**Circular economy**

Closing resource and energy loops

**Low specific adsorption capacity of activated carbon**

**Chromium (VI) in the environment**

Welding, pigments,…
Toxic, mutagenic, carcinogenic
Soluble.

**Production of Brewer's spent grain (BSG)**

85 % of brewery waste
271 kton per year



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# Modication of activated carbons from brewers' spent for chromium(VI) adsorption

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- Introduction

- Production of Activated Carbon (AC)
  - Steam activation
  - Modification

- Chromium(VI) adsorption
  - Isotherm experiment
  - Kinetic experiment

- Conclusion



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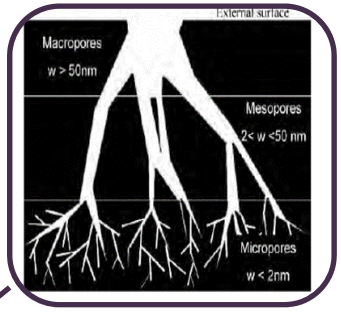
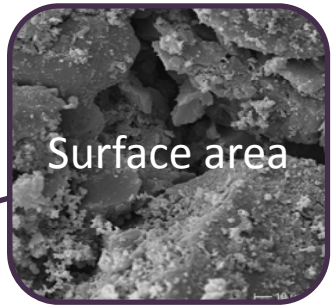
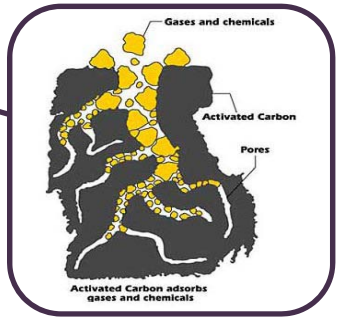
# Production of activated carbon (AC)




Heat
Pressure
Radiation

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# Modification of AC

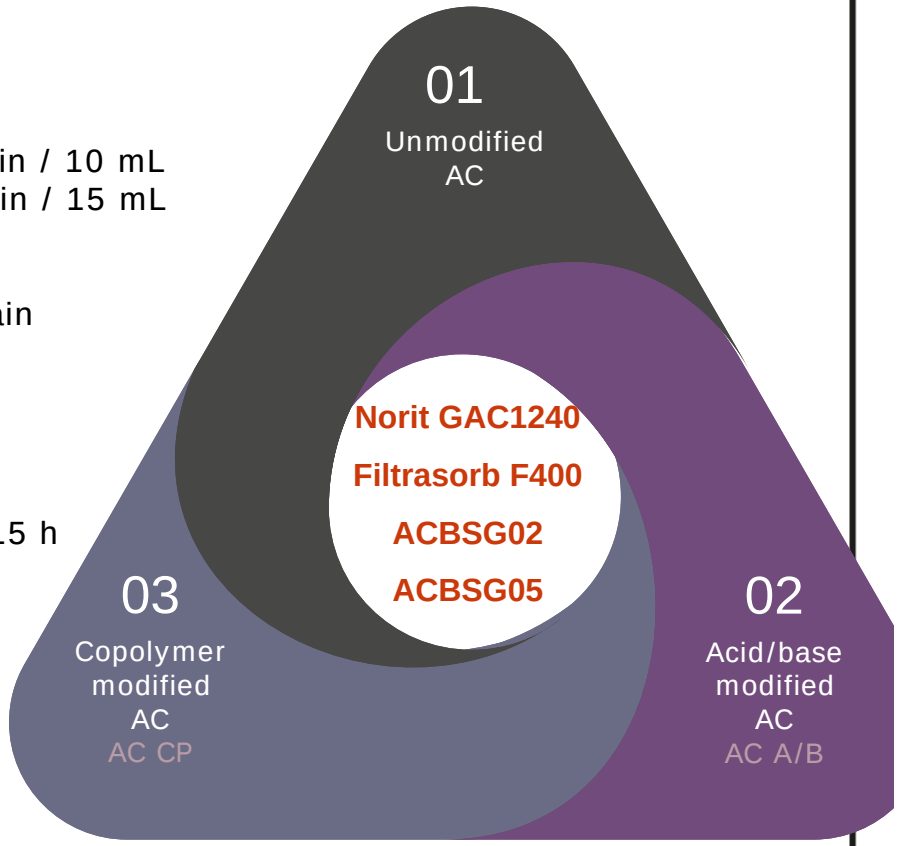
## 01 AC

Norit GAC 1240
Filtrasorb F400

Commercial ACs

ACBSG02: 800 °C / 30 min / 10 mL
ACBSG05: 800 °C / 45 min / 15 mL

AC from brewer's spent grain




## 02 AC A/B

I. 8 g of AC + 40 mL of 7 M $HNO_3$: reflux at 90 C for 15 h
II. Dried at 105 ± 5°C for 24 h
III. + 160 mL 1 M NaOH solution: shake 72 h at room temperature
IV. Washed and dried at 105 ± 5 °C for 24 h

S.X. Liu, X. Chen, X.Y. Chen, Z.F. Liu, H.L. Wang, Activated carbon with excellent chromium(VI) adsorption performance prepared by acid-base surface modification, ournal of Hazardous Materials, (2007) 315-319

## 03 AC CP

I. 2 g of AC 80 °C + 5 mL of N,N- dimethylformamide (DMF) + 5 mL of epichlorohydrin
II. After one hour: + 3 mL of diethylenetriamine + 10 mL of DMF
III. After one hour: + 5 mL of triethyleneamine
IV. After one hour: filtered & washed with Milli-Q, dried in an oven at 70 ± 5 °C for 72 h.

Y. Sun, Q. Yue, B. Gao, Y. Gao, Q. Li, Y. Wang, Adsorption of hexavalent chromium on Arundo donax Linn activated carbon amine-crosslinked copolymer, Chemical Engineering Journal, 217 (2013) 240-247.
X. Xu, Y. Gao, B. Gao, X. Tan, Y.-Q. Zhao, Q. Yue, Y. Wang, Characteristics of diethylenetriamine-crosslinked cotton stalk/wheat stalk and their biosorption capacities for phosphate, Journal of Hazardous Materials, 192 (2011) 1690-1696.



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# Chromium(VI) adsorption experiments

- The Cr(VI) solution
  - $K_2Cr_2O_7$
  - 10 mg/L, pH = 2 (HCl for adjustment)
- Measurements
  - After filtration using ashless Rotilabo A14 filters
  - Total chromium: ICP-AES
    - PE Optima 8300
  - Cr(VI): diphenylcarbazide method (ASTM D6832)
    - Absorbance at 540 nm



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## Equilibrium experiment : adsorption isotherm

- 5 – 100 mg of AC + 25 mL Cr(VI) solution
- Shaken for 24 h at 25°C

- Additional experiments:
  - 100 mg of AC + 100 / 200 / 500 mL of Cr(VI) solution

- Plots (for Cr(VI) and $Cr_{tot}$)
  - Adsorption capacity ($q_e$ – mg/g) versus equilibrium concentration ($c_e$ - mg/L)
  - Percent removal (%) versus AC dosage (g/L)



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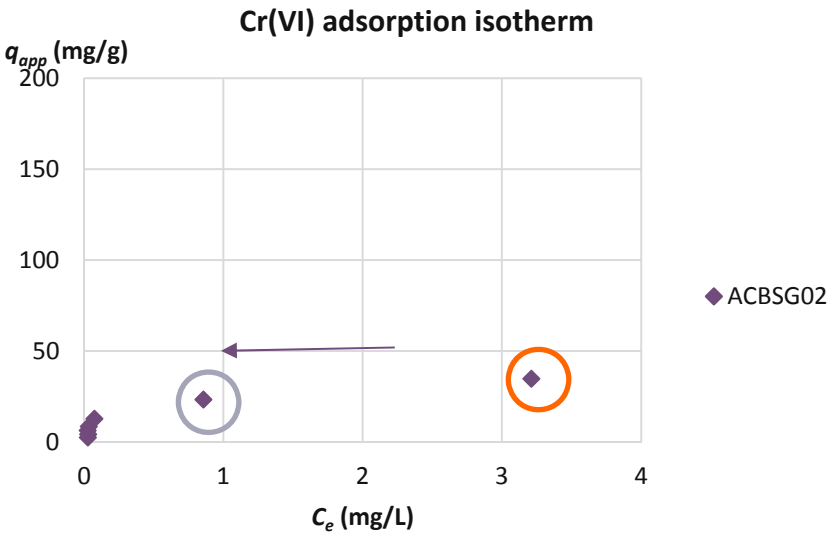
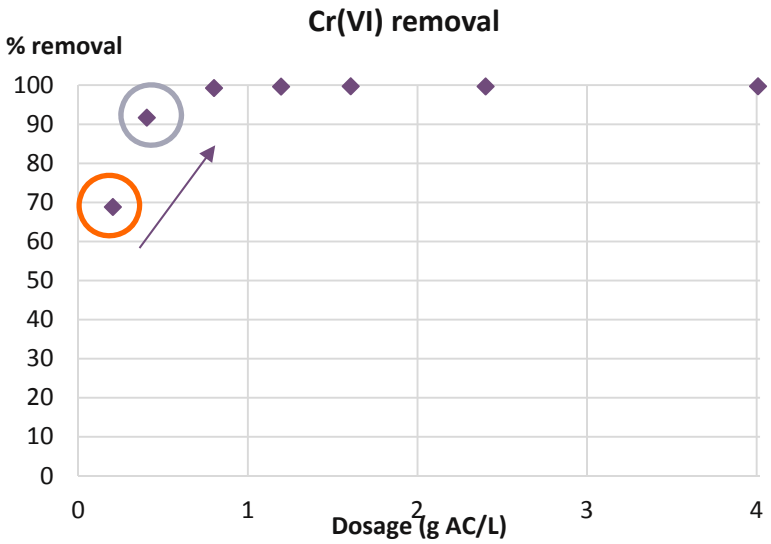
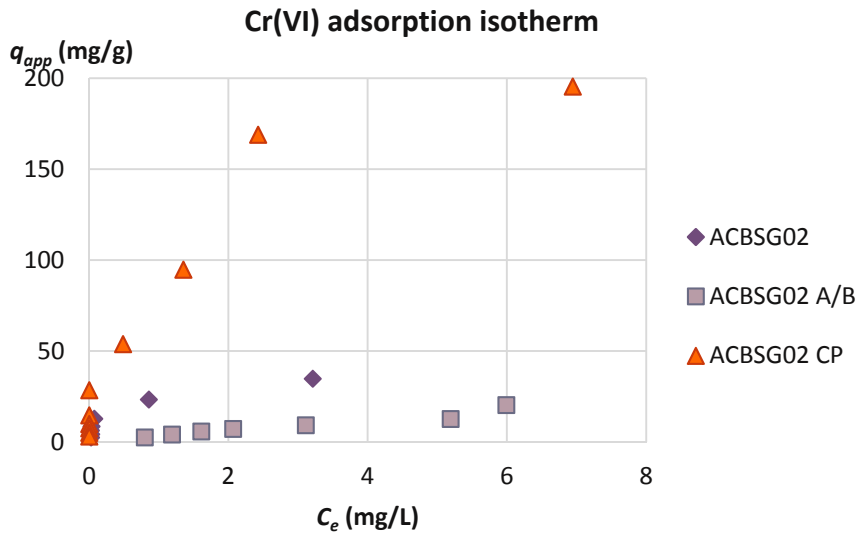
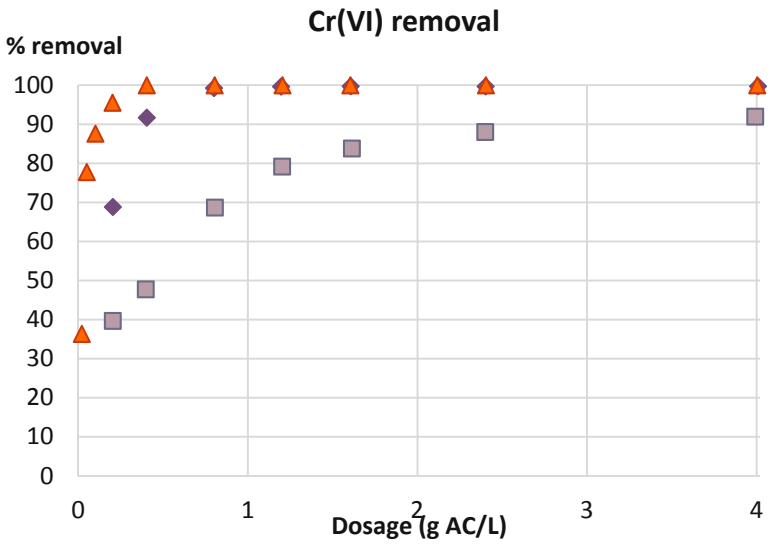
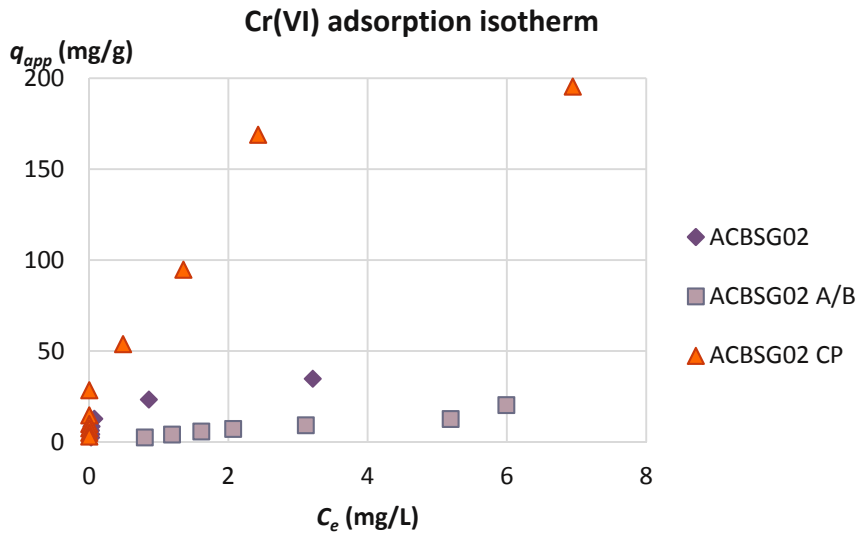
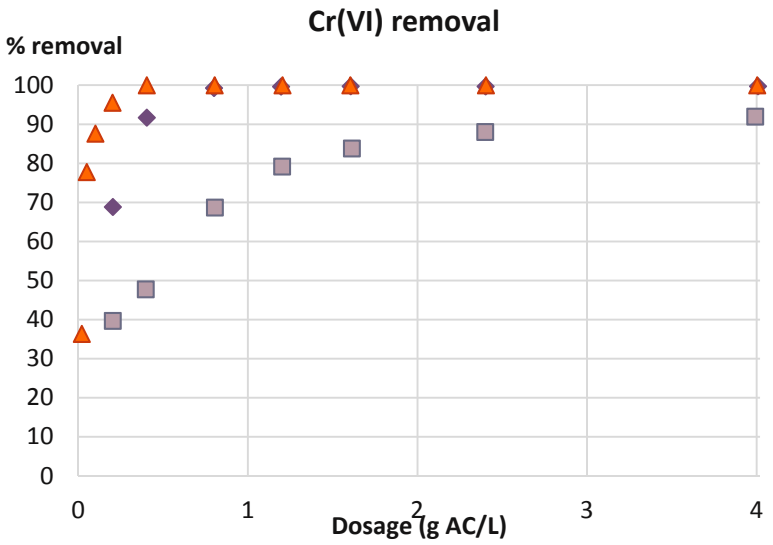

Cr(VI) adsorption isotherm
$q_{app}$ (mg/g)
200
150
100
50
0
0
1
2
3
4
$C_e$ (mg/L)
ACBSG02

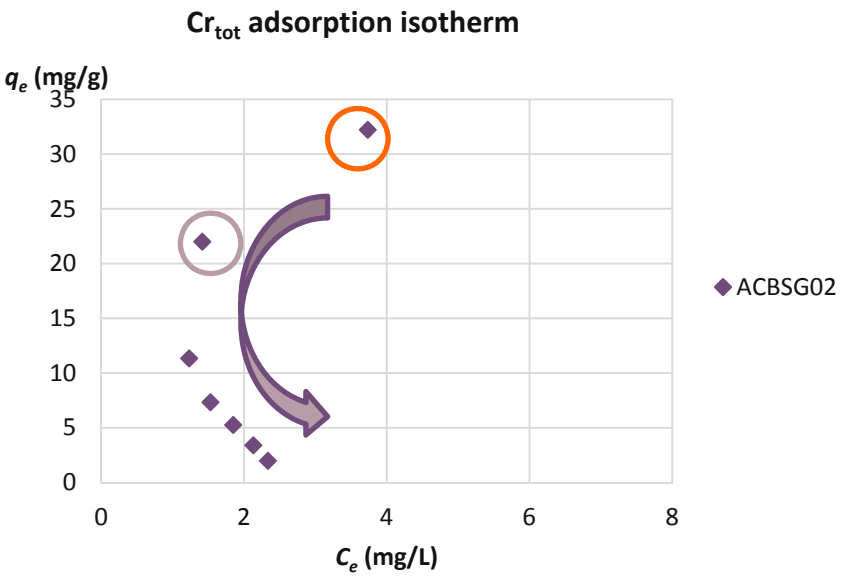

Cr(VI) removal
% removal
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
Dosage (g AC/L)

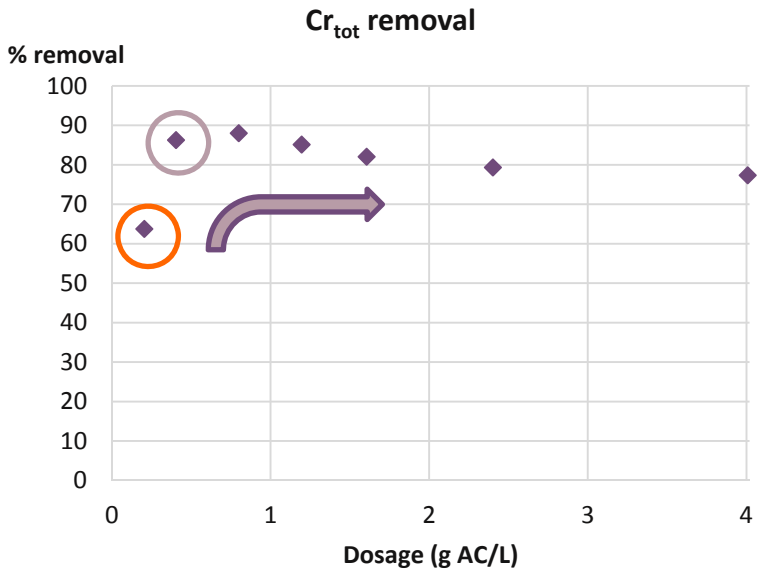

Cr(VI) adsorption isotherm
$q_{app}$ (mg/g)
200
150
100
50
0
0
2
4
6
8
$C_e$ (mg/L)
ACBSG02
ACBSG02 A/B
ACBSG02 CP


Cr(VI) removal
% removal
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
Dosage (g AC/L)



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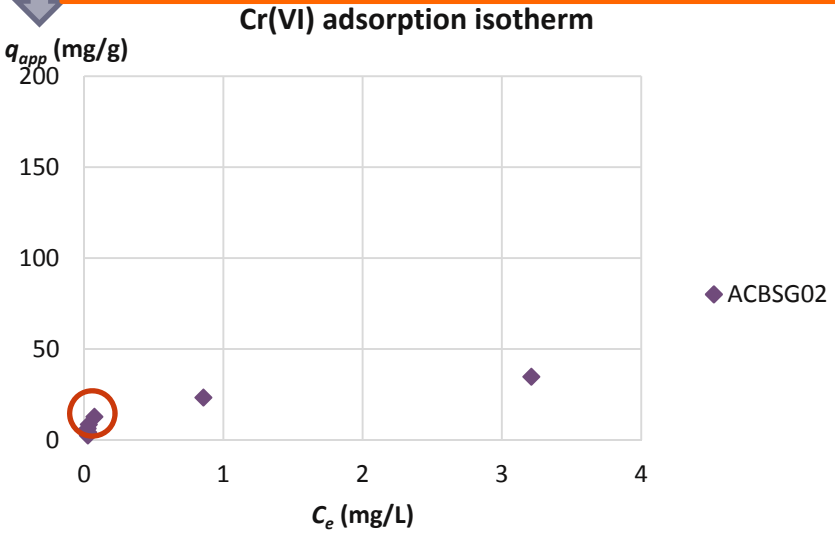
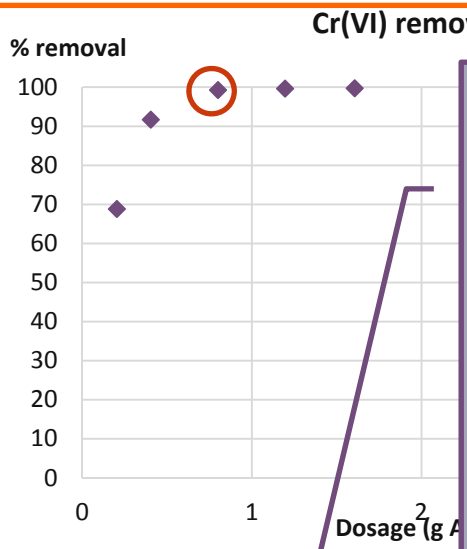
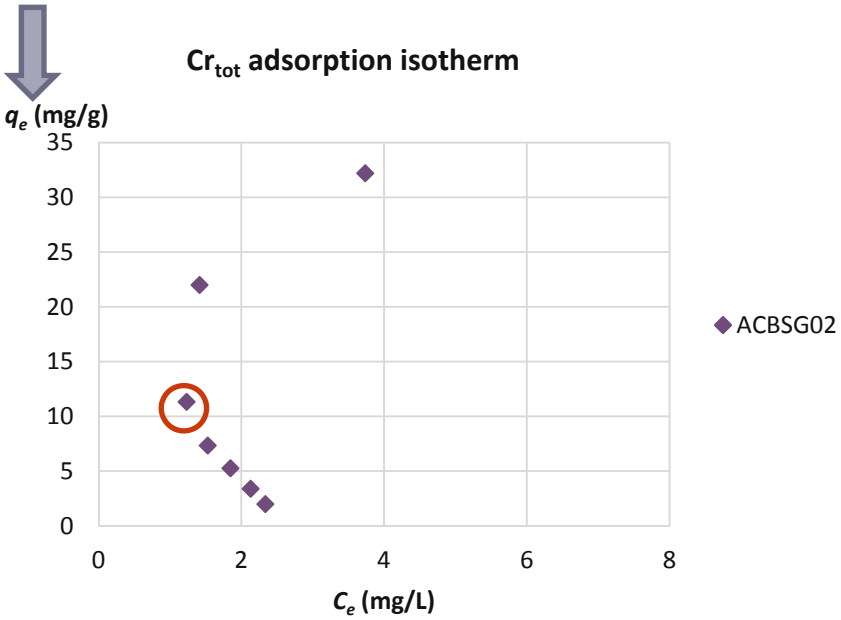
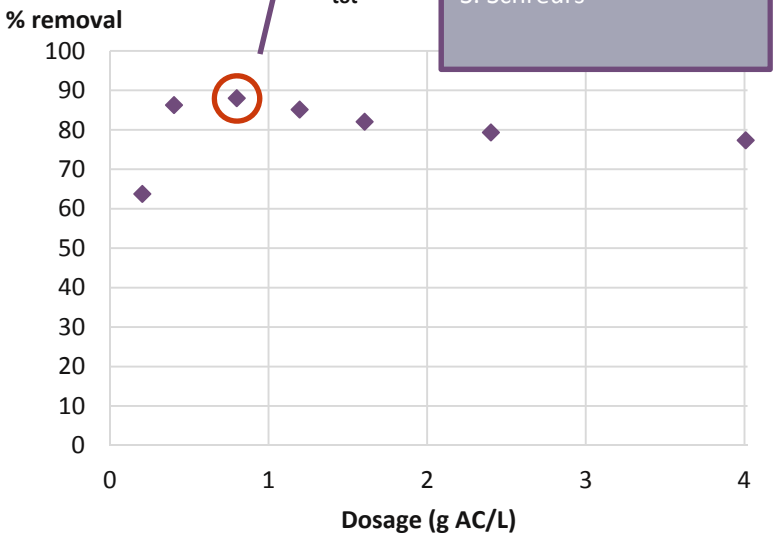
# On a sidenote:




Optimal dosage for removal of all chromium!

**Chromium(VI) removal using activated carbon prepared from brewers' spent grain**

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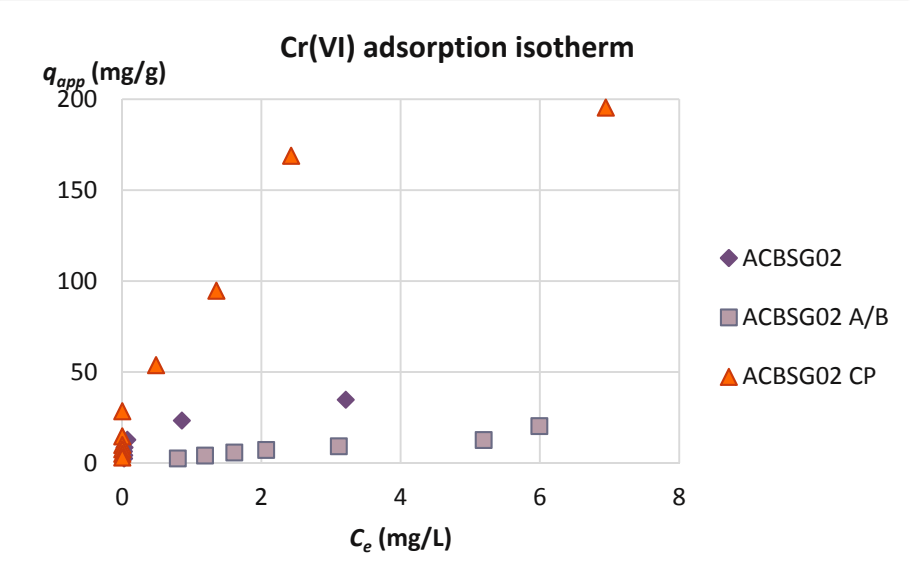


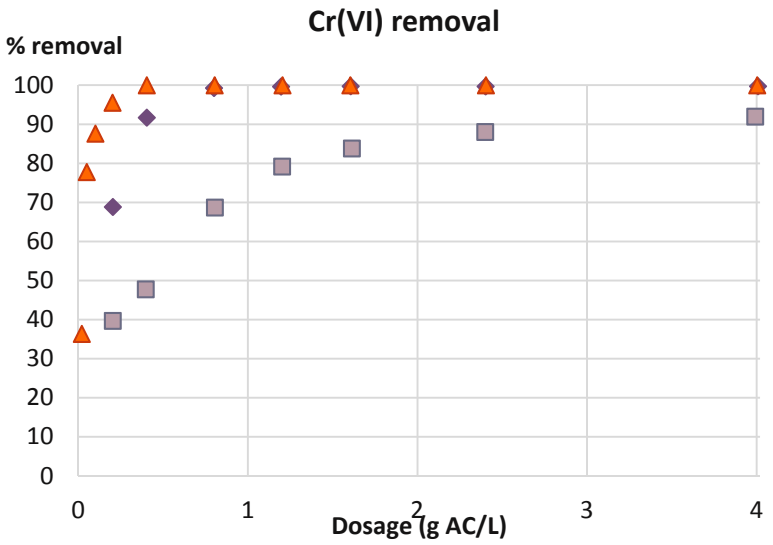


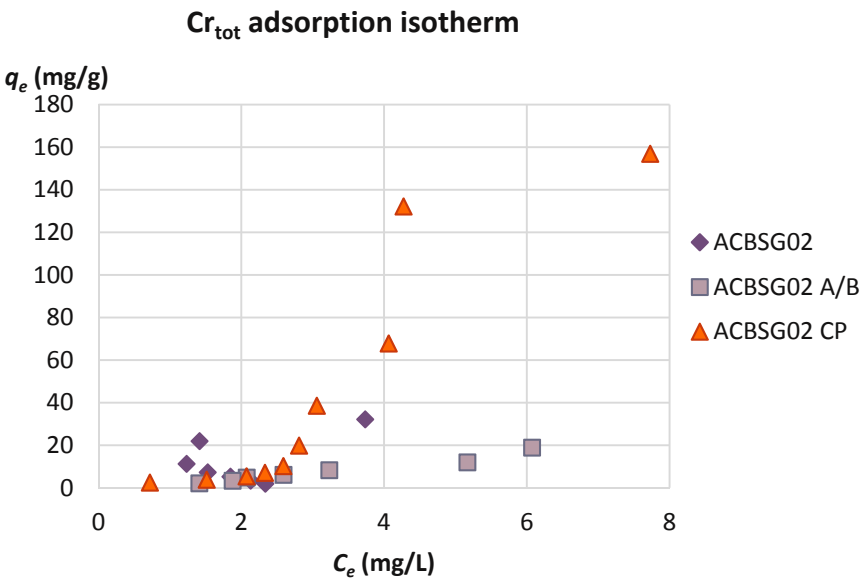


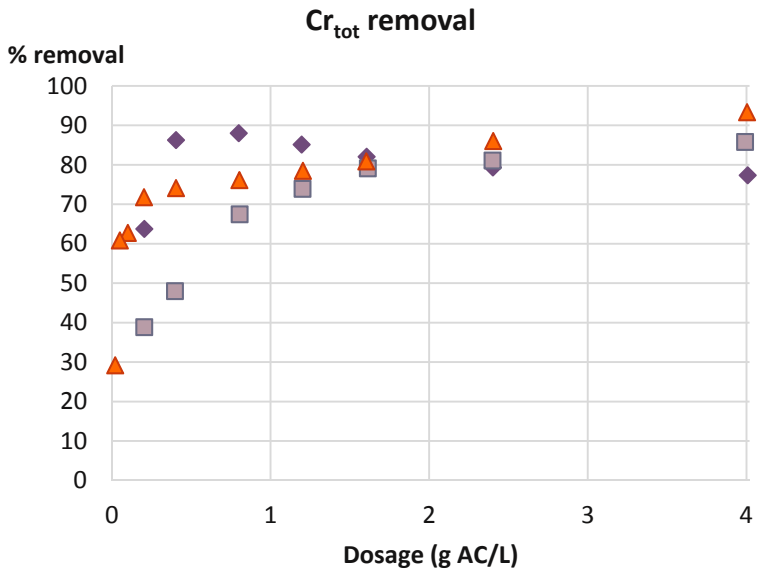




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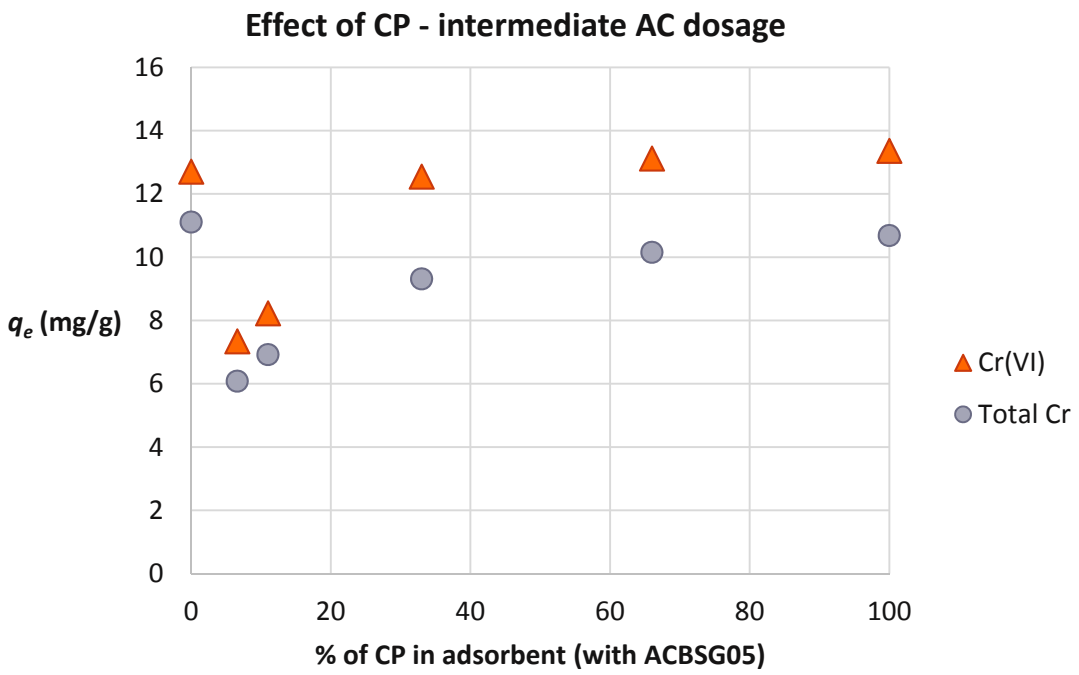
# Influence of AC/copolymer ratio

- Intermediate dosage: 1 g AC/L
  - 25 mg AC + 25 mL Cr(VI) solution



## Kinetics of adsorption

- 20 mg AC + 25 mL Cr(VI) solution
- 11 time intervals:
  - 0.5 / 1 / 1.5 / 2 / 2.5 / 3 / 4 / 5 / 6 / 16 / 24 h

- Pseudo first order model:
  - $q_t = q_e(1 - e^{-k_1 t})$

- Pseudo second order model:
  - $q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t}$



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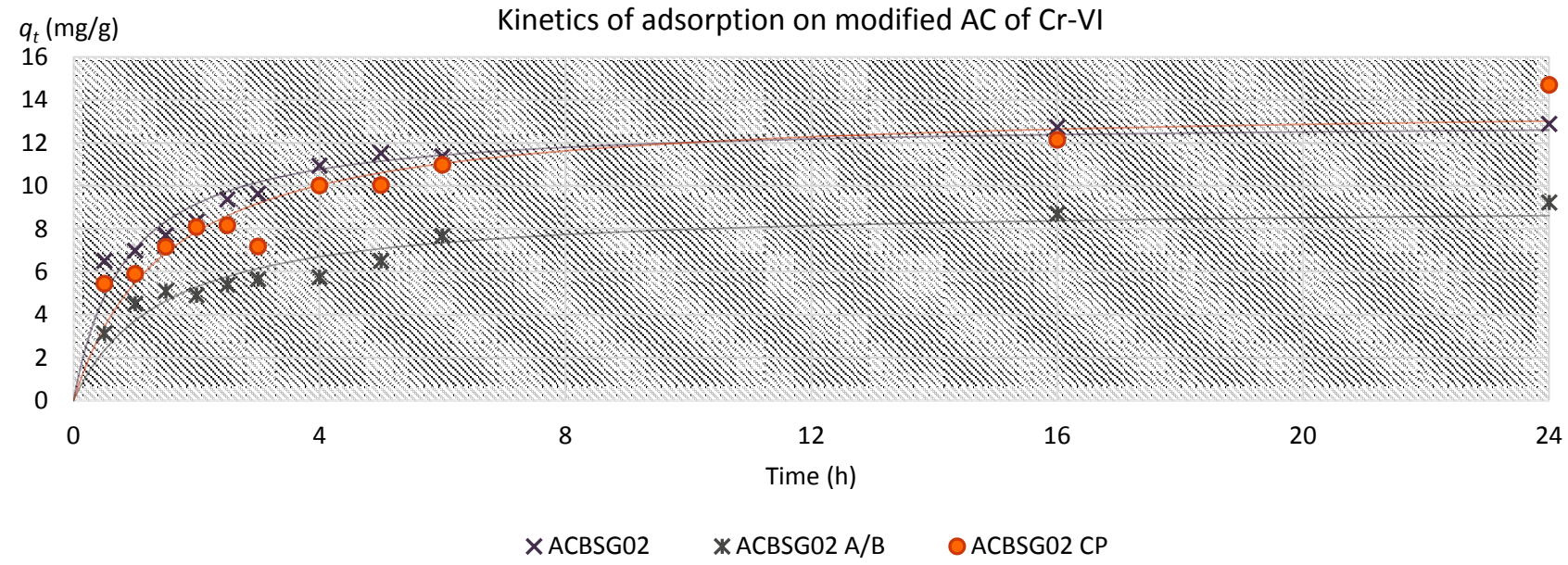
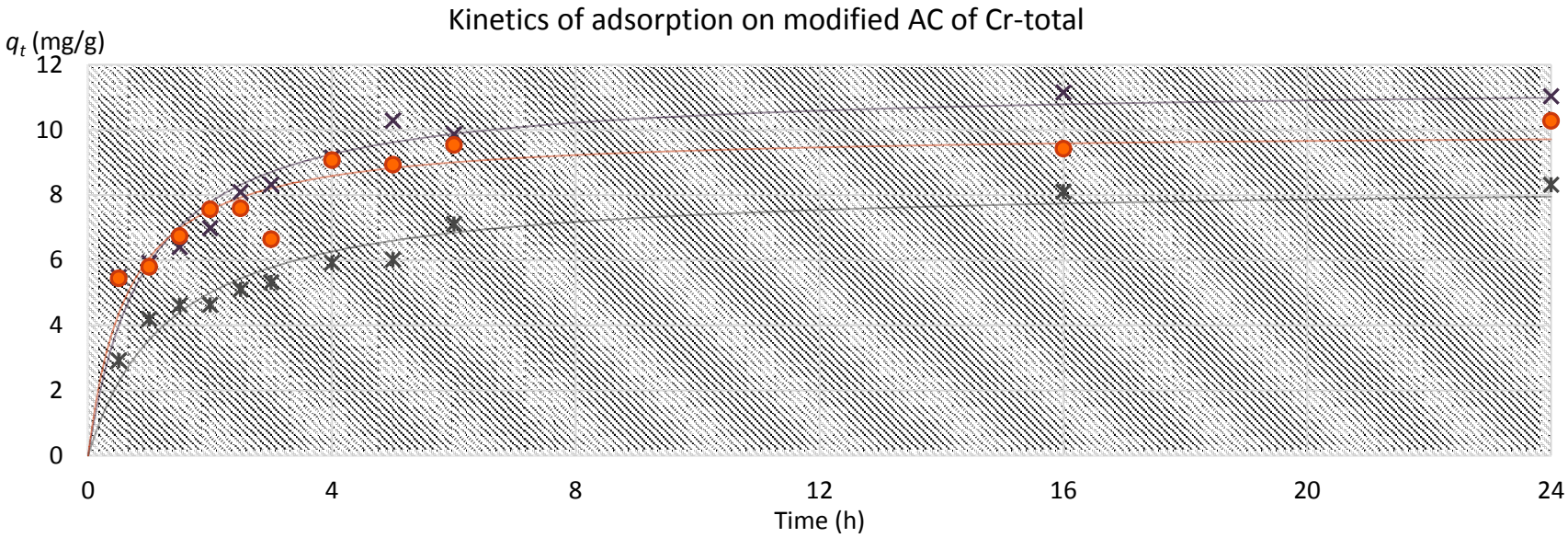
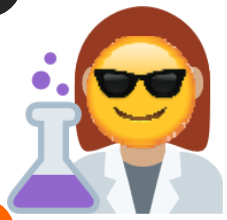

Kinetics of adsorption on modified AC of Cr-VI
$q_t$ (mg/g)
16
14
12
10
8
6
4
2
0
0
4
8
12
16
20
24
Time (h)
ACBSG02
ACBSG02 A/B
ACBSG02 CP


Kinetics of adsorption on modified AC of Cr-total
$q_t$ (mg/g)
12
10
8
6
4
2
0
0
4
8
12
16
20
24
Time (h)

**Circular economy**

Closing resource and energy loops

**Low specific adsorption capacity of activated carbon**



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Toxic, mutagenic, carcinogenic
Soluble.

**Production of Brewer's spent grain (BSG)**

85 % of brewery waste
$271 \cdot 10^{6}$ kg per year



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## Conclusion

- Acid/basic treatment of AC
  - No improvement in adsorption capacity
- Treatment of AC with quaternary ammonium end group
  - Greatly enhanced adsorption capacity
    - Especially at very low dosage
  - Effect is only caused by copolymer
    - No synergy
- Unmodified AC has best removal rate for Cr(VI)
  - But: $Cr_{tot}$ is removed faster by AC/CP



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