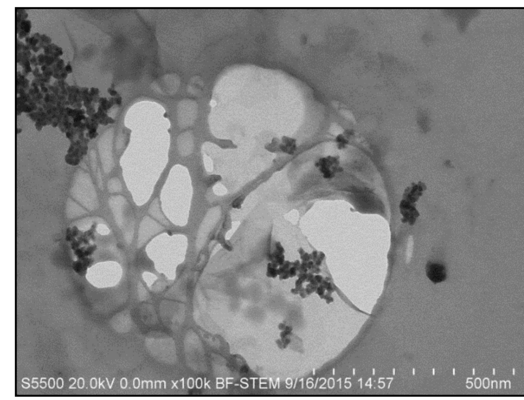


Graphene Copper Composites

Scanning electron micrographs of exfoliated graphene oxide sheets following chemical reduction

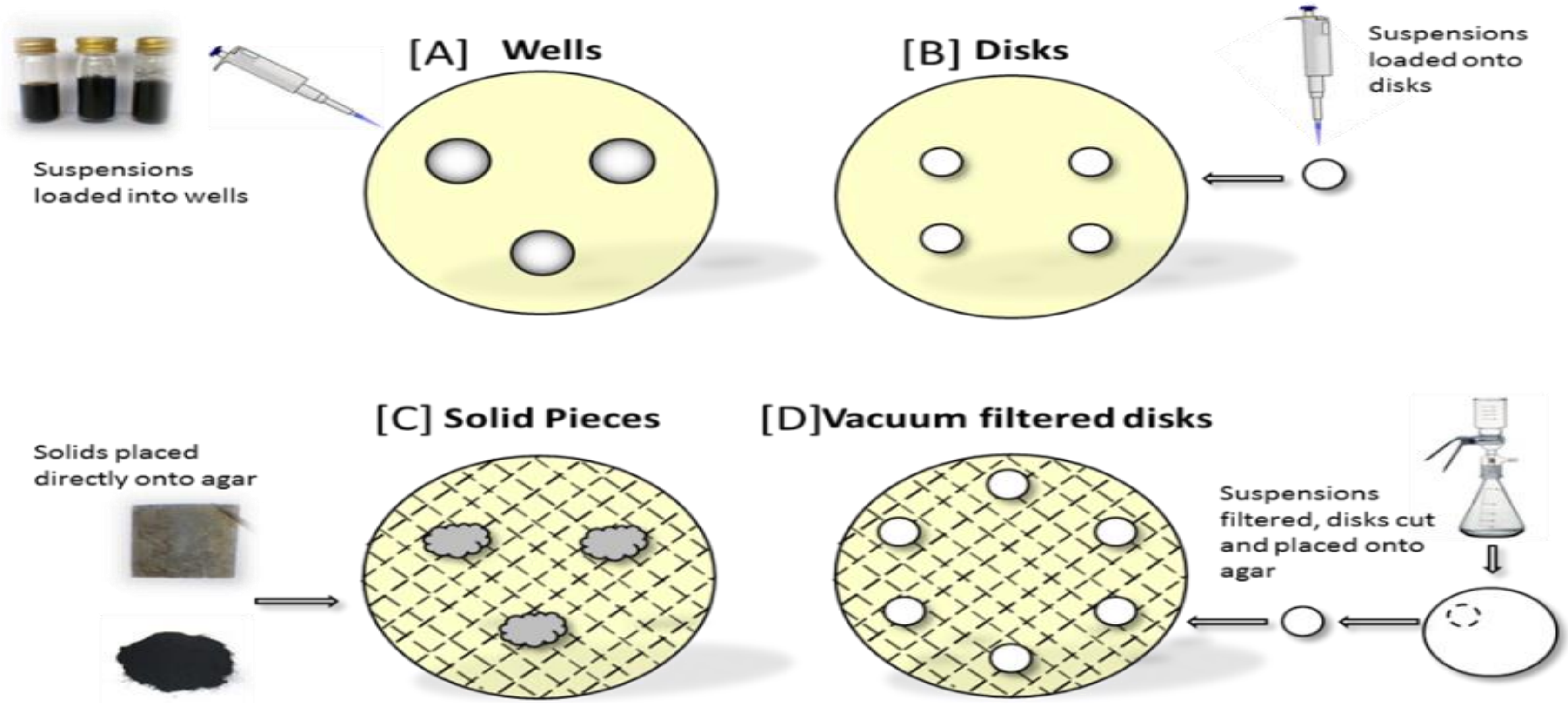
Composite	% Carbon	% Oxygen	% Copper
Graphene Oxide (GO)	50.1	46.3	
Reduced Graphene Oxide (rGO)	68.68	31.32	
Copper Composite (Cu-rGO)	37.16	22.42	40.04
Copper nanoparticles (CuNP)		25.69	74.31





Scanning electron micrographs graphene-copper composite at [A] x500 magnification under second electron mode [B] x100k magnification under transmission mode with copper particles visible

Microbiological Solid Media Studies

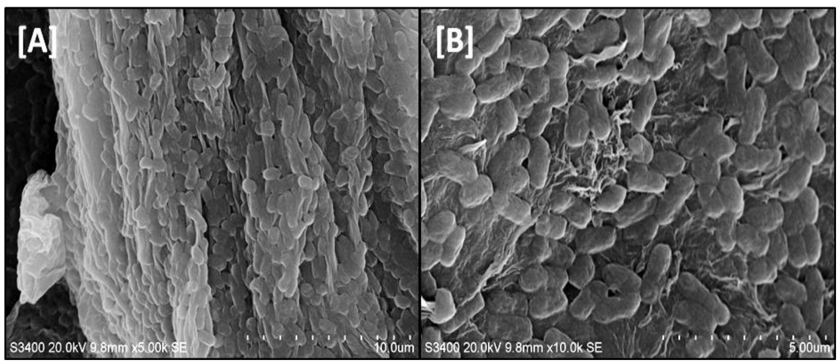


[A] Suspensions added to wells cut into agar [B] Disks loaded with suspensions added onto the surface of the agar [C] Solid pieces of material added to agar with a bacterial lawn and [D] disks cut from membranes vacuum filtered with suspensions of material added to the surface of the agar.

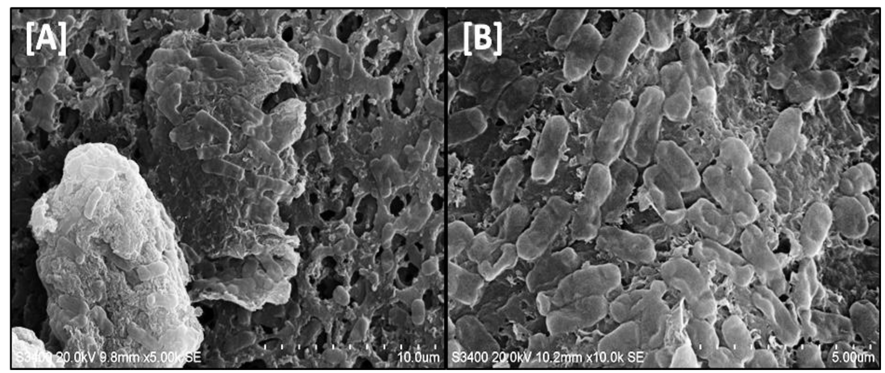
Results of Microbiological Solid Media

Zones of inhibition for each of the material employed in the vacuum-filtered disk assay

Zone size (mm)	E. coli	B. subtilis
Blank	No zone	No zone
GO	No zone	No zone
rGO	No zone	No zone
Cu-rGO	11mm	14mm
$CuCl_2$	14mm	19mm
$CuSO_4$	10mm	15mm
CuNPs	12mm	16mm
Gentamycin	19mm	20mm

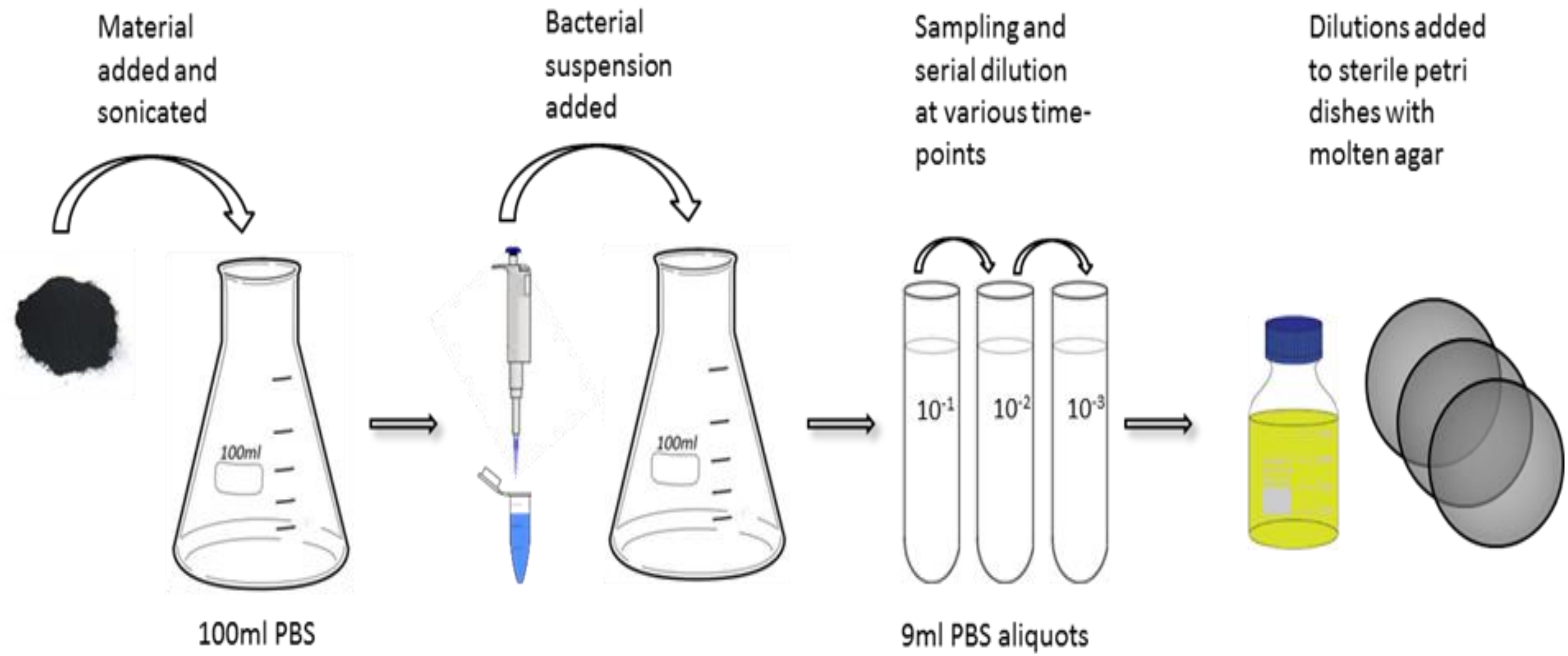


E. coli exposure to the surface of rGO at [A]x5k magnification and [B]x10k magnification



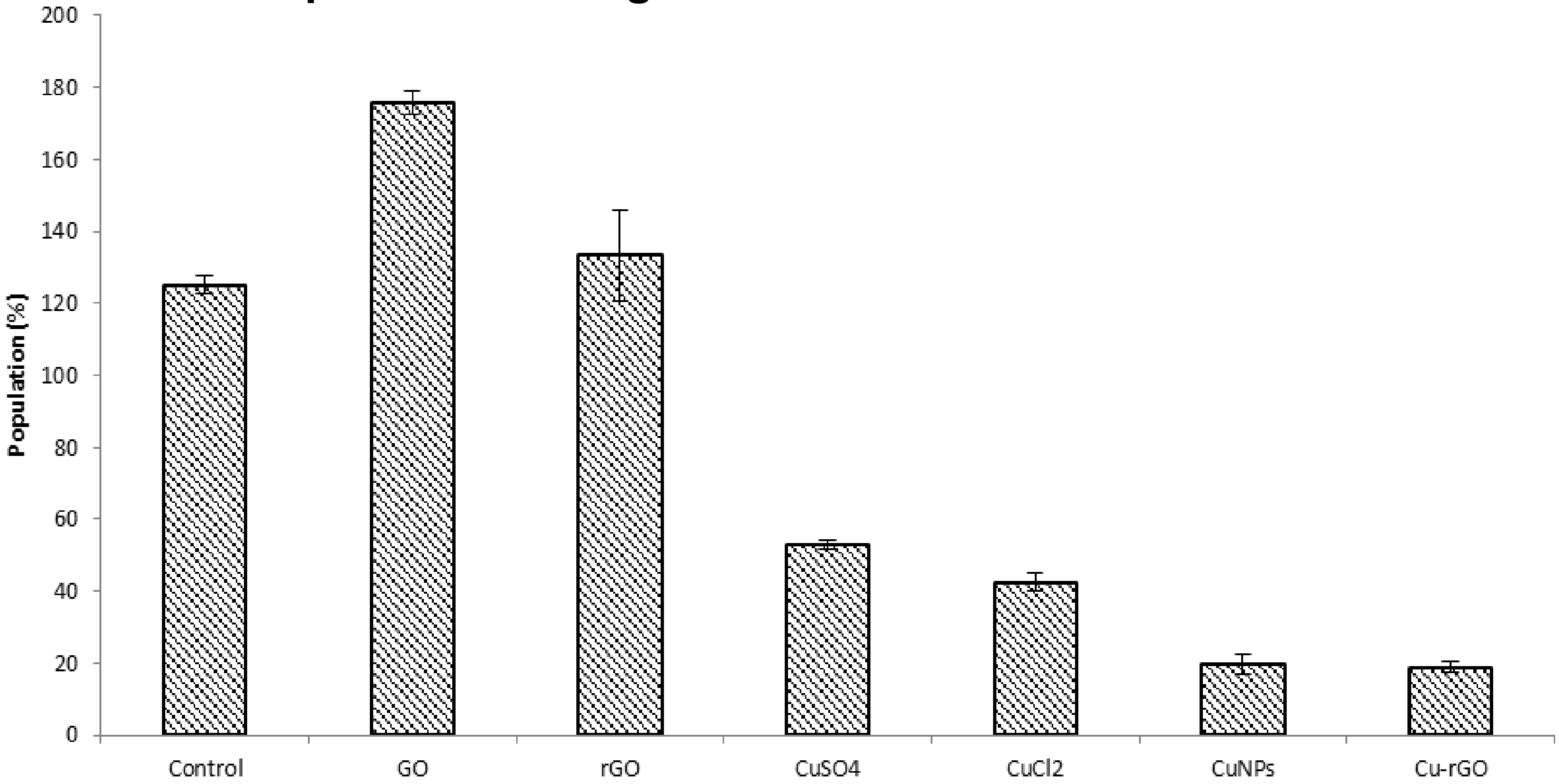
E. coli exposure to the surface of Cu-rGO at [A]x5k magnification and [B]x10k magnification

Shakeflask Studies



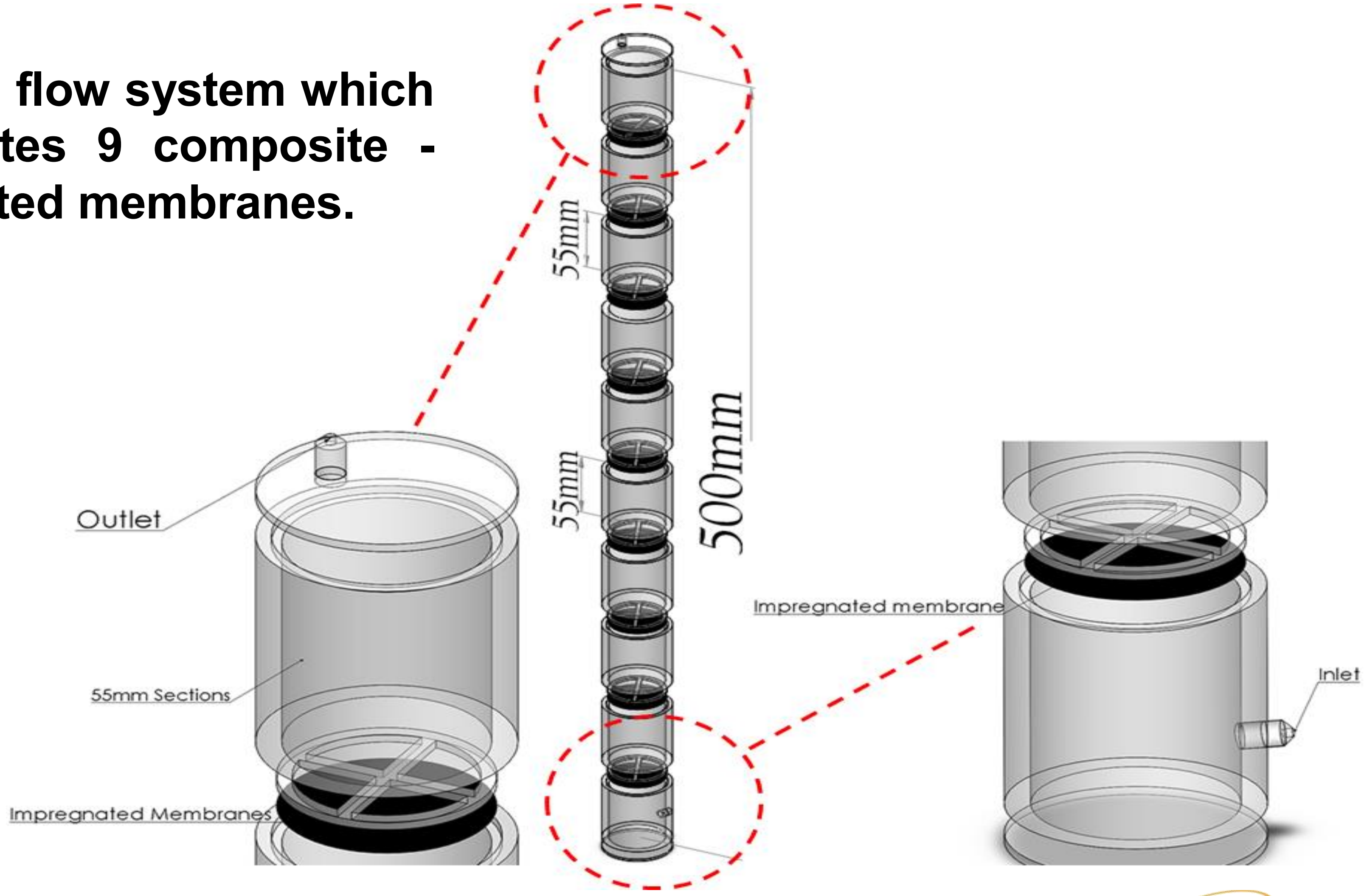
Shake Flask Bio Evaluation of Composites

E. coli **exposure to the various materials: GO, rGO, Cu-rGO, CuNPs ,$CuCl_2$ and $CuSO_4$ in PBS following a 24 hour period at 100mg/L.**

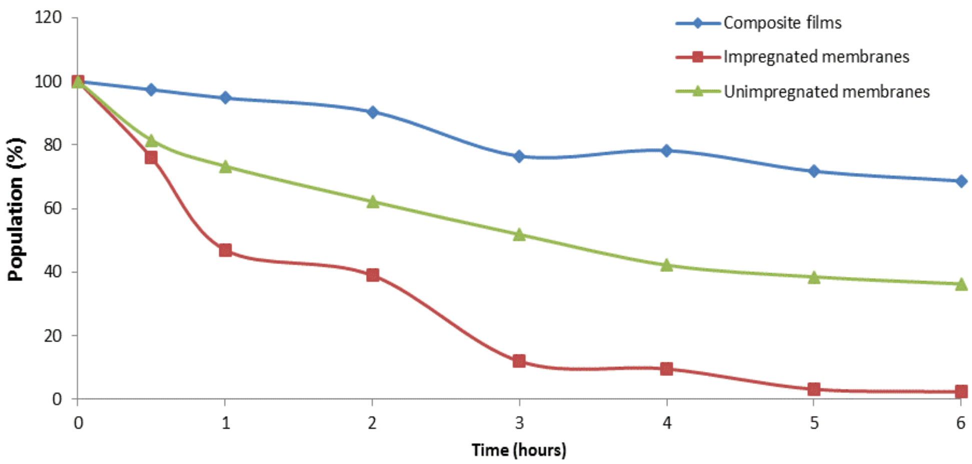


Prototype Development

Prototype flow system which incorporates 9 composite - impregnated membranes.



Performance Overview of new Graphene Composite Flow Filtration System



Bacterial removal by each of the initial prototype tests; the four composite films (blue), glass fibre membranes (green) and composite impregnated glass fibre membranes (red)

#Membranes	Control Membranes		Composite membranes	
	R2A	NB	R2A	NB
1	✓	✓	✓	✓
2	✓	✓	X	X
3	✓	✓	X	X
4	✓	✓	X	X
5	✓	✓	X	X
6	✓	✓	X	X
7	✓	✓	X	X
8	✓	✓	X	X
9	✓	✓	X	X

Viability of bacteria attached to both control membranes (with no composite) and the composite impregnated membranes following unit testing. Where ✓ indicates growth and X indicates no growth

To investigate the response of the prototype to *cryptosporidium*, the unit was challenged with 10L of sterile saline (0.85%) containing 10 oocysts/L. The 10L volume was then passed through the filtramax filtration unit and following microscopic analysis by City Analysts Ltd. no oocysts were detected.

Conclusions

- TiO_2 photocatalysis is effective at mineralising selected pharmaceuticals – some technical issues need solving
- IPCAs with AC and Graphene perform well in the removal of pharma's and Graphene oxide TNT can work efficiently with visible light
- Graphene copper composite based membranes both remove small molecules and are effective at inhibiting biological fouling

The Team

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DCU

Thanks to:

epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

QUESTOR
CENTRE

ATWARM

Tyndall
National Institute
Institiúid Náisiúnta

MARIE CURIE ACTIONS

PEOPLE

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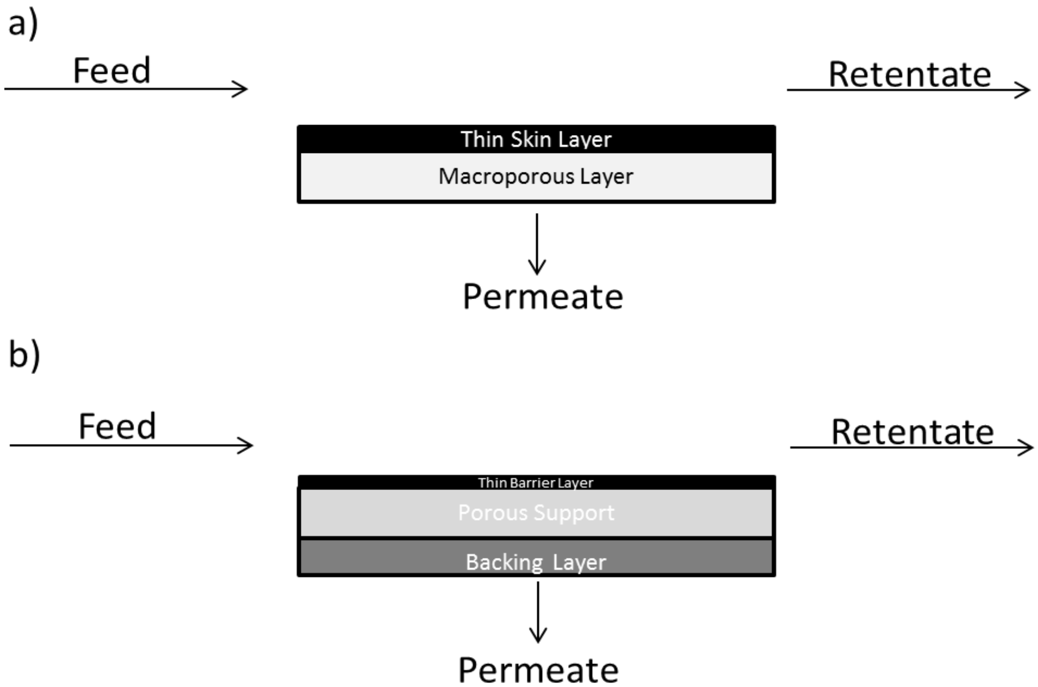

Membrane Structure a) Asymmetric macroporous membrane b) Thin film composite membrane