Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation

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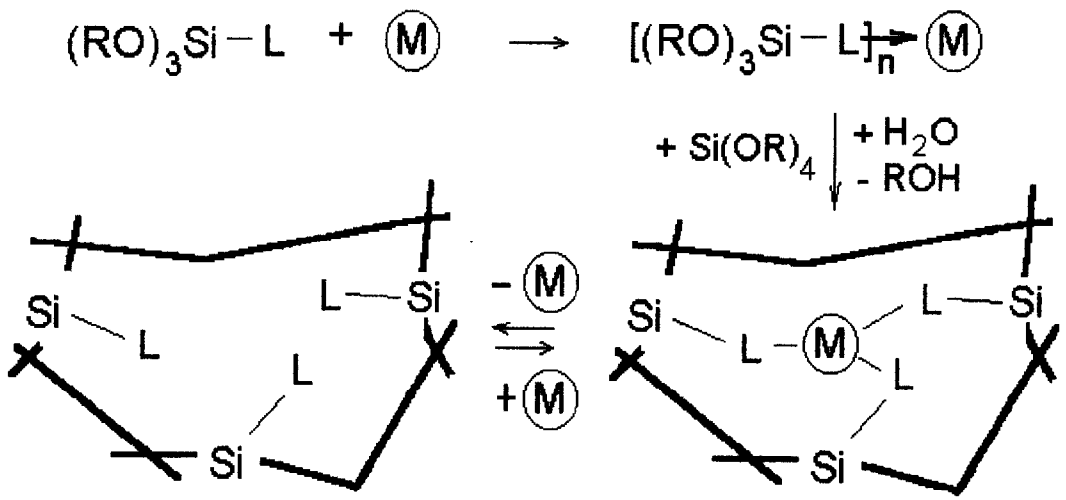
Goals:

- Graft ligands (L) on *inorganic polymers* (SiO_2 or MO_n) by sol-gel method as an alternative to L-grafted organic polymer sorbents
- Utilize the *hydrophilic* SiO_2 or MO_n network with *intrinsic* fast metal ion diffusion
- Use template-imprinting process to enhance capacity and selectivity
- Understand the M-L binding in heterogeneous and anisotropic chemical environment in sol gels

Background:

- Previous studies about inorganic polymers as metal sorbents:
  - Grafting ligands on the *external* surface of *preformed* silica gel
  - Self-assembled monolayers of mesoporous supports (SAMMS)[1]
  - Crystalline silicotitanates (CSTs) for Cs^+ removal[2]
- Organofunctional sol-gels[3] from $[(RO)_3Si\text{-}L]_n \rightarrow M$ have been studied as new metal catalysts and materials for metal separation[3]
- Template-imprinting has been used to prepare, e.g., high-selectivity separation materials, zeolites, and nanoporous silicas[4]

Our approach:



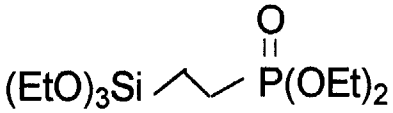
Sol-gel (SiO_2) imprinted with target metal

TMSen

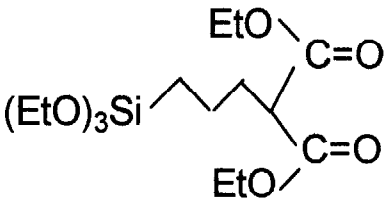
MPTS

CPTS

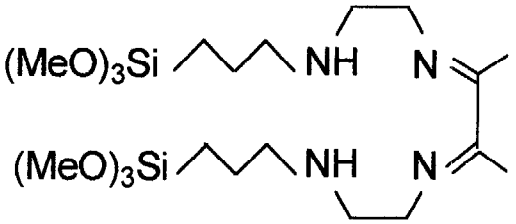
APTES



DMPTS



TSPDM



Schiff Base

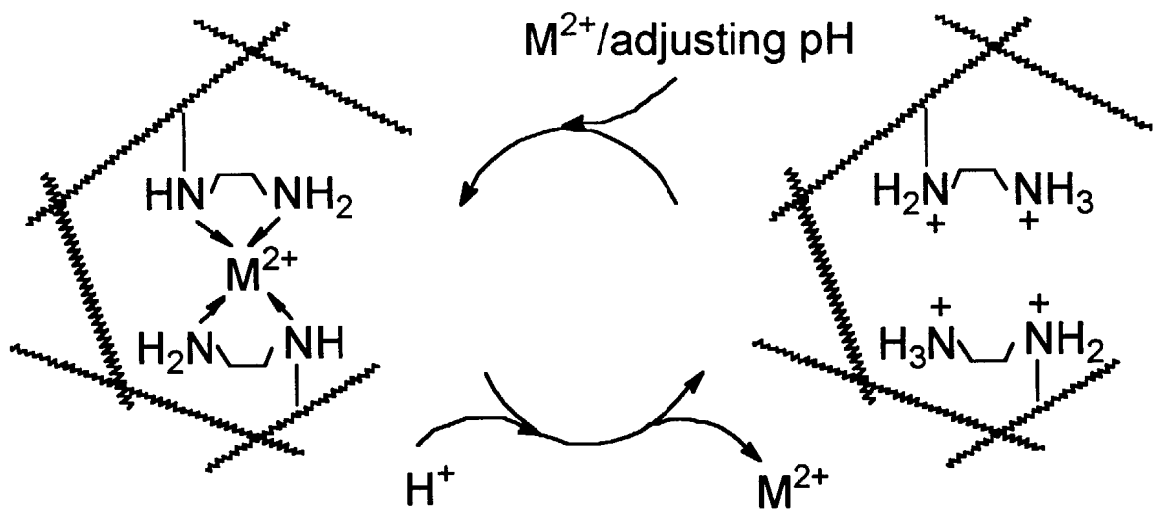
Example:

(A) (B) (C)

Figure 1. *Photographs illustrating the reversible Cu^{2+} binding by a Cu^{2+}-imprinted gel (9 × 8 × 3 mm^3) with grafted ethylene diamine (TMSen): (A) Cu^{2+} saturated gel; (B) 3 min after addition of 1 M HCl to remove Cu^{2+}; (C) 3 min after neutralization with $NaHCO_3$ and re-immersion of the gel in a $CuCl_2$ solution.*

Sol-gels for soft metal ions (Cu^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}):

- EPA priority pollutants and RCRA metals
- Ethylene diamine (TMSen) grafted sol-gels -> reversible binding of these metal ions (e.g., see Fig. 1)
- Metal removal cycles:



Scheme 1.

Cu^{2+} and Hg^{2+}

- Easy gel preparation: prepared from off-the-shelf chemicals in 1 hr
- Loading in *one* cycle: > 0.02 g Cu^{2+}/g of the gel
  0.10 g Hg^{2+}/g of the gel
- Durable and stable for multiple cycles
- Preliminary Cu^{2+} $K_d = 1.4 \times 10^3$
- Fast binding kinetics: reduce 2.09 ppm Cu^{2+} to 0.25 ppm in 5 min
- Fast removal: remove Cu^{2+} from loaded gel in 5 min (Fig. 2)
- No secondary waste during application

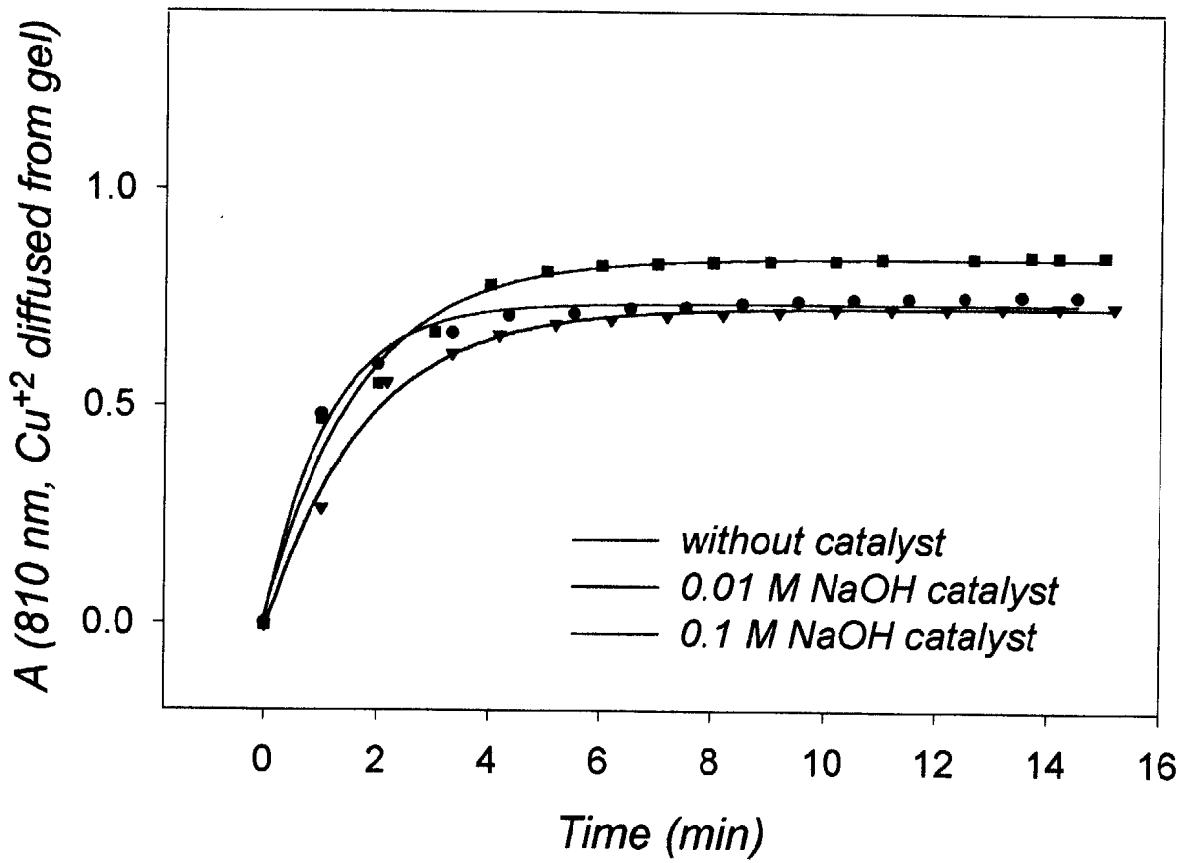
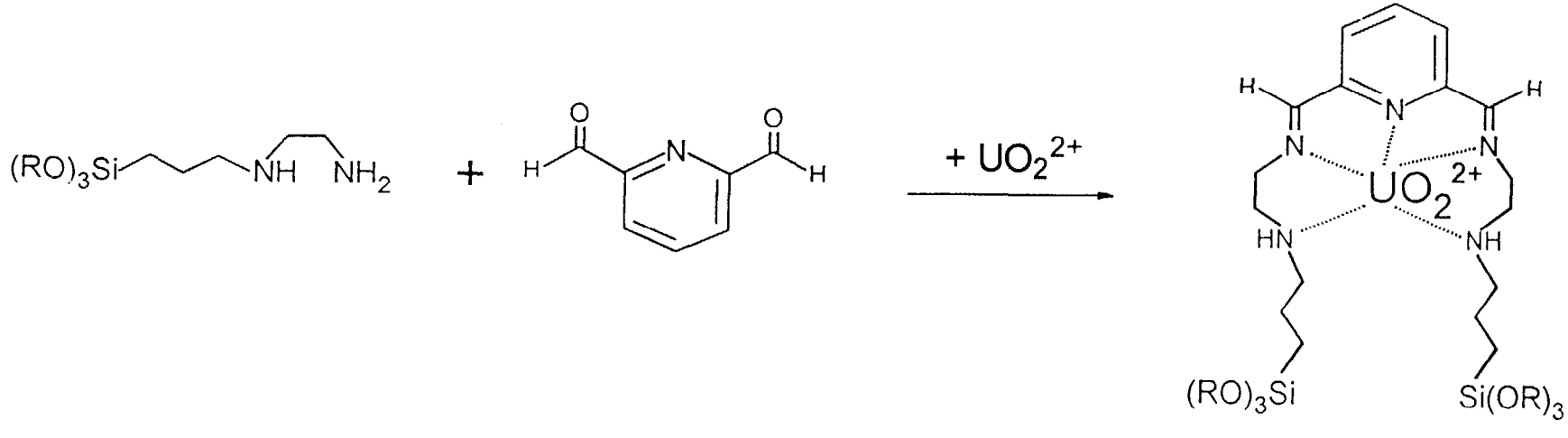


Figure 2. *Cu^{2+} diffusion from sol-gels grafted with ethylene diamine (500 - 595 μm size, TMSen/Si(OMe)$_4$ = 1/12.5, 0.5 g in 2 mL of 6 M HCl).*

successfully prepared through the use of surfactants

- Fast binding kinetics in mesoporous sorbents has been observed
- Multi-dentate Schiff base ligands have been grafted on sol gels (Scheme 2); UO_2^{2+} binding capacity > 60 mg/g of the imprinted gel (Fig. 4)



Scheme 2.

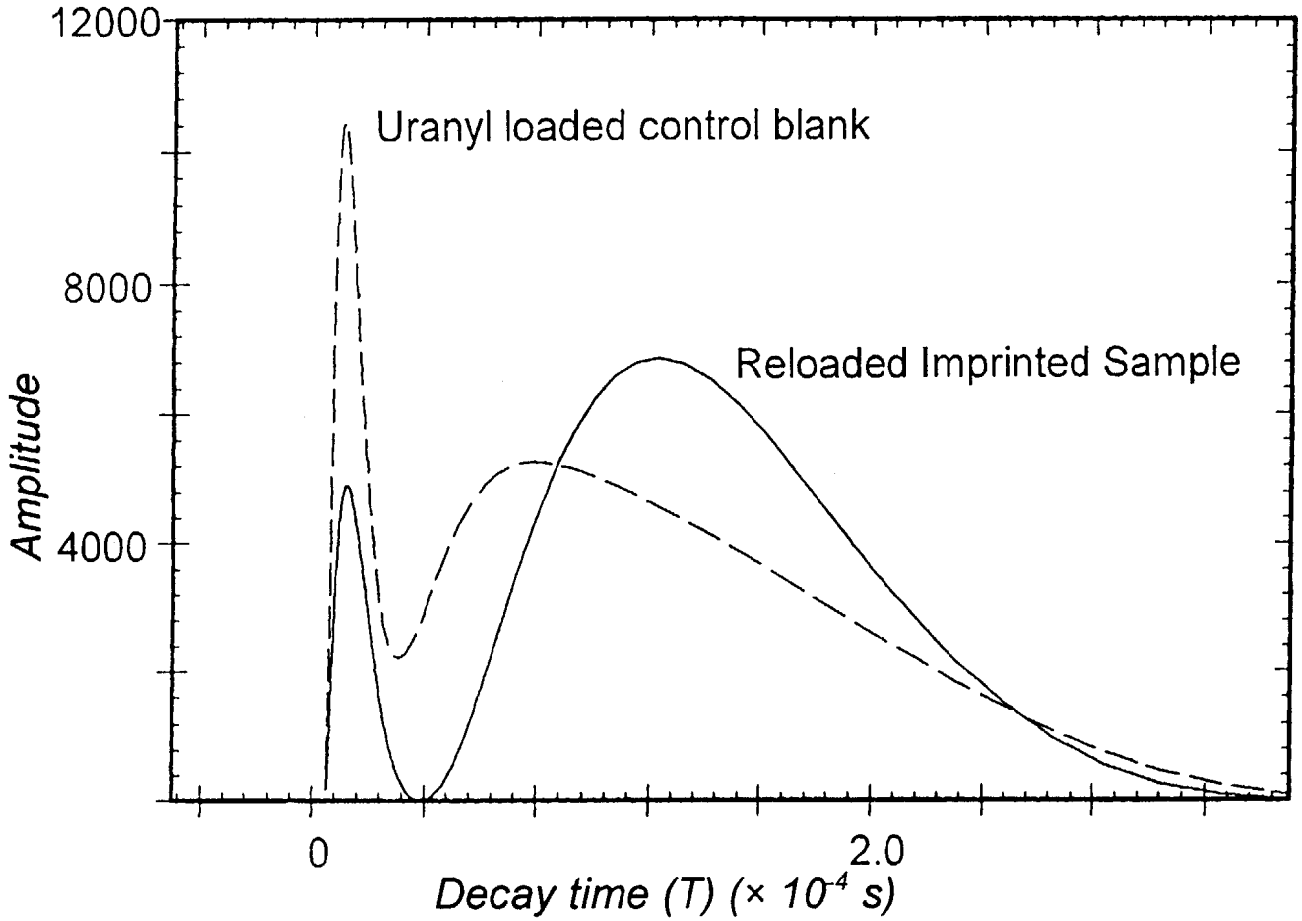


Figure 3. *Time dependence of UO_2^{2+} fluorescence decay in SiO_2 sol gels.*

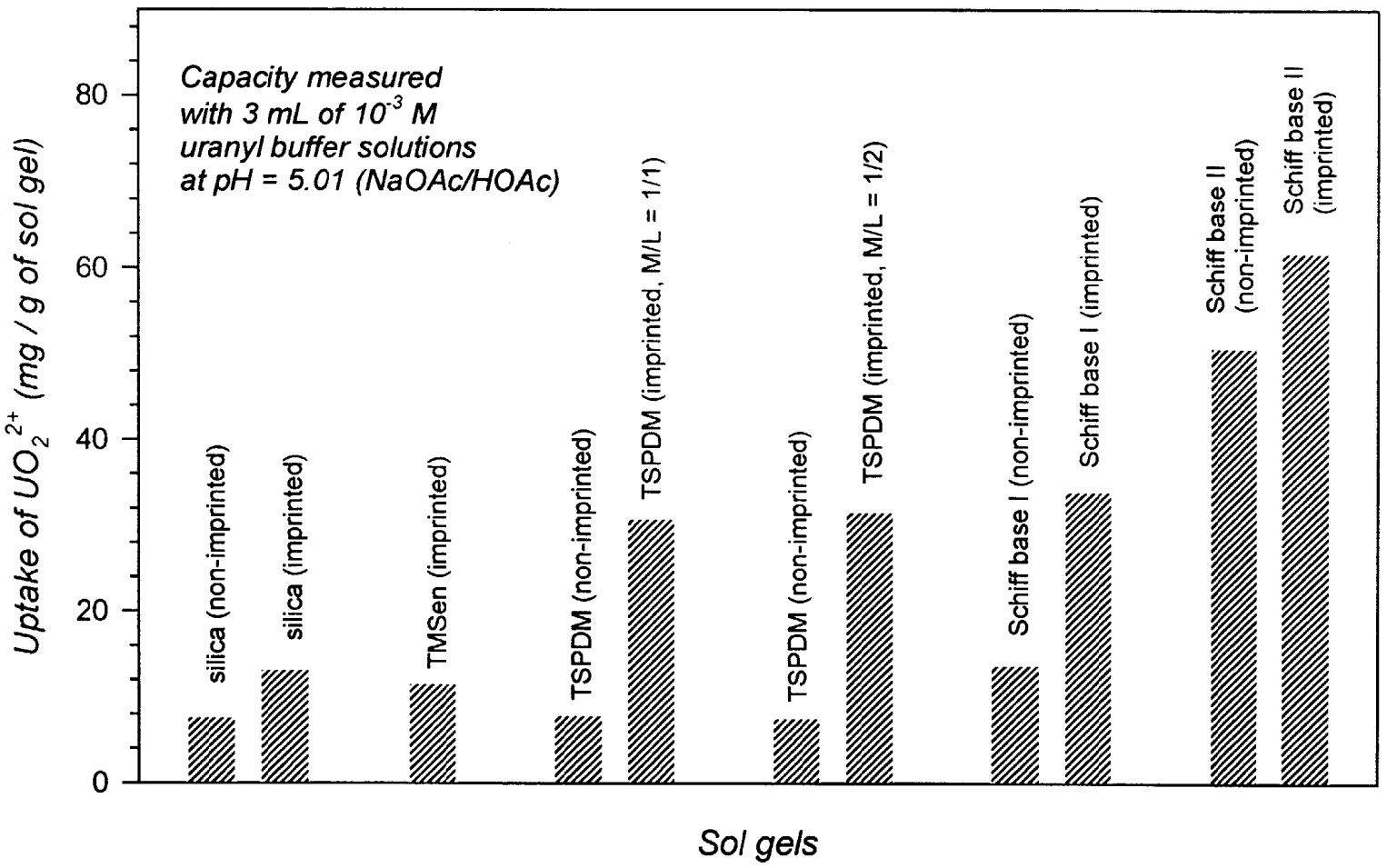


Figure 4. *Adsorption capacities of microporous sol-gels.*

Sr^{2+}

- Ethylene diamine (TMSen) grafted sol-gels -> reversible binding of Sr^{2+} and metal removal cycles (Scheme 1, p. 6)
- Easy gel preparation: prepared from off-the-shelf chemicals in 1 hr
- Loading: > 0.036 g Sr^{2+}/g of the *imprinted* gel in *one* cycle*
- Capacity of *Imprinted* gel -> over 20 times larger than that of *non-imprinted* gel*
- Durable and stable for multiple cycles
- Fast binding kinetics and fast removal
- No secondary waste during application

* Based on preliminary data.

Concluding Remarks:

Our research over the past 10 months shows that

- SiO_2 grafted with ligands by sol-gel method are promising candidates for toxic metal removal, and good alternatives to organic polymer based sorbents
- Many ligands with good affinity for target metal ions can be grafted on SiO_2[5]
- These *hydrophilic inorganic polymers* offer fast metal binding and removal kinetics
- Template-imprinting has shown enhanced metal binding capacity

Acknowledgment

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References

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