At-source hospital wastewater treatment to eliminate harmful pharmaceuticals: A novel immobilised approach using UV-LED activated photocatalytic nanomaterials

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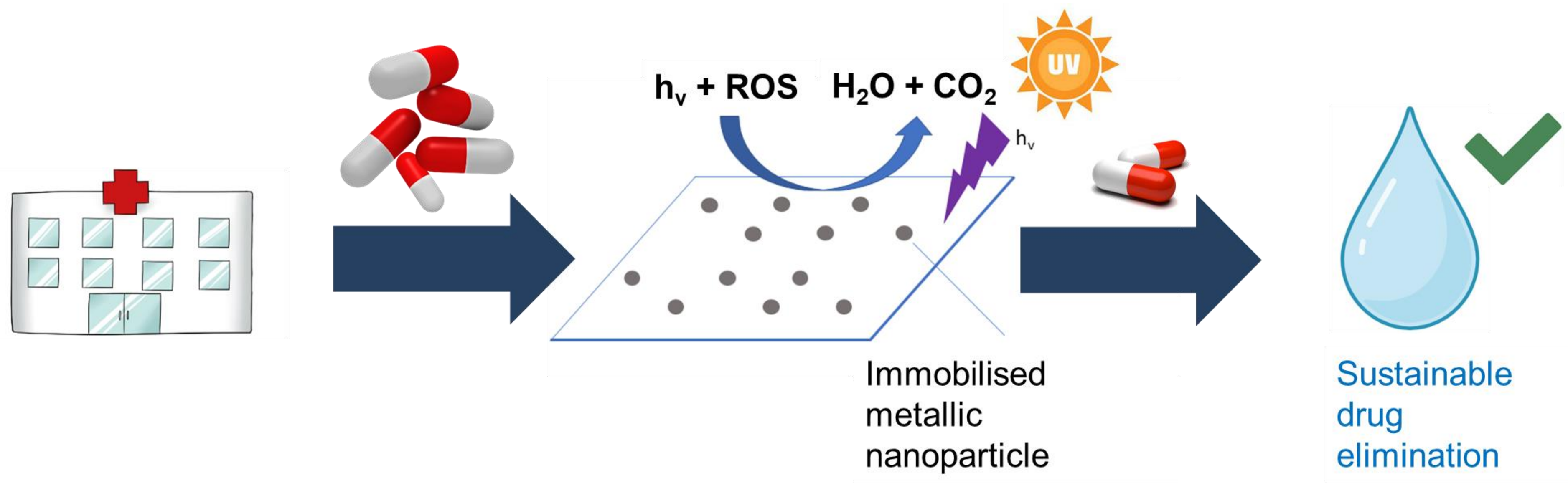
Introduction

Economical UV-LED activated generation of reactive oxygen species (ROS) on the surface of immobilised metallic nanomaterials can continuously oxidise and remove various hospital drugs in wastewater.

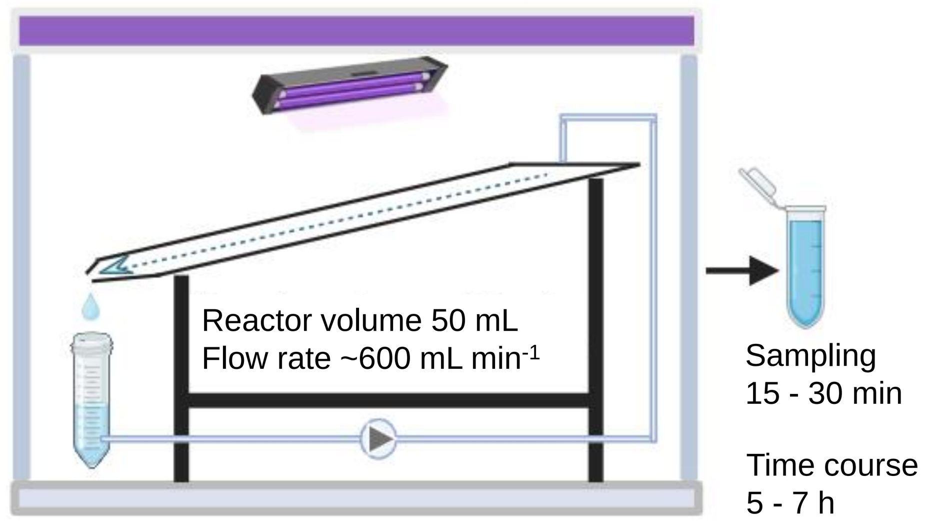
Immobilised photocatalysis, using UV-light effective thin-film nanomaterial coatings on planar borosilicate surfaces is a novel and reusable technique to enable treatment of high volumes of fast-flowing hospital wastewater.



Methods

A recirculating photocatalytic flat-bed reactor build out of 2 mm PMMA and powered by a Pulsatile Blood Pump (Harvard Apparatus) was designed.

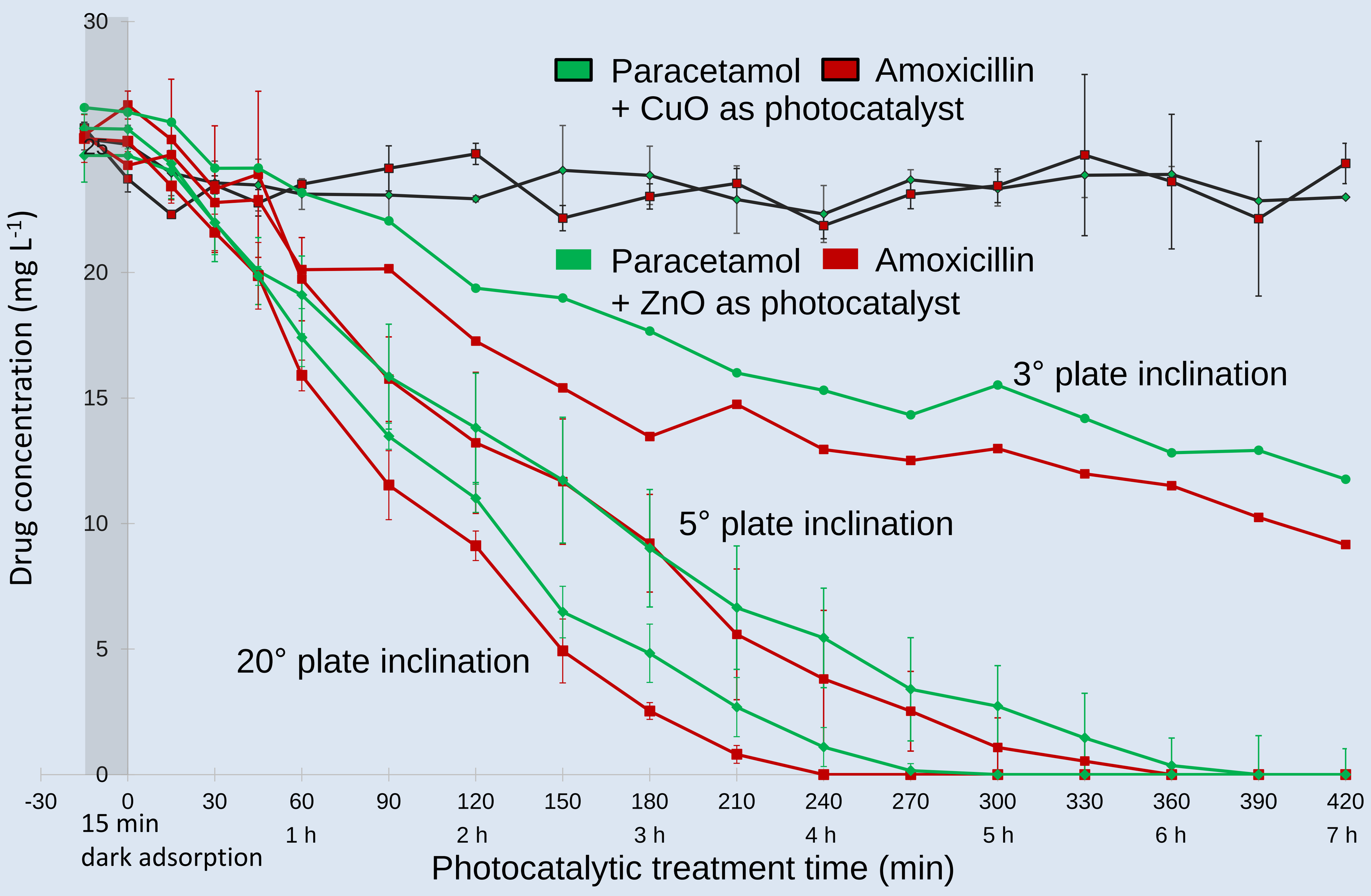
Horizontal illuminating light source:
Upturned box coated on the inside with UV reflective foil and adhesive 24 W 365 nm UV LEDs



Results

Photocatalytic oxidation of test drugs in a flat-bed reactor

~ 96% paracetamol decay after 4 h and
~ 97% amoxicillin decay after 3.5 h photocatalysis



Test nanomaterials:

Wide band gap (3.37 eV) zinc oxide (ZnO)
Narrow band gap (1.2 – 2.1 eV) copper(II)oxide (CuO)

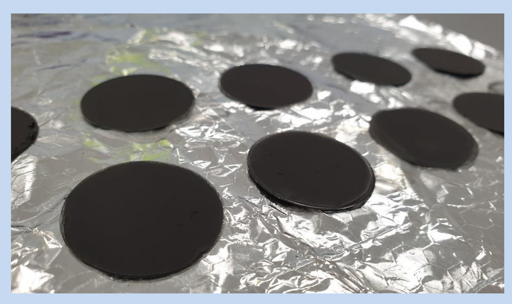
Photocatalytic nanomaterial functionalised onto
Ø 30 mm ~ 0.15 mm borosilicate support

Powdered ZnO

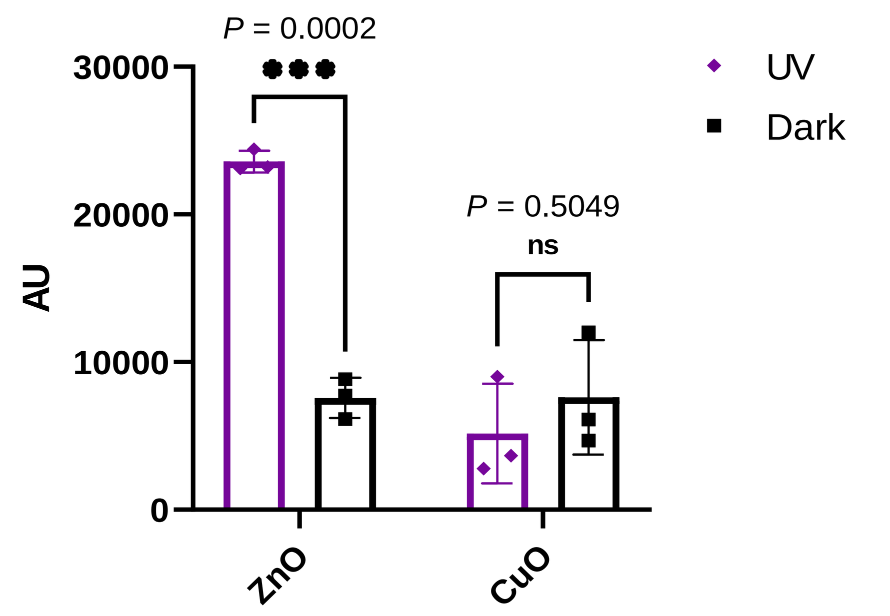
ZnO thin-film coating

Powdered CuO

CuO thin-film coating



Photocatalytic hydroxyl radical (•OH) generation of ZnO vs CuO



Electron Paramagnetic Resonance spectroscopy (EPR) was used to identify principal photocatalytic ROS:

- hydroxyl radicals (•OH) and superoxide radicals ($^•O_2^-$).
- $^•O_2^-$ generation was detected for both test nanomaterials CuO and ZnO.
- •OH generation was detected in ZnO illuminated with UV-light and photocatalytic oxidation of both test drug concentrations was observed.
- No •OH generation was detected in CuO illuminated with UV-light and no photocatalytic oxidation of either drug was observed.

Conclusions / Future

Immobilised photocatalysis using economical 365nm UV-A LEDs and UV-light activated metallic nanomaterials functionalised onto planar borosilicate glass provides an effective, sustainable, reusable solution for the oxidation of toxic hospital drug mixtures in fast-flowing wastewater.
Repeated use of the same ZnO-functionalised substrates has shown reproducibly effective photocatalytic drug removal (in n > 10 replicates).

- EPR experiments identified hydroxyl radicals (•OH) as the ROS to effectively oxidise both test drugs.
- A thin film of wastewater, caused by a high inclination angle of the reactor (20°), is required for effective drug removal and at lower concentrations a first order decrease is observed in both test drug concentrations.

This suggests that the rate of reaction is limited only by the decrease in drug concentration over time.
Photocatalytic ROS (here hydroxyl radicals) may then be generated in excess by ZnO and released in a thin-film of water closest to the drug.

Next immobilised photocatalytic removal of all 5 hospital test drugs amoxicillin, paracetamol, methotrexate, tamoxifen and simvastatin will be assessed at environmental ng L^{-1} drug concentrations using a self-developed sensitive mass spectrometry method.

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