Circular economy
Closing resource and energy loops

Chromium (VI) in the environment
Welding, pigments,...
Toxic, mutagenic, carcinogenic
Soluble.

Low specific adsorption capacity of activated carbon

Production of Brewer’s spent grain (BSG)
85% of brewery waste
271 kton per year
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
Production of activated carbon (AC)

Coal / Biomass + Steam activation → AC

Surface area

Heat Pressure Radiation

"Activated Charcoal" by Mydriatic - Own work. Licensed under CC BY-SA 3.0 via Commons
Modification of AC

01 AC
Norit GAC 1240
Filtrasorb F400
ACBSG02: 800 °C / 30 min / 10 mL
ACBSG05: 800 °C / 45 min / 15 mL
Commercial ACs
AC from brewer’s spent grain

02 AC A/B
I. 8 g of AC + 40 mL of 7 M HNO₃: 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


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.

Chromium(VI) adsorption experiments

- The Cr(VI) solution
  - $\text{K}_2\text{Cr}_2\text{O}_7$
  - $10 \text{ mg/L, pH} = 2$ (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
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 (\(q_e - \text{mg/g}\)) versus equilibrium concentration (\(c_e - \text{mg/L}\))
  - Percent removal (%) versus AC dosage (g/L)
Cr(VI) adsorption isotherm

- $q_{app}$ (mg/g)
- $C_e$ (mg/L)

Cr(VI) removal

- % removal
- Dosage (g AC/L)

- ACBSG02
- ACBSG02 A/B
- ACBSG02 CP
On a sidenote:

Cr(VI) adsorption isotherm

Optimal dosage for removal of all chromium!

Chromium(VI) removal using activated carbon prepared from brewers' spent grain
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Cr$_{\text{tot}}$ adsorption isotherm

Optimal dosage for removal of all chromium!
Cr(VI) adsorption isotherm

Cr(VI) removal

Cr\textsubscript{tot} adsorption isotherm

Cr\textsubscript{tot} removal

Dosage (g AC/L)
Influence of AC/copolymer ratio

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

![Graph showing effect of CP - intermediate AC dosage]
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:
  - \( q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \)
Kinetics of adsorption on modified AC of Cr-VI

Kinetics of adsorption on modified AC of Cr-total
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271 $\times 10^6$ kg per year
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: $\text{Cr}_{\text{tot}}$ is removed faster by AC/CP
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