Silica removal from natural waters on a New Organic-Inorganic Hybrid Ion Exchanger

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Silica in natural waters

- ***Concentration:*** **1 - 20 mg/L as SiO_2 in surface waters**

  0.8 - 63 mg/L as SiO_2 in ground waters

- ***Speciation:***

$$SiO_{2\,(S)} + 2H_2O \rightleftharpoons Si(OH)_4$$

$$Si(OH)_4 \rightleftharpoons Si(OH)_3O^- + H^+$$

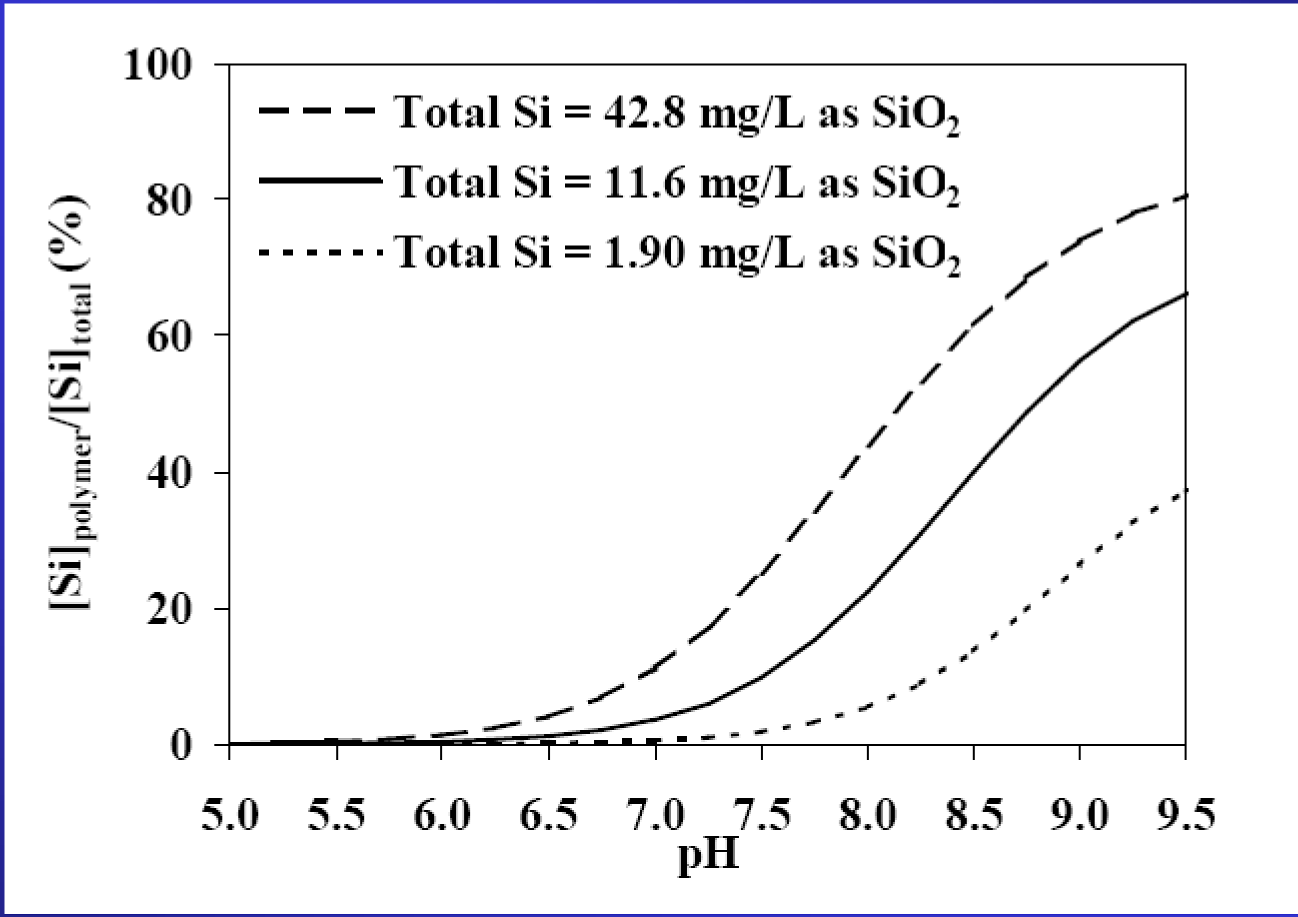
$$2\ Si(OH)_4 \rightleftharpoons (OH)_3SiOSi(OH)_3 + H_2O$$

$$2\ Si(OH)_4 \rightleftharpoons (OH)_3SiOSi(OH)_2O^- + H^+ + H_2O$$

$$n\ Si(OH)_4 \rightleftharpoons \text{polymeric silica} + n\ H_2O$$

Silica in natural waters

$(HO)_3SiOSi(OH)_2O^-$ 99% of the polymeric silicon



C. C. Davies, H. W. Chen, M. Edwards, *Environ. Sci. Technol*. **2002**, *36*, 582-587

Implications for environmental systems

A high silica content in water would be a major problem for:

- **Coagulation-Filtration Technologies**
  - Interactions with Aluminum
  - Interactions with Iron
- **Membrane Separation Technologies** (RO)
- **Ion Exchange Technologies**

Silica removal from natural waters

- Ion exchange – SBA exchange resins
  - Silica removal is suppressed by the competition of other present anions (SO_4^{2-})
- Adsorption – Iron hydroxide media
  - It was found that sorption increases as the silica concentration and pH increase with a maximum adsorption at ~ pH 9 (L. Sigg and W. Stumm, *Colloids Surf*., **1981**, *2*, 101-117)
- Adsorption on hybrid sorbents
  - The polymeric ion exchangers were used as host skeleton for nanoparticles of hydrous ferric oxide for oxyanions removal (L. Cumbal, A.K. SenGupta, *Environ. Sci. Technol.*, **2005**, *39*, 6508-6515)
  - Potential media for silica removal.

The purpose of the present work

- To evaluate the performance of a new organic/ inorganic hybrid ion exchanger, containing nanoparticles of hydrous ferric oxide inside the matrix of a macroporous strong base anion (SBA) resin, for silica removal from natural waters.

Experimental

- Sorption isotherms on the hybrid sorbent and the parent ion exchanger were measured at 1-5 mmol/L Si in NSF-53 solution and DM water at pHs of 6.5, 7.5 and 8.5 at 298ºK using AAS.

New Organic / Inorganic Hybrid Ion Exchanger "D-9908"

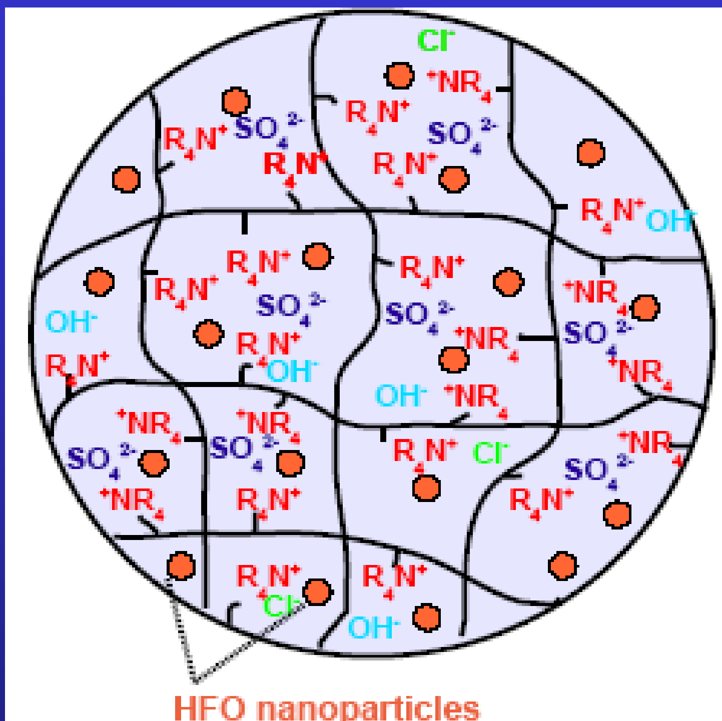
Strong Base Anion (SBA)

- Macroporous matrix
- Quaternary ammonium functional groups (R_4N^+)
- SO_4^{2-} form

D-9908

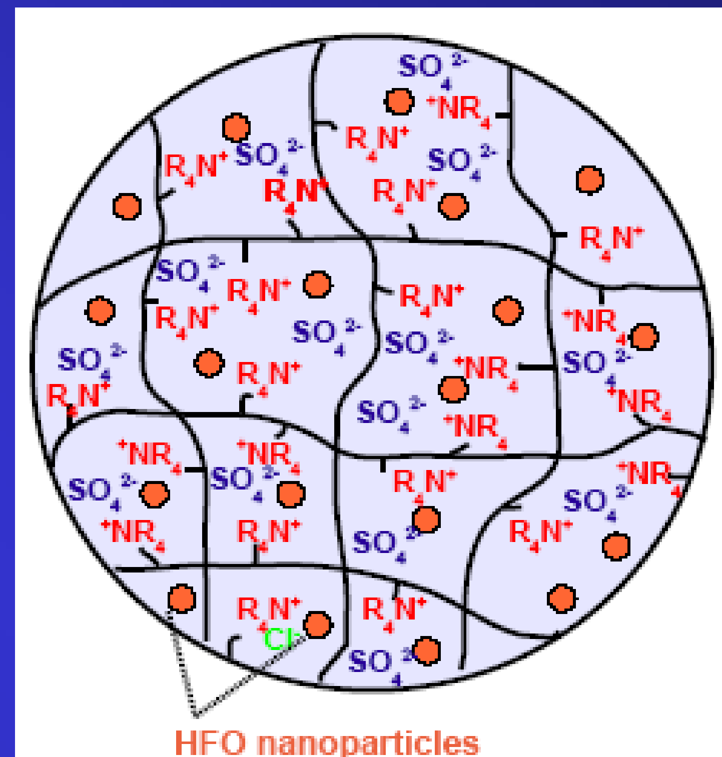
- Hydrous ferric oxide irreversible encapsulated throughout the SBA beads
- 250 mg Fe / g dry resin

New Organic / Inorganic Hybrid Ion Exchanger "D-9908"



excess of Na_2SO_4
1 M solution

→



D-9908 "virgin"

75 % SO_4^{2-}
17 % OH^-
7 % Cl^-

D-9908 (SO_4^{2-})

97.2 % SO_4^{2-}
2.8 % Cl^-

NSF-53 standard test water composition

CATIONS	meq/L	ANIONS	meq/L
Ca^{2+}	2.00	HCO_3^-	2.97
Mg^{2+}	1.04	SO_4^{2-}	1.04
Na^+	3.169	NO_3^-	0.14
		PO_4^{3-}	0.004
		Cl^-	2.00
		F^-	0.052
Total cations:	6.209	Total anions:	6.206

NSF/ANSI-53 Standard for Drinking Water Treatment Units – Health effects, **2003**, *43*, 51-54.

Measured isotherms at 298° K

Resin	C^0_{Si} (mmol/L)	Solution matrix	$pH_{initial}$
D-9908	1	NSF-53	6.5; 7.5; 8.5; 9.5
D-9908	3	NSF-53	7.5
D-9908	5	NSF-53	6.5; 7.5; 8.5
D-9908	1	DMW	6.5; 7.5; 8.5
D-9908 (SO_4^{2-})	1	DMW	6.5; 7.5; 8.5
SBA (SO_4^{2-})	1	NSF-53	6.5; 7.5; 8.5
SBA (SO_4^{2-})	5	NSF-53	6.5; 7.5; 8.5
SBA (SO_4^{2-})	1	DMW	6.5; 7.5; 8.5

Multicomponent ion exchange system

Initial stage

Resin phase

- $FeOH_2^+$
- $FeOH$
- FeO^-
- $CH_2N^+R_3$
  - SO_4^{2-}: 75%
  - HO^-: 17%
  - Cl^-: 7%
  - CO_3^{2-}: 1%

Solution phase

$pH_{initial}$ = 6.5 / 7.5 / 8.5 / 9.5

$Si(OH)_4$
$Si(OH)_3O^-$
$(HO)_3SiOSi(OH)_3$
$(HO)_3SiOSi(OH)_2O^-$

NSF-53

HCO_3^- : 3 meq/L
Cl^- : 2 meq/L
SO_4^{2-} : 1 meq/L
NO_3^- : 0.14 meq/L
F^- : 0.052 meq/L
PO_4^{3-} : 0.04 meq/L

At equilibrium

Resin phase

- $FeOSi(OH)_3$
- $FeOSi(OH)_2O^-$
- $FeOSi(OH)_2OSi(OH)_3$
- $FeOSi(OH)_2OSi(OH)_2O^-$
- $CH_2N^+R_3$ | SO_4^{2-} : 97%

Solution phase

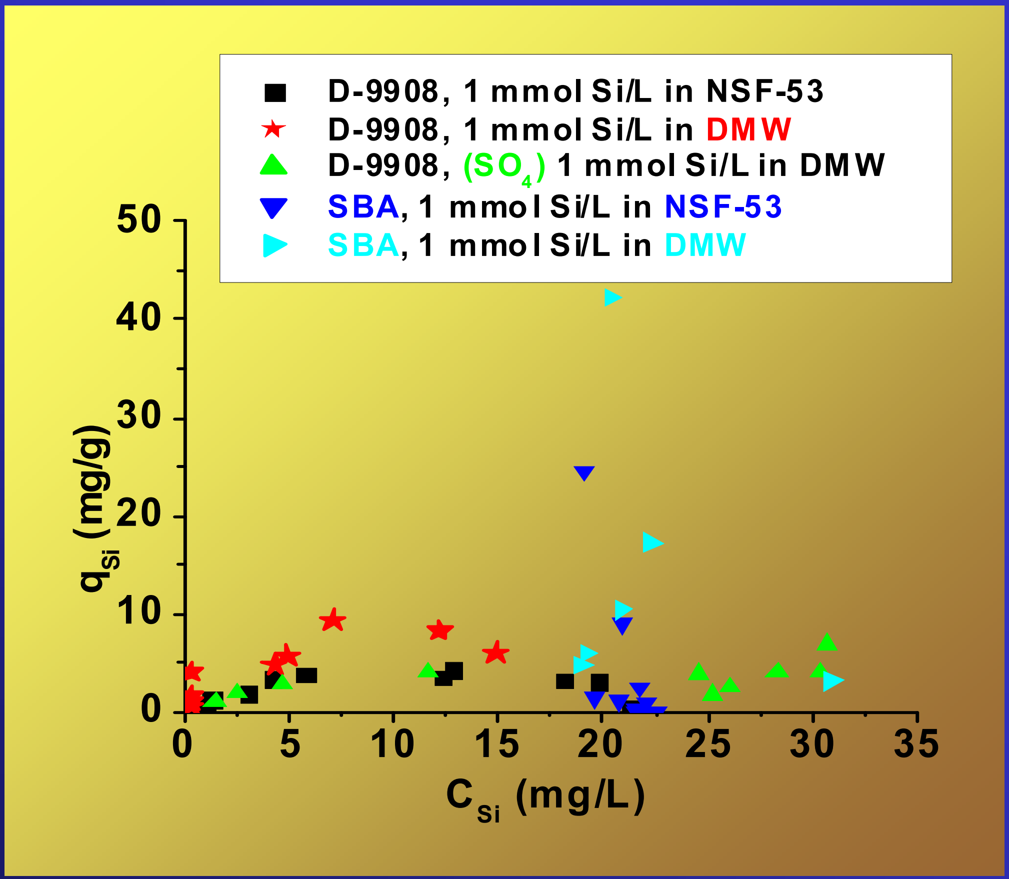
$Si(OH)_4$
$Si(OH)_3O^-$
$(HO)_3SiOSi(OH)_3$
$(HO)_3SiOSi(OH)_2O^-$

NSF-53

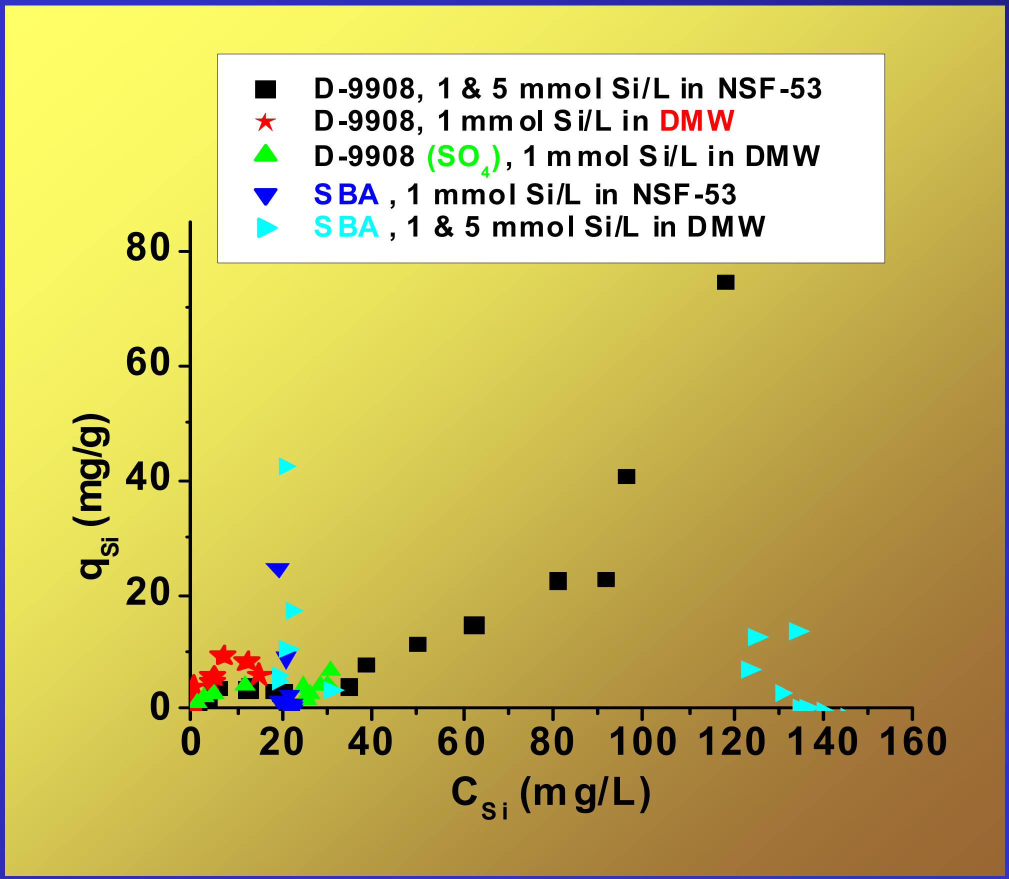
HCO_3^- ; Cl^- ; NO_3^-
F^- ; OH^- ; CO_3^{2-}
SO_4^{2-}; PO_4^{3-}

Sorption isotherms of silica on D-9908 and SBA from NSF-53 and DMW solutions at $pH_{in} = 6.5$

a) 1 mmol / L

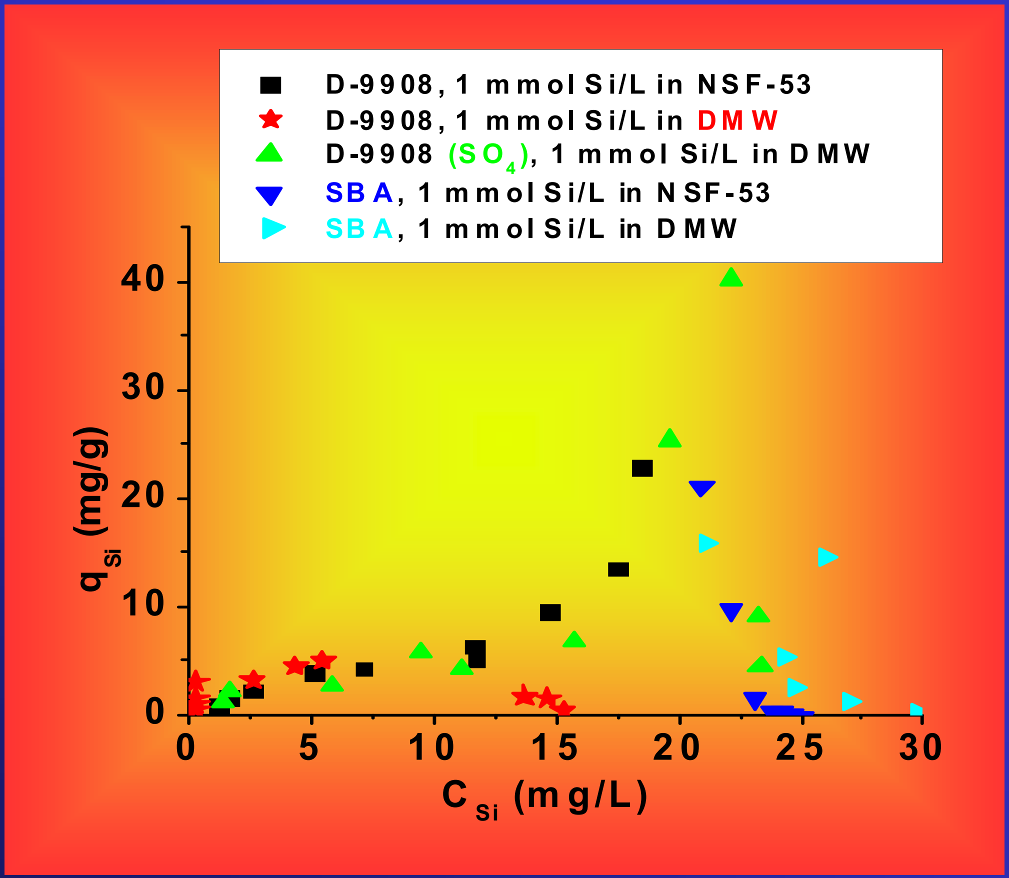


b) 1 & 5 mmol / L

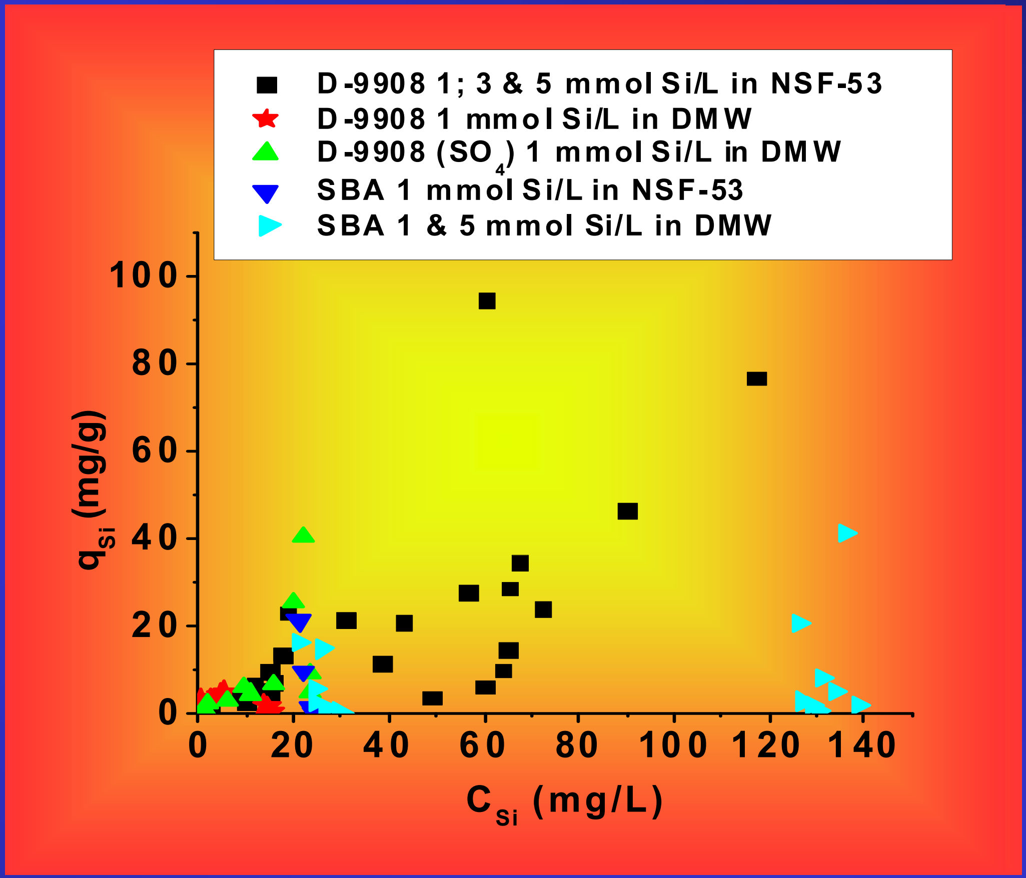


Sorption isotherms of silica on D-9908 and SBA from NSF-53 and DMW solutions at pH_{in} = 7.5

a) 1 mmol / L

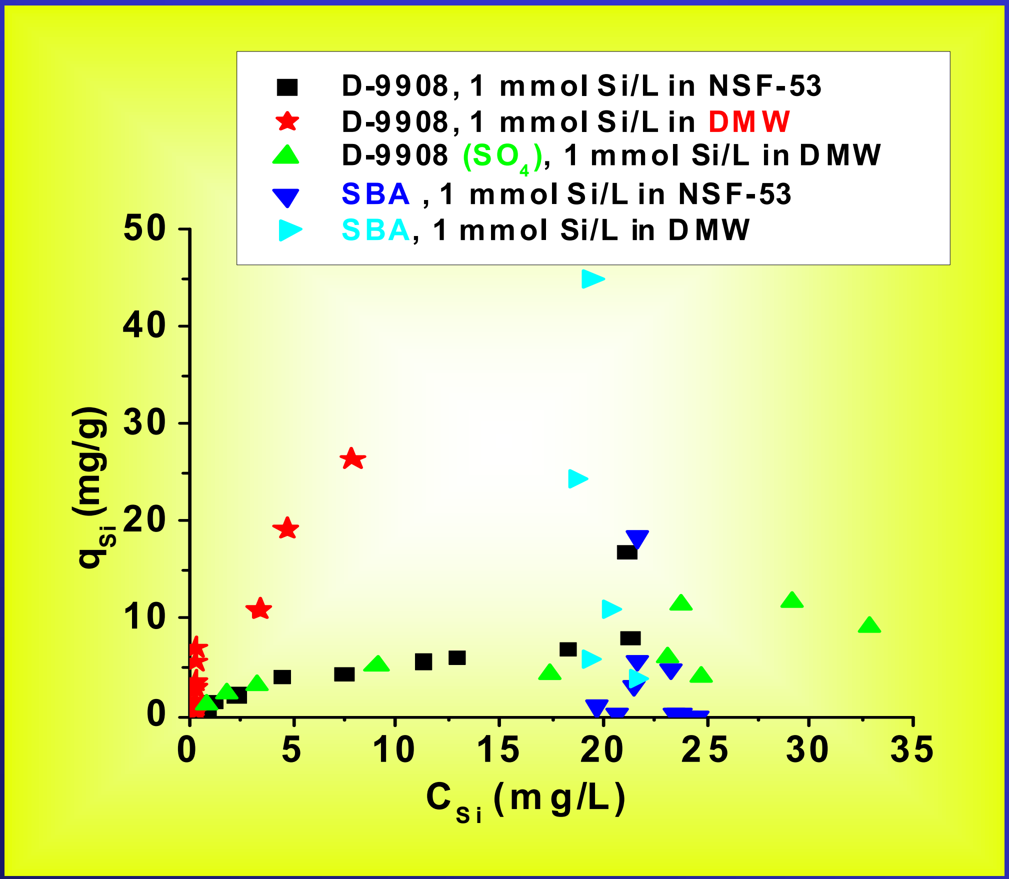


b) 1 & 5 mmol / L

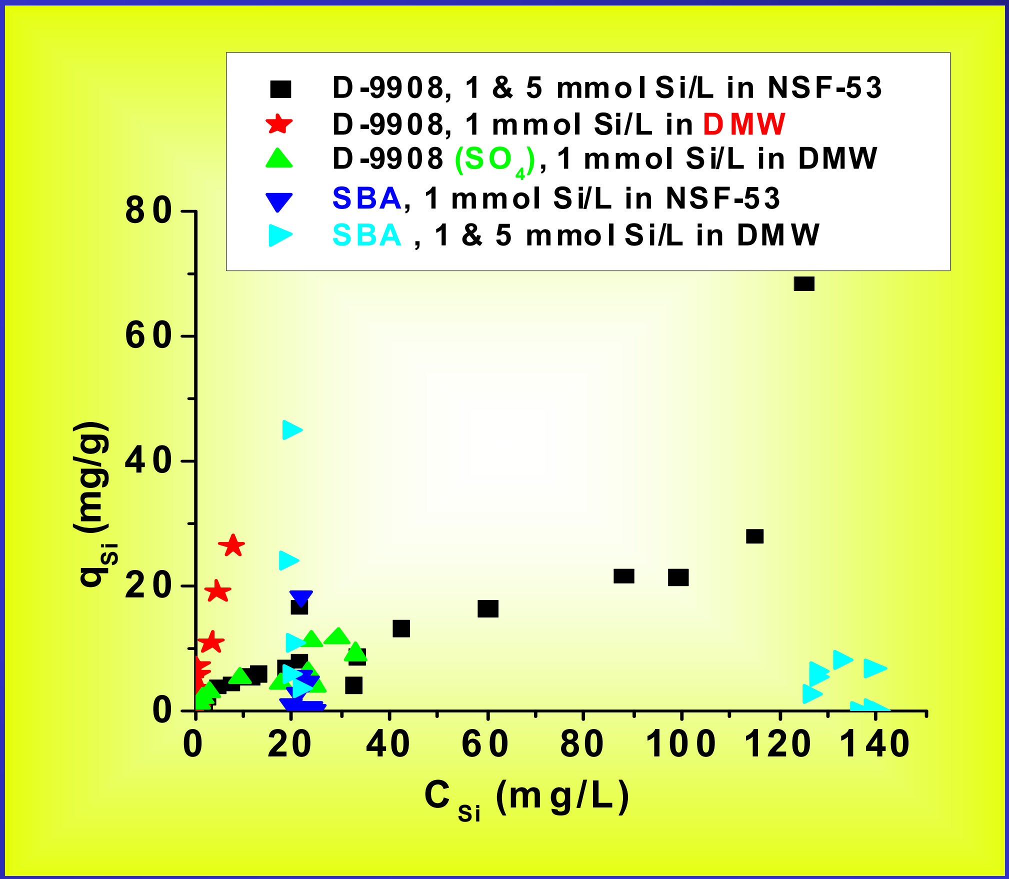


Sorption isotherms of silica on D-9908 and SBA from NSF-53 and DMW solutions at $pH_{in} = 8.5$

a) 1 mmol / L

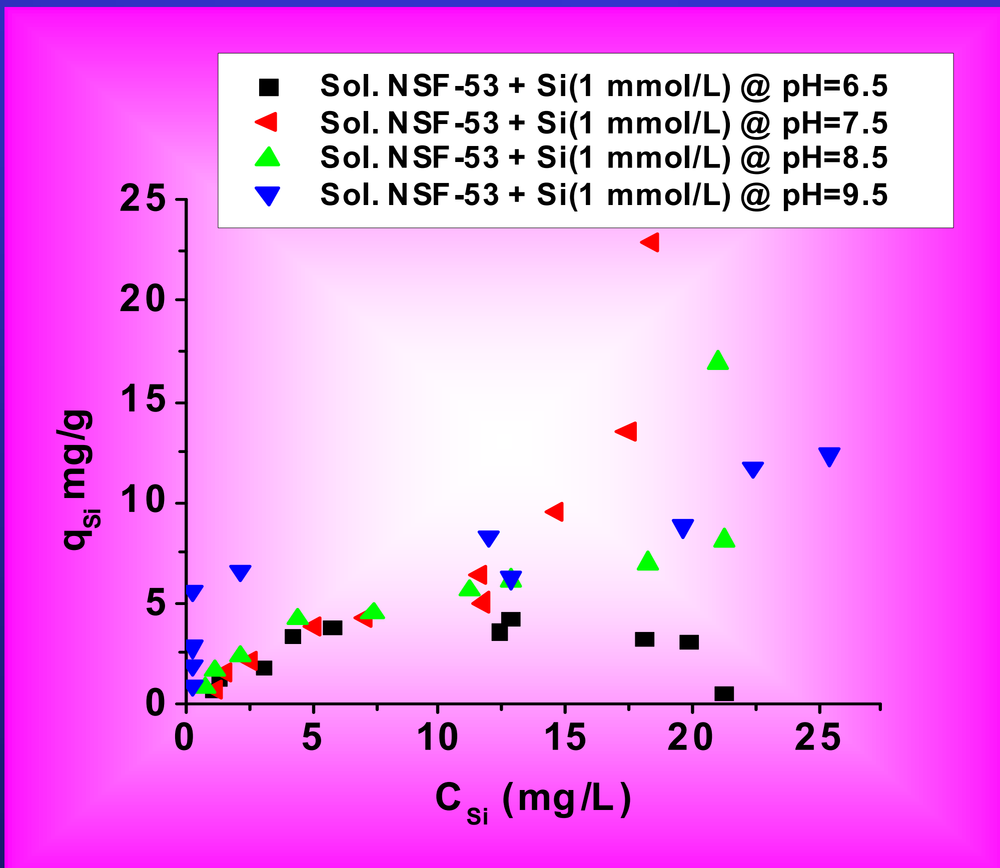


b) 1 & 5 mmol / L

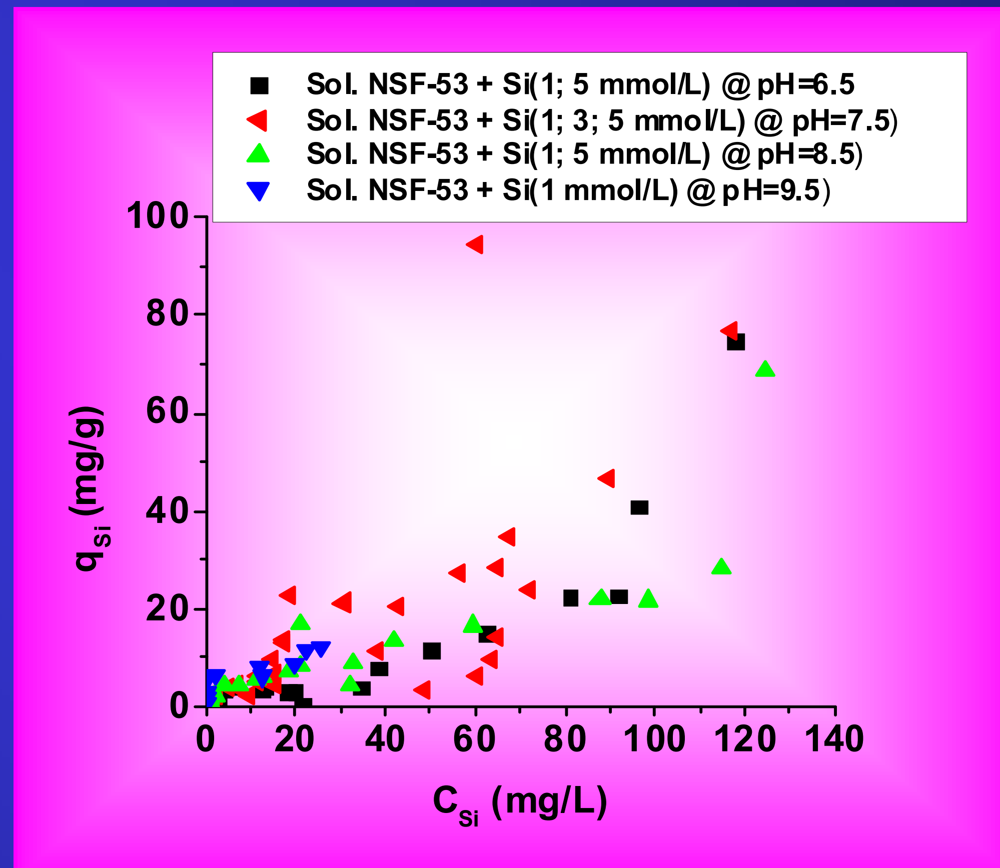


Silica sorption isotherms on the hybrid ion exchanger D-9908 at different pHs

a) 1 mmol/L Si



b) 1 & 3 & 5 mmol/L Si



The series of variation of the loading with silicon of D-9908 at equilibrium at different pHs

C_{Si} / mg/L	loading variation with pH
$0 < C_{Si} < 12$	$9.5 \gg 6.5 \approx 7.5 \approx 8.5$
$12 < C_{Si} < 25$	$7.5 > 9.5 > 8.5 > 6.5$
$25 < C_{Si} < 70$	$7.5 > 8.5 \approx 6.5$
$70 < C_{Si} < 120$	$7.5 > 6.5 > 8.5$

Concluding Remarks

- The performance of a new organic-inorganic hybrid ion exchanger for silica removal from natural waters was evaluated measuring the sorption isotherms at 298 K. The sorbent contains nanoparticles of hydrous ferric oxide encapsulated in a macroporous matrix of a strongly basic anion exchanger. NSF-53 standard test water was used to simulate the composition of the natural water. The total silica concentration was 1, 3 and 5 mmol/L. The initial pH was 6.5, 7.5, 8.5, and 9.5

- The isotherms depict solid-liquid multicomponent systems at equilibrium

- The results show that the new material is a good sorbent for removing silica from natural waters at all investigated pHs and has better properties than the host anion exchanger

- The experiments support the retention of silica on the hydrous ferric oxide nanoparticles of the hybrid material at all investigated pHs

- The presence of other anions in the natural water suppressed the silica removal on the hybrid material; at pH 7.5 the effect is negligible

- The up-take on the hybrid sorbent depends strongly on the initial pH and silica concentration in the natural water, due to silica speciation

- The sorption of silica on the new hybrid ion exchanger seems to be the maximum at pH 7.5.

Thank you for your attention!!!