Polymeric Resins for VOC Removal from Aqueous Systems

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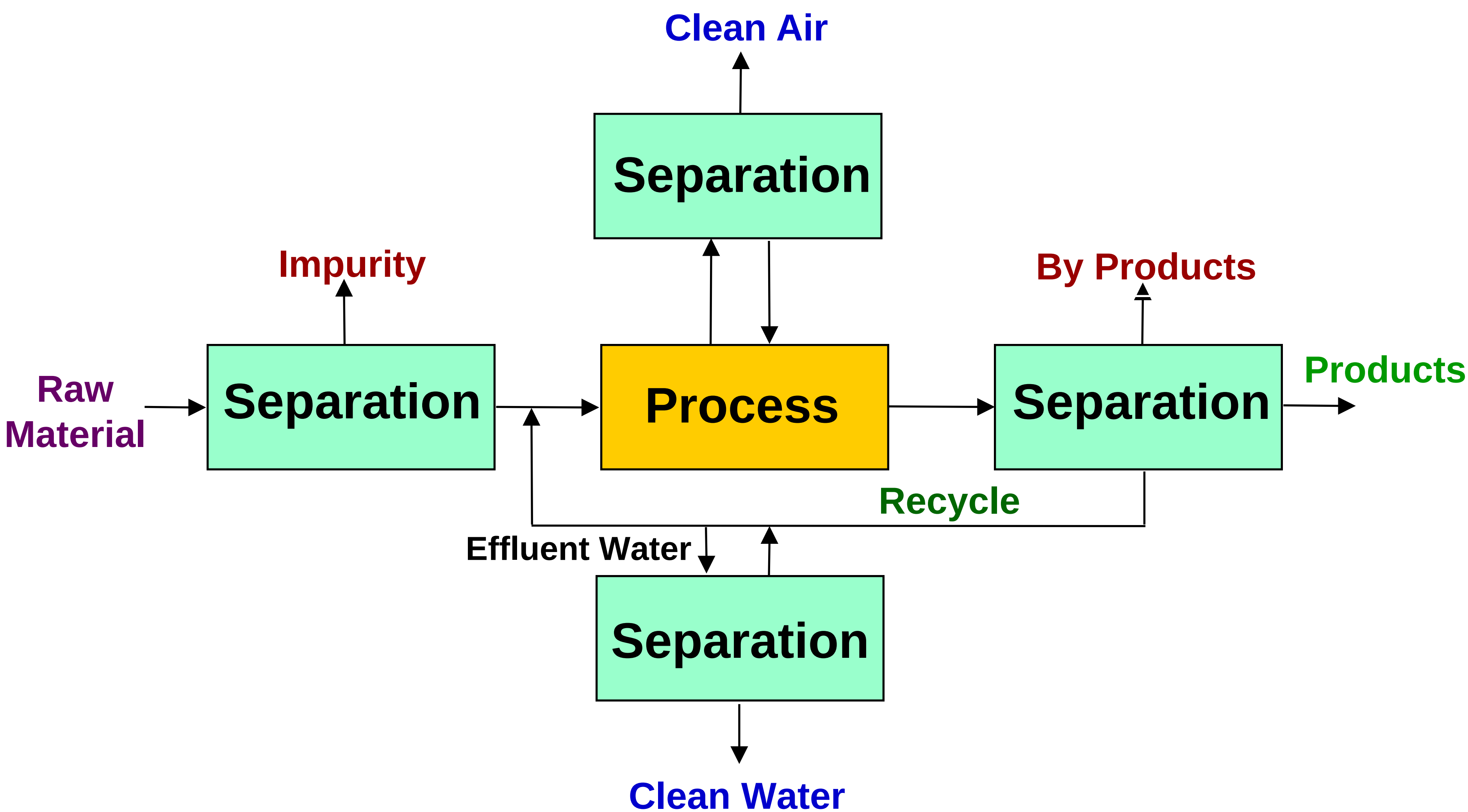
Polymeric Resins for VOC Removal:
Outline

- Motivation
- Attributes of polymeric resins
- Adsorption capacities
- Performance in dynamic column adsorption processes
- Regeneration
- Summary

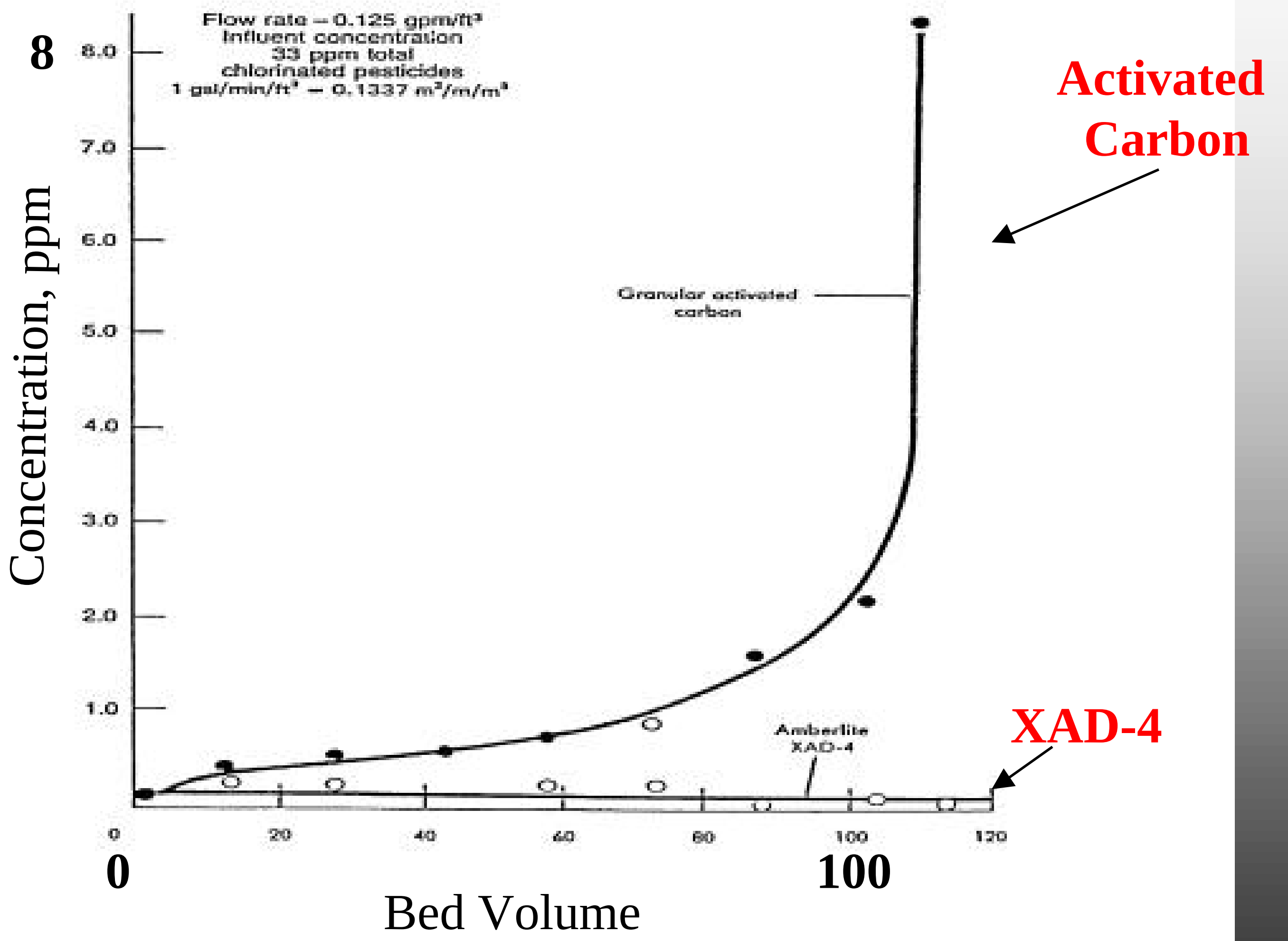
Separation Processes to the Rescue!



Some Application Areas

- Chemical Analysis
- Ion-exchange resins
- Non-adsorbing aqueous size exclusion chromatography (SEC) resins
- Affinity resins for Liquid chromatography
- Adsorption of organics from aqueous systems
- Organic liquid-liquid separations

Adsorption of a Mixture of Chlorinated Pesticides in a Packed-Bed



Source: Fox, C.R., Chem.Eng.Prog., 75, 70 (1979)

Polymer Resins and Activated Carbon

Polymeric Resins

?

Activated Carbon

- High surface area (> 1000 m^2/g)
- High heat of adsorption (>10 kcal/mol)
- Thermal regeneration (e.g., steam regeneration).
- 5%-10% degradation per cycle
- Readily available, low cost (. $2/kg), general adsorbent material
- Spent carbon may have to be treated as hazardous waste

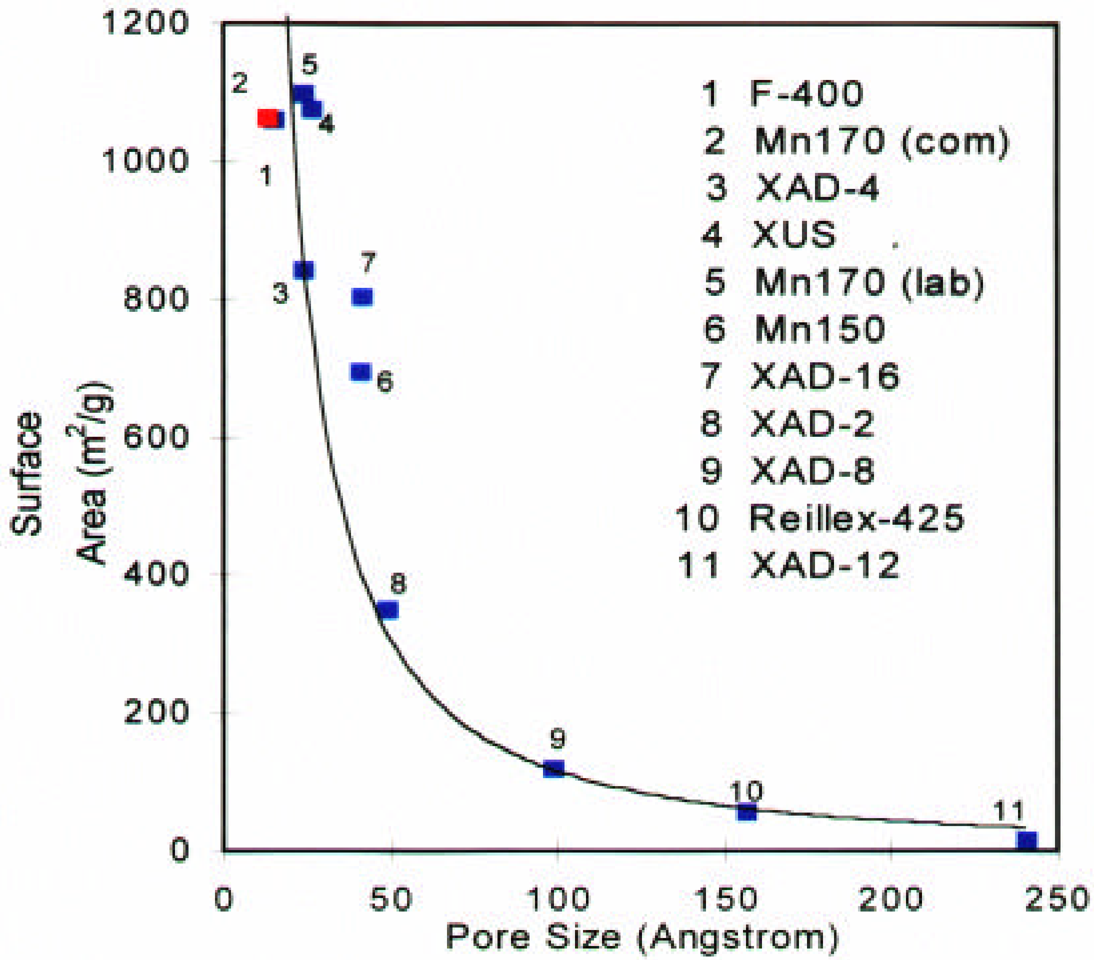
Polymeric Resins: Major Performance Issues

- **Are the surface area and pore size distribution suitable for sorption of VOCs?**
- **Can solute-polymer affinity be controlled?**
- **Can polymeric resins be easily regenerated?**
- **Are polymeric resins stable for cyclic operation?**
- **Are there severe mass transfer limitations?**

Area, Volume and Wettability

- **Pore size/volume distribution**
- **Surface area**
- **Inaccessible pore volume and wettability**

Dependence of the Surface Area of the Polymeric Resins from the average Pore Size



Surface Area Improvements

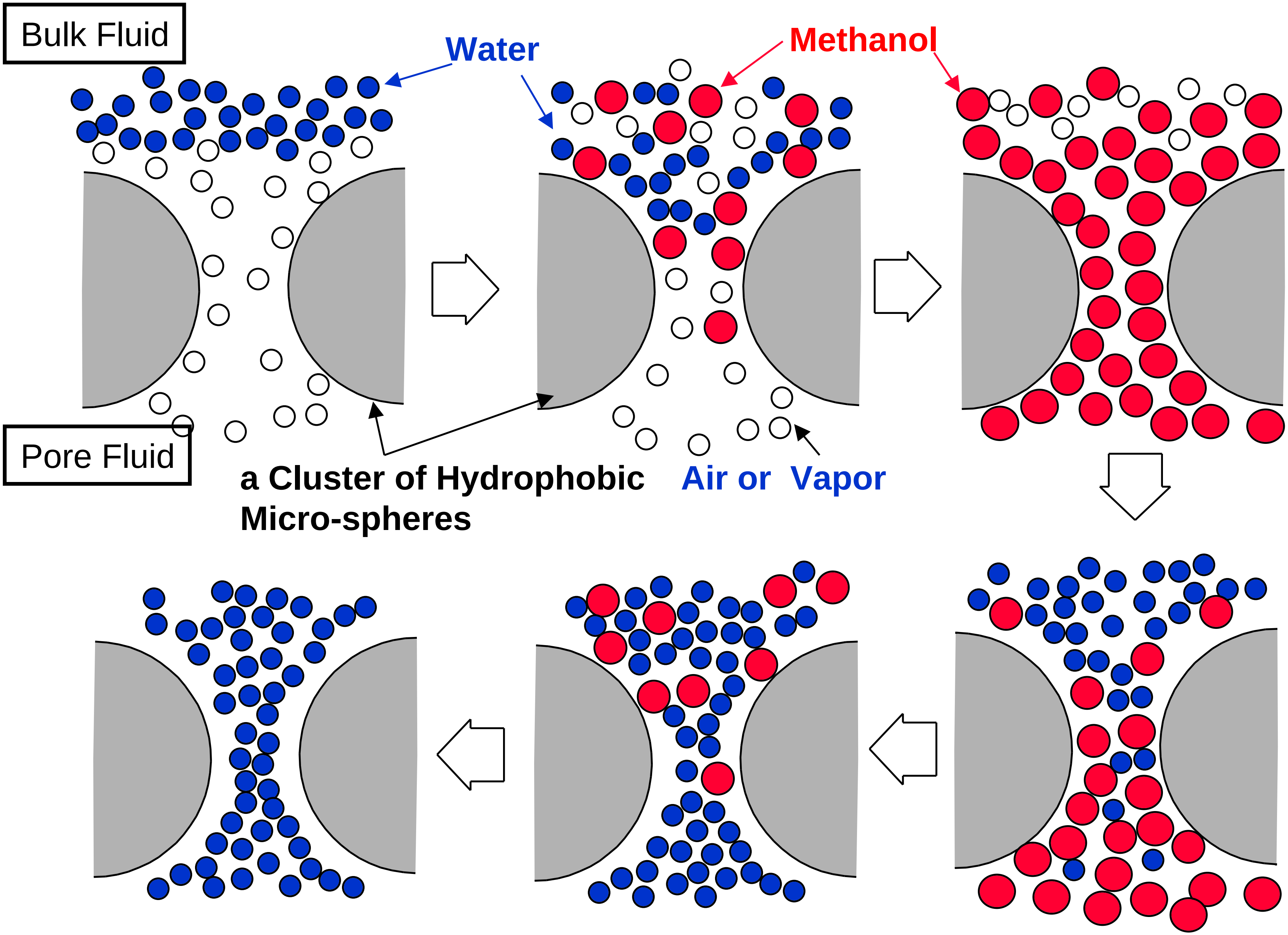
RESIN	SURFACE AREA (M^2/G)	PORE VOLUME (CM^3/G)	PORE RADIUS (Å)
F-400 (Activated Carbon)	1078	0.652	14.7
XAD-2 (SDVB)	353	0.78	48.3
XAD-4 (SDVB)	870	1.18	24.5
XAD-16 (SDVB)	889	1.75	39
XAD-8 (Poly(methylacrylate)[a]	126	0.63	98
Reillex-425 Polyvinylpyridine-divinylbenzene	110	0.63	156
Polyclar-AT Polyvinylpyrrolidone, crosslinked[b]	1.2	<0.004	<10
XUS (43493.01)	1100	1.3	23.5
MN-150	821	1.01	39.9
MN-170	1066	1.4	26

Macropores, Micropores and Inaccessible Pore Volume

Resin	A_{total} (cm^2/g)	A_{micro} (cm^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{ina}/V_{total} (cm^3/g)
XUS	1100	772	1.30	0.39	0.11
Mn150	698	554	1.01	0.30	0.05
Mn170[a]	1066	836	1.40	0.43	0.31
XAD-4	845	114	1.10	0.05	0.43
XAD-16	889	71	1.75	0.02	0.46

[a] Laboratory grade

Prewetting of Hydrophobic Resins

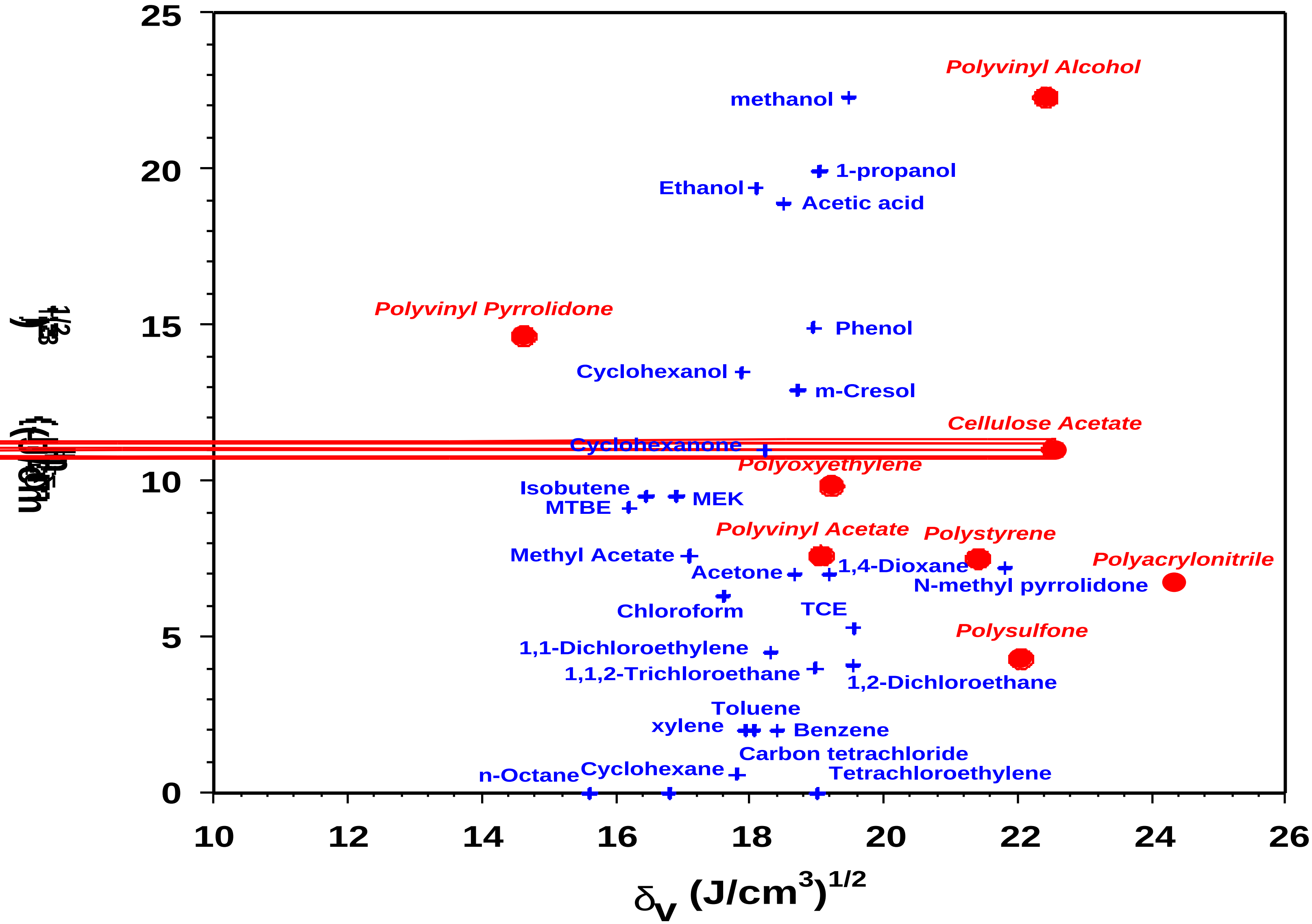


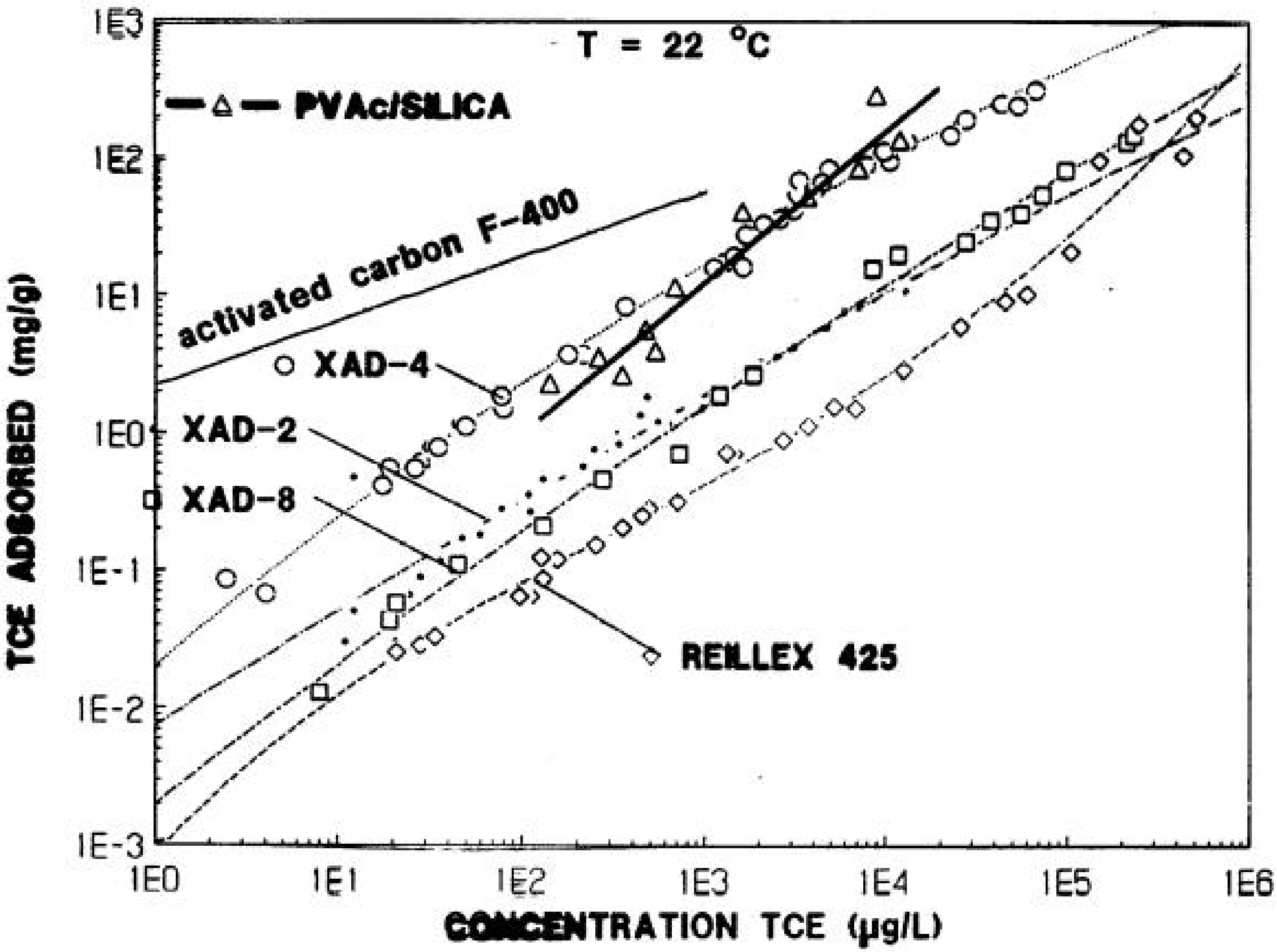
Solute-Polymer Affinity

- Hanson solubility parameter approach
- Adsorption and swelling (absorption)
- Unexpected multi-solute behavior

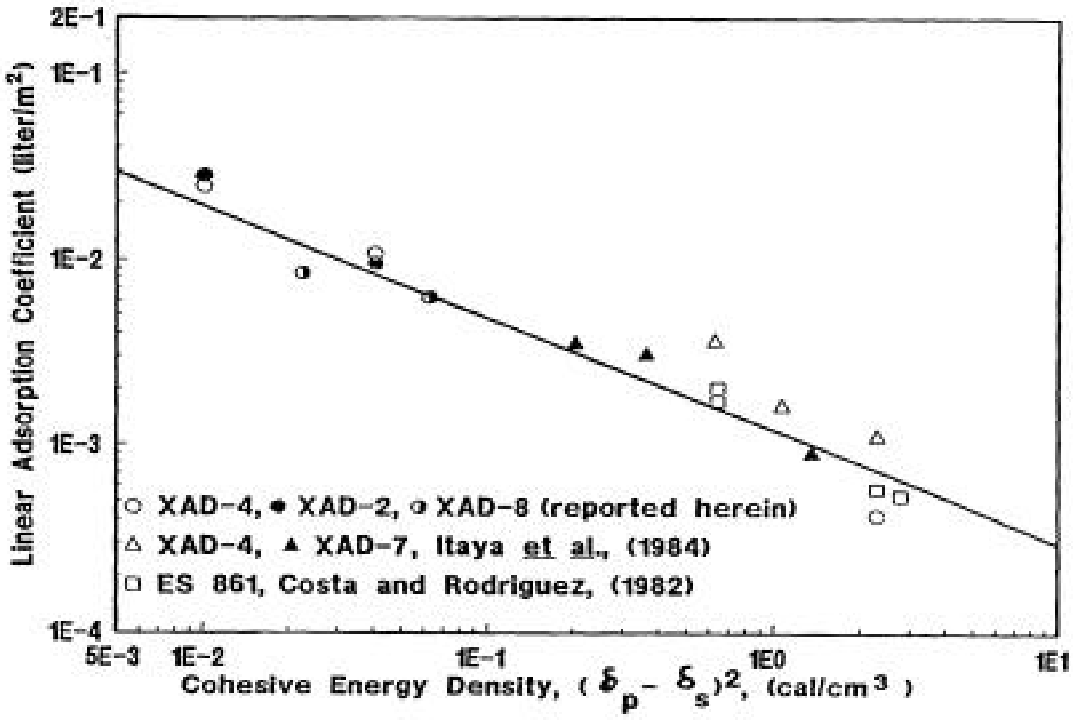
Selecting the Polymer Phase

Hansen Solubility Map

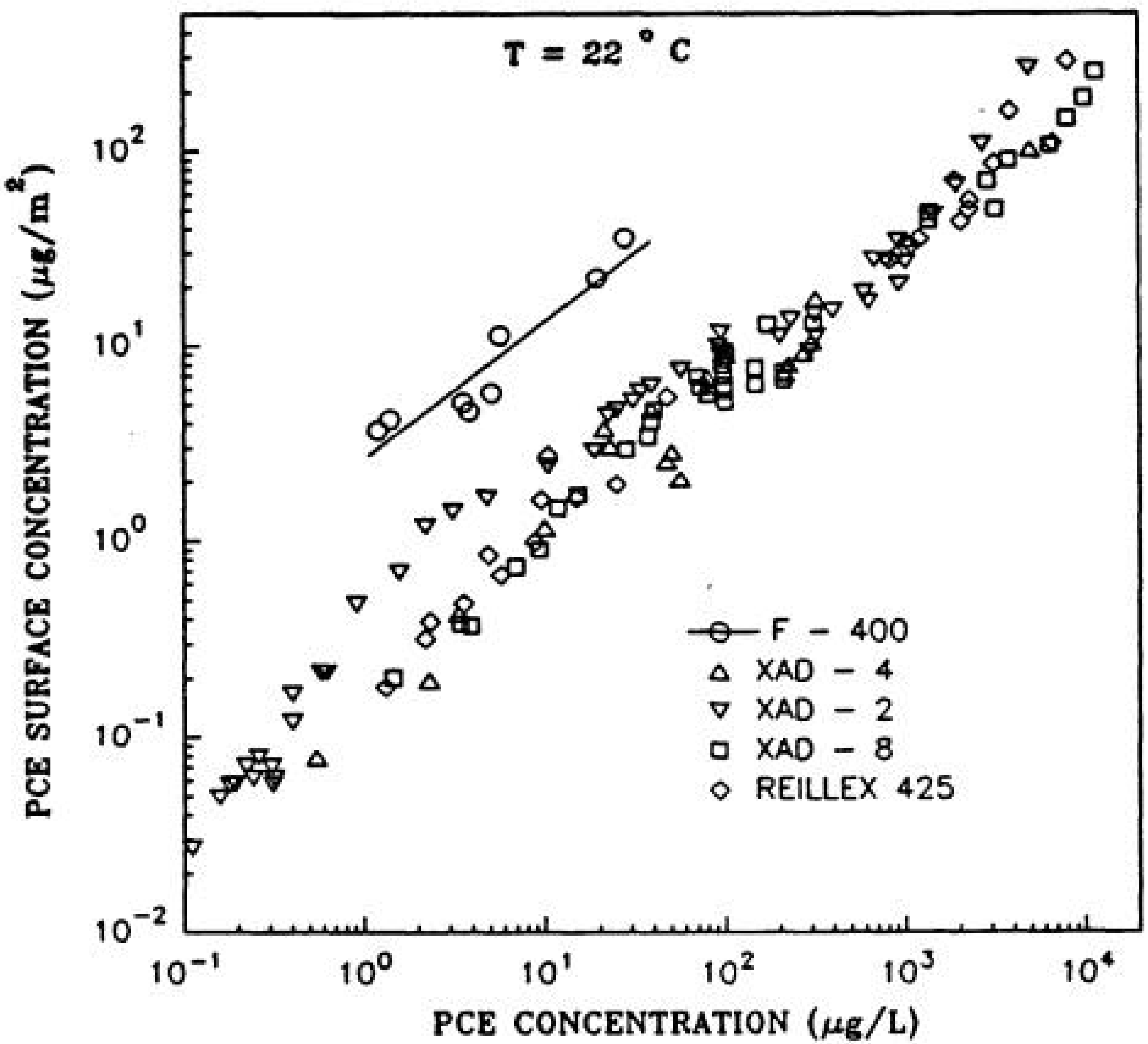


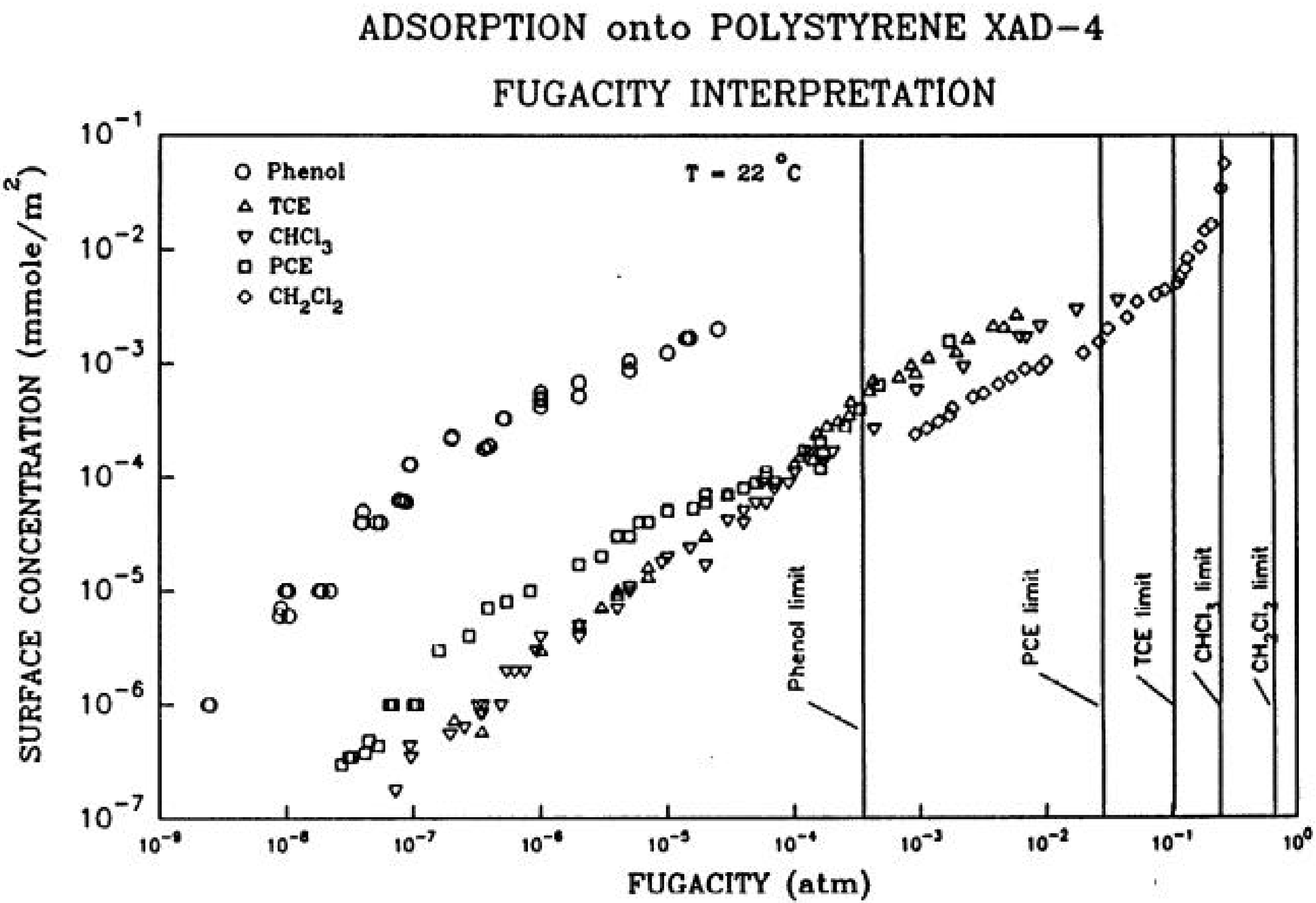

T = 22 °C
PVAc/SILICA
activated carbon F-400
XAD-4
XAD-2
XAD-8
REILLEX 425
TCE ADSORBED (mg/g)
CONCENTRATION TCE (μg/L)
1E3
1E2
1E1
1E0
1E-1
1E-2
1E-3
1E0
1E1
1E2
1E3
1E4
1E5
1E6

Adsorption of VOCs onto Polymeric Resins - A Simple Correlation

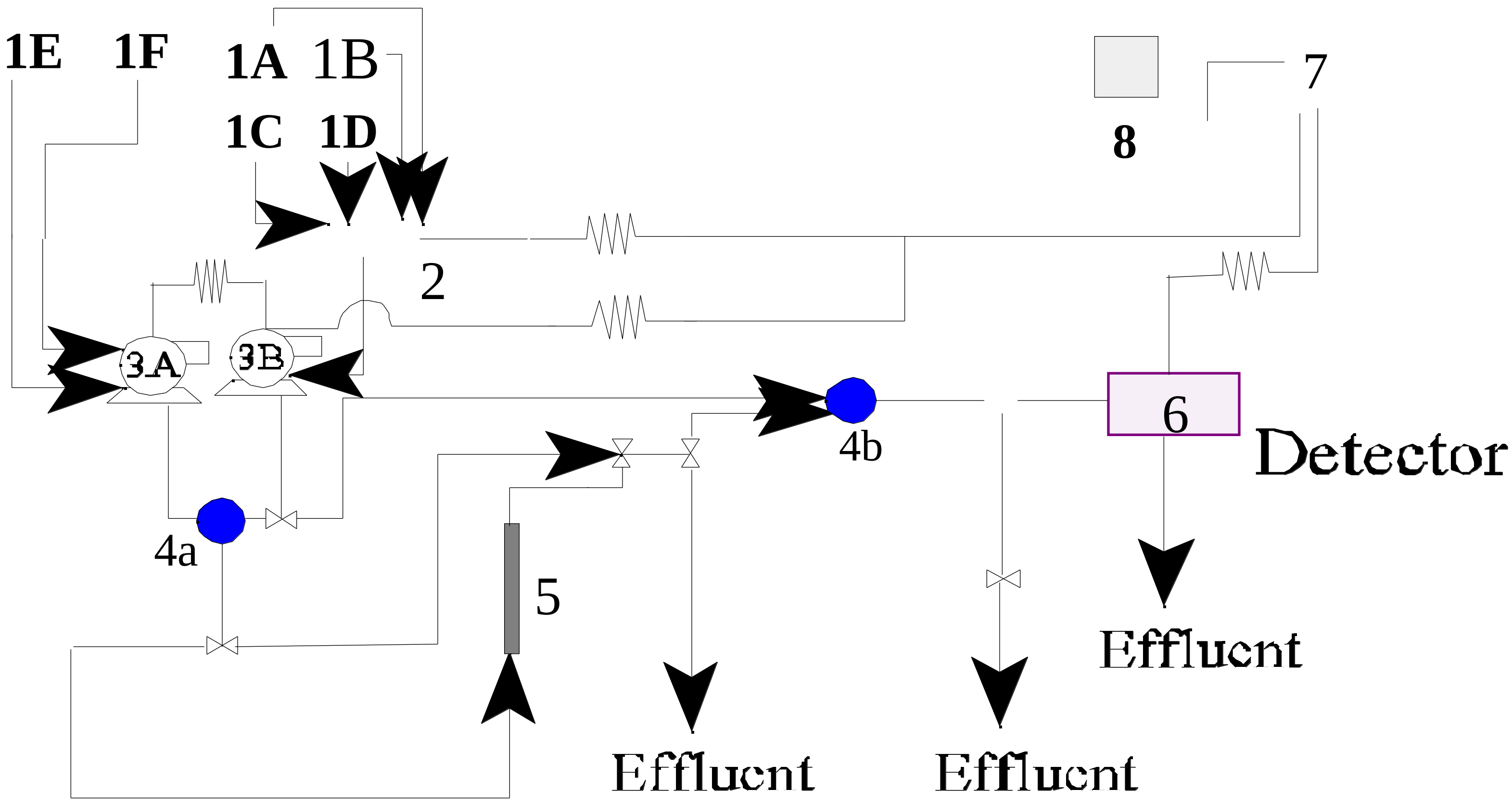


PCE Adsorption Isotherms



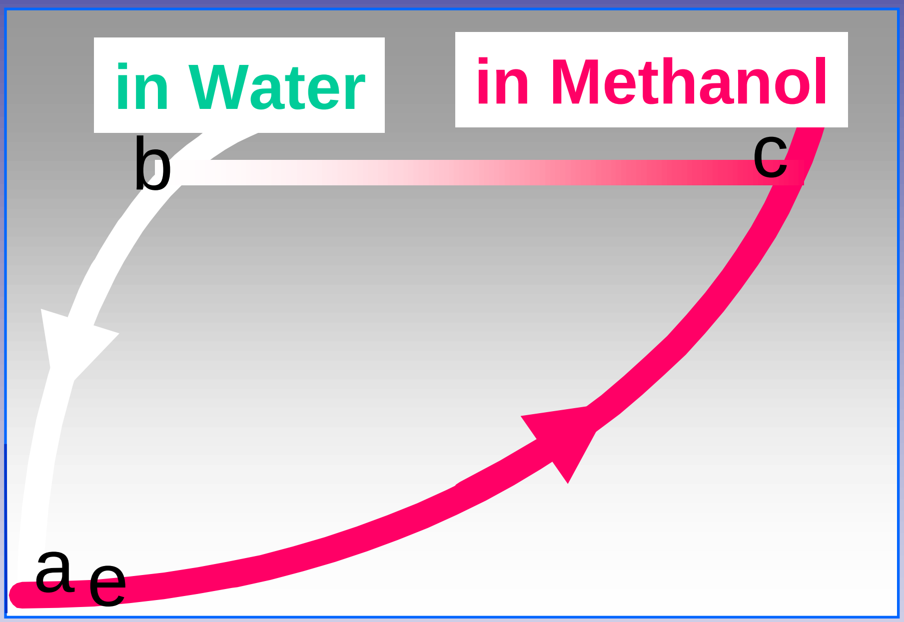

ADSORPTION onto POLYSTYRENE XAD-4
FUGACITY INTERPRETATION
Phenol
TCE
CHCl3
PCE
CH2Cl2
T = 22 °C
Phenol limit
PCE limit
TCE limit
CHCl3 limit
CH2Cl2 limit
SURFACE CONCENTRATION (mmole/m2)
FUGACITY (atm)

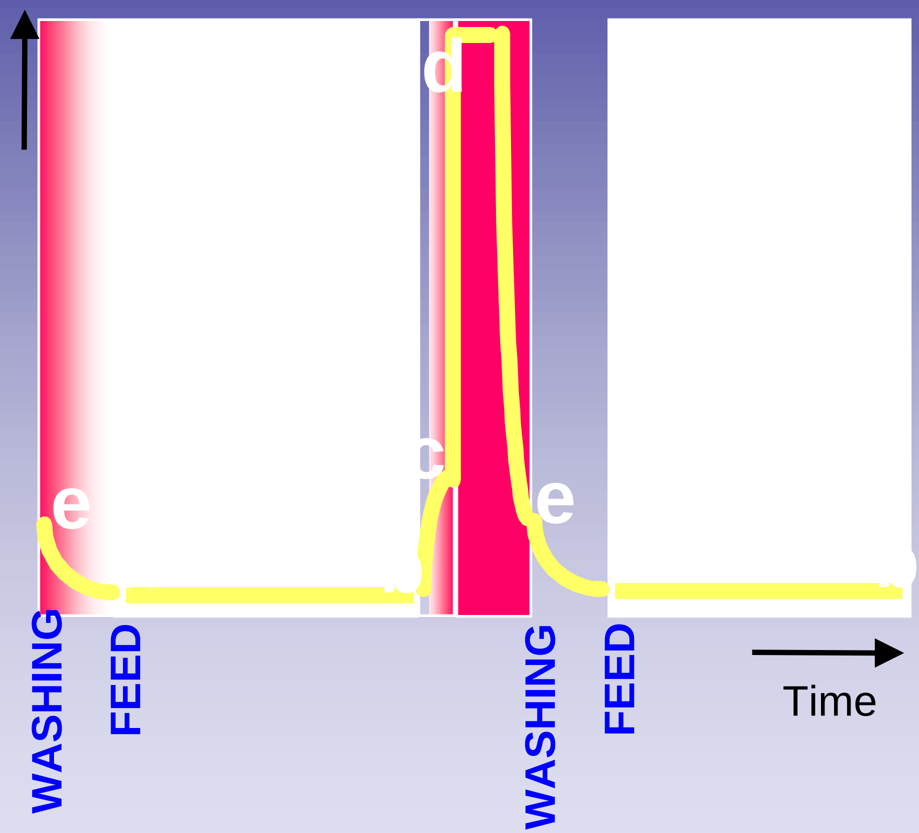
Adsorption/Regeneration System



1 a-f Solvent Reservoirs
2 Solvent Select Valve
3 a,b Piston Pumps
4 a,b High Pressure Mixer
5 Adsorber column
6 UV Detector
7 SIM Box
8 386sx Computer

Cyclic Adsorption/Regeneration Process

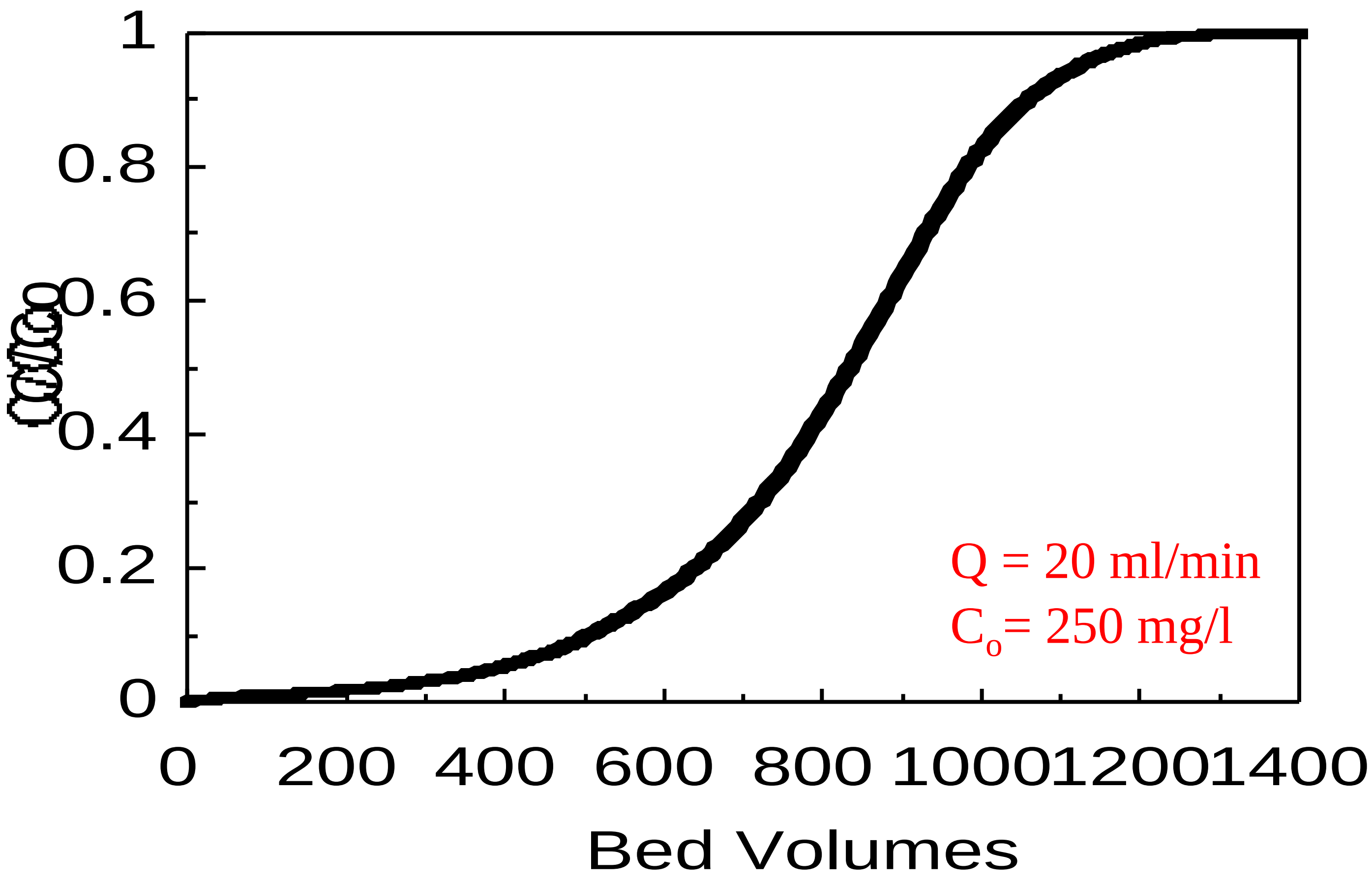




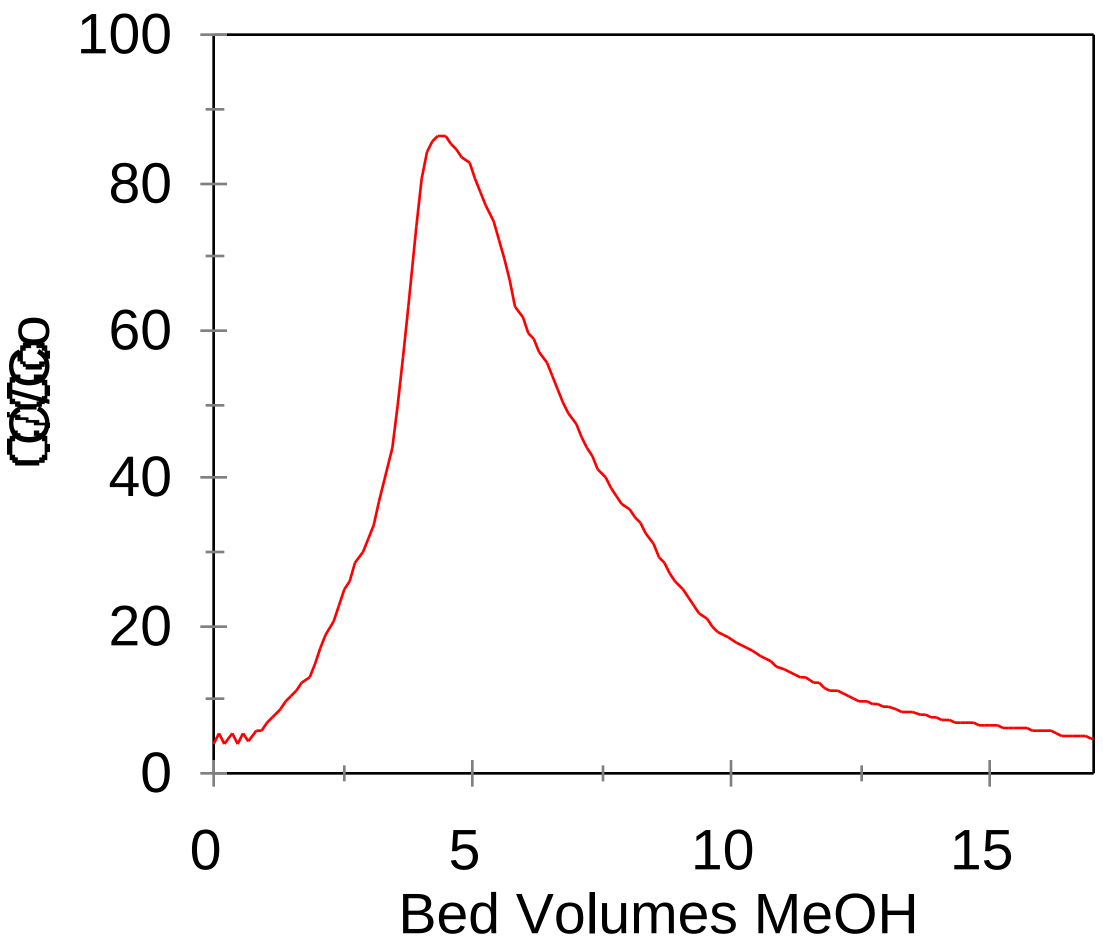
Column Regeneration

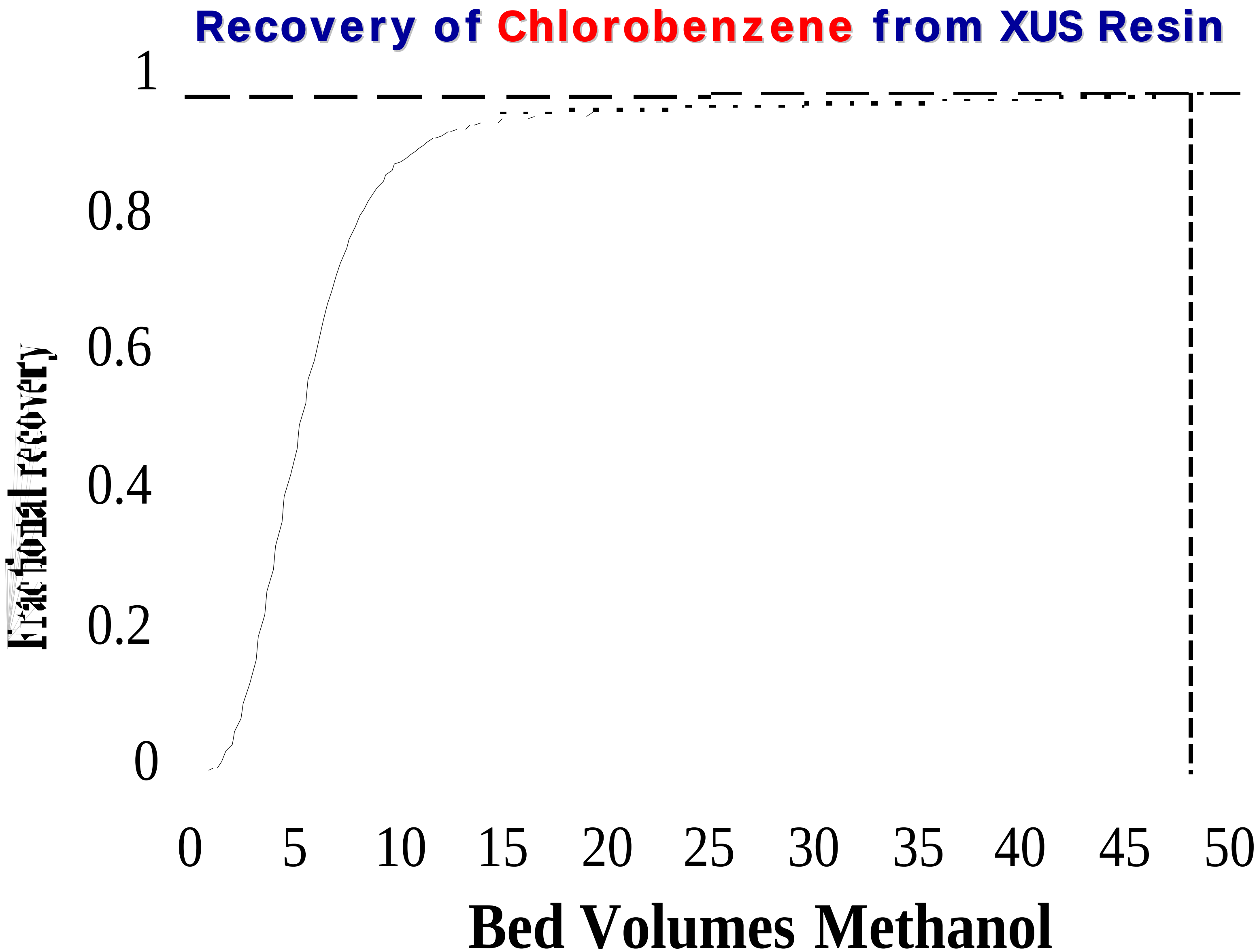
- **In-situ solvent regeneration of resin with aliphatic alcohols**
- **Cyclic Adsorption/regeneration process**

Breakthrough Curve for Chlorobenzene in XUS Column

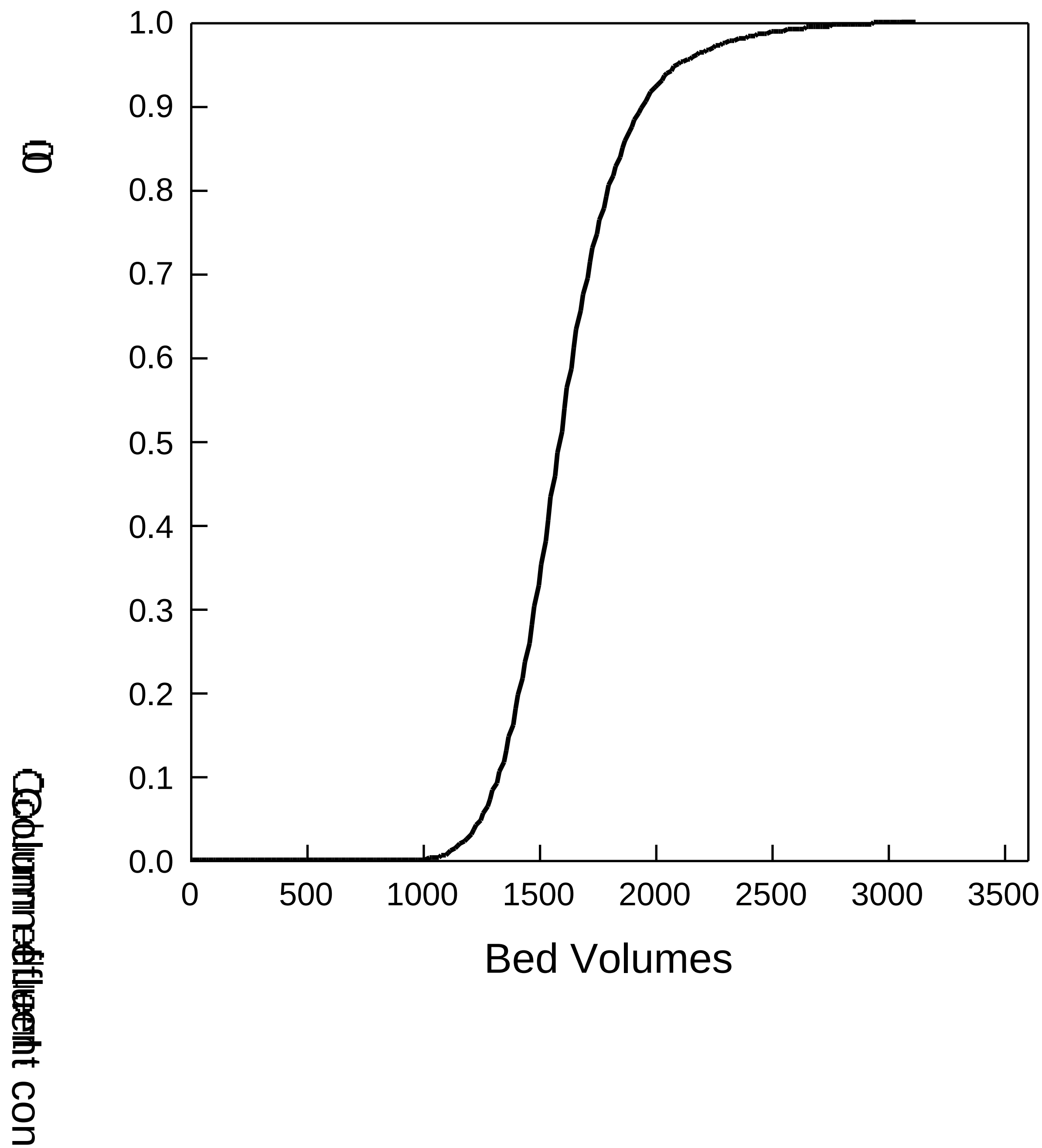


Regeneration Curve for Fixed-Bed XUS Column Saturated with Chlorobenzene.





Recovery of Chlorobenzene from XUS Resin
Fractional recovery
1
0.8
0.6
0.4
0.2
0
0
5
10
15
20
25
30
35
40
45
50
Bed Volumes Methanol

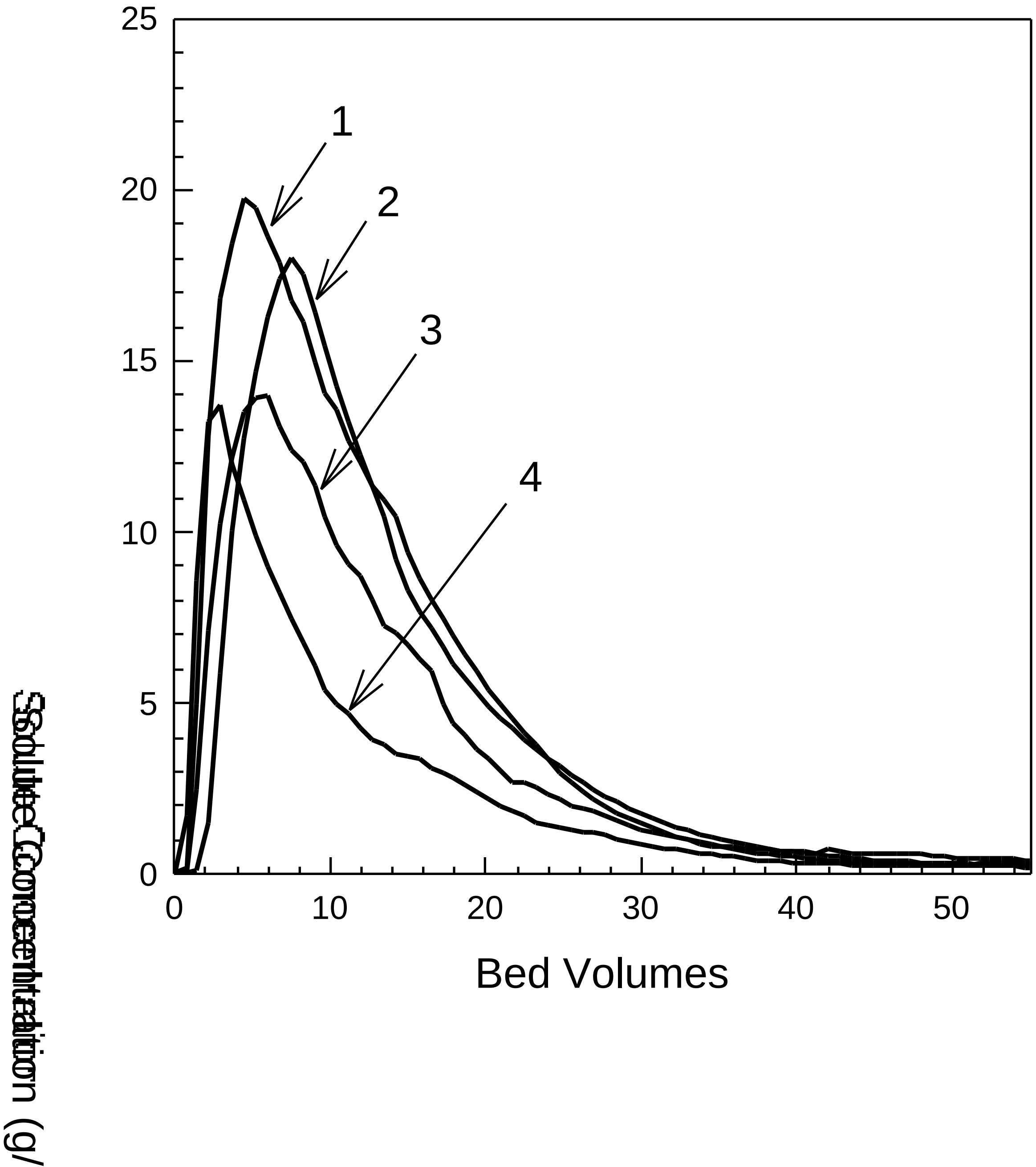


Adsorption of Benzoic Acid onto MN-170

Flow rate=2 ml/min

Bed volume 3.53 cm^3

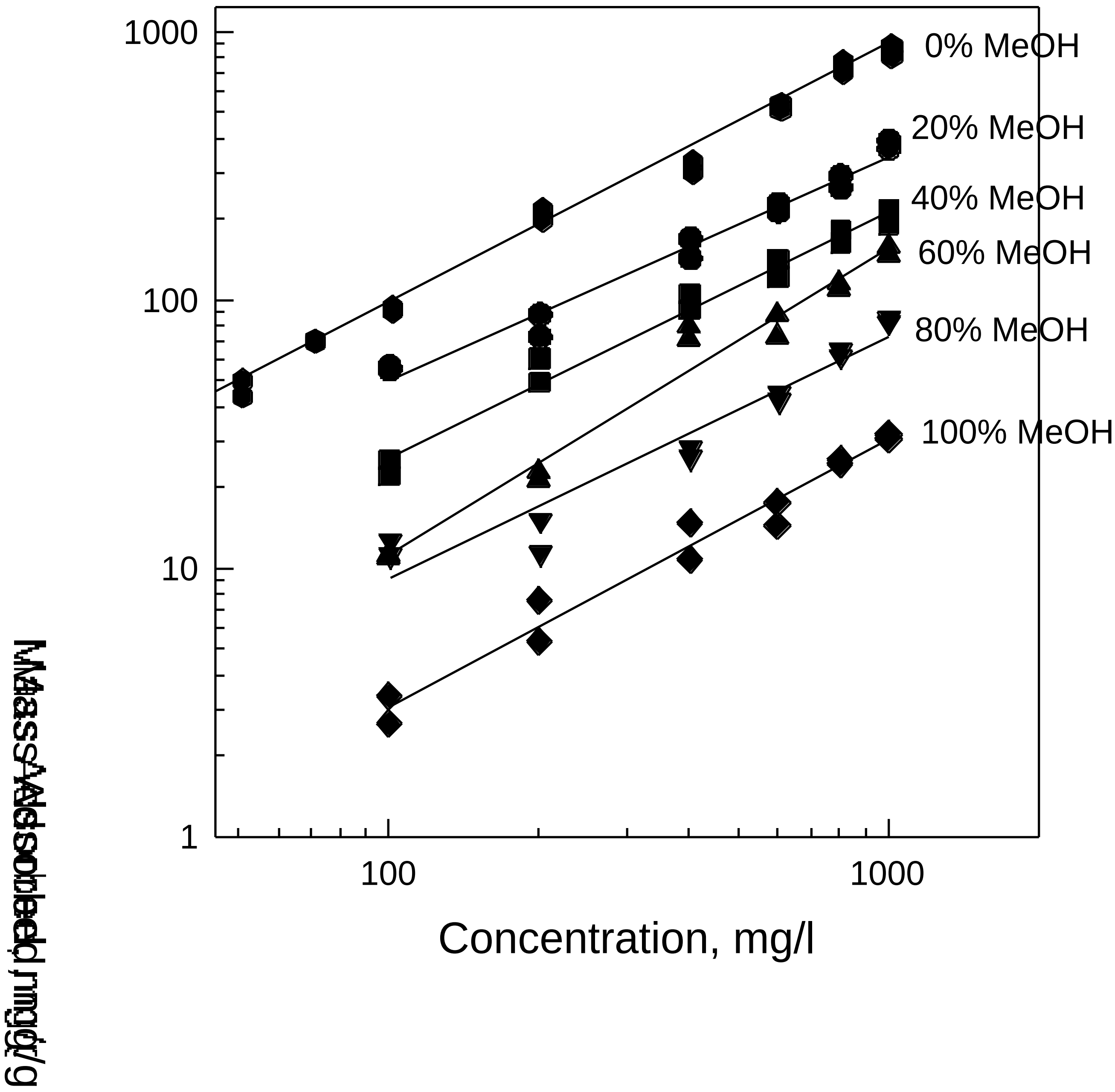
C_o= 400 mg/l

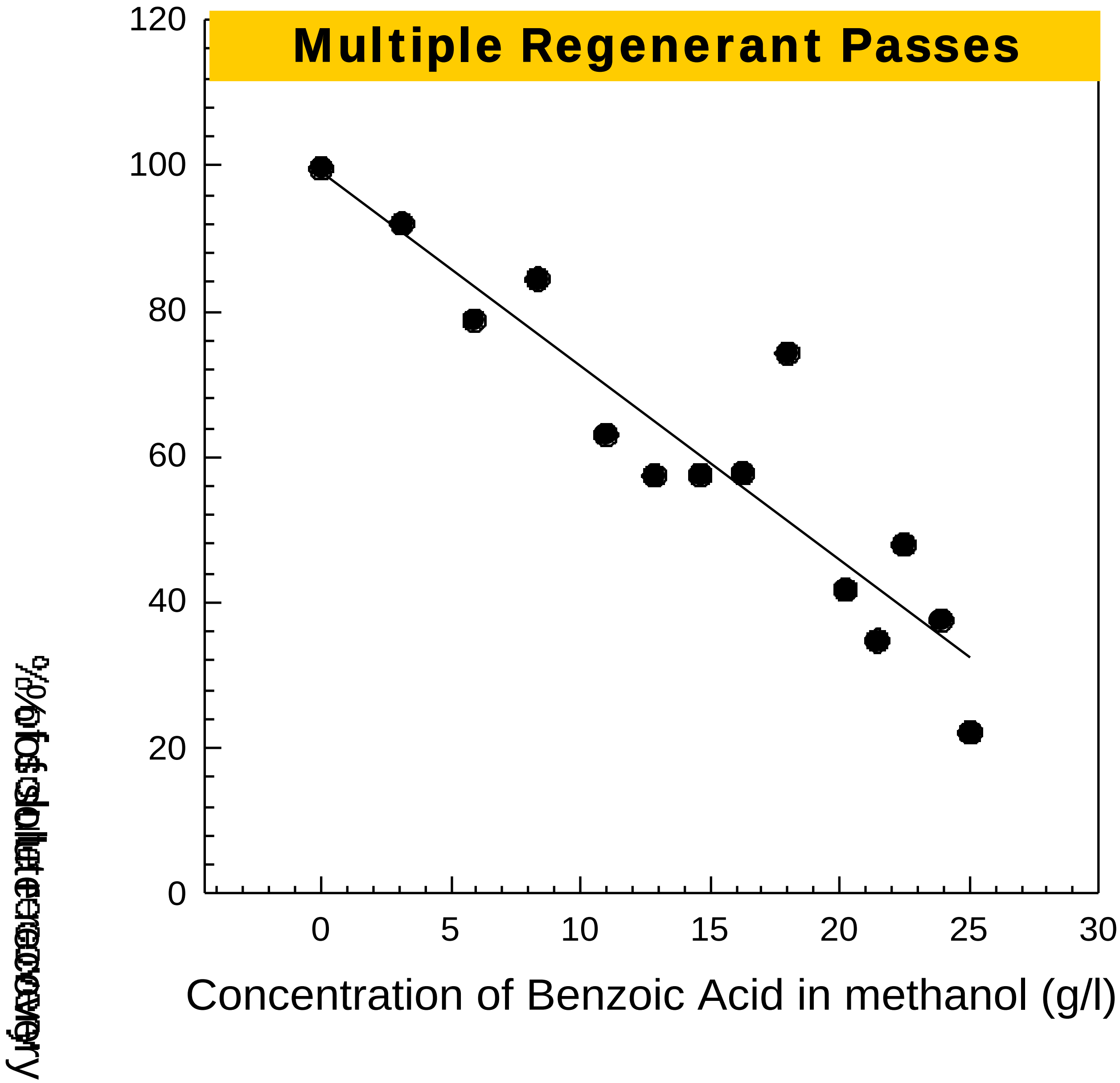


Regeneration of MN-170 Column Saturated with Benzoic Acid

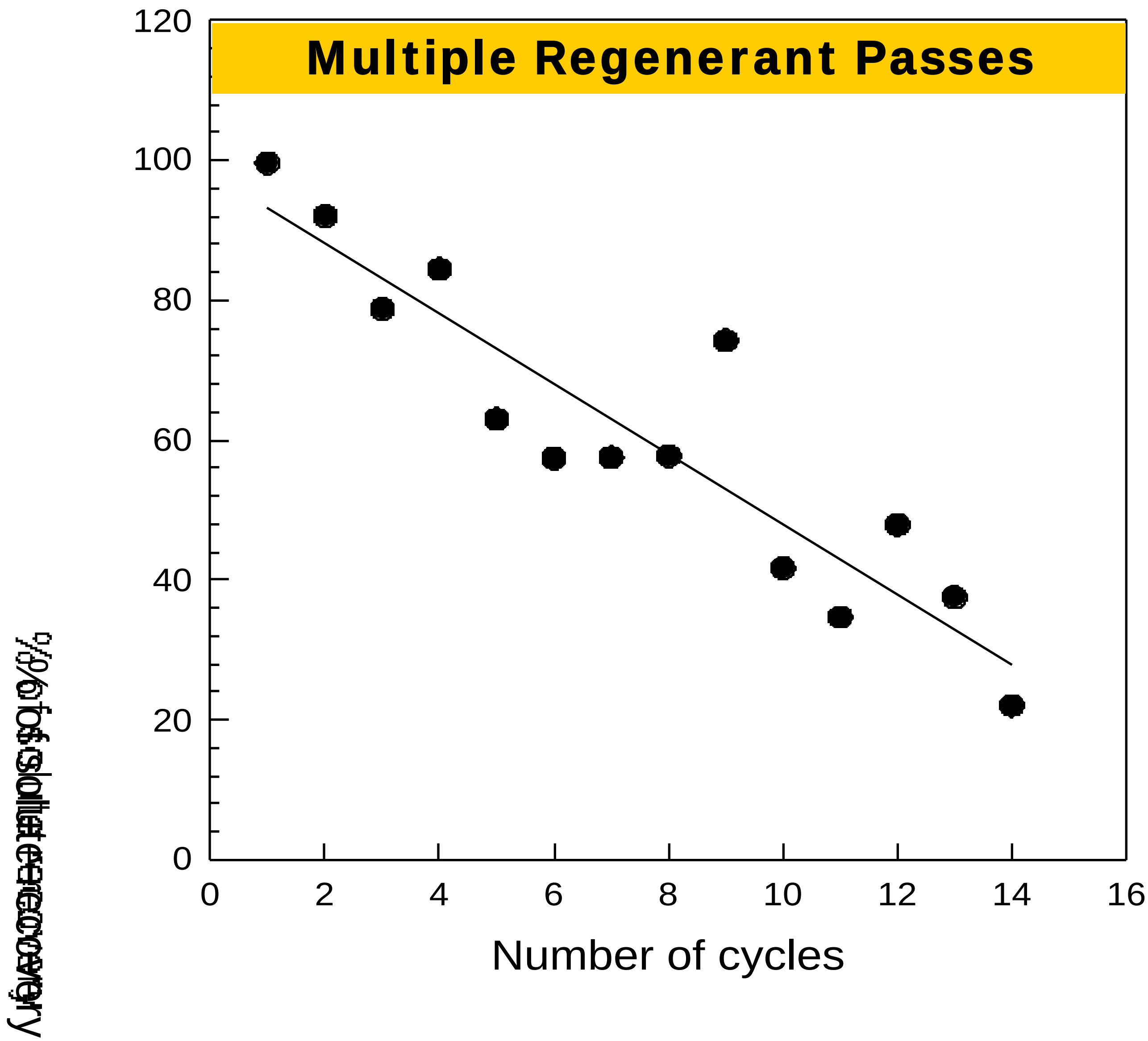
1 - 400 mg/l
2 - 300 mg/l
3 - 200 mg/l
4 - 100 mg/l

Isotherms: Benzoic Acid Adsorption onto MN-170





Benzoic Acid Recovery from MN-170 column using a recycled Methanol Stream



Benzoic Acid Recovery from MN-170 column using a recycled Methanol Stream

Solute Recovery and Solvent Regeneration

- Solute is concentrated in the regenerating stream
- Concentration factor: 10-100
- Solvent can be recycled up to 3-4 cycles
- Regenerate solvent using appropriate separation method

Resin Stability

Chlorobenzene Dynamic Adsorption Capacity over Repeated Adsorption/regeneration Cycles

q/q^{ref}

Chlorobenzene adsorption on MN-150 in a column relative to the initial equilibrium adsorption capacity. Every other cycle is plotted for clarity.

Column Adsorption Regeneration Cycles

Relative mass of chlorobenzene adsorbed onto XUS resin for repeated adsorption/regeneration cycles

Resin Stability

Resin Stability

Resin's Performance for Repeated Adsorption/Regeneration Cycles

Relative mass of benzoic acid adsorbed onto XUS resin over repeated process cycles

Resin Stability

- **Adsorption capacity is retained over many adsorption/regeneration cycles**

Mass Transfer Limitations

Source	Adsorbent	Temperature (K)	Intraparticle Diffusivity x10^{11} [m^2/s]
This study	Macronet	293	1.05
Huang et al. (1994)	Macroreticular	300	2.71
Takeuchi and Suzuki (1984)	Activated Carbon	298	0.41

Polymeric Resins and Activated Carbon

Polymeric Resins

- High surface area (>1000 m^2/g)
- Low heat of adsorption (<4 kcal/mol)
- Solvent regeneration (e.g., using aliphatic alcohols)
- No loss in performance over many cycles
- Limited choice and high cost (- $20/kg)
- Chemical selectivity is feasible

Activated Carbon

- High surface area (> 1000 m^2/g)
- High heat of adsorption (>10 kcal/mol)
- Thermal regeneration (e.g., steam regeneration).
- 5%-10% degradation per cycle
- Readily available, low cost (. $2/kg), general adsorbent material
- Spent carbon may have to be treated as hazardous waste

SUMMARY

- Polymeric sorption resins can be regenerated in-situ by solvent regeneration or thermal recovery.
- Cyclic adsorption/regeneration process is feasible.
- Solvent regeneration and solute recovery from the solvent may be the costly part of the process.
- The dominance of low cost activated carbon is an important reason for the small market share of polymeric resins and thus their high cost.

SUMMARY (Cont'd)

- Capital cost for polymeric resin packed-beds should is expected to be at the same level as for granular activated carbon adsorption.
  - Virtually no attrition of resin
  - Resin stability is maintained over many cycles
  - Regeneration can be done in-site under mild conditions
- Pilot-scale demonstration is the next step

STUDENTS

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SPONSORS

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Pertinent Publications:

- **Cohen, Y. and T. E. Browne, "Aqueous Phase Adsorption of Trichloroethylene and Chloroform by Polymeric Resins and Activated Carbon,"** ***Industrial and Engineering Chemistry Research*****, 29, 1338-1345 (1990).**
- **Gusher, M. G., T. Browne and Y. Cohen, "Sorption of Organics from Aqueous Solution onto Polymeric Resins,"** ***Industrial and Engineering Chemistry Research*****, 32, 2727-2735 (1993).**
- **Browne, T. and Y. Cohen, "Polymer-Grafted Silica: A Screening System for Polymeric Adsorption Resin Development,"** ***Industrial and Engineering Chemistry Research*****, 32, 716-725 (1993).**
- **Cohen, Y. And J. Klein, "Removal of Organics from Aqueous Systems," in Novel Adsorbents and Their Environmental Applications, AIChE Symposium Series, 91, 72-78 (1995).**