Adsorption isotherm and kinetics study of acid-extractable organics removal from oil sands process-affected water on biochar and activated carbon

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Outline

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- Conclusions

2.2 volumes of freshwater are required for each volume of bitumen produced

Oil sands process-affected water (OSPW) contains salts, heavy metals, phenols, benzene, toluene, and organic acids (e.g., naphthenic acids (NA))

NA above 5 mg/L can cause toxicity to a variety of organisms

For environmental discharge and reclamation process, NA needs to be reduced in OSPW


Naphthenic acids

- NA is a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids \(^{1}\)
- Both a hydrophilic (carboxylic group) and a hydrophobic (non-polar aliphatic) end \(^{1}\)
- Empirical formula \(C_nH_{2n+z}O_2\), n carbon number included R, \(CH_2\) and ring carbons \(^{1}\)
- Acid extractable organics (AEO) considered as NA \(^{2}\)
- AEO Fourier Transform Infrared (FTIR) spectrum is identical to commercial NA \(^{2}\)

Naphthenic acid structure \(^{2}\)

2. Grewer et al., 2010. *Sci. Total Environ.* 408(23), 5997-6010
**Benefits-Biomass**
- Biomass has significant carbon content (60 million ton C/yr in 2003) 1
- Confine atmospheric carbon 2

**Drawbacks-Biomass**
- Yield is very low (15-20% fixed carbon content in biomass) 3
- Transportation cost: Fixed cost is $5/ton; variable cost is $0.12/ton-km 4

**Benefit- Biochar vs activated carbon (AC)**
- Production cost: $245/ton biochar vs $1500/ton AC 5

**Drawback- Biochar vs AC**
- Adsorption capacity: Biochar (0-30%) vs AC (70-95%)

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2. Lehmann, J., Joseph S., **2009. Biochar for Environmental Management: Science and Technology.**
The main objective of this study is

- To obtain AEO adsorption isotherm and kinetics data required for process design using biochar and activated carbon
Preparation of biochar and AC

**Commercial activated carbon (AC)**
- Norit AC - coal based, steam activated and powder
- ColorSorb G5 - wood based, steam activated and powder
- Darco AC - coal based, steam activated and granular

**Biochar, Acidified biochar and CO₂ Aspen AC**

Biomass → Pyrolysis at vertical down-flow packed bed reactor

- 600°C, N₂ for 0.5 h

Aspen biochar → Activation

- 800°C, CO₂

CO₂ Aspen AC

Wheat straw or Hemp shives biochar → Pyrolysis at rotary drum pyrolyzer → Drying at 105°C for 12 h

- 600°C, no gas for 0.5 h

- 13% impregnation of H₂SO₄

Acidified Hemp shives biochar
Characterization and Adsorption tests

- Physical property analysis - N₂ adsorption
- Batch adsorption - incubating shaker
- Analysis - Total organic carbon analyzer

**Batch adsorption procedure**

- **0.02/0.4 g of biochar or AC sample**
  - Adsorption isotherm
  - 0.01-1.5 g of biochar or AC sample

1. **Mixing**
2. **Shaking at 225 rpm, 25°C for 24 hrs**
3. **Filter**
4. **TOC analysis**

**Batch adsorption procedure**

\[
AEO \text{ removal (mg/g)} = \frac{C(\text{feed}) - C(\text{after adsorption})}{\text{adsorbent dose}}
\]

\[
AEO \text{ removal (%) } = \frac{C(\text{feed}) - C(\text{after adsorption})}{C(\text{feed})} \times 100%
\]
Norit AC had the highest adsorption capacity of 49 mg/g

All biochar had very low adsorption capacity (1.2-2.1 mg/g)

CO₂ activated Aspen AC had adsorption capacity of 41 mg/g
Commercial AC and CO₂ activated AC removed more than 90% AEO

Acidified Hemp shives removed 41% AEO compare to 4% without acidification

Wheat straw biochar removed 21% AEO
Adsorption isotherms

Adsorption isotherm - describing a phenomenon to retention or mobility of a substance from aquatic media to a solid phase at constant temperature and pH

**Langmuir isotherm**

\[ q_e = \frac{a_0 b C_e}{1 + b C_e} \]

**Freundlich isotherm**

\[ q_e = K_F C_e^n \]

- \( q_e \) - amount AEO adsorbed in solid surface
- \( C_e \) - equilibrium concentration
- \( a_0 \) and \( b \) - Langmuir constants
- \( K_F \) and \( n \) - Freundlich constants
Norit AC isotherm data were fit well with both Langmuir ($R^2 = 0.99$, $RMSE = 2.8$ & $\chi^2 = 1.3$) and Freundlich isotherm model ($R^2 = 0.98$, $RMSE = 4.5$ & $\chi^2 = 3.6$)

Acidified Hemp shives isotherm data were not fit well by either the Langmuir ($R^2 = 0.72$, $RMSE = 0.4$ & $\chi^2 = 0.5$) or Freundlich model ($R^2 = 0.74$, $RMSE = 0.4$ & $\chi^2 = 0.4$)
Design of single-stage batch adsorption system

**Batch adsorption process**

AEO Initial Concentration, $C_o=65$ mg/L, time $t=0$

AEO Equilibrium concentration, $C_e=1.5$ mg/L, time $t=t$

- Norit AC required : 12 kg
- Acidified biochar required : 212 kg
- Biochar required : 2690 kg

**Design equation**

$$\frac{M}{V} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{a_0 b C_e} \frac{1}{1 + b C_e}$$

**Adsorption isotherm curve for Norit AC**

- $(21$ mg/g, $6.5$ mg/L)
- $(5.5$ mg/g, $1.5$ mg/L)
- $(49$ mg/g, $18.8$ mg/L)
AEO adsorption kinetics study

- Pseudo first-order model:
  
  \[ \ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \]

- Pseudo second-order model:
  
  \[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \]

- Intra-particle diffusion model:
  
  \[ q_t = k_{pi} t^\frac{1}{2} + c_i \]

- \( q_t \) - amount AEO adsorbed in solid surface at time, \( t \)
- \( k_1 \) – pseudo first-order rate constant
- \( K_2 \) – pseudo second-order rate constant
- \( K_{pi} \) – intra-particle diffusion model
- \( c_i \) - constant applicable for stage i
The kinetic data for Norit AC and wheat straw biochar were both fit well by the pseudo-2nd order model. Both chemisorption and physisorption were involved. After 200 min both samples reached equilibrium, and the kinetic rate constants were high (0.03 g/mg.min)

Design of column adsorption process

Thomas equation for an adsorption column

\[
\frac{C_e}{C_0} = \frac{1}{1 + e^{\frac{k_2 (q_e M - C_0 V)}{Q}}}
\]

\[
\ln \left( \frac{C_0}{C_e} - 1 \right) = \frac{k_2 q_e M}{Q} - \frac{k_2 q_e V}{Q}
\]

- Norit AC required: 33 kg
- Biochar required: 2080 kg

Conclusions

- Norit AC adsorption data were fit well with both Langmuir isotherm and Freundlich isotherm.
- In batch adsorption, 12 kg Norit AC, 212 kg acidified biochar and 2690 kg biochar are required to treat 1000 L of OSPW containing (Initial: 65 mg/L AEO, desired: 1.5 mg/L).
- The kinetic data for Norit AC and wheat straw biochar were both fit well by the pseudo-second order model and the samples reached at equilibrium after 200 min.
- In column adsorption, 33 kg Norit AC and 2080 kg biochar are required to treat 1000 L of OSPW with 10 L/min flowrate (Initial: 65 mg/L AEO, desired: 1.5 mg/L).
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