Media Performance: Laboratory Studies (Impact of Water Quality Parameters on Adsorbent Treatment Technologies for Arsenic Removal)

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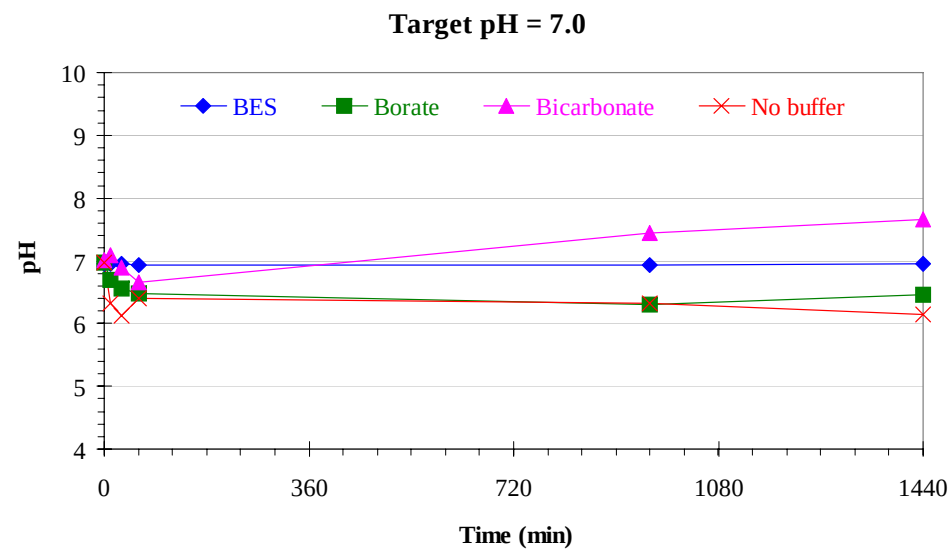
Experimental Approach

- Batch Tests
  - Preliminary Screening of Candidate Adsorbents
    - Selection of Non-Adsorbing Buffer
    - Kinetics (contact time)
    - Isotherms (absence of interferants)
  - Intensive Testing of Selected Adsorbents
    - Physical-Chemical Properties of Adsorbents
    - Isotherms (presence of interferants)
    - NSF Challenge Water and Utility-Supplied Waters
- Column Tests
- TCLP/WET Tests

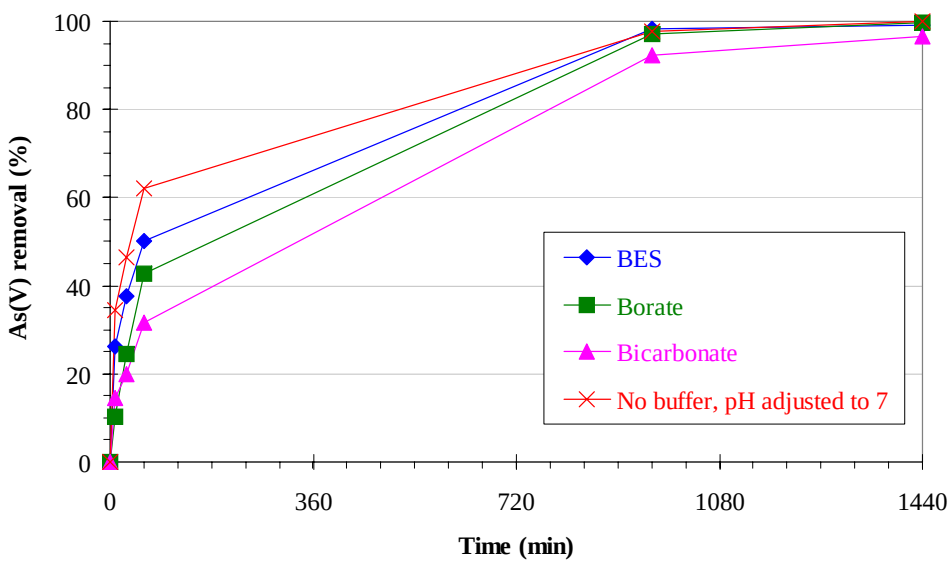
Preliminary Screening Experiments – Candidate Adsorbents

- AA-400G (activated alumina (AA))
- AA-FS50 (iron impregnated AA)
- MIEX (amagnetized ion exchange resin)
- Bayoxide E33 (granular ferric oxide (GFO))
- Granular Ferric Hydroxide (GFH)
- Metsorb (titanium dioxide)
- Z33-Revision B (iron modified zeolyte)
- ARM 100 (alumina based, with proprietary promoters)
- Sulfur Modified Iron Version III (SMI)
- ViroClear Bauxsol F3 (Bauxite Clay)
- Geothite (α-FeOOH)
- Pyrolusite (β-MnO_2)

Non-Adsorbing Buffer (w/ GFH)

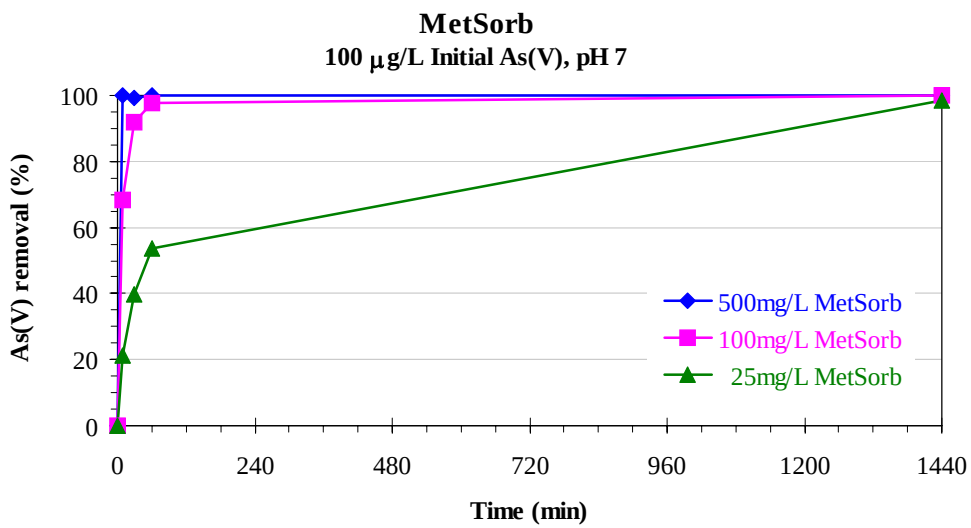


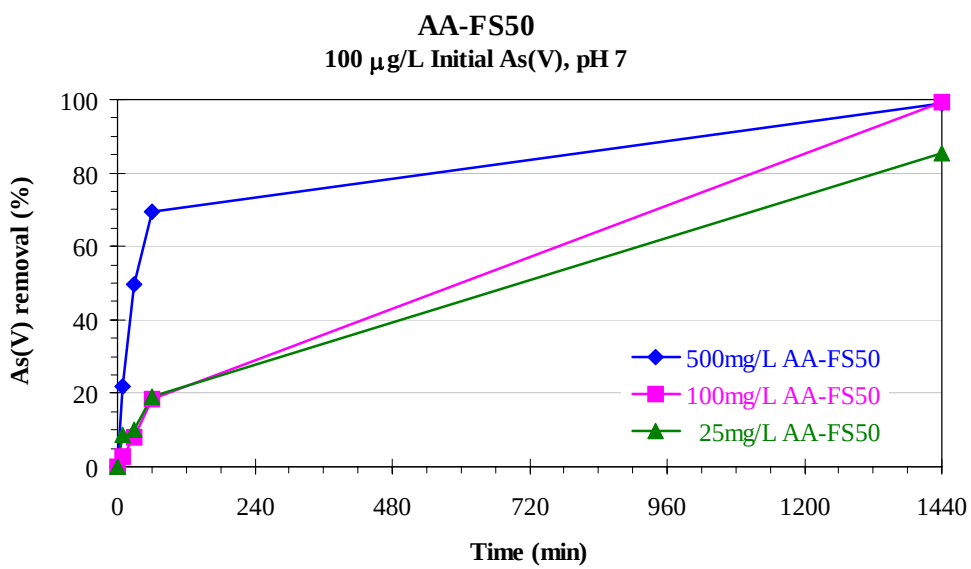
None (Milli-Q)
Bicarbonate
Borate
BES
(N,N-Bis(2-hydroxyethyl)-2-aminoethanesulfonic Acid)



2 mM BES Buffer

Kinetics



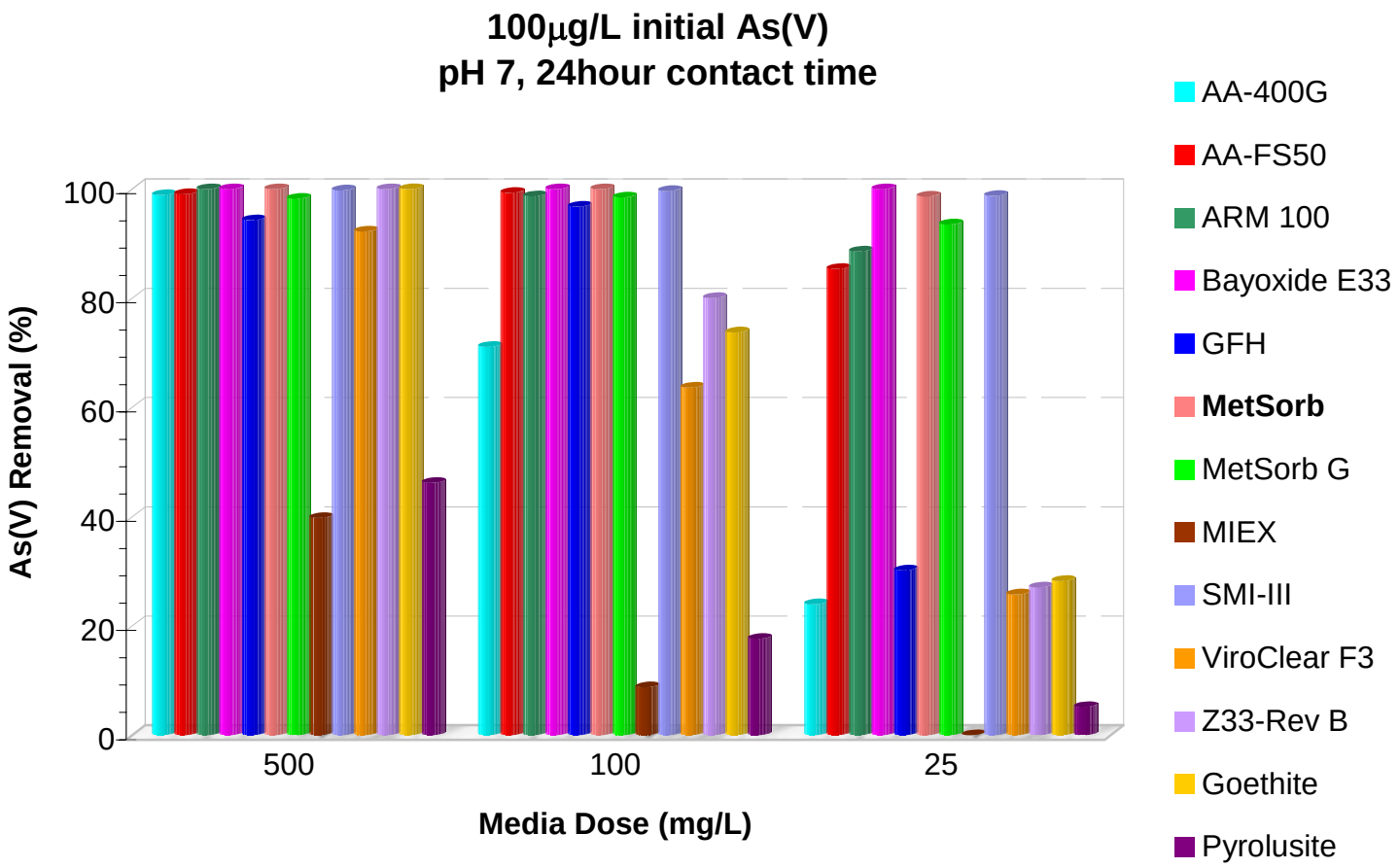


Rapid Kinetics:
Bayoxide E33
ARM 100
Metsorb
MIEX
Pyrulosite

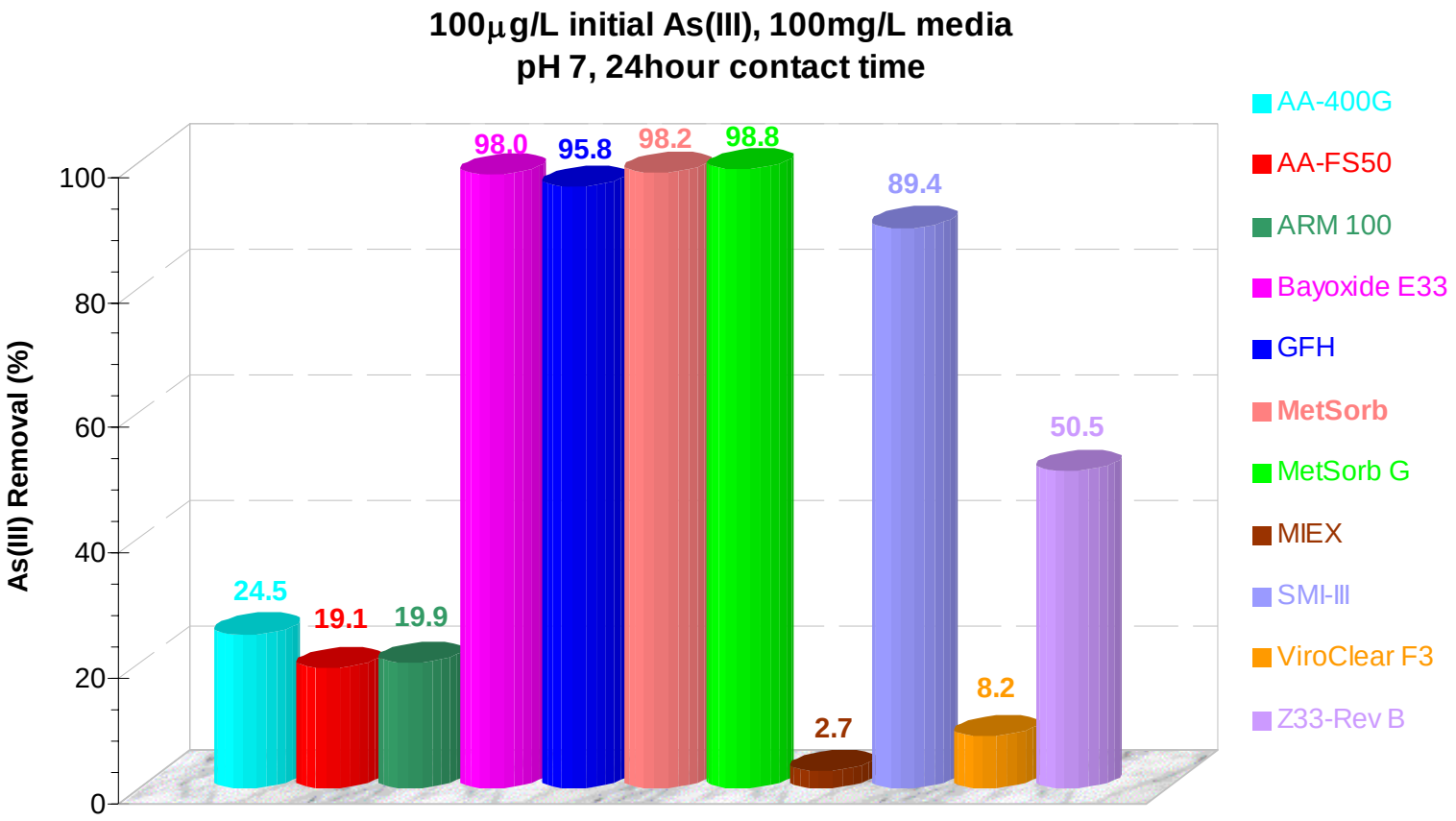
24 hours ⇨ Pseudo-Equilibrium

Slower Kinetics:
AA-400G
AA-FS50
GFH
Z33
Goethite

Preliminary Screening Experiments – % Removal of As(V) by Candidate Adsorbents



Preliminary Screening Experiments – % Removal of As(III) by Candidate Adsorbents



Intensive Testing – Selected Adsorbents

- Bayoxide E-33
- GFH
- MetSorb G
- AA-FS50
- Z33 (Revision b)

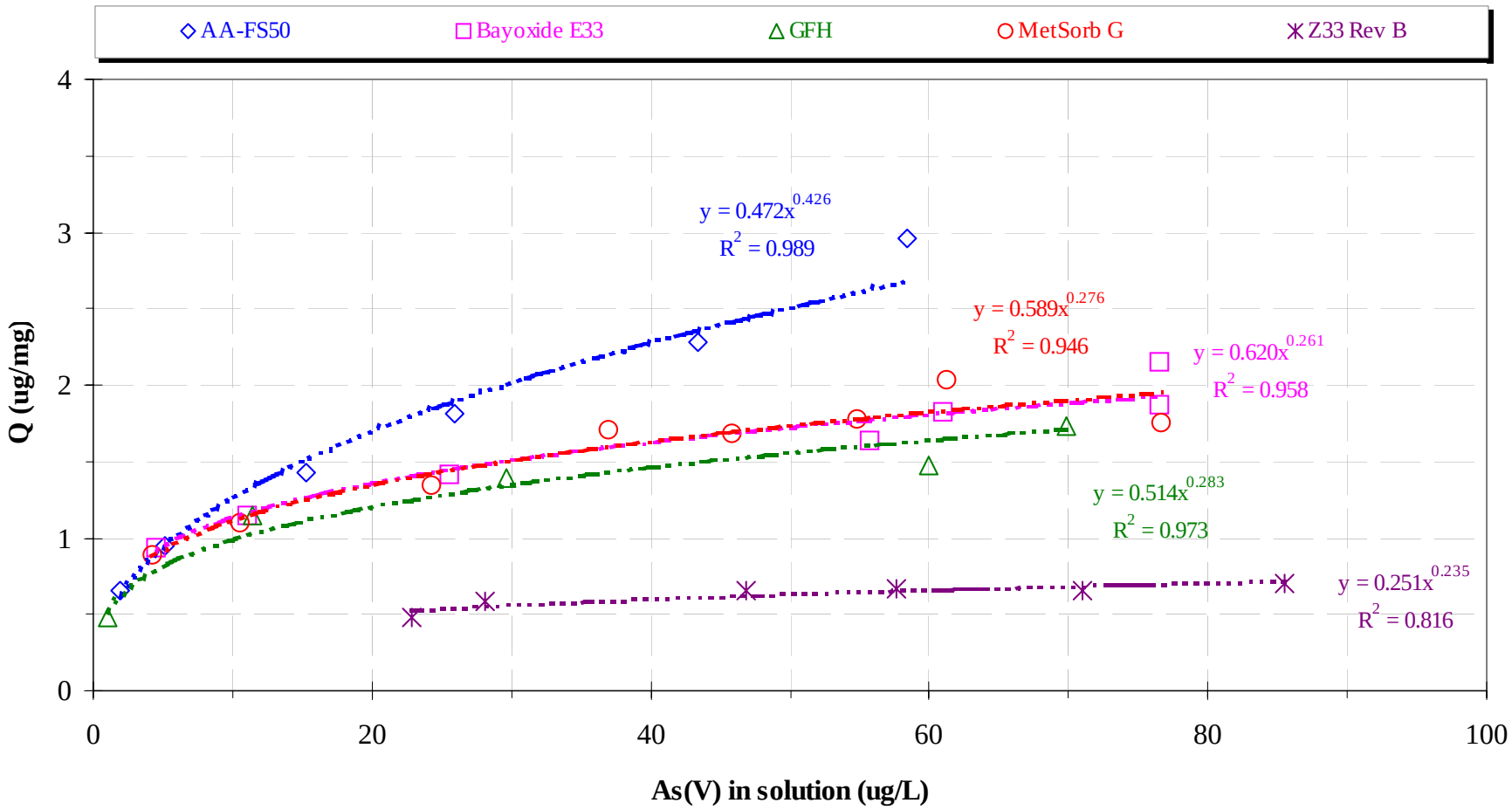
Criteria: As(V) capacity, As(III) capacity, and other factors

Physical/Chemical Properties of Adsorbents

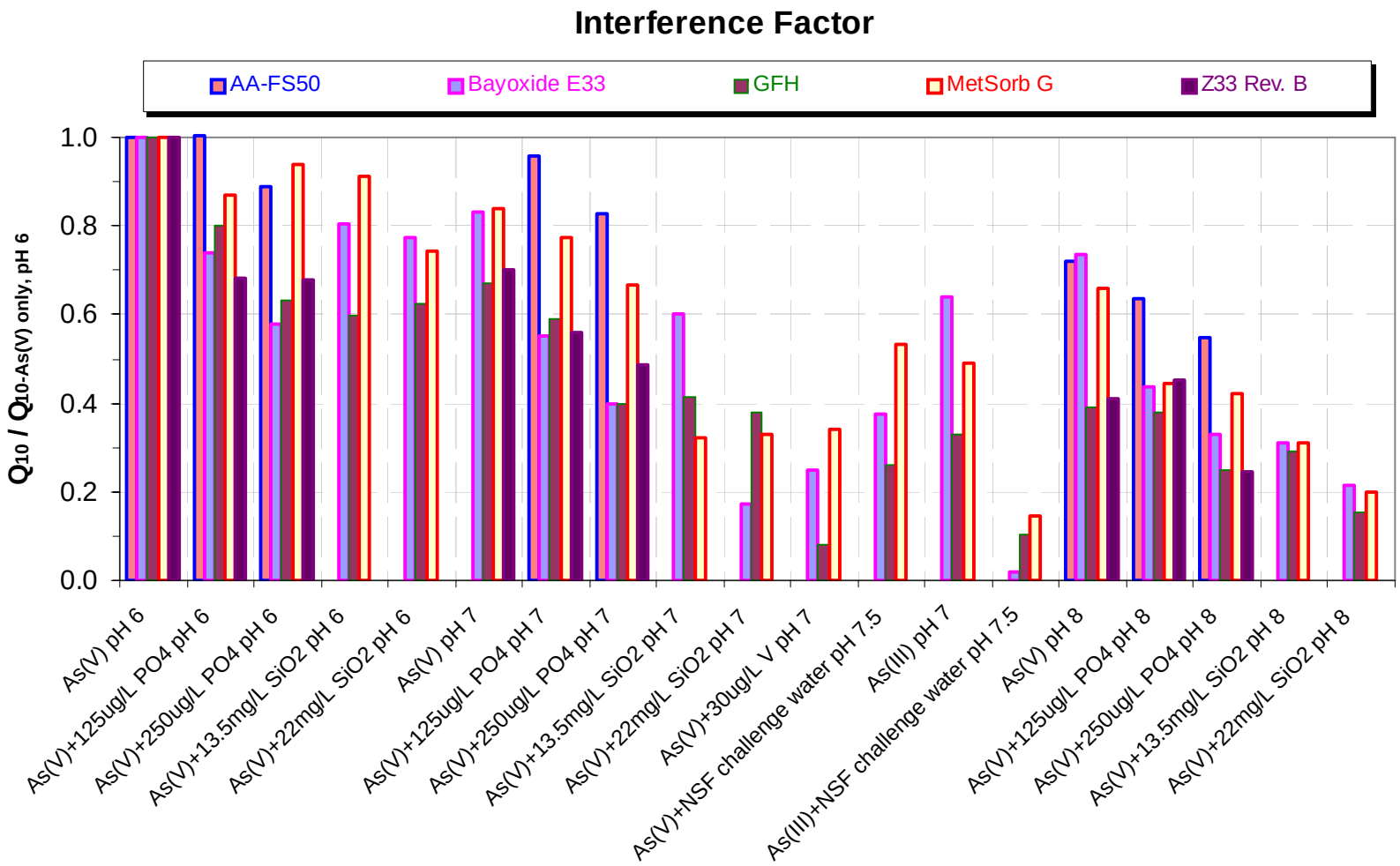
Adsorbent	Property				
	Grain Size (mm or mesh)*	Bulk Density (g/mL)	pH_{ZPC}	Surface Area (m^2/g) (BET)	Mineral Identity (by XRD)
AA-FS50	28-48 mesh	0.75 (dry)	7.28	246	Aluminum oxide Hydrate (Boehmite)
E33	0.5 – 2.0 mm (10-35 mesh)	1.19 (wet)	8.28	119	Iron oxide hydrate (Goethite)
GFH	0.32 - 2.0 mm	1.19 (wet)	7.57	242	Iron oxide (Akaganeite)**
Metsorb G	16 – 50 mesh	0.78 (dry) 0.88 (wet)	4.68	166	Titanium oxide (Anatase)
Z33	100-140 mesh	0.88	4.79	36.9	Calcium aluminum silicate hydrate (Heulandite)
SMI	n/a	2.15	n/a	4.46	n/a

*10 mesh = 0.1 inches = 0.254 cm = 2.54 mm
**Traces of Hematite and Geothite also identified in contrast to previous studies

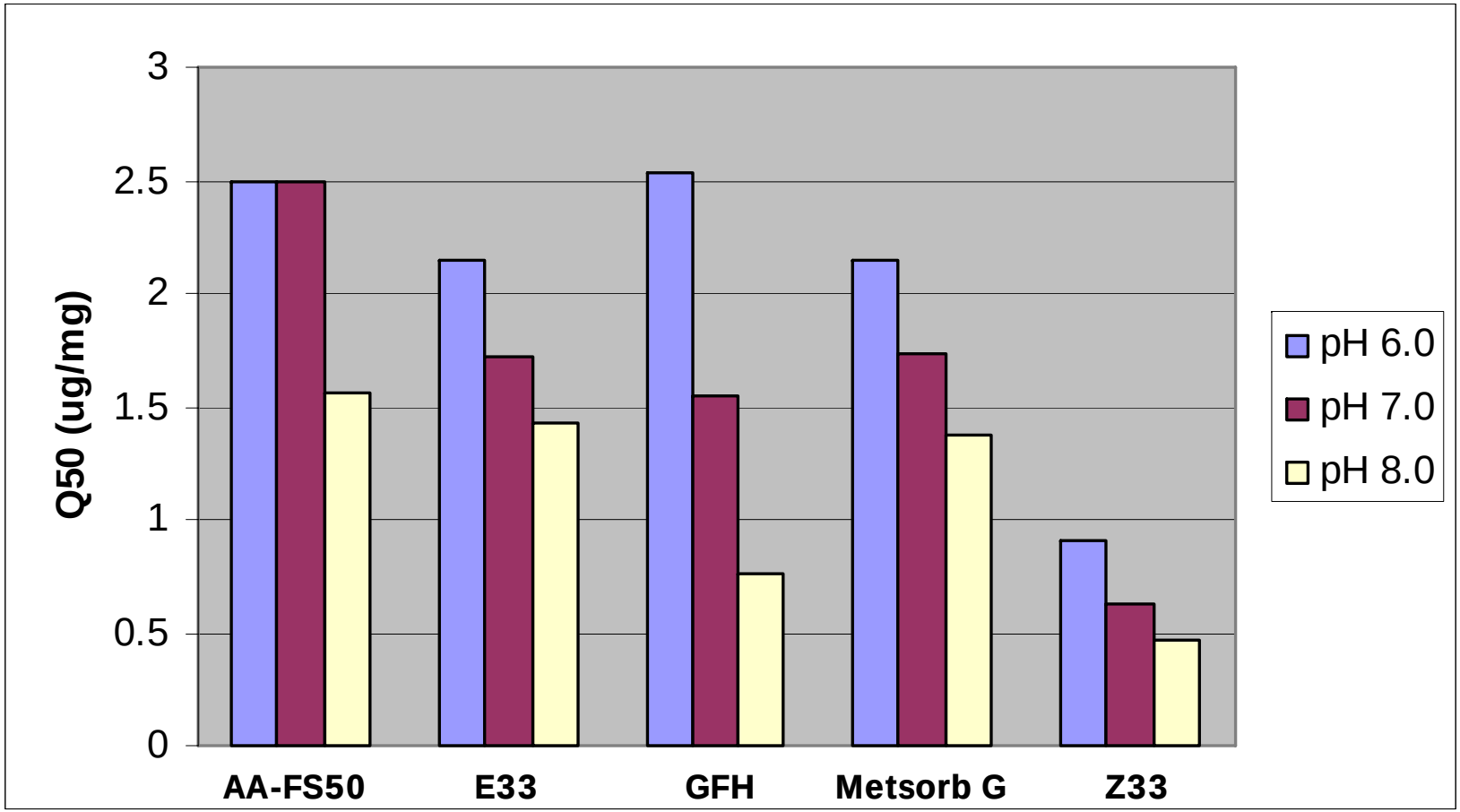
As(V) Adsorption Isotherms @ pH 7.0
(Single Solute)



Summary of Interference Factors (Ratio of As(V) Capacity to that at pH 6.0 in the Absence of Interferents)



As(V) Adsorption: pH Effects on Q_{50} (Q_{50} in equilibrium with C = 50 ug/L)

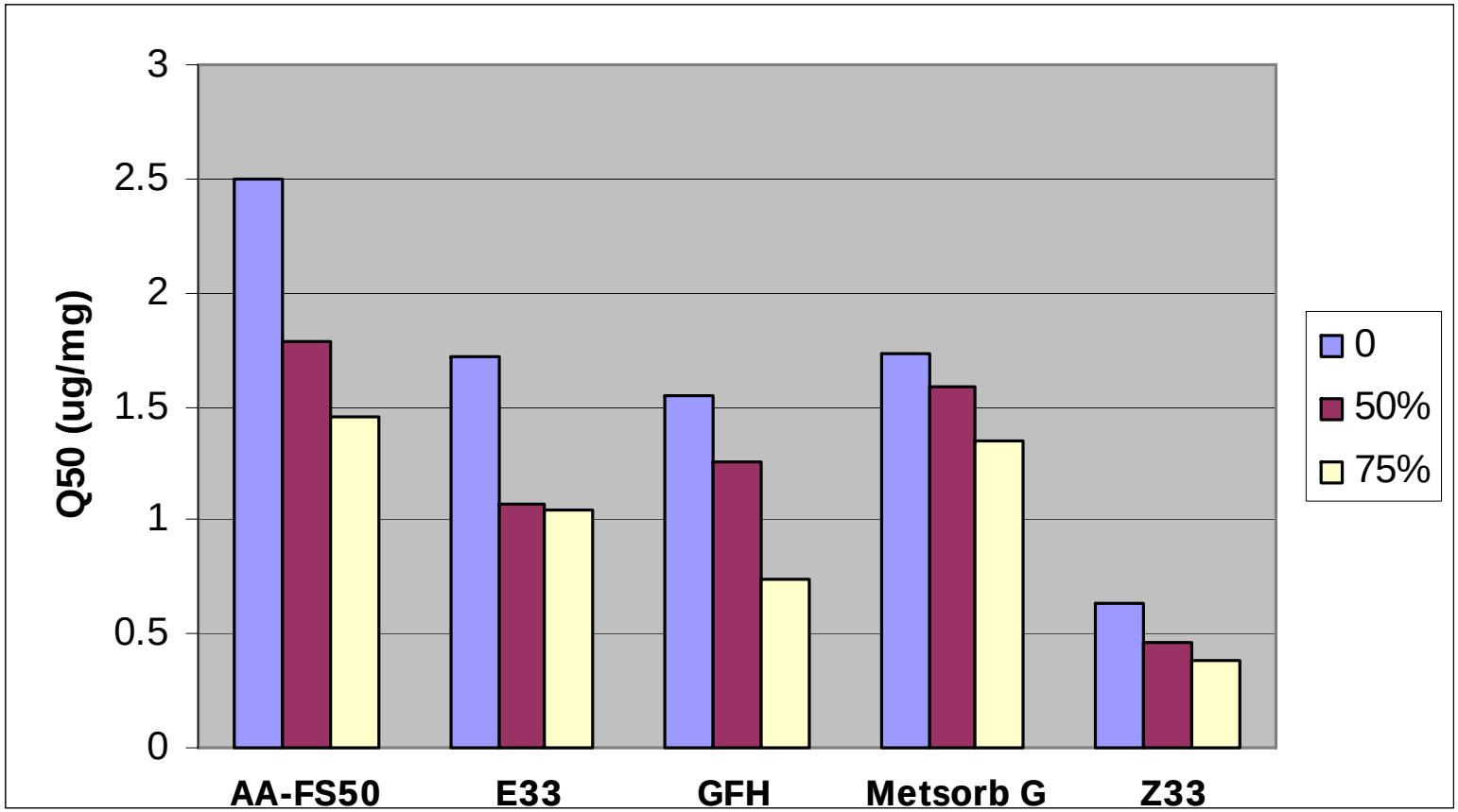


Concentrations of Interferents based on U.S. Co-Occurrence Survey

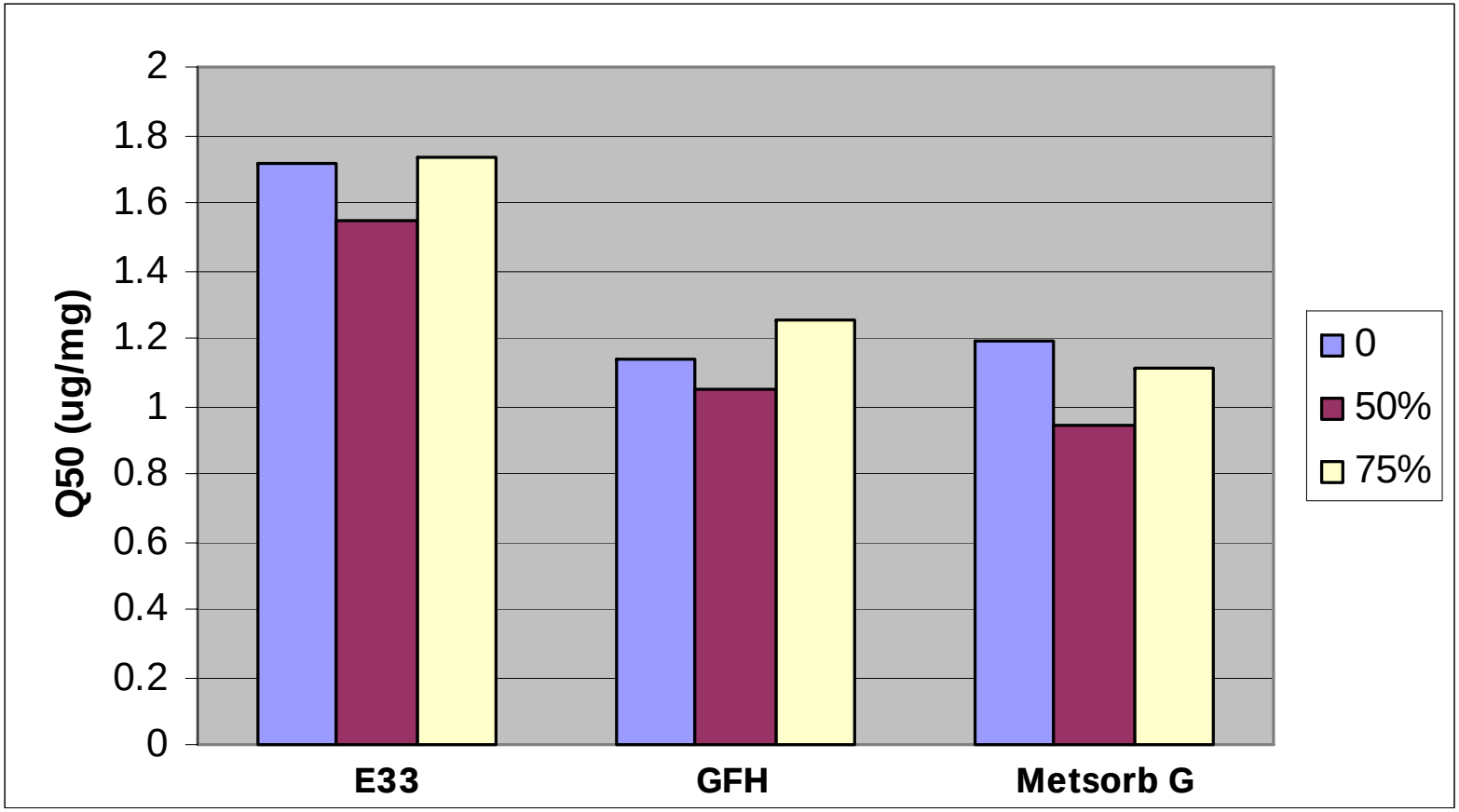
Component*	Units	50 Percentile Concentration	75 Percentile Concentration
Phosphate	ug/L as PO_4^{3-}	125	250
Silicate	mg/L as SiO_2	13.5	22
Vanadate	ug/L as V	18	30

*Others: Fluoride, Sulfate, Carbonate

As(V) Adsorption: PO_4^{3-} Effects @ pH 7.0

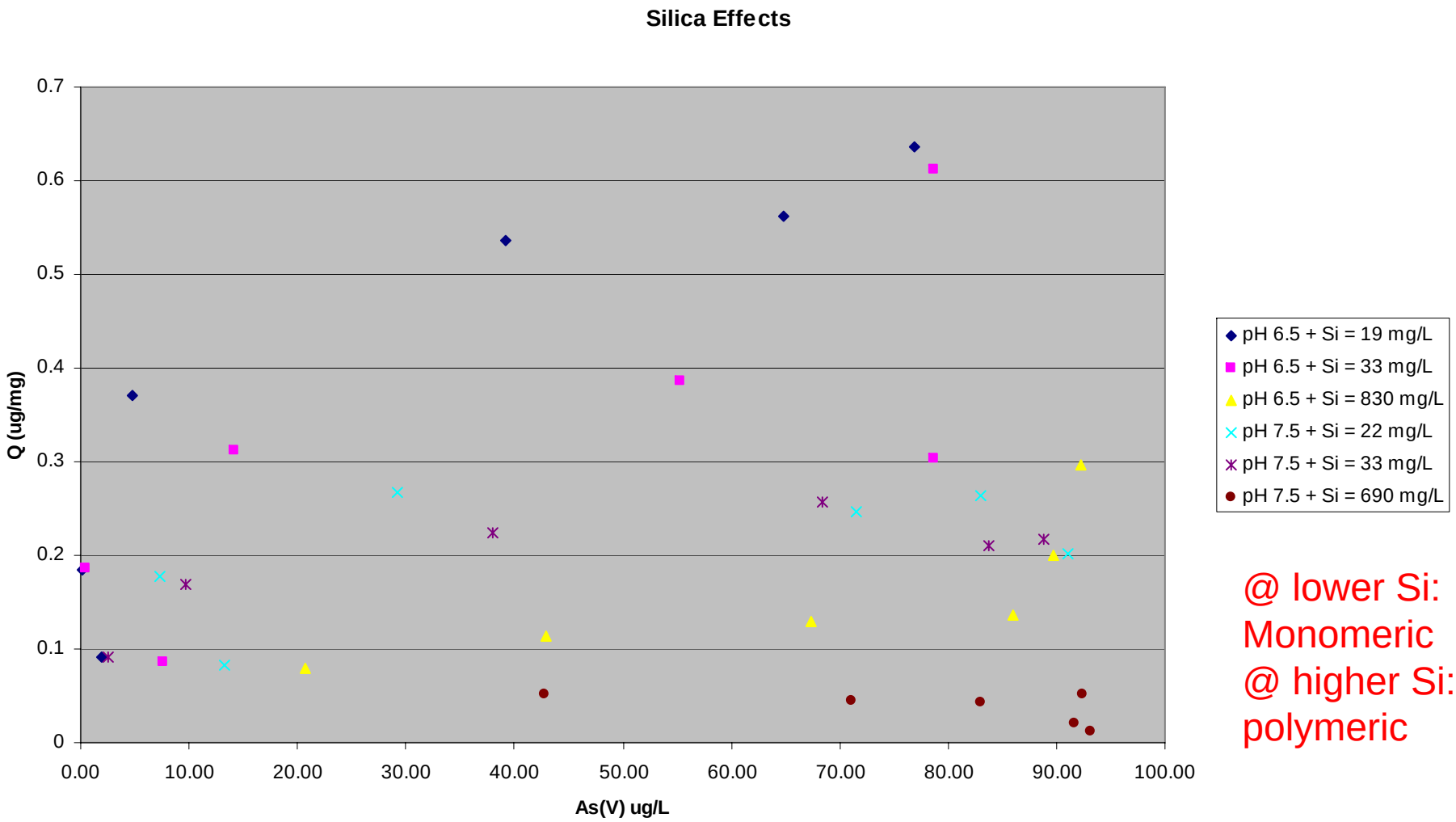


As(V) Adsorption: SiO_2 Effects @ pH 7.0



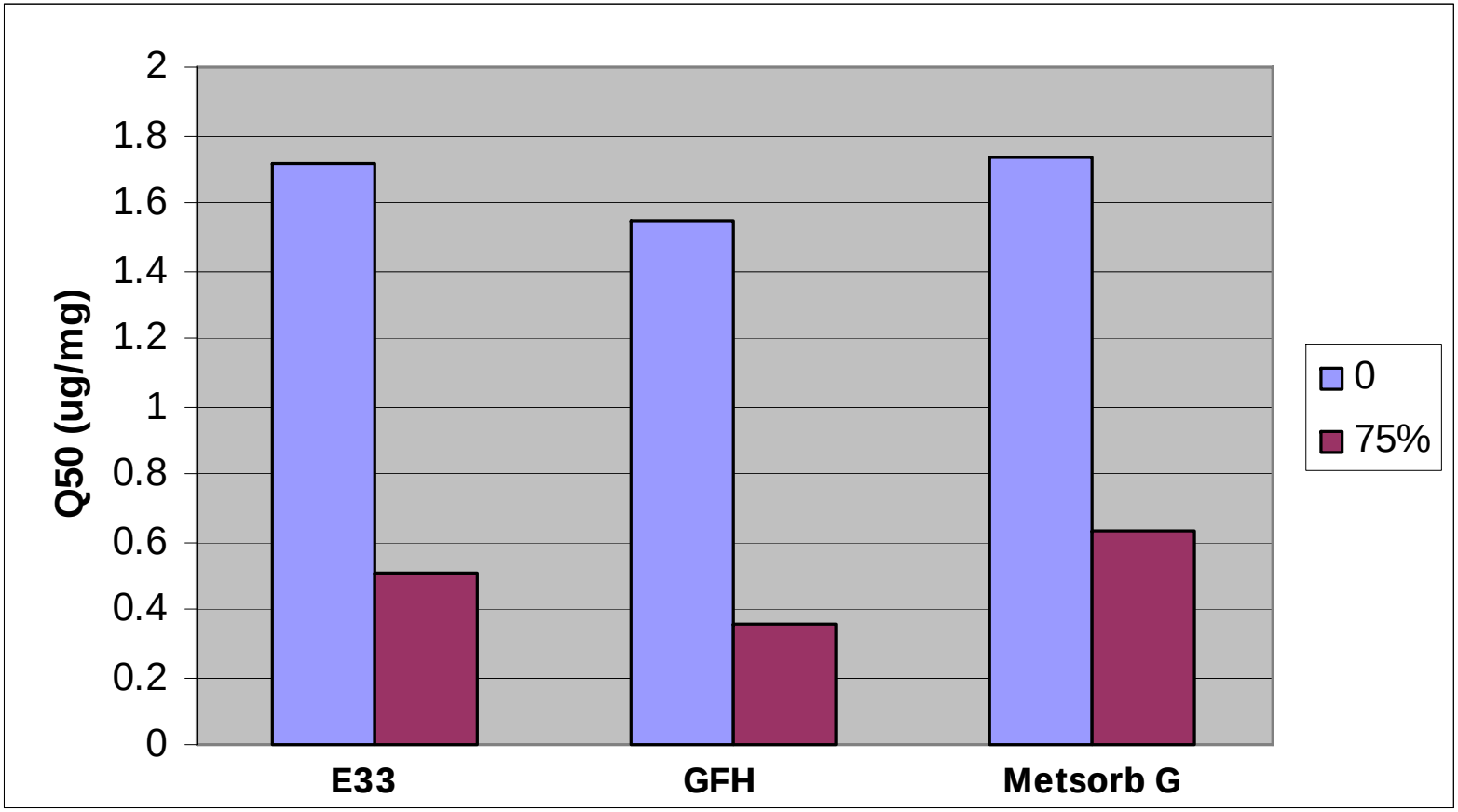
Monomeric vs. Polymeric Silica?

Isotherms for GFH with As(V) at Varying pH Levels and Silica Concentrations

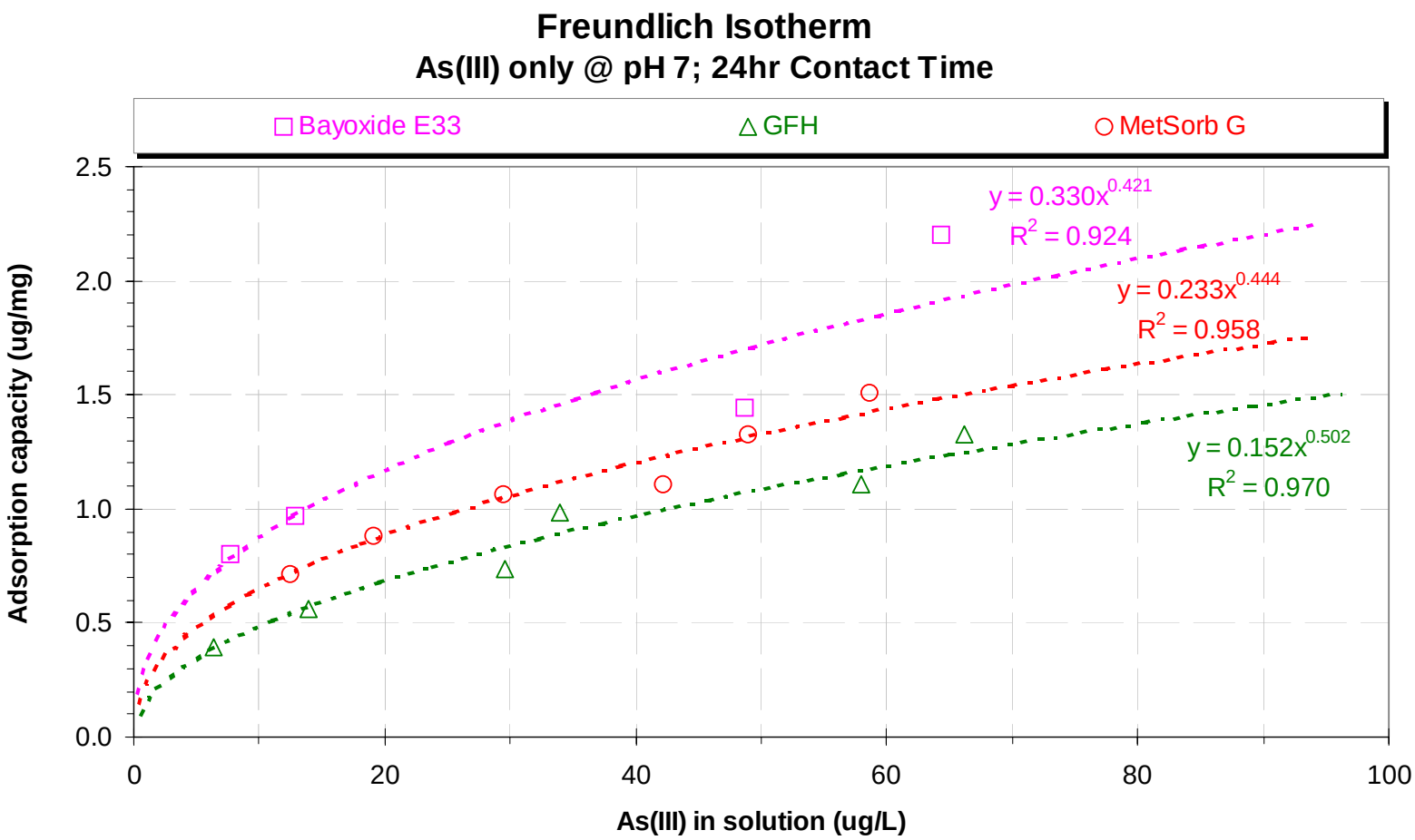


@ lower Si: Monomeric
@ higher Si: polymeric

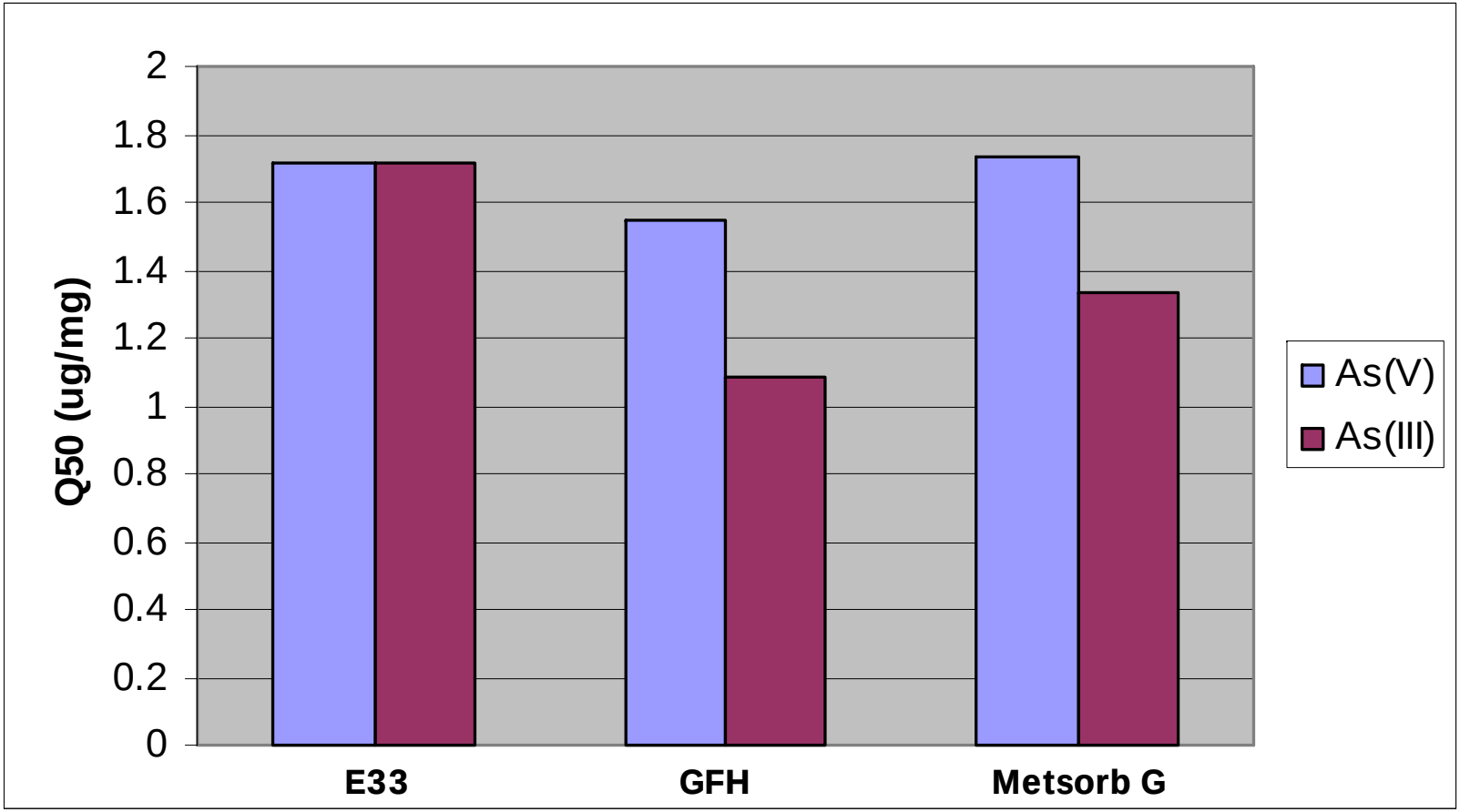
As(V) Adsorption: V Effects @ pH 7.0



Isotherms for As(III) at a pH of 7.0: Absence of Interferants.



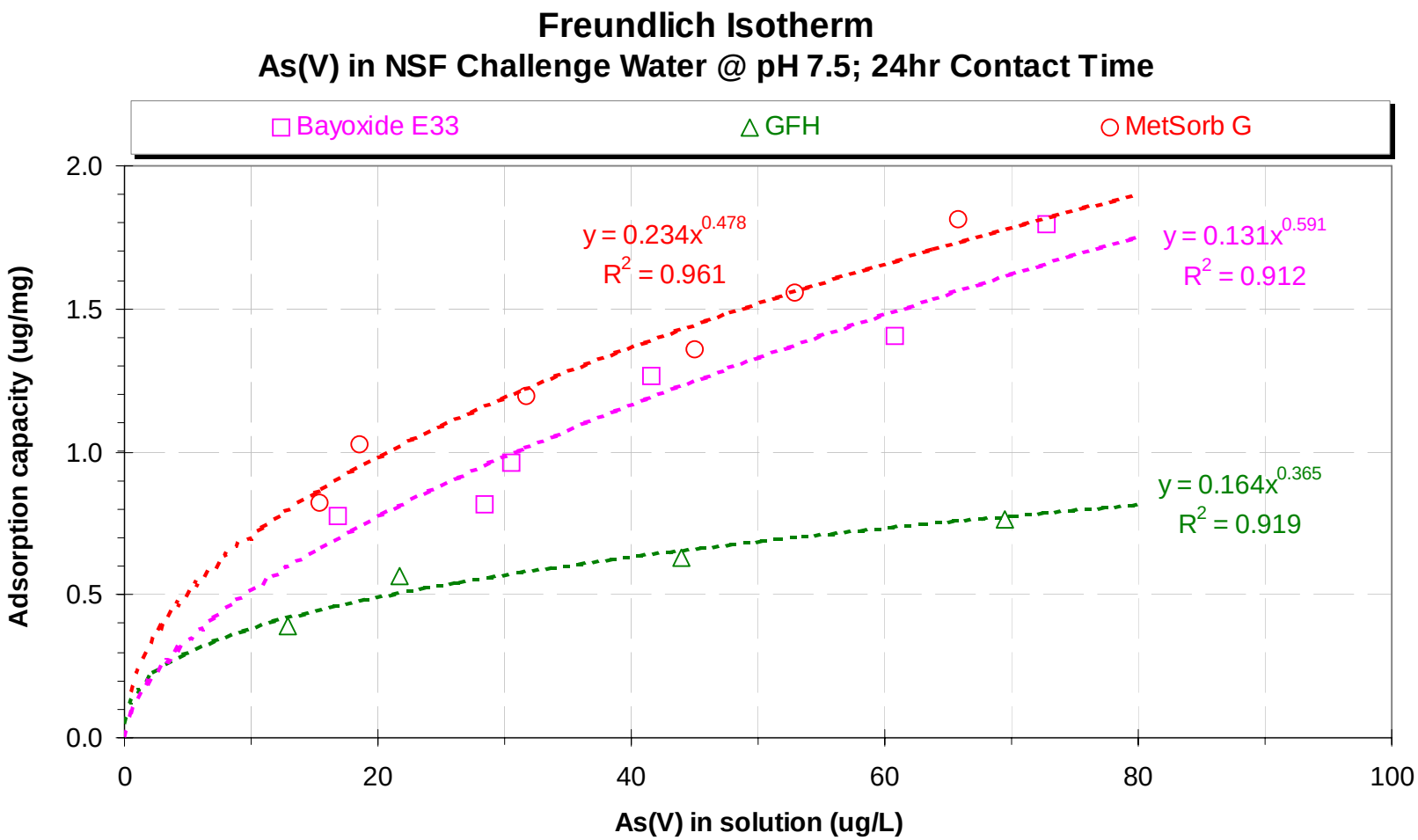
As(V) vs. As(III) Adsorption @ pH 7.0



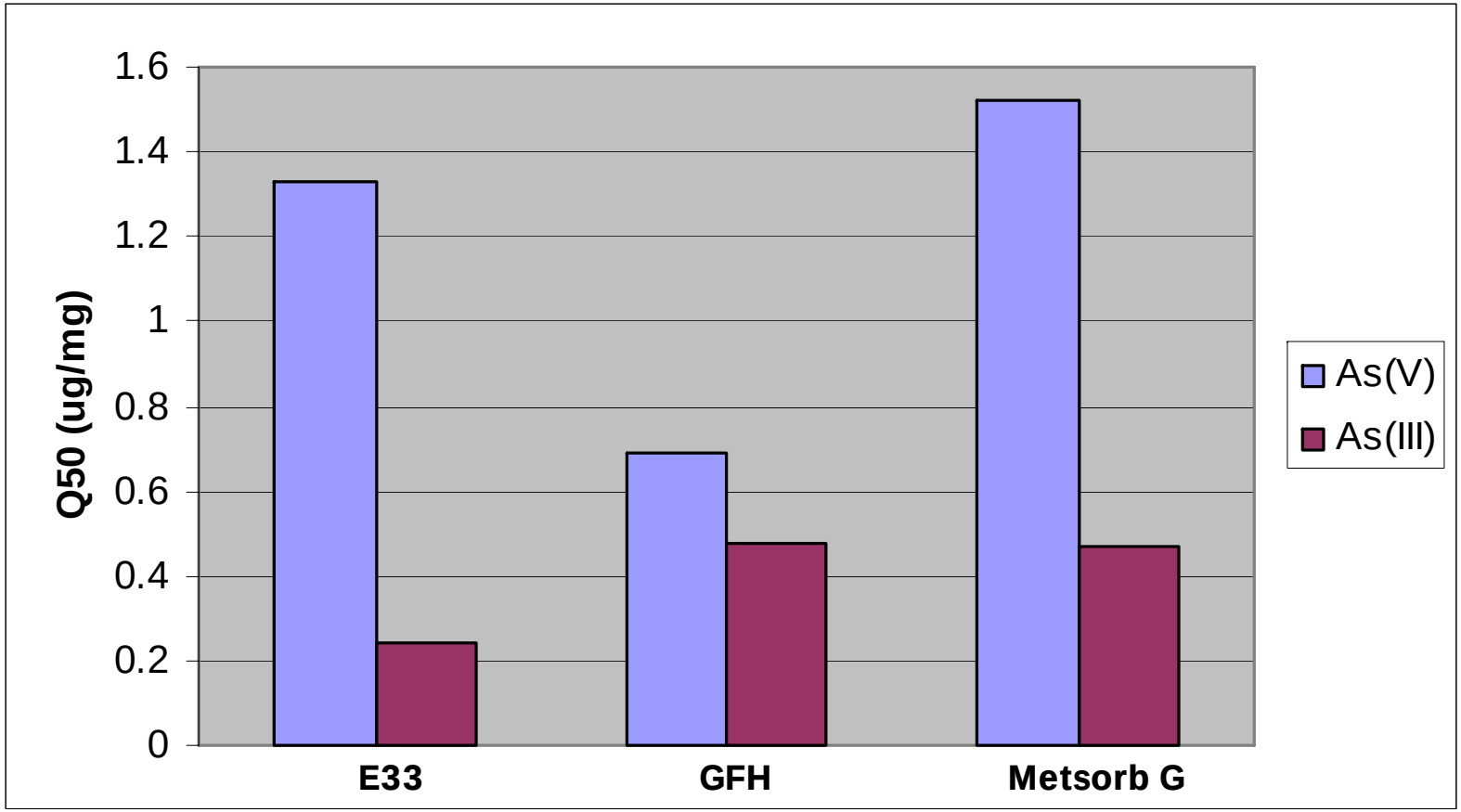
Ionic Composition of Standardized (NSF) Challenge Water (pH = 7.5)

Component	Concentration (mg/L)	Component	Concentration (mg/L)
Na^+	74	SO_4^{2-}	50
Ca^{2+}	40	NO_3^--N	2.0
Mg^{2+}	13	F^-	1.0
HCO_3^-	183	PO_4^{3-}-P	0.04
Cl^-	71	SiO_2	20

Isotherms for As(V) in NSF *Challenge* Water



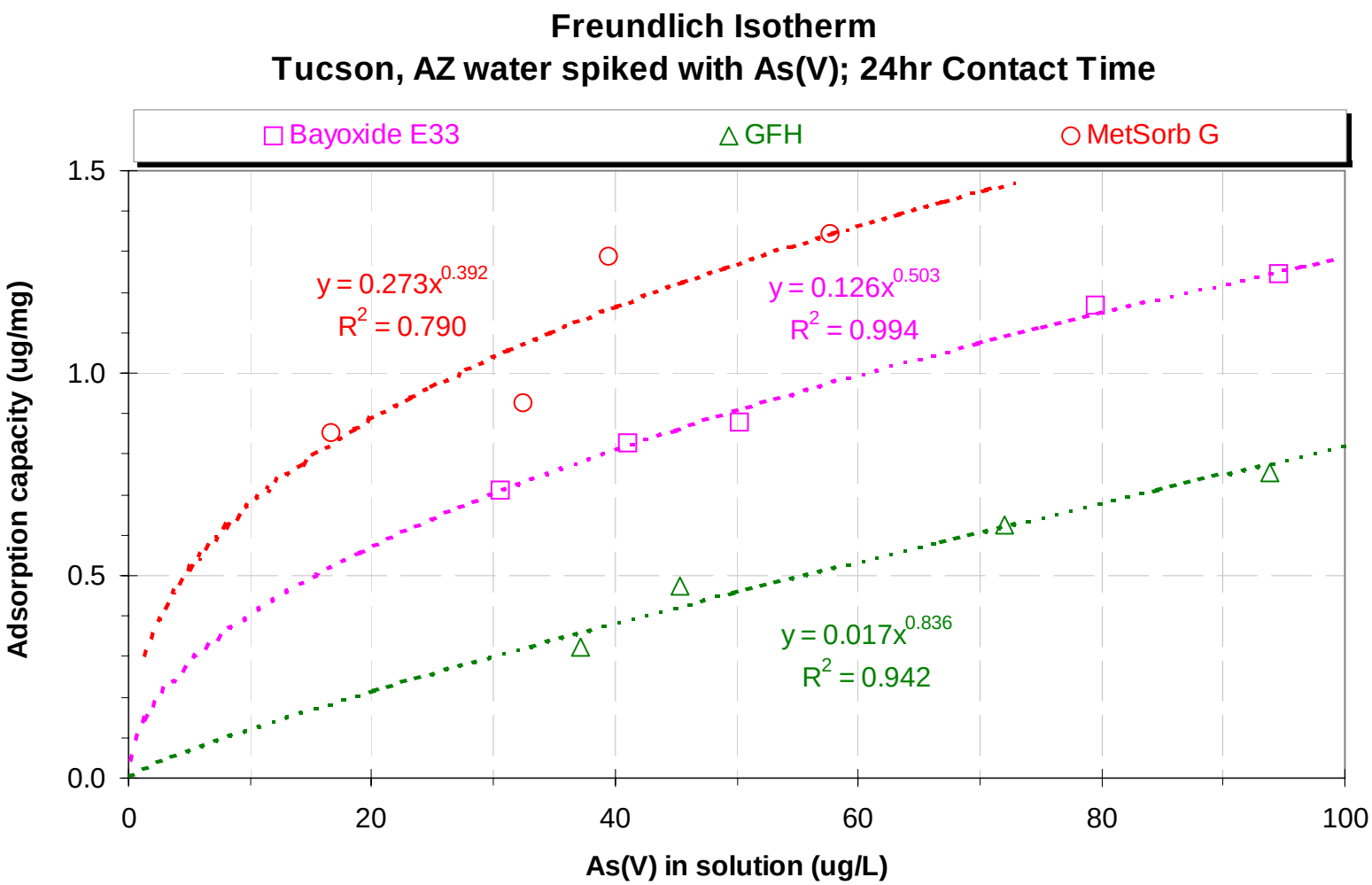
As(V) vs. As(III) Adsorption: NSF Test Water



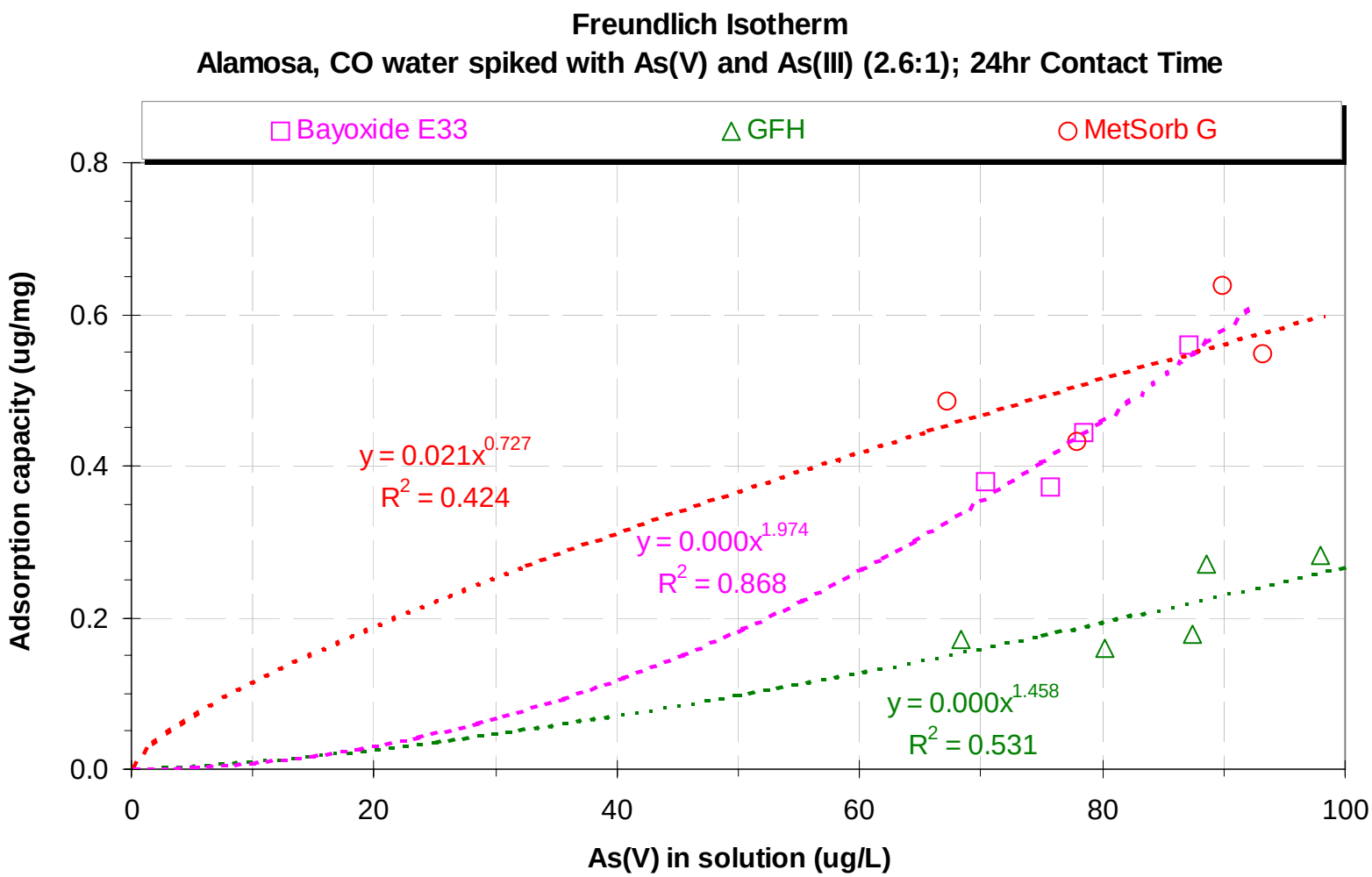
Water Quality Summary of Utility-Supplied Waters

Parameter	Water			
	Tucson AZ	LADWP CA	El Paso TX	Alamosa CO
V (ug/L)	66	5	6	125
SiO_2 (mg/L)	28	28	28	93
PO_4^{3-} (ug/L)	18	78	35	26
pH	7.9	7.7	8.5	8.3
As_{total} (ug/L)	12.6	25.6	22.9	40.9
As(V) (ug/L)	12.6	25.6	12.4	29.6
As(III) (ug/L)	0	0	10.5	11.4

Isotherms for Utility-Supplied Water: Tucson AZ Groundwater



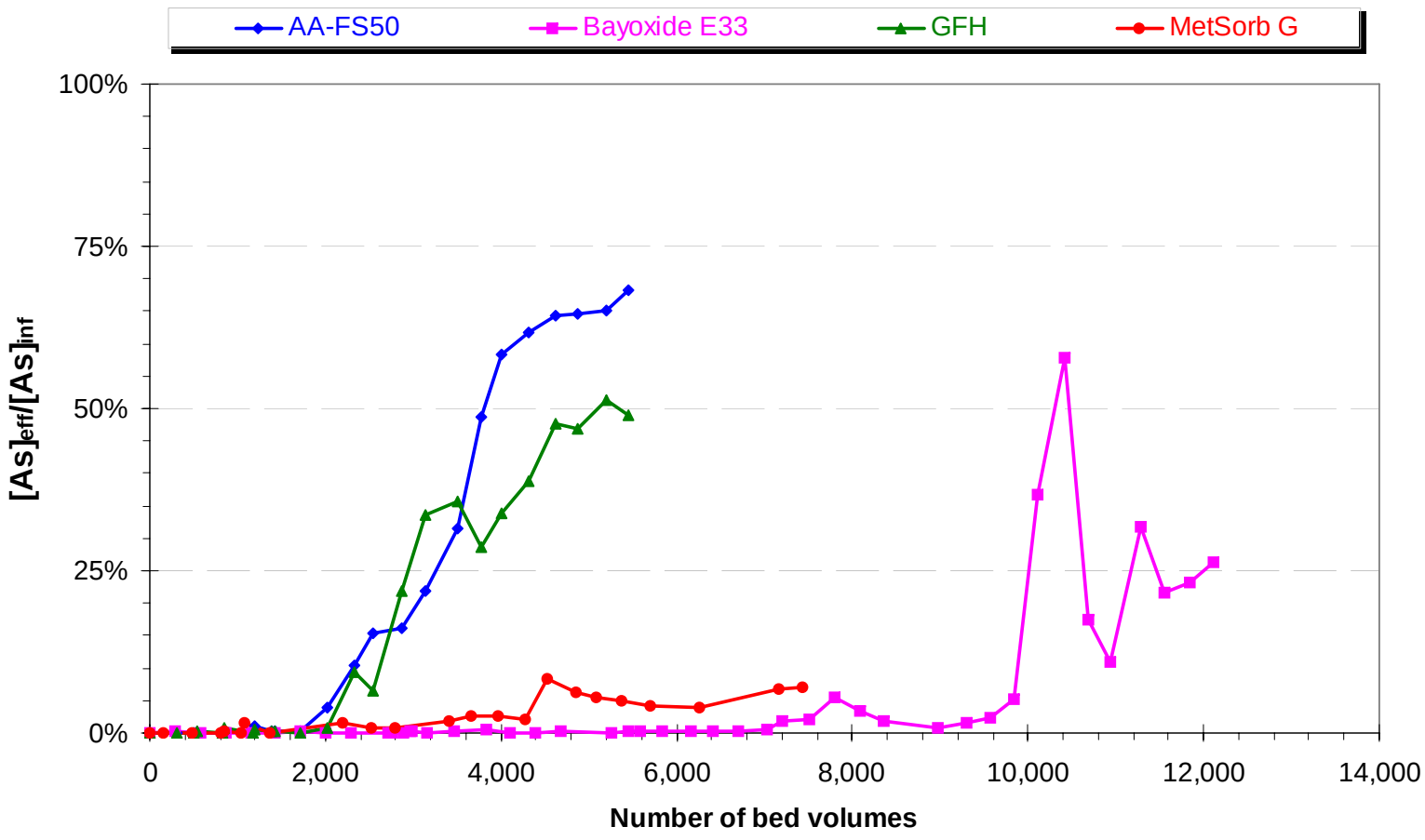
Isotherms for Utility-Supplied Water: Alamosa CO Groundwater



Experimental Conditions Employed in Column Tests

	Adsorbent			
	Bayoxide E33	AA-FS50	GFH	Metsorb G
EBCT (min)	5	5	5	5
HLR (cm/min)	8.2	4.1	2.0	2.0
D (cm)	40	20	10	10
A (cm^2)	1.3	5.1	5.1	1.3
Media mass (g)	20	110	59	9.3
BV/hour	12	12	12	12
$As(V)_0$ (ug/L)	250	1,000	1,000	1,000

Breakthrough Curves (BTCs) for Column Tests with NSF Challenge Water



Column-mode versus Batch-mode Capacities

Adsorbent	Column-Mode (ug/mg) (integration of BTC)	Batch-Mode (ug/mg) (Q_{100} from isotherm)
Bayoxide E33	6.55	1.99
AA-FS50	3.46	n/a
GFH	3.51	0.87
Metsorb G	9.44	2.11

- High initial As concentration in column tests
- 24-hour psuedo-equilibrium time in batch tests
(inadequate in establishing true equilibrium for porous adsorbents?)
- another mechanism of As(V) removal other than adsorption (e.g., surface precipitation)

TCLP and WET results for spent media from column tests

	TCLP As (ug/L)		WET As (ug/L)	
	Avg	Std dev	Avg	Std dev
Bayoxide E33	0.3	0.0	88	1.4
GFH	0.1	0.2	1023	32
AA-FS 50	12.8	1.1	1337	37
Metsorb	1.6	0.1	129	13

Summary

- Each Adsorbent Independently
  - AA-FS50 showed moderate decrease in capacity as pH increased, significant decrease in capacity in the presence of fluoride (results not shown), and small impact by phosphate
  - Bayoxide E33 media showed only slight pH effect but exhibited significant impacts by phosphate and vanadium with some silica effects
  - GFH showed a decrease in performance as pH increased, with phosphate, silica, and vanadium exhibiting adverse effects
  - MetSorb G showed a decrease in performance as pH increased, with phosphate, silica, and vanadium exhibiting effects, although the interferent effects were less at lower pH
  - Z33 performance decreased as pH increased and phosphate had a significant effect

Summary – cont.

- Adsorbent Comparisons
  - The two iron oxide media (Bayoxide E33 and GFH) and Metsorb G generally showed comparable capacities although GFH performance dropped sharply at highest pH; interferant effects were lowest for Metsorb G (pH_{ZPC}: E33 > GFH)
  - The iron-modified activated alumina (AA-FS50) showed higher capacity than the two iron oxide media and Metsorb G at lower pH, but a lower capacity at higher pH, indicating more of a pH dependency
  - The iron-modified zeolite (Z33) generally exhibited the lowest capacity (lowest specific surface area)
  - As(III) capacity:
    - As(V) > As(III)
    - E33 > Metsorb G > GFH

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