Optimising the Removal of Steroid Hormones and Pharmaceutical and Personal Care Products (PPCPs) from Aqueous Media Using Low Cost Biosorbents

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INTRODUCTION

Endocrine Disrupting Chemicals (EDCs) and Pharmaceutical and Personal Care Products (PPCPs) have been detected ubiquitously in the aquatic environment due to insufficient removal by conventional activated sludge processes in wastewater treatment plants. The adverse effects of EDCs include reproductive disturbance, developmental problems in wildlife and humans at ultra-trace, part per trillion (ppt) concentrations, and exposures to PPCPs have been linked to the development of acquired antibiotic resistance in pathogenic and non-pathogenic bacteria and other miscellaneous biological effects. As such, some EDCs and PPCPs have been added to the Watch List of the EU Environmental Quality Standards Directive and continued research into monitoring and the development of more efficient methods for their removal from wastewaters is required. Where usage reduction of these substances is not possible, alternative 'end of pipe' solutions are required. Biosorption has been shown to have potential as a low-cost effective alternative to more expensive tertiary treatment methods for the removal of some contaminants like dyes or heavy metals from aqueous media, but has not been extensively evaluated for EDCs and PPCPs.

This project aims to utilize a variety of recycled industrial, domestic and agricultural by-products as low cost biosorbents for the removal of EDCs and PPCPs from wastewater. These will be used to develop dynamic, rechargeable column systems for wastewater effluents in pilot studies with Scottish Water and the Chinese Academy of Sciences. It is anticipated that the polishing treatment system will be applicable in rural or semi-rural (low flow) WWTPs in a fast and inexpensive way.

References

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Acknowledgements:
Project funded by The Hydro Nation Scholarships Programme

METHODS

15 prioritized EDCs and PPCPs have been selected through comprehensive prioritization approaches as shown in the table below.

Class	Compounds	Usage statistics[4]	Legislation	Removal efficiencies	Environmental ocurrance (ppt)	PNEC
Antiinfectives	Trimethoprim	487128	No	0-50%	10-3050	500
Macrolide antibiotic	Clarithromycin	268489	Yes[1,2,3]	0-24%	3.5-621	250
Fluoroquinolone Antibiotic	Ciprofloxacin	99441	Yes[1,3]	45-78%	6-2500	100
Anti-bacterial agent	Triclosan	10-1000 tons per year in EU	Yes[3]	45-93%	3.9-434	200
NSAID	Ibuprofen	915788	Yes[3]	72-100%	44-990000	1650
	Diclofenac	595709	Yes[1,2,3]	9-60%	10-510000	3310
SSRI	Fluoxetine	816346	Yes[3]	3-60%	2.1-2000	110
Antiepileptics	Carbamazepine	223601	Yes[3]	0-53%	290-4596	420
Carbamazepine metabolite	Carbamazepine-epoxide	n/a	Yes[3]	n/a	8-2100	n/a
ß-blockers	Propranolol	557628	Yes[3]	34-80%	108-1130	244
blood-lipid regulators	Atorvastatin	1637000	Yes[3]	40-80%	10-210	86
Antidiatetics	Metformin	1140162	Yes[3]	~85%	100-4000	12000
Synthetic Hormone	17α-ethynyl estradiol	298045	Yes[1,2,3]	60-85%	0-4.3	0.35
Natural Hormone	17β-Estradiol	n/a	Yes[1,2,3]	0-87%	0.72-51	2
	Estrone	n/a	Yes[1,2,3]	0-61%	1.8-60	6

1Inclusion in Watch list under EU Environmental Quality Standards Directive2 in EU Priority Watch List 3 in Scottish Water Chemical Investigation Programme list 4 Items prescribed in Scotland in 2014/15; SSRI-selective serotonin reuptake inhibitors; NSAID-Nonsteroidal anti-inflammatory drugs; PNEC-Predicted no-effect concentration

The determination and quantification methods for target compounds have been developed by Liquid chromatography-tandem mass spectrometry (LC-MS/MS). Good chromatographic separation of 10 analytes has been achieved in the positive ionization mode as shown in Figure 1 while other 5 chemicals have been detected in negative ionisation mode. The instrumental limit of detection (LOD) ranges from 0.13 to 3.61 µg/L, providing robust detection methods for the evaluation of biosorption study. These detection limits will be lowered considerably when an optimised solid phase extraction (SPE) stage is incorporated into the methodology.

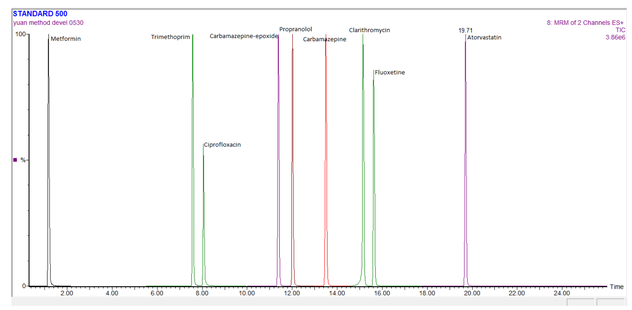
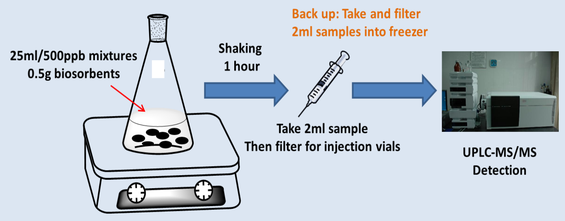


Figure1. Liquid chromatography of positive ionised PPCPs

RESULTS – Initial Biosorbent Screening

Eleven low-cost biosorbents derived from mainly Scottish industrial and agricultural wastes such as spent grains, crab shells, biochars, coffee wastes and algae, as well as a reference activated carbon, have been screened for the biosorption of target compounds, initially at relatively high concentrations (100 µg/L, 500 µg/L and 2mg/L).



The removal efficiencies of each analyte by each biosorbent is present in Figures 2 and 3 (500 µg/L data shown as example). Among them, an Italian biochar derived from Orchard pruning residues provided satisfactory removal rates (above 69% for all target compounds), close to the performance of activated carbon. Other non-pyrolysis materials such as green compost, coffee waste, oak wood chippings and algae derived materials have showed promising removal efficiencies for a number of target analytes.

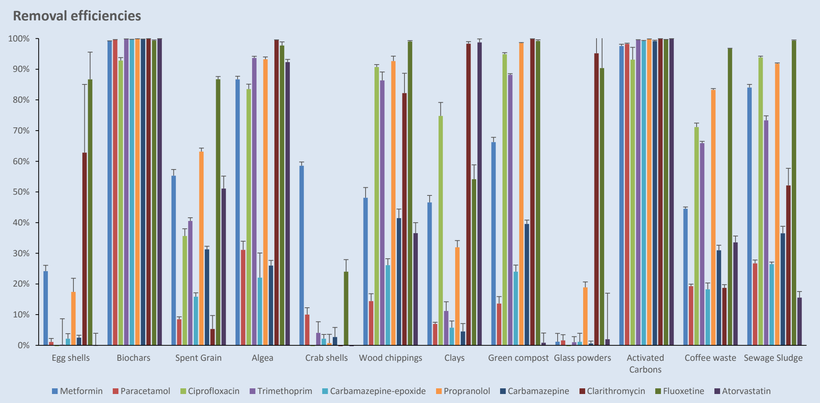


Figure2. Mean removal efficiencies of positively ionised target compounds by 12 tested biosorbents (vertical error bars stand for 1 standard deviation)

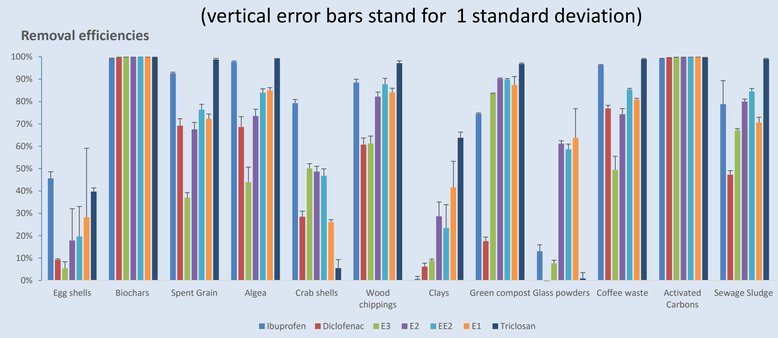


Figure3. Mean removal efficiencies of negatively ionised target compounds by 12 tested biosorbents (vertical error bars stand for 1 standard deviation)

CONCLUSIONS AND FUTURE WORK

- Some biosorbent materials showed promising removal efficiencies for target compounds such as Italian biochar (> 69% for all 15 analytes), algae (> 58% for 13), sewage sludge (> 67% for 11), spent grain (> 62% for 10), coffee waste (>50% for 11) and 61% by wood chippings (above 61% for 10).
- Further experiments will be carried out to investigate biosorbent performance for compounds at environmental concentrations; to determine the physicochemical properties and surface micro-structure of the biosorbents studied to understanding the underlying mechanisms of adsorption.
- Based on those results, 3-5 promising biosorbents will be selected for further evaluation of their robustness under typical environmental conditions, analyte adsorption isotherms and kinetics.
- The dynamic column treatment system will be developed using the most promising biosorbent material or mixtures of materials and their mechanical and fluid dynamic properties will be assessed under realistic environmental conditions. The removal of all prioritised compounds from real wastewater effluents containing environmentally relevant analyte concentrations will be optimised.

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