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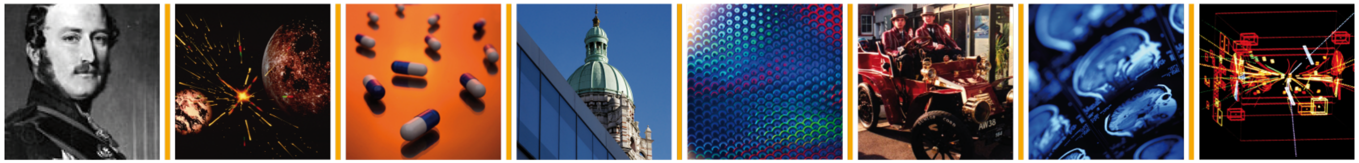
Sewage sludge as source of activated carbon for the removal of endocrine disrupting chemicals in wastewater



G. D. Fowler, S. Pullket, K. M. Smith & N. J. D. Graham
Environmental and Water Resources Engineering
Department of Civil and Environmental Engineering, Imperial College London
SW7 2AZ

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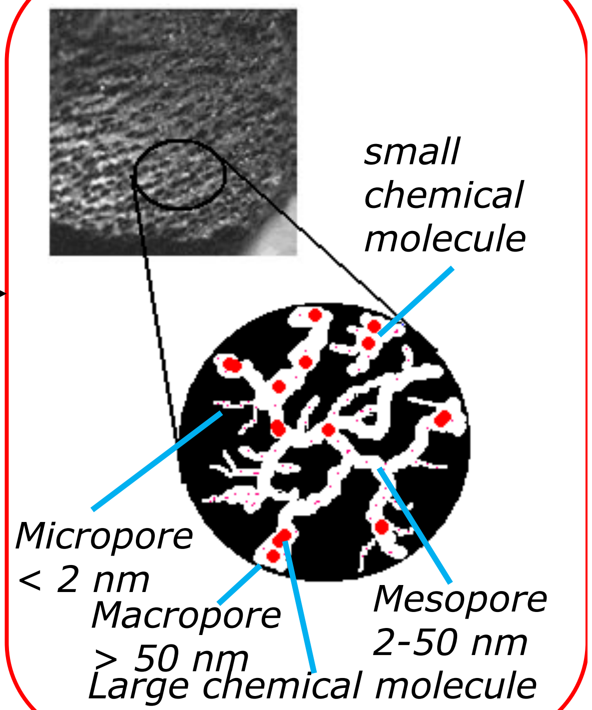
Project aims – Sludge valorisation and reuse

Sewage Sludge

Physical Activation
(Sequential Pyrolysis & Partial gasification)

Chemical Activation
(Simultaneous Pyrolysis & Activation)

Activated Carbon
"added value product"



Adsorption of Endocrine Disrupting Chemicals from Waste Water

- **Determine optimal conditions to maximise surface area & Bisphenol A adsorption**
- **Explain any differences in sludge response to optimised activation conditions**

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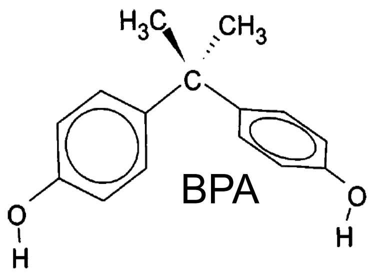
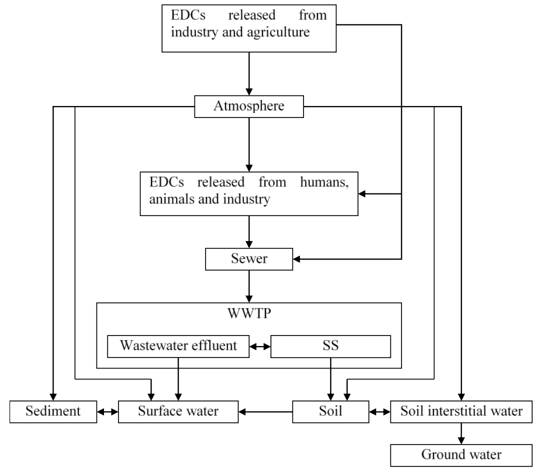
EDCs & Bisphenol A – molecular probe of choice



- The World Health Organisation defines *EDCs* as: "exogenous substances or mixture that alter function(s) of the endocrine system and consequently cause adverse health effects in intact organism, or its progeny or (sub)-populations"
- Solubility (hydrophilicity) of BPA is among the highest compared to the other potent EDC compounds.
- This nature (when compared among the other EDC) also imply that it is by far the most difficult EDC to remove from the aqueous phase.
- The molecular size of BPA is mid-range of EDCs of concern
- Recent research has identified that BPA shows equal potency of action to estradiol, a natural hormone.
- It is one of the highest volume manufactured chemicals, worldwide.
- Its occurrence is widespread:
  - In: wastewater derived from manufacturing applications using BPA
  - In: Landfill leachate



Compound	Formula	MW (g/mol)	Water solubility (mg/l)	Log K_{ow}	RBA (AR)[c]	RBA (ER)[d]
Estrone (E1)	$C_{18}H_{22}O_2$	270.4	12.42[a]	3.43[a]	1.3×10^{-3}	0.44
17β-estradiol (E2)	$C_{18}H_{24}O_2$	272.4	12.96[a]	3.94[a]	0.66	1
17α-Ethinylestradiol (EE2)	$C_{24}H_{20}O_2$	296.4	4.83[a]	4.15[a]	3.2×10^{-4}	0.33
Estriol (E3)	$C_{18}H_{24}O_3$	288.4	13[a]	2.81[a]	4.82×10^{-3}	1.4
Nonylphenol (NP)	$C_{15}H_{24}O$	220.3	3.9[b]	5.76[b]	1.26×10^{-4}	1.4×10^{-3}
Octylphenol (OP)	$C_{14}H_{22}O$	206.3	3[b]	5.50[b]	1.25×10^{-4}	1.24×10^{-3}
Bisphenol A (BPA)	$C_{15}H_{16}O_2$	228.3	120-300[a]	3.4[a]	3.01×10^{-4}	2×10^{-3}

a: Birkett, J.W. and Lester J.N., Endocrine disrupters in wastewater and sludge treatment processes. 2003, London: Lewis publishers. 295 pages.
b: Tan, B.L.L., Chemical and biological analyses of selected endocrine disruptors in wastewater treatment plants in South East Queensland, Australia. Australian School of Environmental Studies, Faculty of Environmental Sciences, 2006, Griffith University
c: RBA (AR) is relative binding affinity determined by androgen receptor ligand competitive binding assay
d: RBA (ER) is relative binding affinity determined by estrogen receptor ligand competitive binding assay

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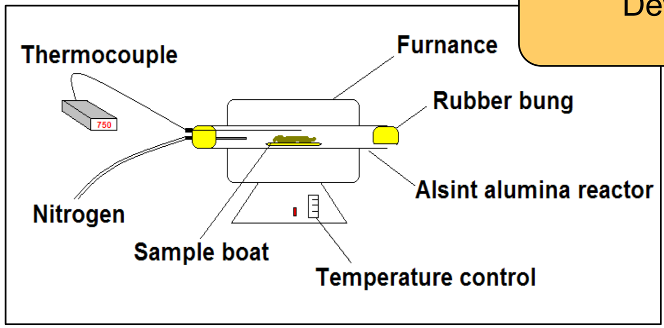
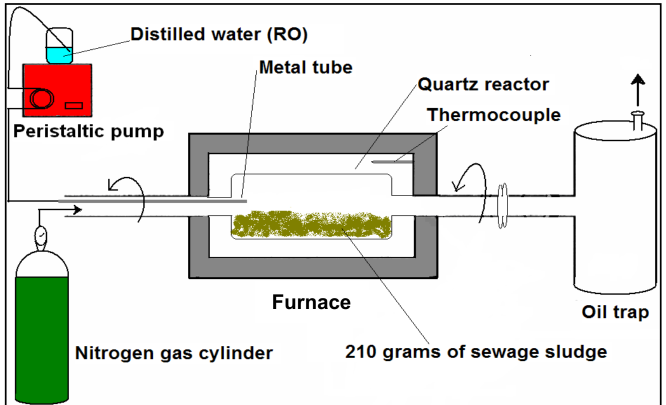
Methodology – Optimised production conditions





"DRAW"
Dewatered raw filter cake

"DMAD"
Dewatered Mesophilic Anaerobically Digested

Dry at 105^{o}C, then crush<10mm

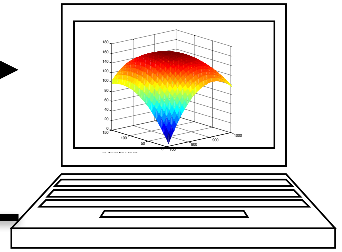
Carbonisation & Activation by steam or chemicals

Response **S**urface **M**ethodology (**RSM**)
Experimental points designed for each sludge/activation method
Activation Temp: up to 940^{o}C
Activation Time: 0-120 mins
(water flow rate of 0.7 ml/min or impregnation ratio up to 3.5 (by wt)

Sludge Based Adsorbents (SBAs)

Surface area characterisation & BPA adsorption

Total surface areas (BET) BPA adsorption



Optimised production conditions
ACTIVATION TIME & TEMP

Highest BET surface area

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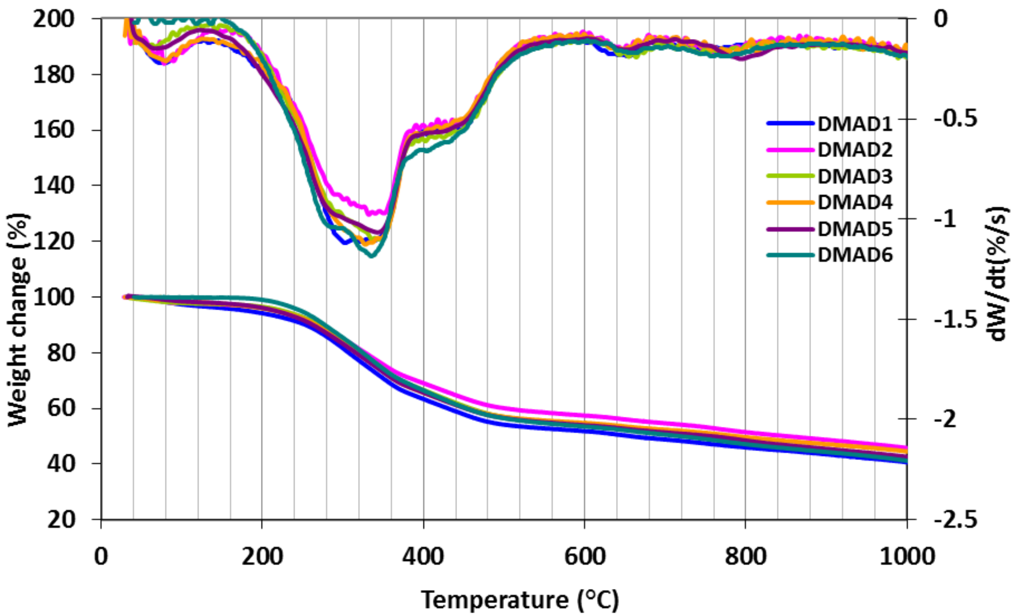
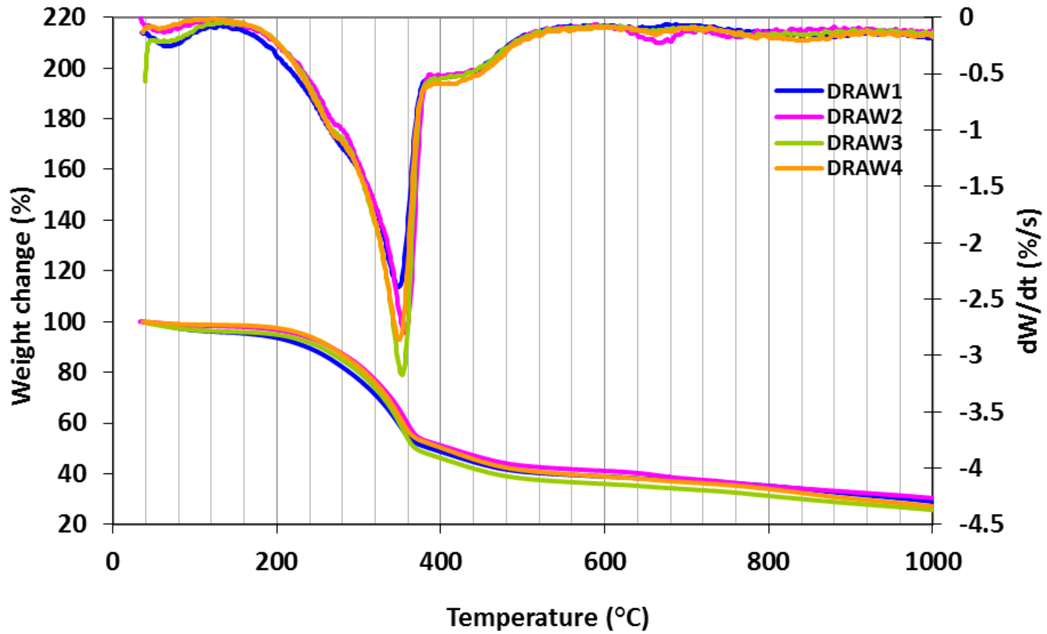
Seasonal variation of sludge: Assessed by TGA response





(heating rate: 5°C/min)

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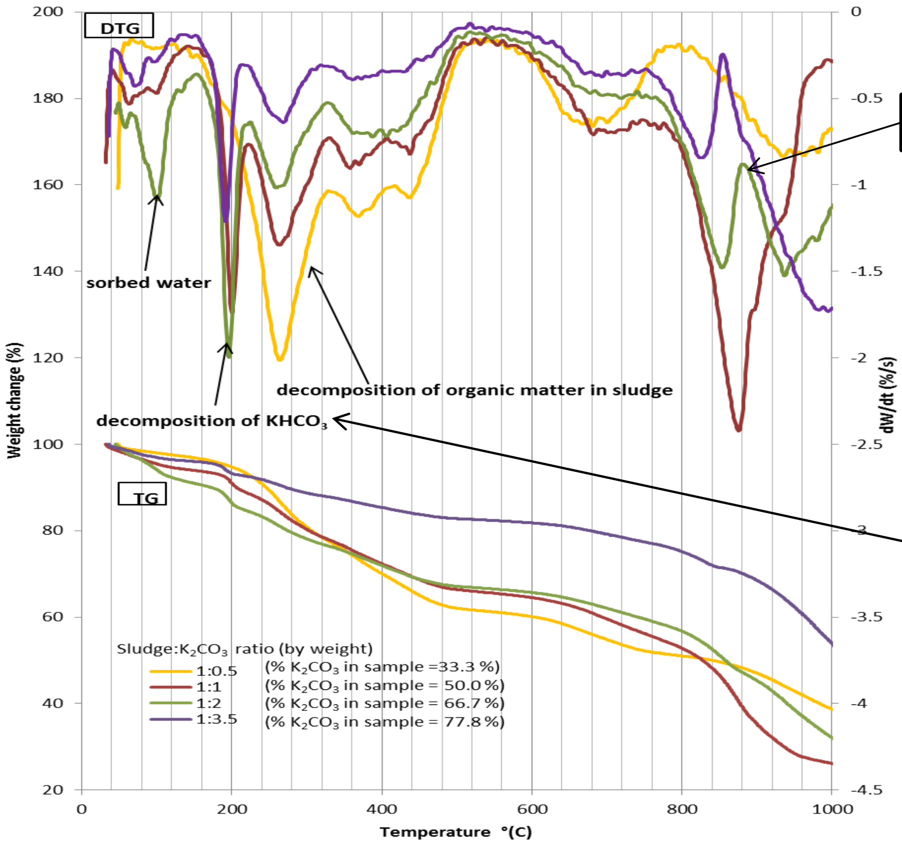
Thermal analysis of DMAD sludge impregnated with K_2CO_3



Secondary reactions between activating agent and sludge char

$$2C + K_2CO_3 \rightarrow 2K + 3CO$$

Notable effect of K_2CO_3 upon thermal events during sludge decomposition

$$K_4H_2(CO_3)_3.15H_2O \rightarrow K_2CO_3.15H_2O + 2KHCO_3$$

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2$$

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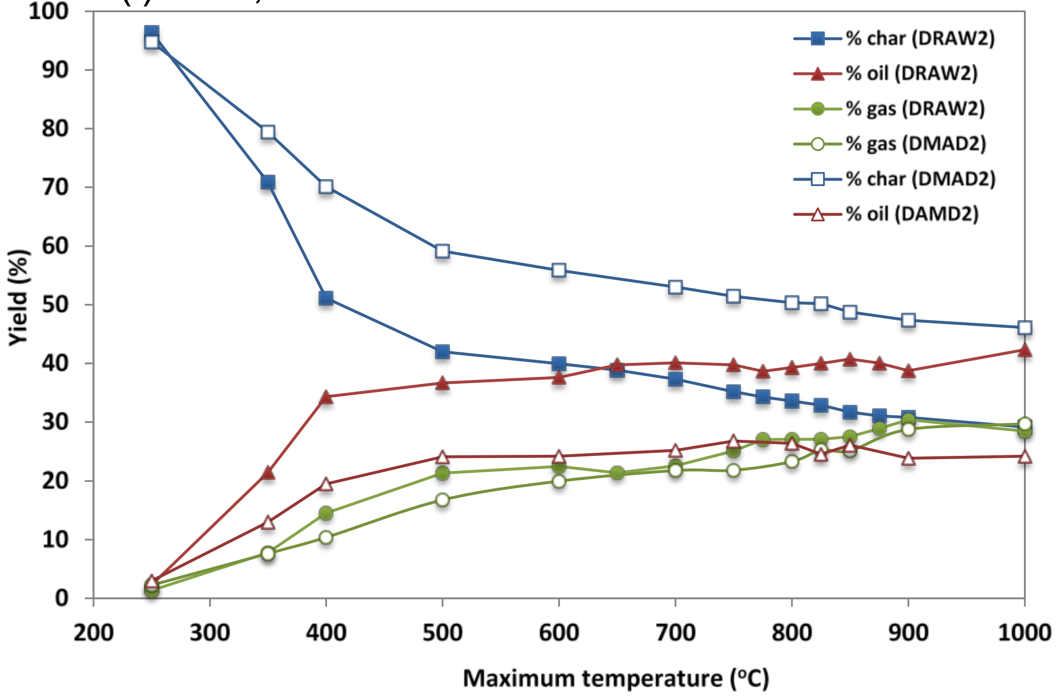
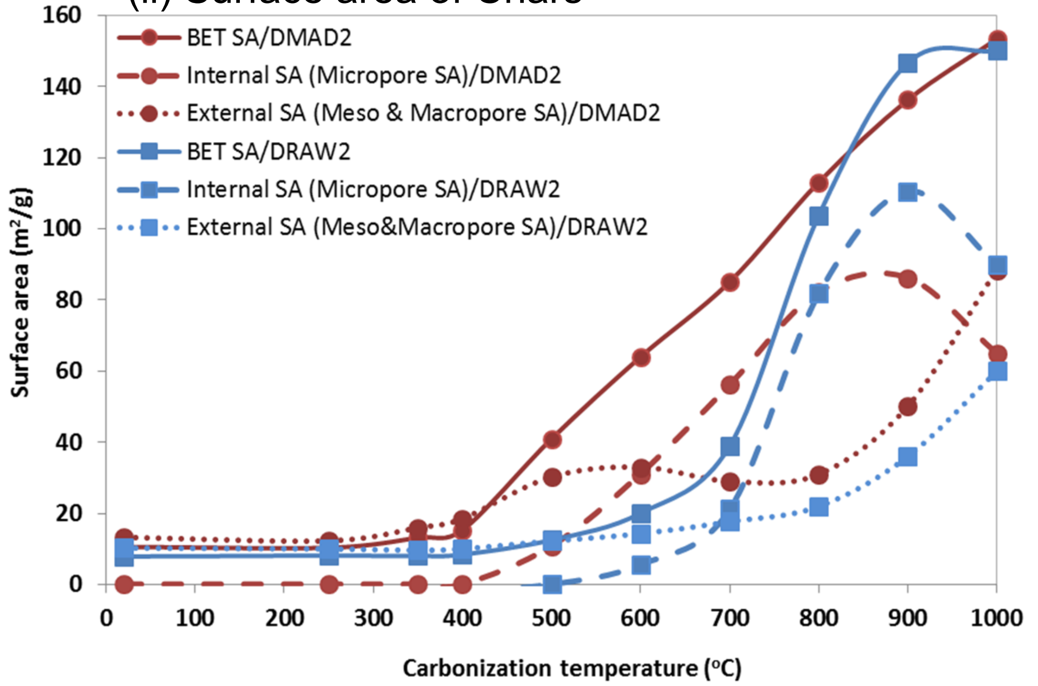
Effect of Temperature upon: (i) Char, oil & gas yields; (ii) Surface Area

(i) Char, Oil & Gas Yields



(ii) Surface area of Chars



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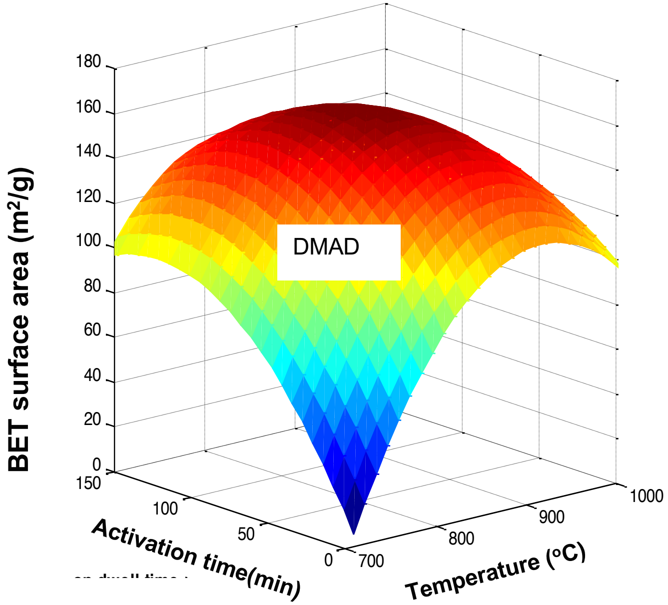
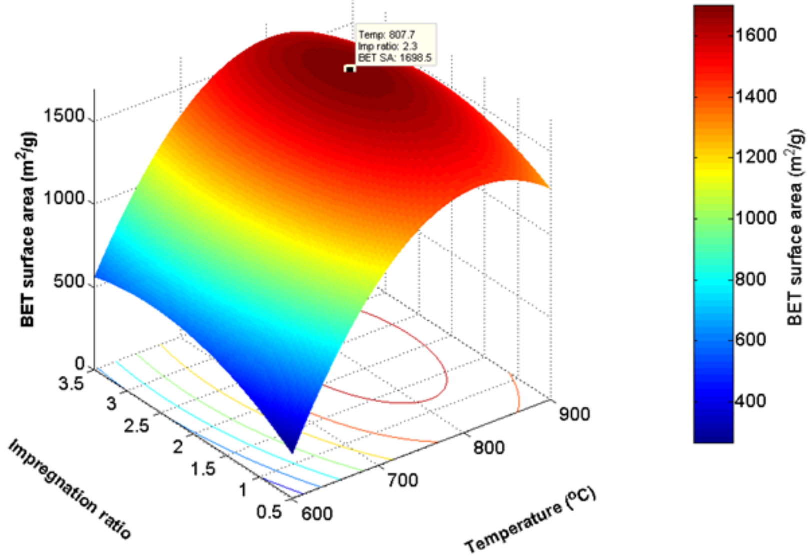
Response Surface Methodology Activation optimisation





Optimum conditions – Steam Activation

- DRAW: 838°C, 80 mins, Highest BET: 271 m^2/g
- DMAD: 838°C, 73 mins, Highest BET: 167 m^2/g

Optimum conditions – K_2CO_3 activation

- DMAD: 807.7°C, 1:2.3 Impregnation ratio

Highest BET: 1698.5 m^2/g

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BPA adsorption capacity

Sludge Based Adsorbent	Langmuir Q_{max} (mg/g)	Sludge Based Adsorbent	Langmuir Q_{max} (mg/g)
DR + K_2CO_3/900 – Acid Washed	714	DM + $MgCl_2$/600 – Acid Washed	115
DR + K_2CO_3/750 – Acid Washed	625	DM + $CaCl_2$/750 – Acid Washed	105
DR + KOH/750 – Acid Washed	555	DM + KCl/900 – Acid Washed	91
DM + K_2CO_3/750 – Acid Washed	455	DR Steam Activated	85
DM + $ZnCl_2$/600 – Acid Washed	333	DM Steam Activated	55
DM + KOH/750 – Acid Washed	303	DM + HNO_3/900 – Acid Washed	47
DM + $FeCl_3$/900 – Acid Washed	243	DR Carbonised at 1000 ^oC	45
DM + H_3PO_4/900 – Acid Washed	159	DM Carbonised at 1000 ^oC	40
Chemviron Filtrasorb 400 –Commercial Activated Carbon			**400**

Conclusions

- The highest surface area SBA and BPA adsorption was produced by K_2CO_3 chemically activating undigested (DRAW) sludge. Obtained from DR+K_2CO_3/900-A: BET SA = 1979 m^2/g and BPA adsorption capacity (based on Q_{max}) = 714 mg/g.

- Nevertheless, Steam activation of sludge could be attractive depending on the mode of application (as a powdered carbon vs granular material).

- Sewage sludge adsorbents have significant BPA adsorption capability and could provide opportunities to the water industry: further beneficial reuse of sludge; control options for emerging pollutants; sustainable energy generation.

Acknowledgements

- Thank you to….

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Thank you – Questions?

- Geoff Fowler
- Environmental and Water Resources Engineering
- Department of Civil and Environmental Engineering
- South Kensington Campus
- London SW7 2AZ
- Phone: +44 (20) 7594 5973
- Email: g.fowler@ic.ac.uk