Activated Carbon Classifications and Selection Criteria for Water and Wastewater

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OTCO Procrastinator's Workshop

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Agenda

- Activated carbon basics
- Uses for activated carbon treatment
- Activated carbon manufacturing
- Carbon adsorption kinetics
- General properties for activated carbon products
- Why proper carbon selection is important
- Carbon dosing and usage predictions
- Selecting activated carbon products for performance

Activated Carbon Basics

- Activated carbon has two basic classifications
  - Powdered activated carbon (PAC)
  - Granular activated carbon (GAC)
    - Generally GAC out performs PAC in all cases, but should it always be preferred?
- Carbon selection is complex and site specific
  - PAC generally used or seasonal treatment issues, one time use
  - GAC typically used when source contaminants persist year round, run carbon to breakthrough
- Cost effective solutions utilize carbon selection according to treatment performance and NOT according to unit cost

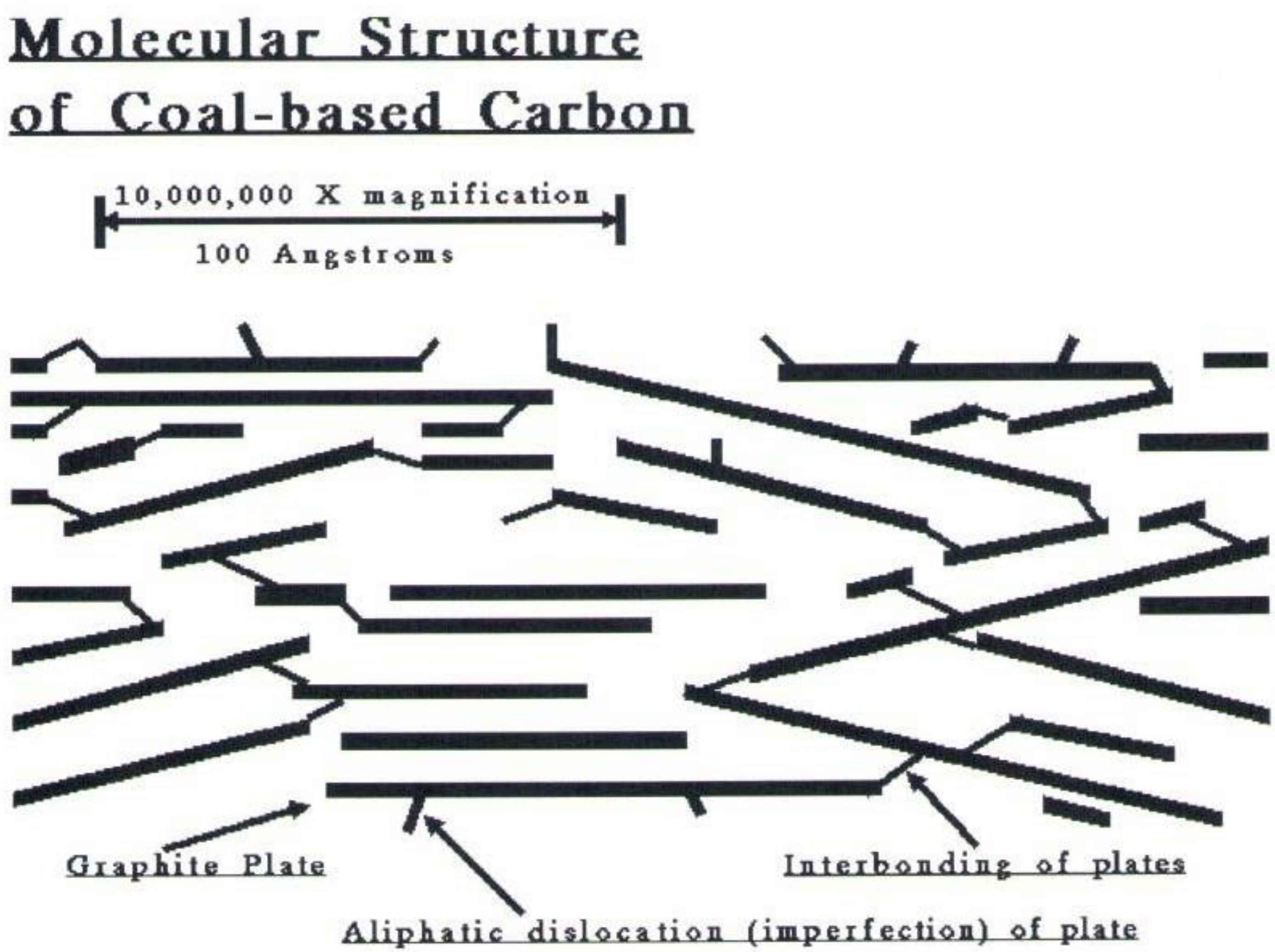
Activated Carbon Basics

- Activated carbon treatment is an adsorption process that removes organic contaminants from aqueous solutions
  - Adsorption involves adherence of the adsorbate to the surface structure of the carbon
    - Occurs in the micropores of the carbon material deep within the carbon particle, not on the particle surface
    - Carbon ionic bonding holds contaminants within the pores
  - Organics can be desorbed (pushed off) from carbon
    - When more active organic material is introduced into the system
    - If inlet concentration decreases significantly
  - Organics can be removed from carbon by chemical and thermal means (reactivation processes)

Activated Carbon Basics

- Activated carbon is a hybrid mixture of a wide variety of graphite platelets interconnected by carbon bonding organized in a random fashion (definition from Calgon Carbon)
- Pathways between the platelets make up the carbon pore structure
  - Configuration of the platelets influenced carbon source material
    - Generally determines pore structures, internal surface area, and surface chemistry
  - Density of the source carbon develops into an extensive platelet structure of the final product
    - Dense materials create tighter platelet structures with smaller pores
    - Ease of transport needed for contaminants to reach the adsorption sites

Activated Carbon Basics



Courtesy of Calgon Carbon Corporation

Activated Carbon Basics

- Unique trimodal pore structure of carbons

TYPICAL PORE SIZES IN ACTIVATED CARBONS		
Category	Size in nanometers (nm)	Size in Angströms (Å)
Micropores	<2	<20
Mesopores	2 to 50	20 to 500
Macropores	>50	>500

Activated Carbon Basics

- Bituminous-based carbons
  - Good development of micropore, mesopore, and macropore mixtures
  - Good transport capabilities
  - Good adsorptive capacity
    - 500 mg/g to 1,100 mg/g IN
  - Relatively high surface area
    - 600 m^2/g to 1,400 m^2/g

GAC

PAC

Activated Carbon Basics

Lignite coal (brown coal)

- Lignite-based carbons
  - Good development of macropores with less development of mesopores and micropores
  - Good transport capabilities for smaller molecules (MW 1,650 or less)
  - Lower adsorptive capacity
    - Up to 600 mg/g IN
  - Relatively lower surface area
    - Up to 1,250 m^2/g

Activated Carbon Basics

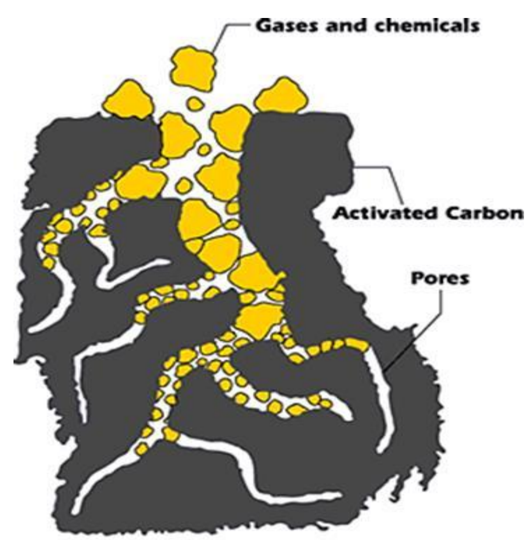
- Wood-based carbons
  - Good development of micropore, mesopore, and macropore mixtures
  - Good transport capabilities
  - Good adsorptive capacity
    - 500 mg/g to 1,100 mg/g IN
  - Relatively high surface area
    - Up to 1,480 m^2/g

Activated Carbon Basics

- Coconut-based carbons
  - Good development of micropores with less development of mesopores and macropores
  - Lower transport capabilities, but good for smaller molecules (MW 700 or less)
  - Good adsorptive capacity
    - Up to 1,100 mg/g IN
  - Relatively high surface area
    - Up to 1,480 m^2/g

Activated Carbon Basics

- Adsorption occurs in the micropore structures of carbon
- Adsorbates must travel (transport) from the outer surface of the carbon particle to the internal surface area of the carbon
  - Macropores and mesopores responsible for transport
  - High transport capabilities are needed for molecules to enter the internal spaces

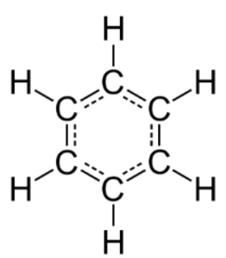


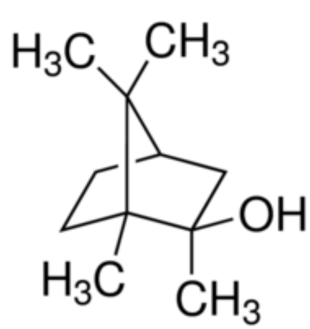
Activated Carbon Basics

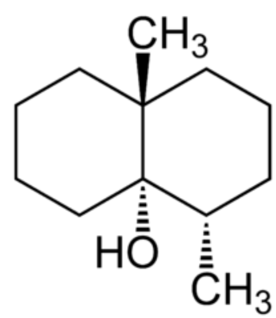
- EMT (external mass transfer) delivers adsorbates to the outer surface of carbon (film diffusion)
- IMT (internal mass transfer) conveys adsorbates to micropore adsorption sites (carbon bonding)
- EMT and IMT are driven by the concentration gradient of the solution
  - Adsorption typically involves chemical bonding to the carbon
  - Poor transport develops into carbon fouling (blocking of pore structures)

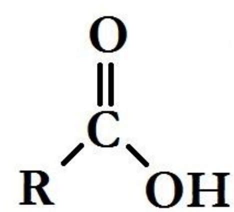
Activated Carbon Basics

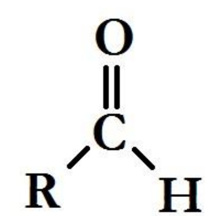
- Very general demonstration of available pore size
  - Micropores should be **1.3 to 1.8** times larger than the molecular size of the adsorbates to be removed
  - Mesopores should be about **5** times larger than the molecular size of the adsorbates to be removed
    - Think of adsorbates as spheres rather than elongated shapes

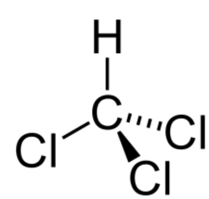


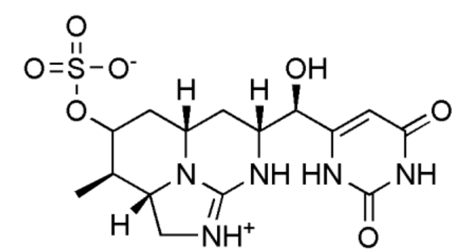












Activated Carbon Basics

- General sizing of adsorbates according to molecular weight
  - Spherical shape has a volume
  - Volume has associated diameter and radius
  - The diameter of the sphere must fit between the pores to reach adsorption sites

$$V = \frac{(0.73\frac{cm^3}{g})(\frac{10^{21}nm^3}{cm^3})}{6.023 * 10^{23}MW/g} * MW = 1.212 * \frac{10^{-3}nm^3}{MW} * MW$$

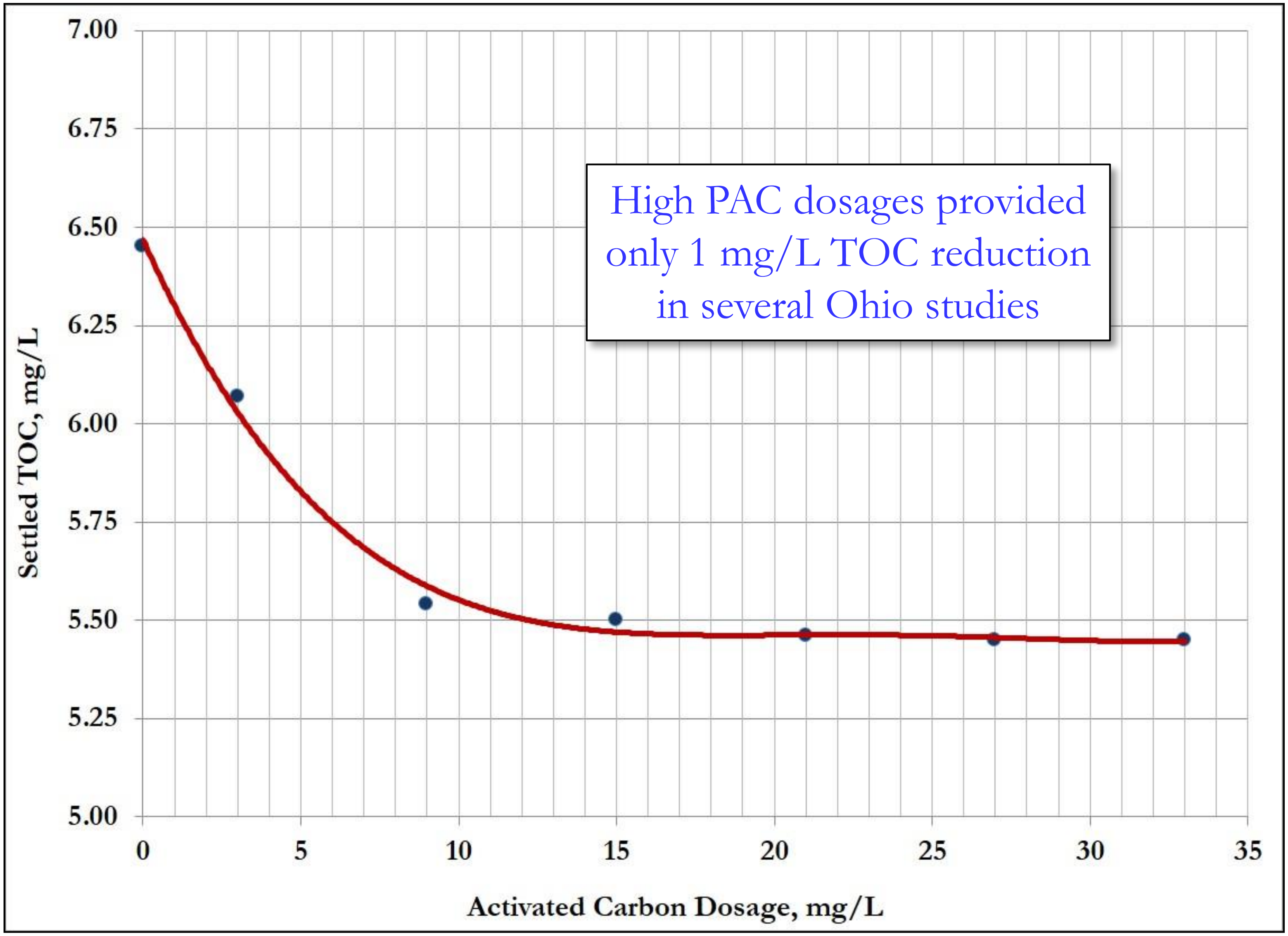
$$R_{min} = \left(\frac{3V}{4\pi}\right)^{1/3} * MW = 0.066 * MW^{1/3}$$

$$D_{min} = 2 * R_{min} * MW$$

Activated Carbon Basics

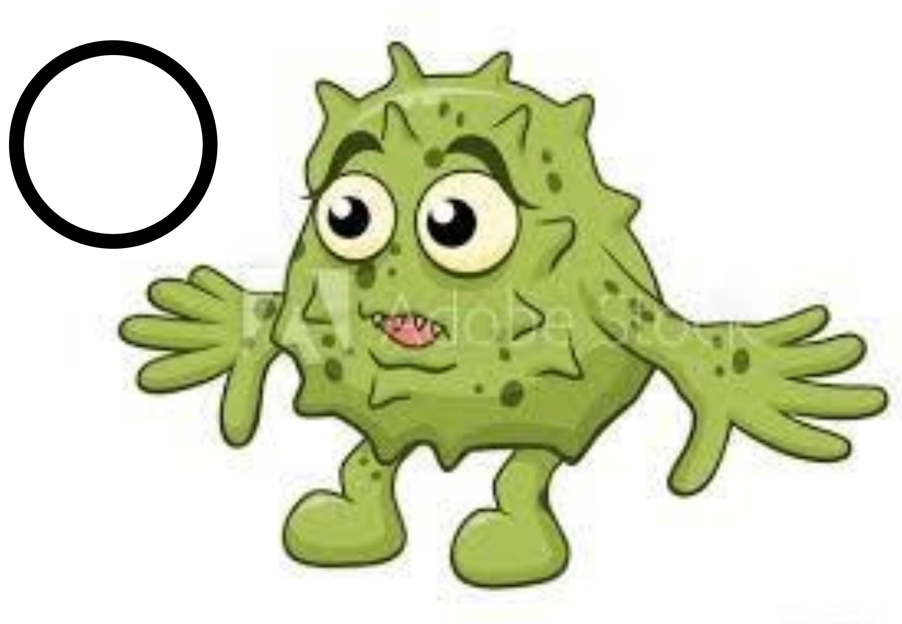
Contaminant	Formula	Molecular weight	Approx. diameter, nm	Transport pore size, nm	Adsorption pore size, nm
2-Methylisoborneol	$C_{11}H_{20}O$	168.3	**0.73**	**3.7**	**1.31**
Geosmin	$C_{12}H_{22}O$	182.3	**0.75**	**3.8**	**1.35**
Atrazine	$C_8H_{14}ClN_5$	215.7	**0.79**	**4.0**	**1.42**
Alachlor	$C_{14}H_{20}ClNO_2$	269.8	**0.85**	**4.3**	**1.53**
MTBE	$C_5H_{12}O$	88.2	**0.59**	**3.0**	**1.06**
Mucidone	$C_{11}H_{16}O_2$	180.2	**0.75**	**3.8**	**1.35**
Isobutyl mercaptan	$C_4H_{10}S$	90.2	**0.59**	**3.0**	**1.06**
Dimethyl sulfide	C_2H_6S	62.1	**0.52**	**2.6**	**0.94**
Methyl mercaptan	CH_3SH	48.1	**0.48**	**2.4**	**0.86**
Fulvic acids	-	>3,500	**2.01**	**10.1**	**3.6**
Humic acids	-	>100,000	**6.14**	**30.7**	**11.1**
Benzene	C_6H_6	78.1	**0.57**	**2.9**	**1.03**
Toluene	C_7H_8	92.1	**0.60**	**3.0**	**1.08**
Xylene	C_8H_{10}	106.2	**0.63**	**3.2**	**1.13**
Ethylbenzene	C_8H_{10}	106.2	**0.63**	**3.2**	**1.13**
Microcystin	$C_{49}H_{74}N_{10}O_{12}$	1,040	**0.67**	**3.4**	**1.21**
Cylindrospermopsin	$C_{15}H_{21}N_5O_7S$	415.4	**0.49**	**2.5**	**0.88**
Anatoxin-a	$C_{10}H_{15}NO$	165.2	**0.36**	**1.8**	**0.65**
Saxitoxin	$C_{10}H_{17}N_7O_4$	299.3	**0.88**	**4.4**	**1.58**
Trihalomethanes (THMs)	varies	119 - 253	**0.65 – 0.84**	**3.3 – 4.2**	**1.2 – 1.5**

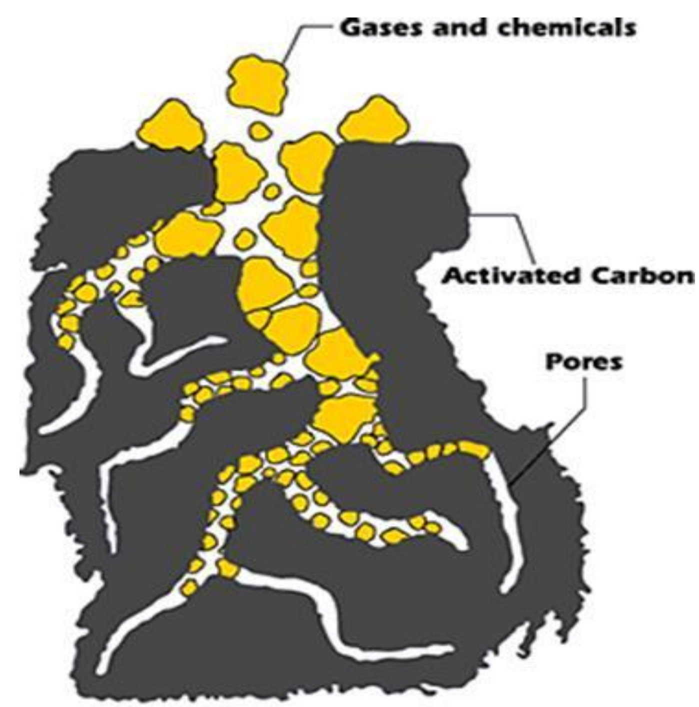
Activated Carbon Basics



Activated Carbon Basics

- Molecules that are too large must either be fractionated or elongated to fit through the pore, otherwise they will block the carbon pore structure preventing adsorption





Uses for Carbon Treatment - Water

- Taste and odor control
- Reductions in VOC's, SOC's, pesticides
- DBP's and precursor removal
- Reduction of PFAS (per-fluoroalkyl & poly-fluoroalkyl substances)
- Removal of BTEX (benzene, toluene, ethylbenzene, xylene) and other hydrocarbons
- Removal of cyanotoxins and other algal byproducts
- Removal of EDC's (endocrine disrupting compounds)
- Organics control (water and air)
- Removal of some PPCP's (pharmacueticals & personal care products)

Uses for Carbon Treatment - WW

- Reduction of COD, BOD, TOC
- Reductions in AOX (assimilable organic halides)
- Treatment for water reuse
- Flue gas treatment
- Removal of heavy metals (Ni, Cd, Cr, Pb, Zn, Hg)
- Removal of cyanides (CN)
- Treatment for bioassay and toxicity requirements
- Treatment for landfill leachate
- Removal of trace organics and micropollutants

Activated Carbon Manufacturing

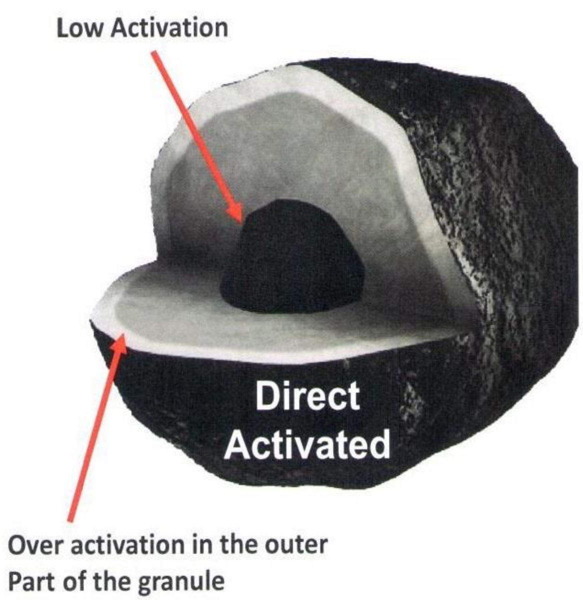
- Common starting materials
  - Bituminous coal
  - Sub-bituminous coal
  - Lignite coal
  - Wood products
  - Coconut shells (and other nut shells)
- Raw material type
  - Affects internal pore structures
  - Impacts relative surface area and adsorption capability
  - Develops specific carbon surface chemistry

Courtesy of Calgon Carbon Corporation

Activated Carbon Manufacturing

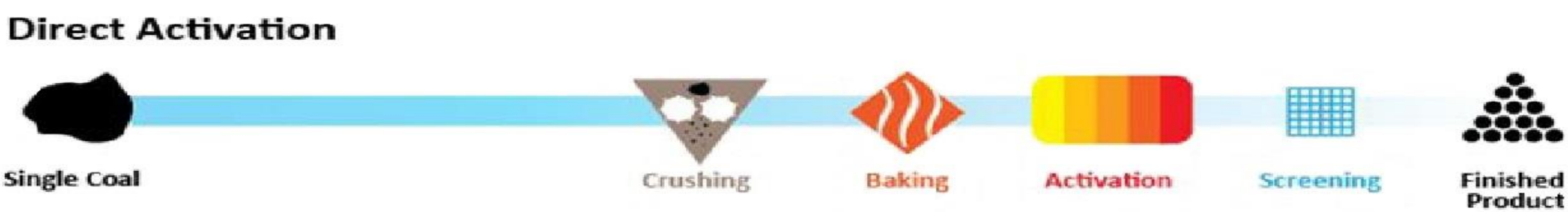
- Two step process
  - Step 1 - **Carbonization**
    - Heating to 500°C to 800°C without oxygen
    - Drives off undesirable organics and inorganics
    - Aligns crystalline structures
  - Step 2 - **Activation**
    - Heating to 850°C to 1,000°C with steam or CO_2
    - Increases pore sizes
    - Creates trimodal pore structures
    - Increases internal surface area

Activated Carbon Manufacturing (GAC)



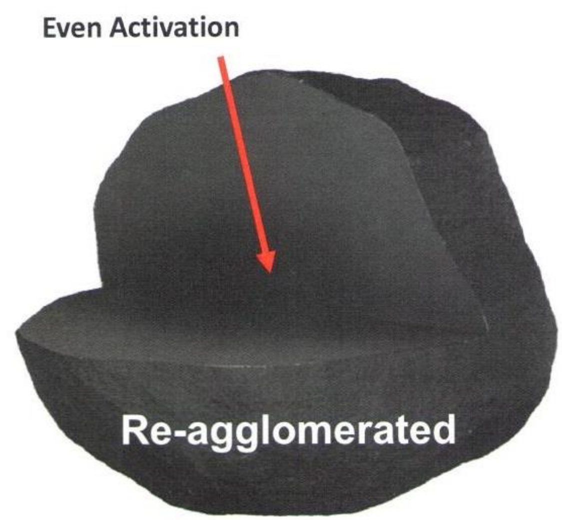
Graphics courtesy of Calgon Carbon Corporation

- Cheaper alternative
- Incomplete activation
  - Can increase carbon usage
  - Generally shorter life cycle
  - May increase treatment costs



Activated Carbon Manufacturing (GAC)

- More costly alternative
  - About 20% higher unit cost
- More even activation
  - Can decrease carbon usage
  - Generally longer life cycle
    - Up to double useful life observed
  - May reduce treatment costs



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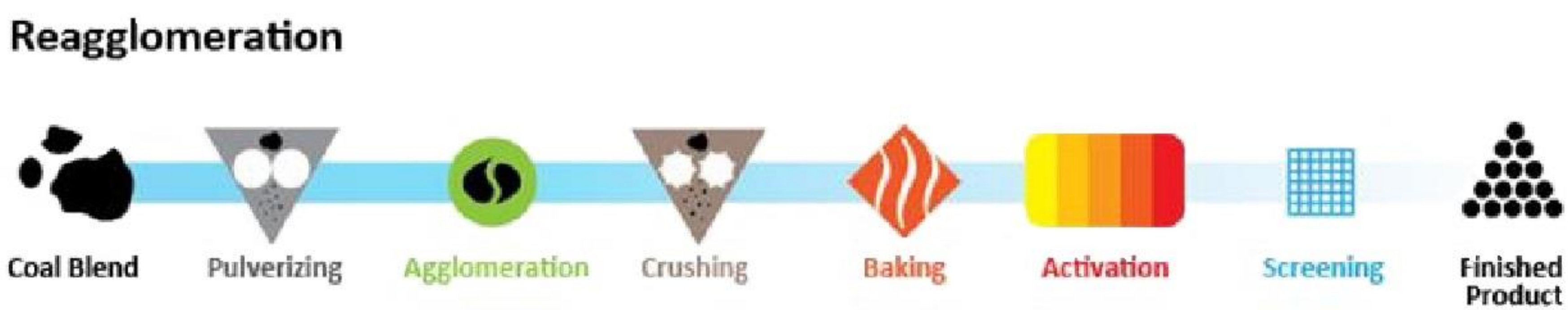
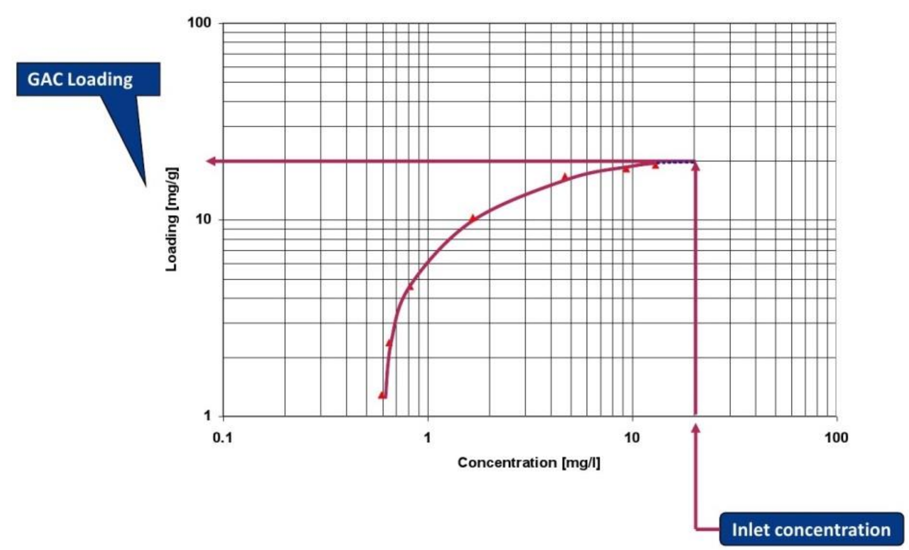


Carbon Adsorption Kinetics

- Different adsorbates removed at different rates
  - Adsorption approaches equilibrium levels in solution
  - Desorption can occur if multiple adsorbates are in solution
    - Highest K tends to win the activation site
- Water pH and temperature play an important role (equilibrium conditions)
  - pH levels greater than 8 and temperature <8°C
    - Hinder adsorption
    - Increase contact time and dosing
    - Particularly important for powdered carbon treatment

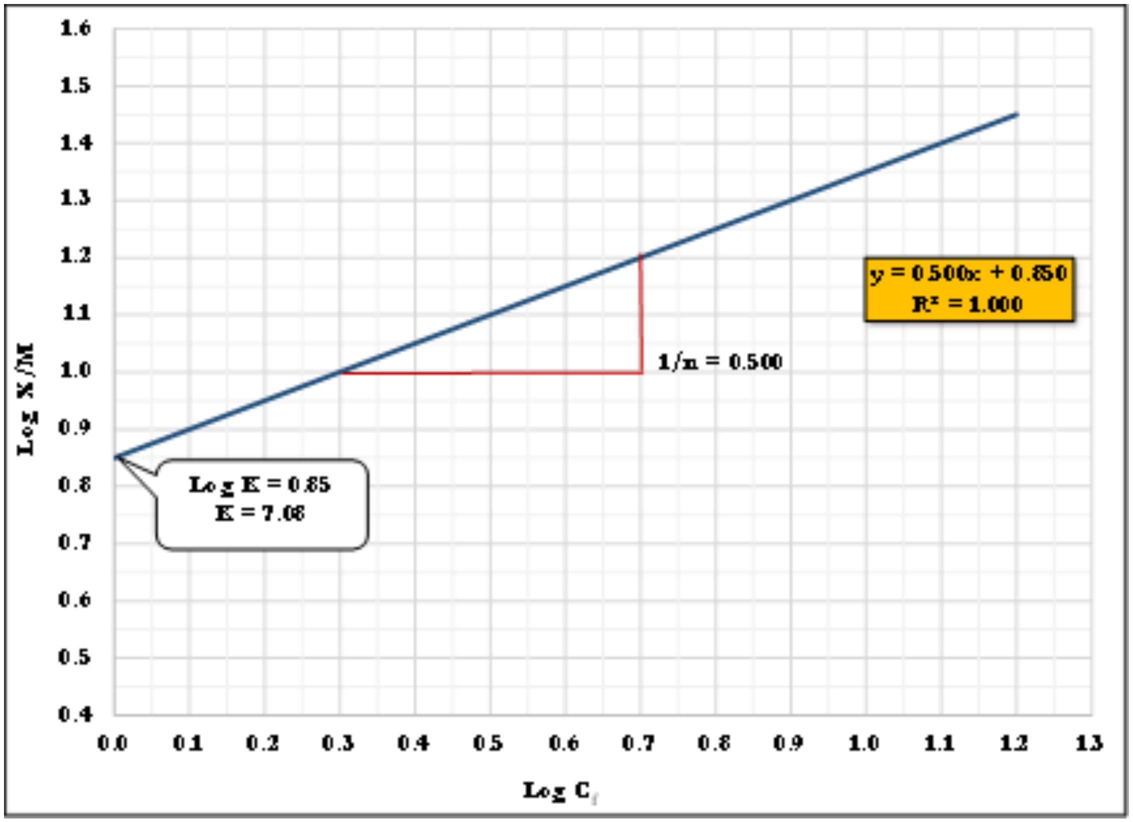
Carbon Adsorption Kinetics

- Adsorption isotherms predict carbon use rate
  - Define adsorptive capacity and intensity coefficients
  - Based on equilibrium conditions between carbon surface, adsorbate concentration, and adsorbate equilibrium concentration
  - Developed from experimental data
    - Specific activated carbon products
    - Specific adsorbates
    - Log-log plot of experimental data
  - Caution using isotherms
    - Multiple adsorbates
    - NOM impacts



Courtesy of Calgon Carbon Corporation

Carbon Adsorption Kinetics



- K and 1/n generated by isotherm log-log plot
  - **K** - adsorption capacity onto carbon
  - **1/n** - adsorption intensity (rate)

$q = K\,C_f^{1/n}$

q = adsorption coefficient, μg/g

K = adsorptive capacity, (μg/g)(L/μg)$^{1/n}$

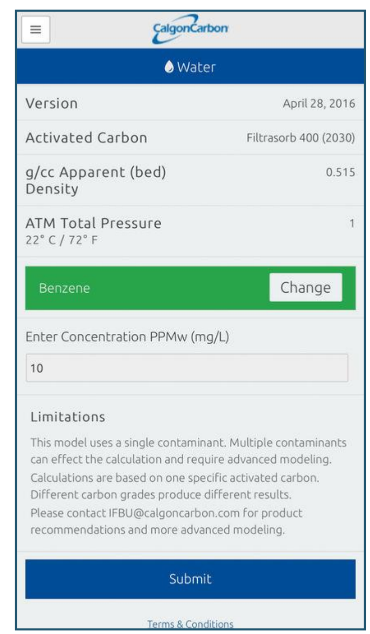
C_f = final adsorbate level, μg/L

$1/n$ = adsorption intensity

$C_i - C_f / q$ = *carbon dosage*

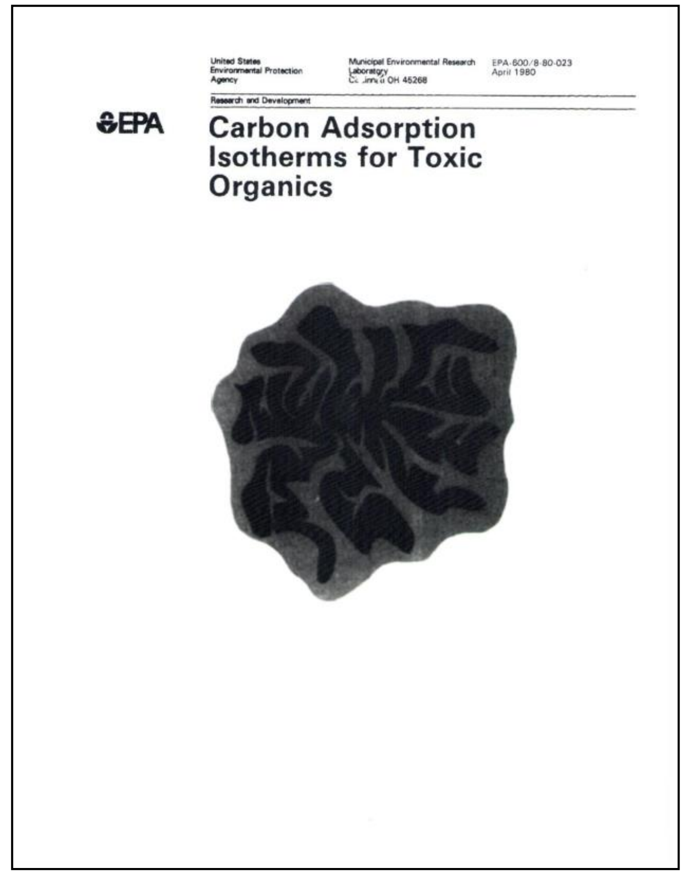
Carbon Adsorption Kinetics

- Published K and 1/n values
  - 70 common adsorbates in Water Quality and Treatment, 6th Edition, Chapter 14
  - Specific adsorbates might be obtained from carbon manufacturer
    - Some success experienced, but don't expect your contaminant to be tested by manufacturers
  - Activated carbon usage rate estimator (iPhone/iPad app)
    - Calgon Carbon Corporation free download in app store (CCURE)
      - – Terms and conditions apply
      - – Predicts usage rate in pounds per 1,000 gallons for many substances

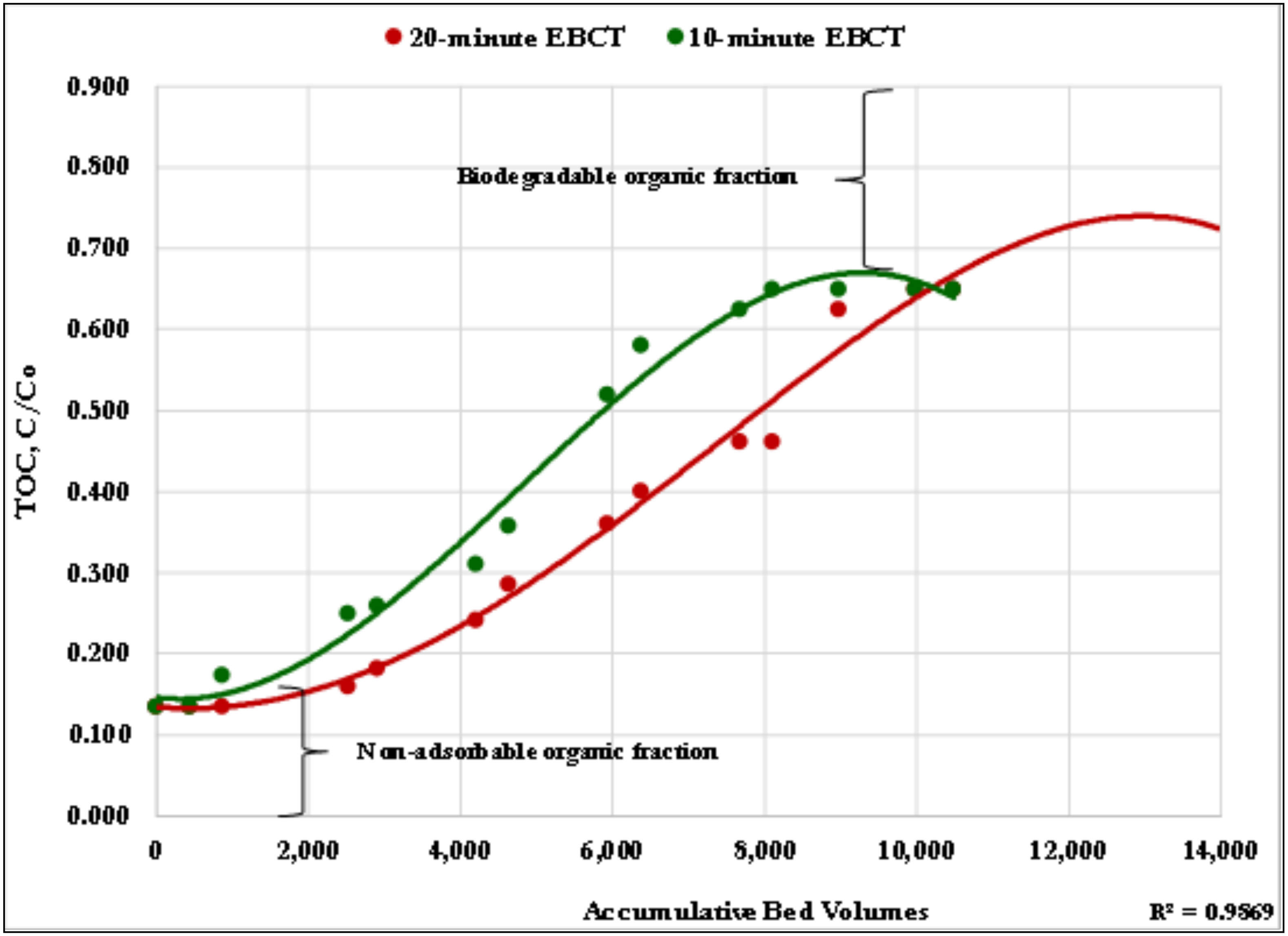


Carbon Adsorption Kinetics

- Published isotherms
  - USEPA "Carbon Adsorption Isotherms for Toxic Organics" 1980
  - Contains 130 organic substances with adsorption activity rates and isotherms developed from experimental data



Carbon Adsorption Kinetics GAC



Carbon Adsorption Kinetics GAC

- Adsorption continues in operation
  - Breakthrough reached on GAC bed
  - Desorption occurs
- EBCT important
  - Based on reaction rates and carbon type
    - T&O, TOC, DBP precursors – 10 minutes
    - Cyanotoxins – 15 minutes
    - DBP's, PFC's – 20 minutes

GAC reactors Greater Ouachita, Louisiana

General Properties of Carbon Products

GENERAL ACTIVATED CARBON PROPERTIES ACCORDING TO RAW MATERIAL				
Property	**Coconut-based**	**Bituminous coal-based**	**Lignite coal-based**	**Wood-based**
Micropore volume	High	High	Medium	Low to medium
Mesopore volume	Medium	Medium to High	Low to Medium	Medium to High
Macropore volume	Low	Low	High	High
GAC Hardness	High	High	Low	Medium
Ash content	Up to 5%	3% to 8%	Up to 20%	3% to 8%
Apparent density	0.35 to 0.50 g/cm^3	0.32 to 0.60 g/cm^3	0.2 to 0.36 g/cm^3	0.24 to 0.39 g/cm^3
Iodine number	Up to 1,100 mg/g	Up to 1,000 mg/g	Up to 600 mg/g	Up to 1,100 mg/g
Relative surface area	Up to 1,480 m^2/g	Up to 1,400 m^2/g	Up to 1,250 m^2/g	Up to 1,480 m^2/g
GAC Regeneration capability	Good	Good	Poor	Fair

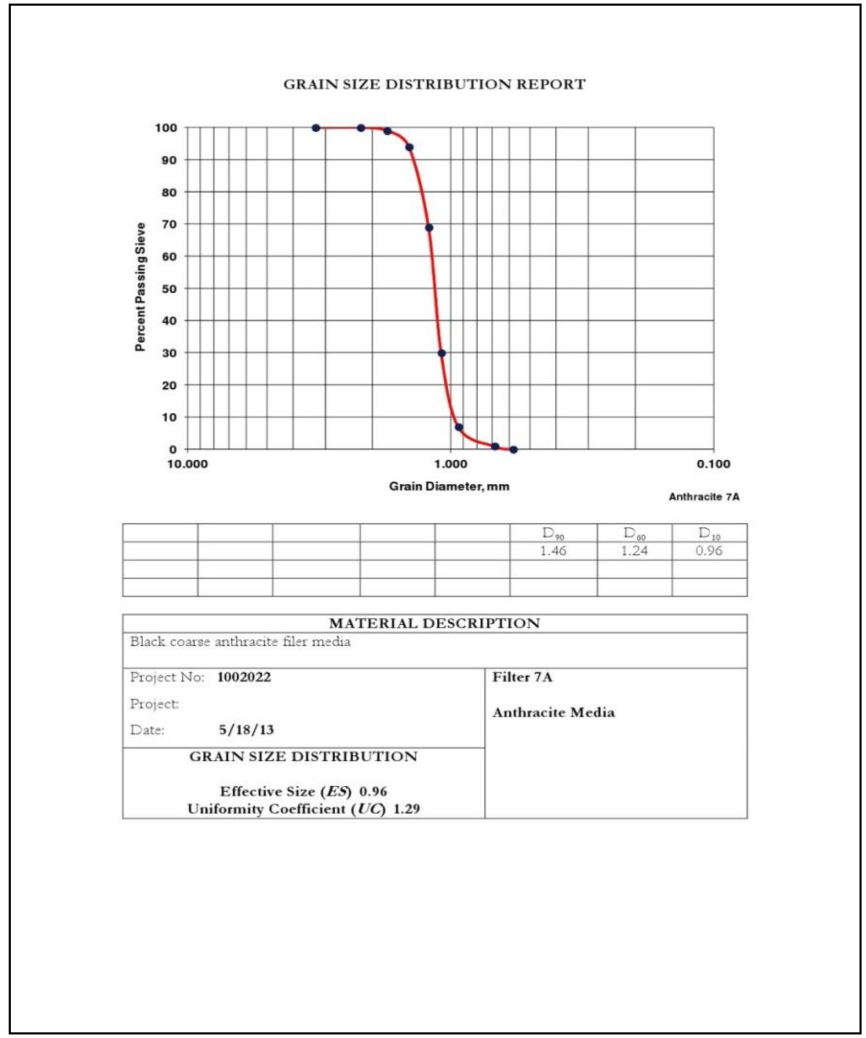
General Properties of Carbon Products

- Ash content (PAC/GAC)
  - Reduces adsorption activity
  - Reduces reactivation efficiency
  - Should be less than 10%

- Abrasion number (GAC only)
  - Ro-Tap abrasion test common
  - Structural strength of GAC to withstand shear
    - Backwash impacts
  - Should be greater than 75

General Properties of Carbon Products

- Effective size(GAC only)
  - Grain size distribution in mm similar to filter media
  - Differs depending on process use
    - Filter GAC caps should be matched to sand for bed expansion (1.0 mm to 2.0 mm ES)
    - GAC contactors usually 0.5 mm to 0.8 mm ES
- Uniformity coefficient (GAC only)
  - Typical 1.8 to 2.1 for GAC products
  - Assists in controlling backwash rates
  - Obtain fluidization curve from your GAC manufacturer

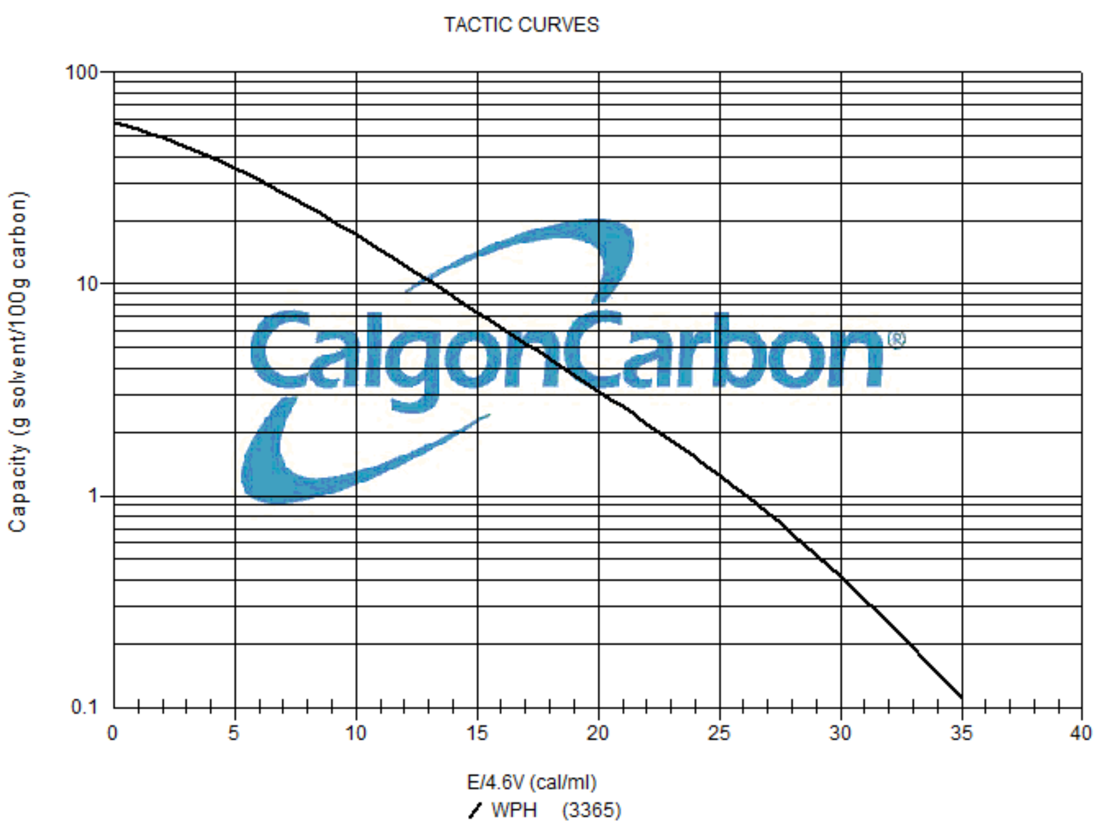


General Properties of Carbon Products

- Trace capacity number TCN (PAC/GAC)
  - Measures high energy sites needed for adsorption (micropores)
  - Greater than 9 grams/cm^3

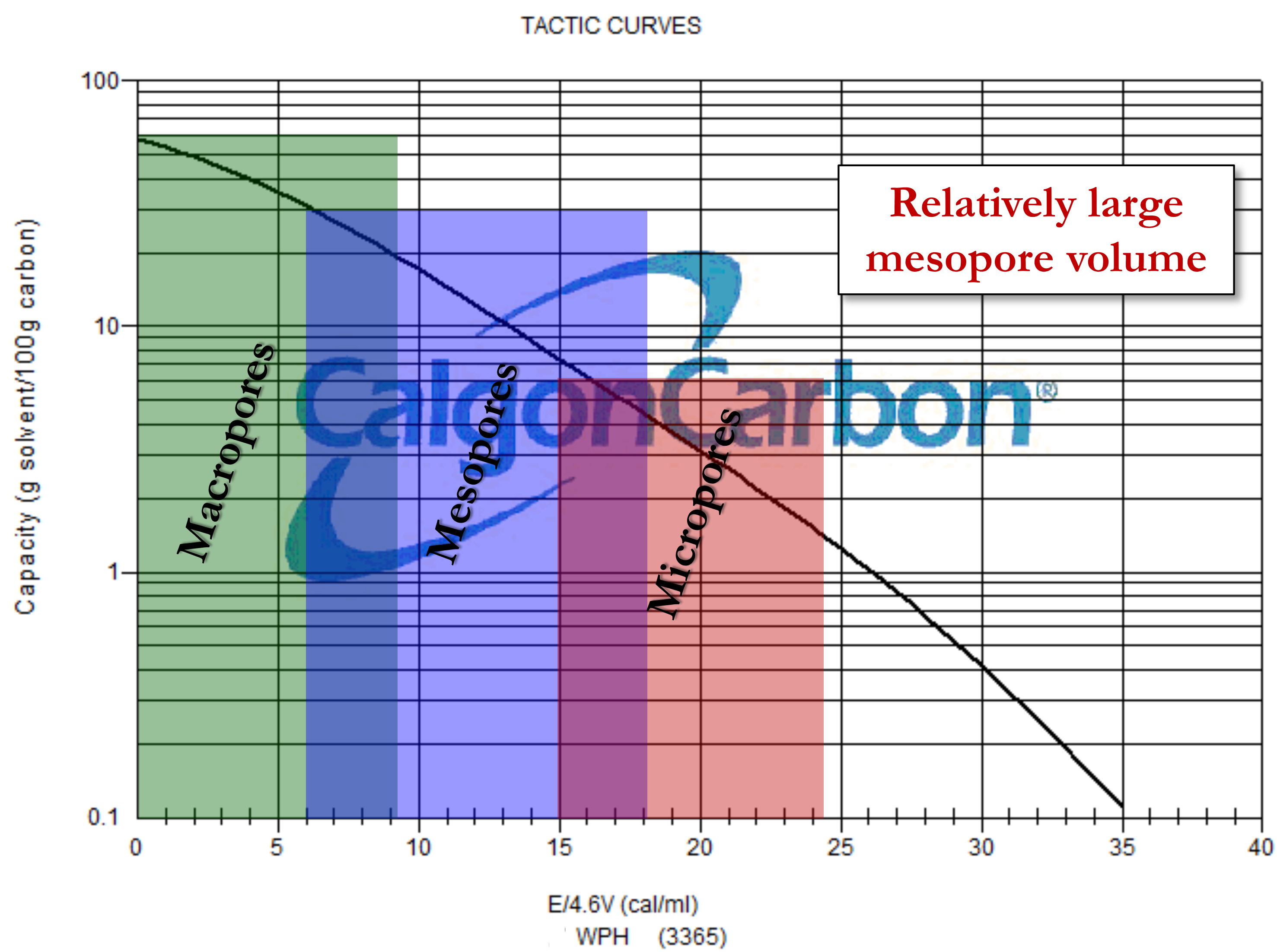
- Iodine number IN (PAC and GAC)
  - Indicates relative surface area and activity level
  - Up to 1,200 mg per gram
    - 800 mg/g to 1,000 mg/g common for good quality carbons
  - Higher numbers suggest better quality carbon
  - **1 gram has surface area up to about 0.36 acres (nearly 16,000 ft^2)**

General Properties of Carbon Products

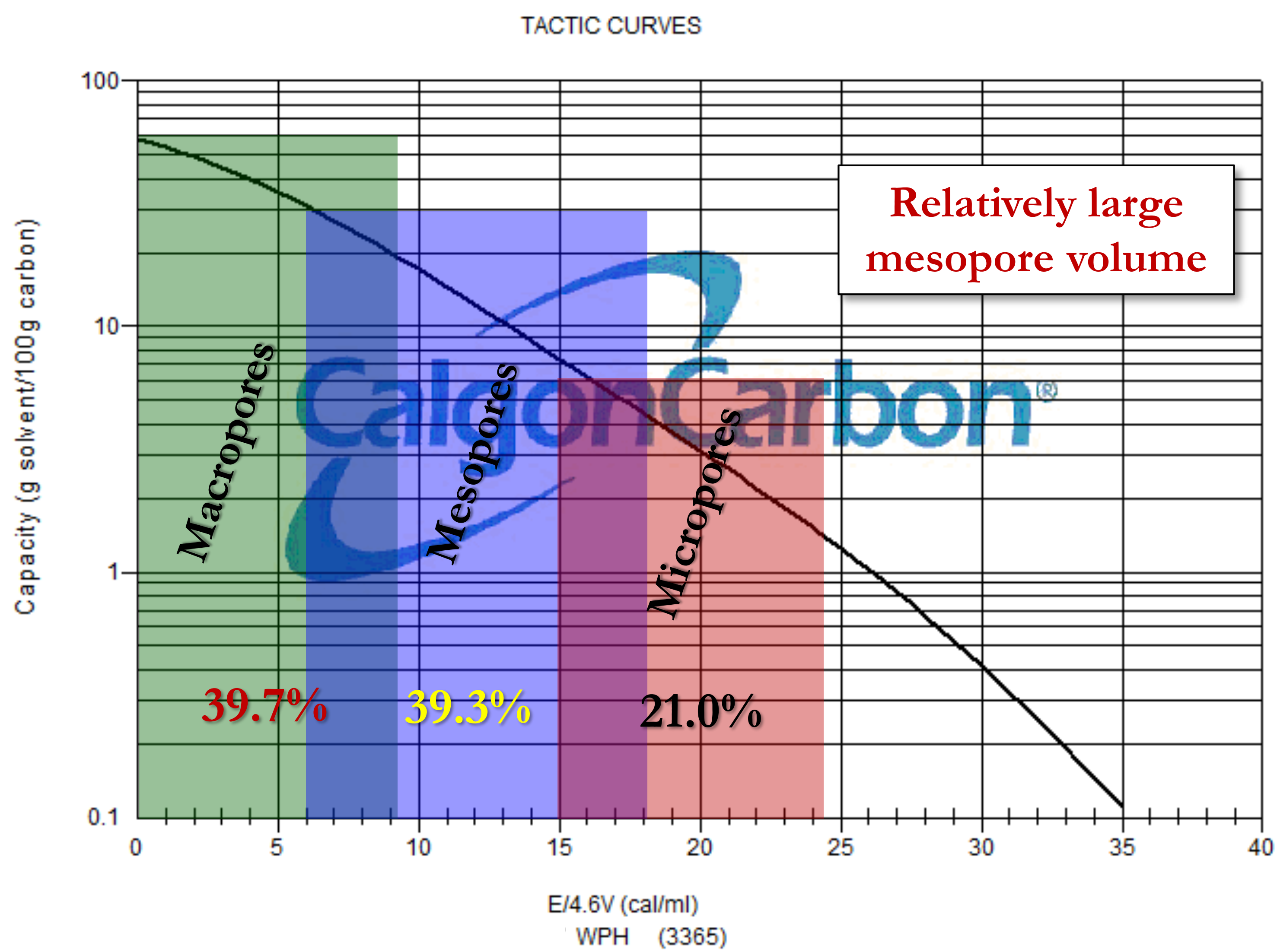


- TACTIC (PAC/GAC)
  - Total Adsorbent Characterization via Temperature Influenced Correction (Calgon Carbon)
  - Fingerprint of carbon surface energy
    - Macropores – 0 cal/mL to 9 cal/mL
    - Mesopores – 6 cal/mL to 18 cal/mL
    - Micropores – 15 cal/mL to 24 cal/mL

General Properties of Carbon Products



General Properties of Carbon Products

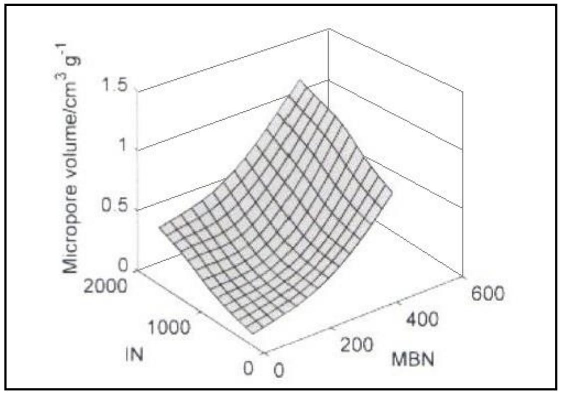


General Properties of Carbon Products

- Methylene blue number MBN (PAC/GAC)
  - Measures adsorption of methylene blue dye
  - Suggests micropore volume
  - Ranges from 150 g/g to 450 g/g
  - Values can be used to calculate volumes using IN-MBN ratios
- Molasses number (PAC/GAC)
  - Measures adsorption of molasses
  - Suggests mesopore and macropore volume
  - Ranges from 95 to 600
  - Relative to carbon surface area based on IN-MBN ratios

General Properties of Carbon Products

- Computer modeling pore volumes

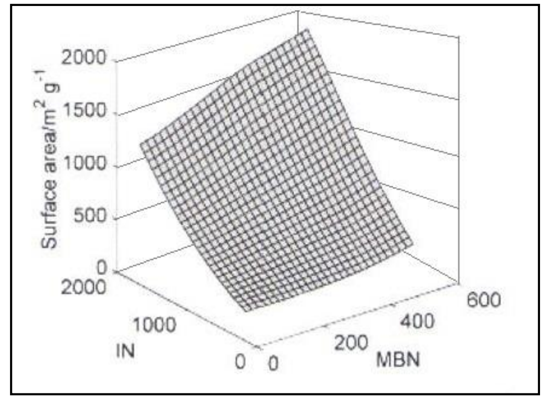


From Nunes-Guerreiro 2011

$$Vm, cm^3/g = 5.6 * 10^{-2} - 1.01 * 10^{-3} MBN + 1.55 * 10^{-4} IN + 7 * 10^{-6} MBN^2 + 1 * 10^{-7} IN^2 - 1.18 * 10^{-7} MBN * IN$$

$$Vt, cm^3/g = 1.37 * 10^{-1} - 1.9 * 10^{-3} MBN + 1 * 10^{-4} IN$$

- Computer modeling surface areas



From Nunes-Guerreiro 2011

$$SA, m^2/g = 2.28 * 10^2 - 1.01 * 10^{-1} MBN + 3 * 10^{-1} IN + 1.05 * 10^{-4} MBN^2 + 2 * 10^{-4} IN^2 + 9.38 * 10^{-4} MBN * IN$$

General Properties of Carbon Products

- Estimate of pore volumes and surface area
  - Iodine number 900 mg/g
  - Methylene blue number 150

  - Total pore volume 0.26660 cm^3/g
  - Micropore volume 0.1114 cm^3/g (41.8%)
  - Meso/Macropore volume 0.15527 cm^3/g (58.2%)
  - Surface area 852 m^2/g (0.21 acres)

Why Proper Selection is Important

- Activated carbon should be properly match carbon performance to its targeted adsorbates
  - Adsorbate molecular size must fit within the pore structures to reach adsorption sites
    - Large molecules may not reach adsorption sites and can block pore structures
  - Poor treatment performance results in higher organics concentrations in drinking water and may lead to customer complaints and/or non-compliance issues
  - Improper carbon type increases chemical treatment dosages and treatment costs
  - Take care to avoid oxidant/carbon interactions
    - Oxidation byproducts block pore structures

Carbon Dosing and Usage Equations

- PAC dosages can be predicted using empirical equations from research literature
  - Caution – many tests carried out in lab pure water with one organic substance
    - Source water dosing can be double the predicted values
    - Best practices suggest safety factor of 2 if TOC >5 mg/L
  - Multiple adsorbates create different kinetics and adsorption efficiencies
    - Interferences often observed when multiple adsorbates are in solution
    - Desorption can occur if higher K substance enters carbon particle

Carbon Dosing and Usage Equations

- Freundlich equation
  - Predicts single adsorbate removal dosing for carbon treatment

$$q = K\, C_f^{1/n}$$

q = adsorption coefficient, µg/g
K = adsorptive capacity, (µg/g)(L/µg)$^{1/n}$
C_f = final adsorbate level, µg/L
$1/n$ = adsorption intensity

$$C_i - C_f \,/\, q = \textit{carbon dosage}$$

Estimated PAC for Microcystin Removal to 0.3 µg/L

K	1/n	Ci	Dose, mg/L
6,309	0.56	50	16
3,630	0.9	50	41
1,259	1.0	50	132

Carbon Dosing and Usage Equations

- Carbon usage rate (CUR) published WRF 1998

$$CUR, \frac{lbs}{1{,}000} gallons = \frac{EBCT * \rho GAC * 10^3}{T * 7.48 * 1{,}440}$$

Where CUR = Carbon Usage Rate, pounds per 1,000 gallons

EBCT= empty bed contact time, minutes

ϱGAC = carbon density, pounds/cubic foot

T = breakthrough time in days

7.48 = 7.48 gallons per cubic foot

1,440 = 1,440 minutes per day

Carbon Dosing and Usage Equations

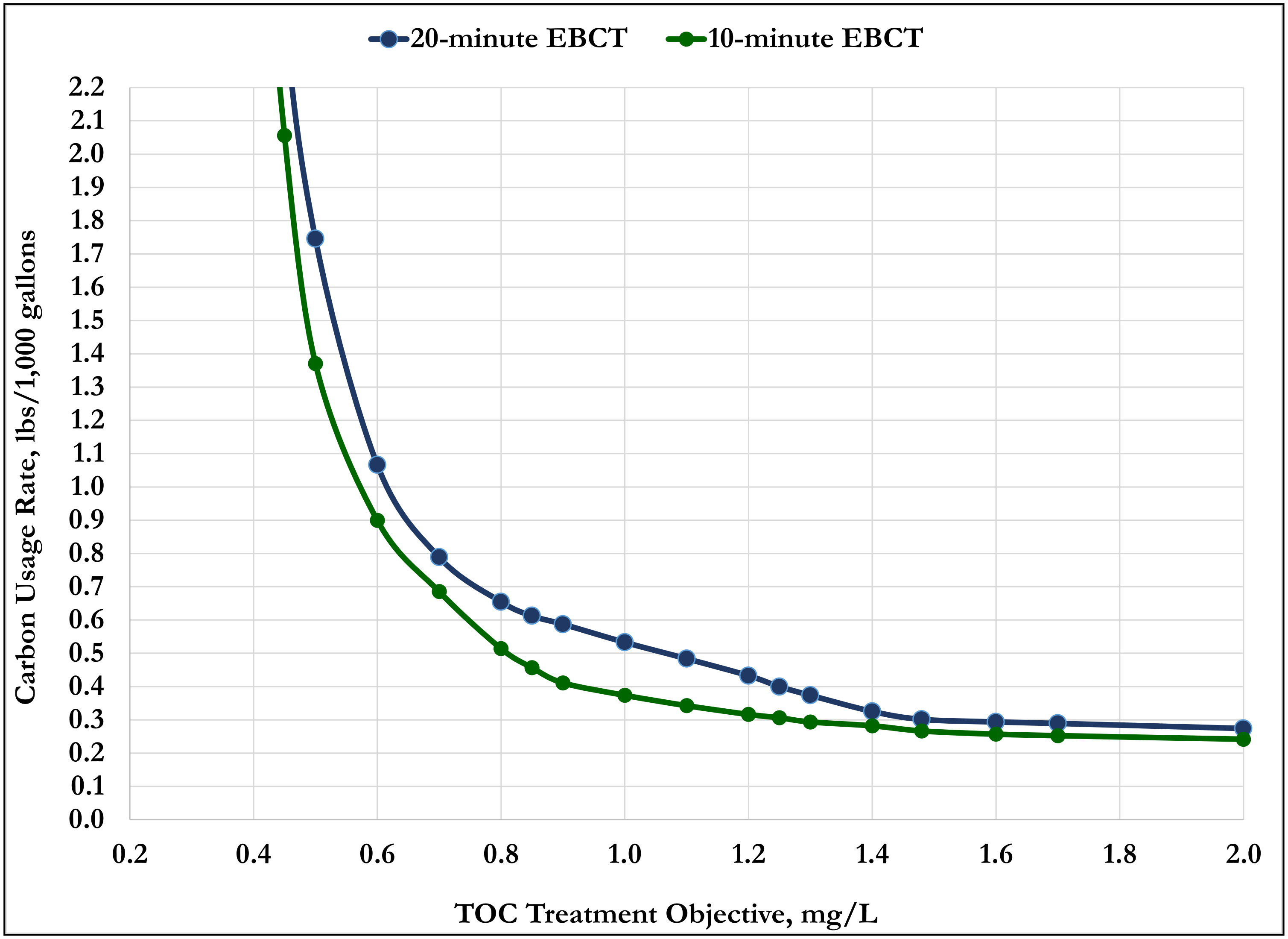
- Carbon usage rate (CUR) example

$$CUR, \frac{lbs}{1{,}000} gallons = \frac{EBCT * \rho GAC * 10^3}{T * 7.48 * 1{,}440}$$

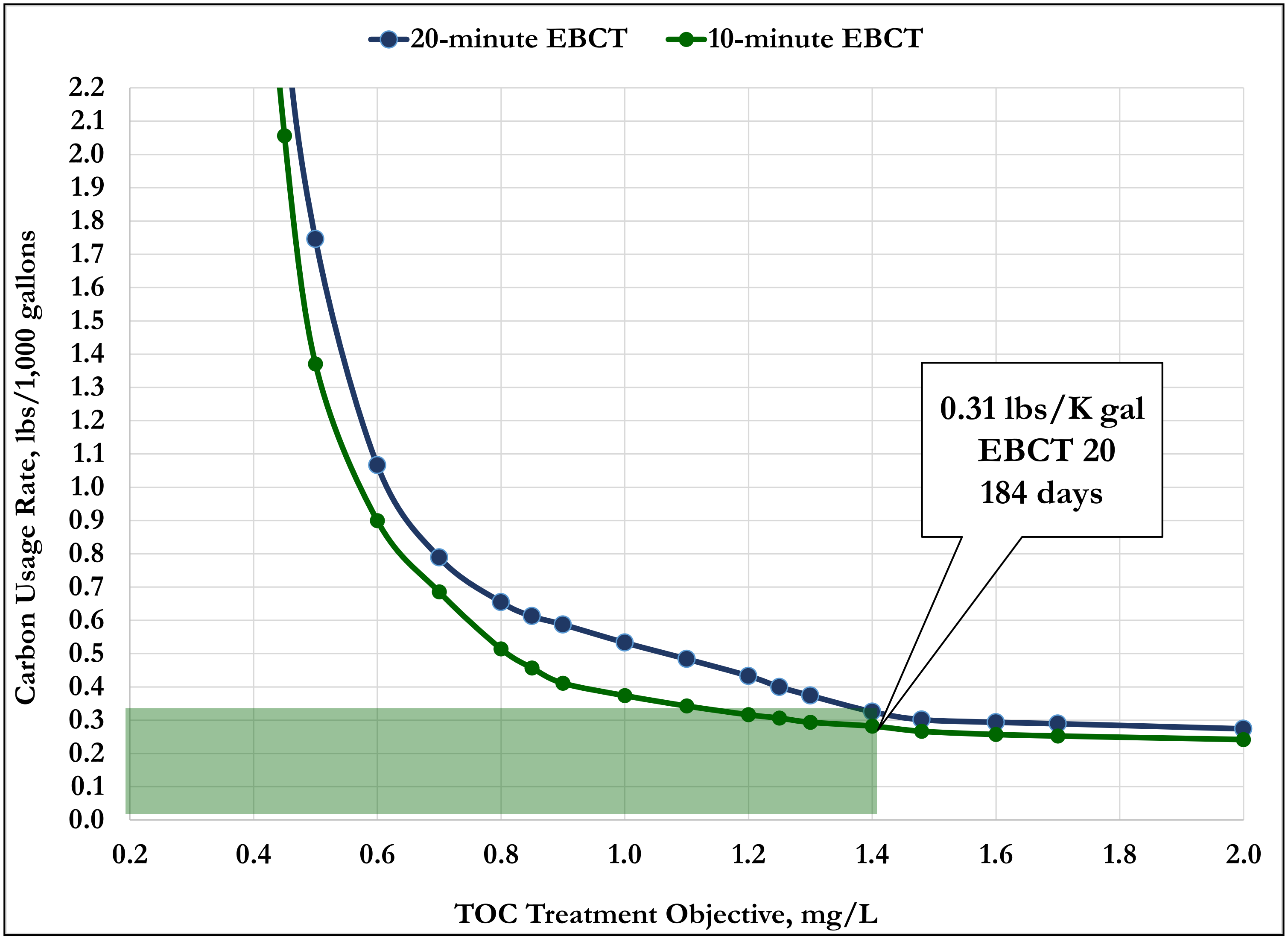
- EBCT - 20 minutes, 184 days breakthrough

$$CUR = \frac{20 * 31 * 10^3}{184 * 7.48 * 1{,}440} = 0.31 \frac{lbs}{1{,}000} gal$$

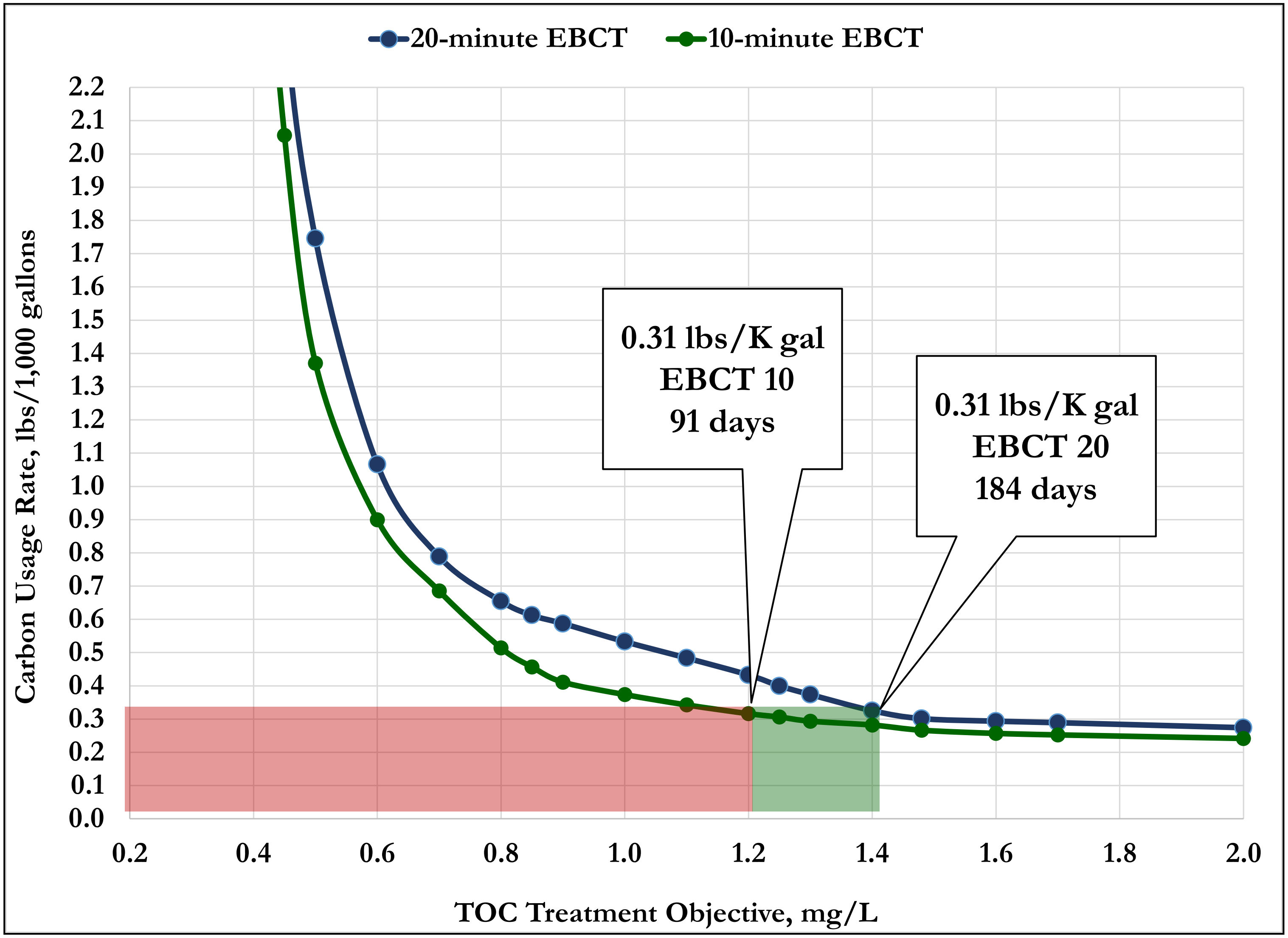
Carbon Dosing and Usage Equations



Carbon Dosing and Usage Equations

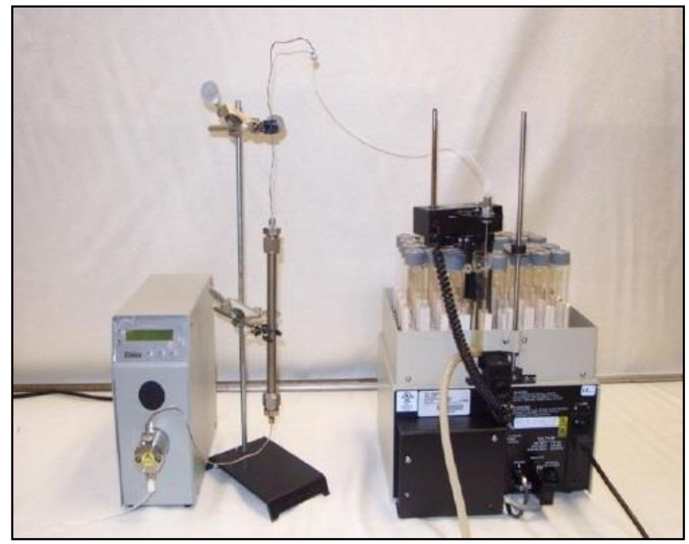


Carbon Dosing and Usage Equations



Selecting Carbons for Performance

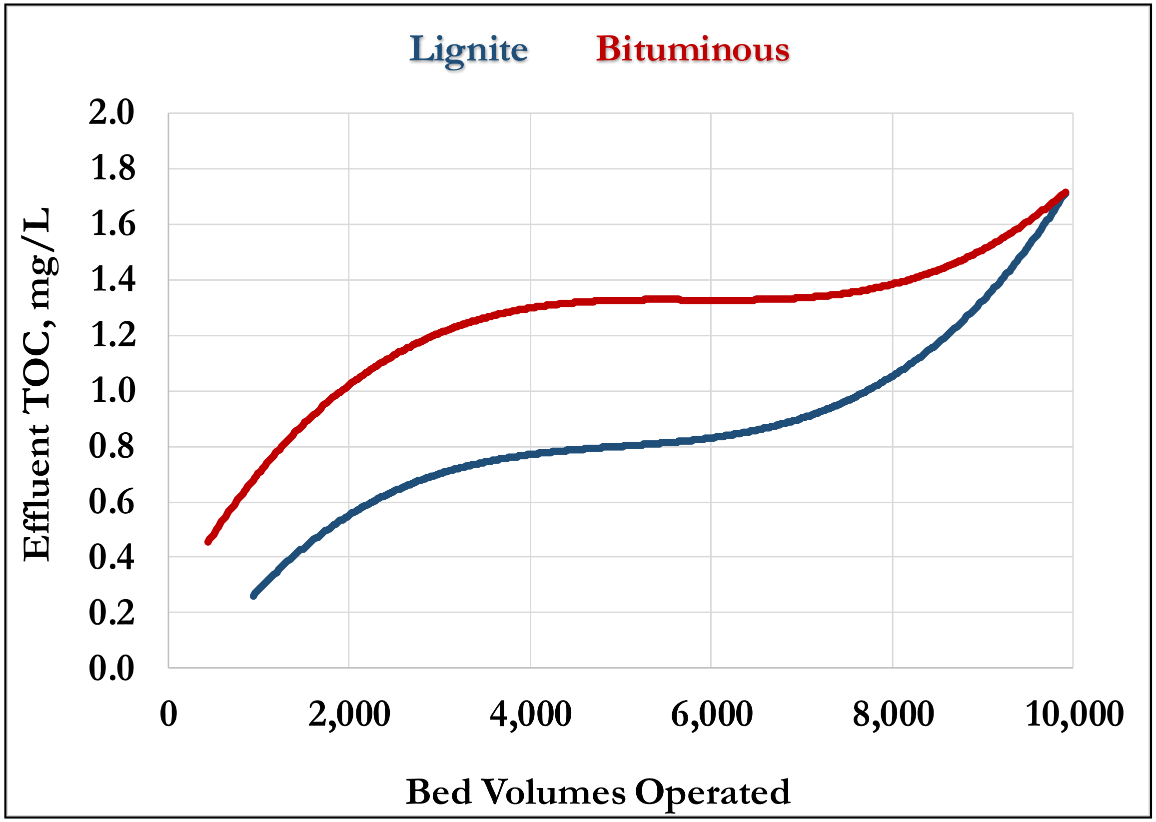
- Experimental testing is best means to determine carbon dosing
  - RSSCT, ACT, or pilot scale for GAC
  - Jar testing for PAC
- Multiple adsorbates create removal difficulties
  - Competing adsorption reactions
  - NOM tends to block adsorption sites and transport pathways
  - Desorption can occur
  - Oxidants create byproducts tending to block adsorption sites



Selecting Carbons for Performance

- Contact time and mixing important
  - PAC up to 4 hours possible
  - GAC EBCT determined from demonstration study
  - pH and temperature also play a role in treatment efficiencies
  - Dosing difficult to calculated (predicted) values if multiple adsorbates present
    - Freundlich equations
    - Dosing estimators
    - Dosage needed could be double

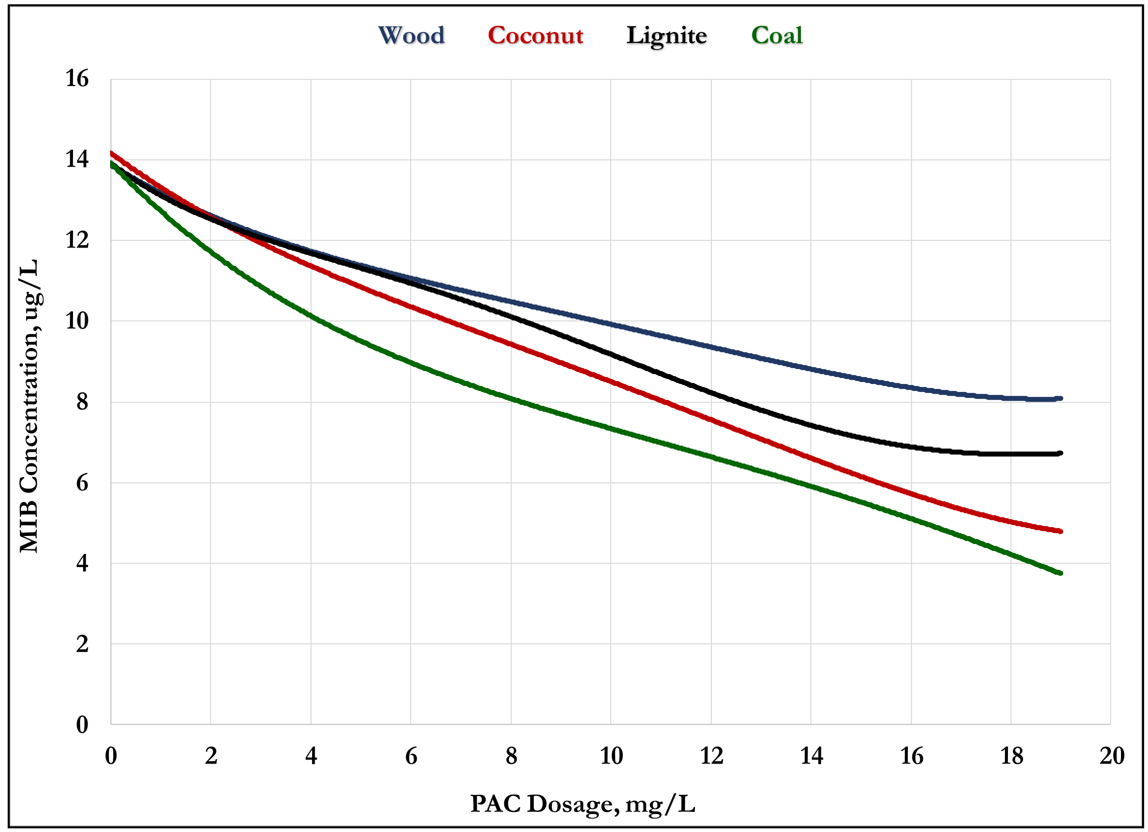
Selecting Carbons for Performance



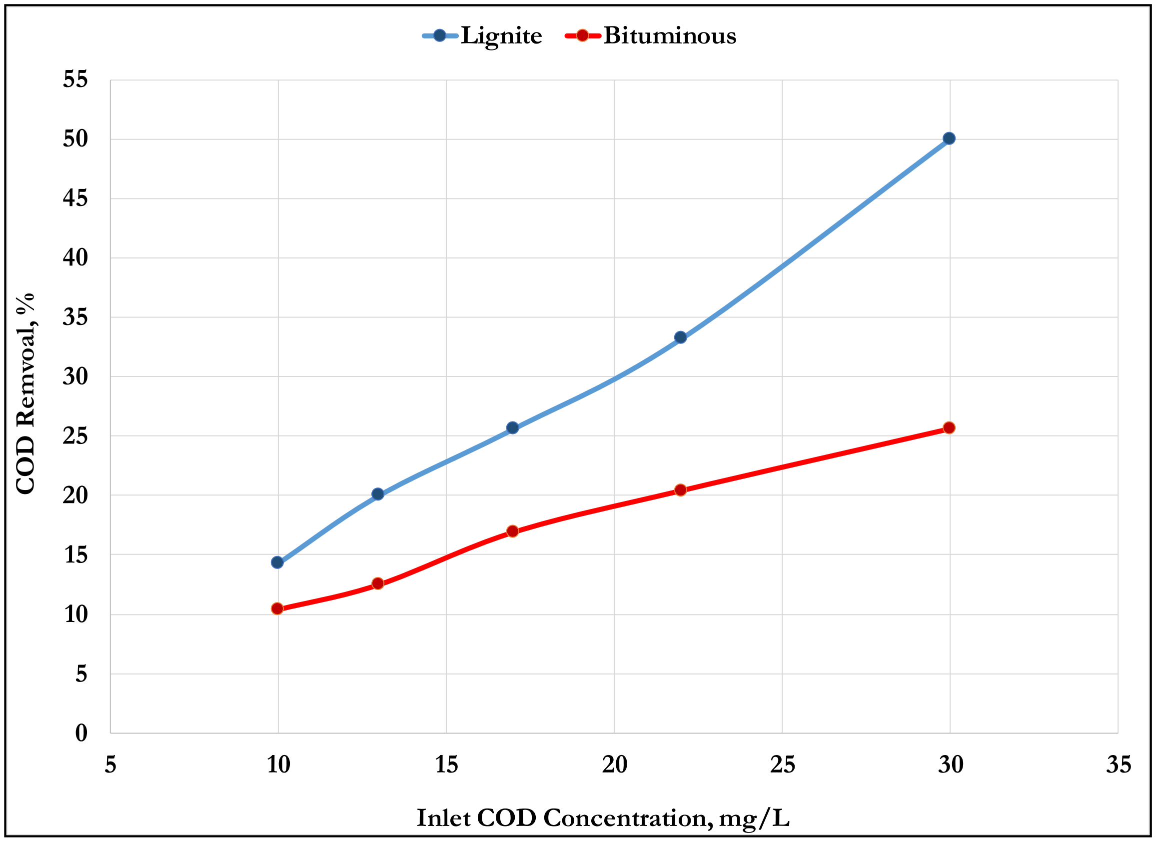
- Not all carbons behave the same
  - Filter capped with GAC's
    - Same iodine number
  - **Lignite** appeared to outperform the **bituminous** (lower TOC until breakthrough)
  - Breakthrough (1.7 mg/L) appeared to occur at the same bed volume throughput

Selecting Carbons for Performance

- Not all carbons behave the same
  - PAC's for MIB reductions
    - Same iodine numbers
  - Bituminous coal appeared to outperform the other carbon products
    - Likely have better removals at lower dosages based on this study



Selecting Carbons for Performance



- Not all carbons behave the same
  - PAC treatment of COD in wastewater
  - **Lignite** appeared to outperform the **bituminous** (greater COD removals)
    - Iodine numbers and PAC dosages not given in literature
    - General PAC dosing for wastewater is 10 mg/L or greater

Selecting Carbons for Performance

- Determine target adsorbate(s) and concentrations
- Define seasonal or prolonged occurrence in treatment
  - Select a PAC or GAC product accordingly
- Consider kinetics of process
  - Adsorption isotherms give a best guess
  - Published isotherm data can predict dosing
  - Choose carbon matched to the adsorbate molecular size
    - May need larger mesopore volume for treatment efficiency (40% or higher)
    - Use other carbon criteria to properly remove target contaminant
    - Conduct testing and life cycle costs for final product selection
- Buy carbon based on performance, not purchase price

Questions

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