Desorption of Mercury(II) on Kaolinite in the Presence of Oxalate and Cysteine

Wasana U Senevirathna[1, 2], Hong Zhang[1,2*], Baohua Gu[3]

[1]Department of Chemistry, and [2]Center for the Management, Utilization, and Protection of Water Resources, Tennessee Tech University (TTU), Cookeville, TN 38505, USA

[3]Environmental Sciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA

Introduction

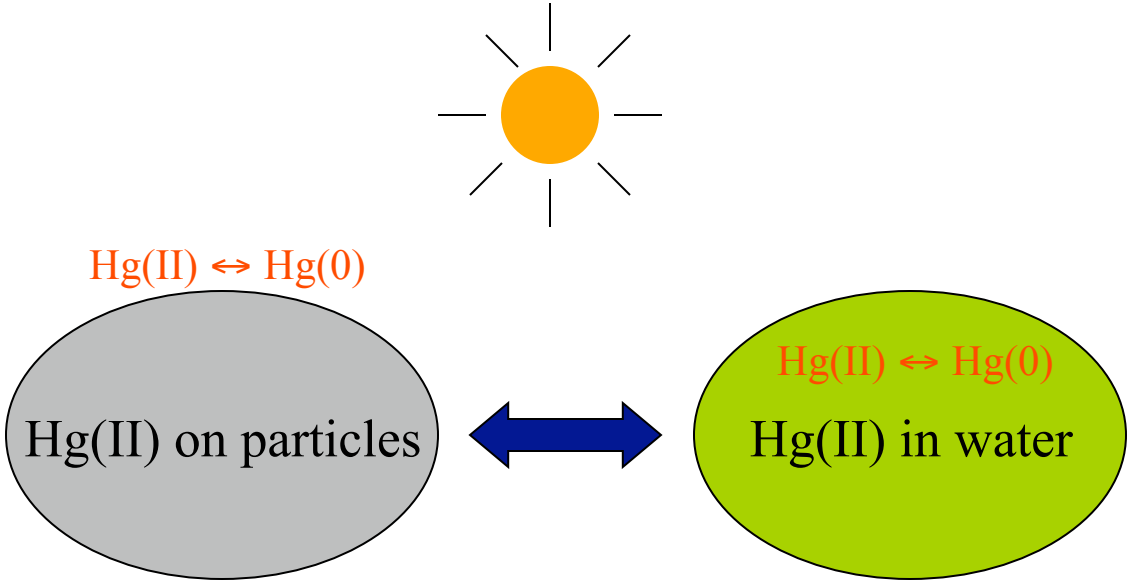
Origin of This Study

- Hg is associated with particulates abundantly.
- Particulate Hg is a source of dissolved Hg in water.
- Desorption can be a pathway for Hg to transport from particular phase to water phase, where Hg can undergo photoredox.
- But, if Hg stays on particles, it can undergo photoredox on particle surface, which may act as catalyst.
- The fate of Hg is thus of interest.

Introduction

Origin of This Study

Hg in aquatic system



Introduction

Origin of This Study

- Kaolinite is a typical clay mineral present in southern aquatic systems as well as soils.
- Low-molecular-mass (LMM) organic ligands can complex with Hg(II) and thus may affect Hg(II) desorption (and adsorption).
- Oxalate is a typical LMM organic ligand with carboxylic group that has a low affinity for Hg(II).
- Cysteine is a typical LMM organic ligand with thiol group that has a high affinity for Hg(II).
- Desorption of Hg(II) on kaolinite in the presence of oxalate or cysteine is thus of interest.

Introduction

Purposes of This Study

Major purposes of this study:

- To investigate the effect of oxalate and cysteine on desorption of Hg(II) from kaolinite, and
- To compare the roles of these two contrasting organic acid ligands.

Introduction

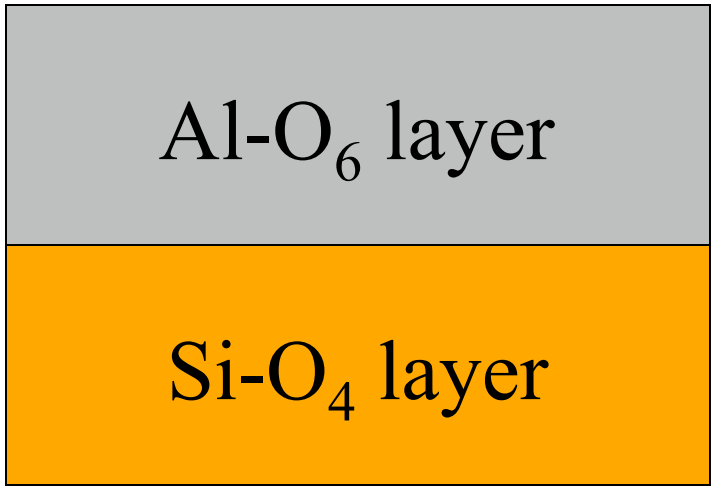
Approach of This Study

- The investigation was accomplished by following the kinetics of desorption of Hg(II) at various pHs, ligand concentrations, and temperatures.
- Kaolinite was chosen as the model mineral particle.
- Oxalate and cysteine were chosen as the model organic ligands.

Introduction

Approach of This Study

Basic mineral structure of kaolinite



Aluminol surface:

>Al-O$^-$ (or >Al-OH, pH dependent)

Silanol surface:

>Si-O$^-$ (or >SOH, pH dependent)

Introduction

Approach of This Study

Important properties of oxalic acid and cysteine

Organic Acid	MM	pK_a	Log$K$*
oxalic acid	90.1	1.24 (pK_{a1}), 4.28 (pK_{a2})	9.66
cysteine	121	1.96 (-COOH), 8.18 ($-NH_3^+$), 10.28 (-SH)	14.4

MM: molecular mass in a.m.u.
*Log$K_{Hg(II)\text{-}complex}$

Oxalic acid (Ox): 1.5 < pH < 4: $^-$OOC-COOH; pH > 5: $^-$OOC-COO$^-$

Cysteine (Cys): 2 < pH < 8.5: $^-$OOC-CH(NH_3^+)-CH_2SH

Experimental

Adsorption of Hg(II) on kaolinite

- The isotherms for adsorption of Hg(II) on kaolinite were obtained at 293 ± 5 K using solid-water suspensions (28 g L^{-1} of kaolinite and 0.01 M $NaNO_3$, pH 5.5).
- The final Hg(II) concentrations were 0.4, 0.6, 0.8, 1.0, 1.2, and1.5 mg L^{-1} (1.99-7.48 μM $Hg(NO_3)_2$).
- The suspensions were shaken overnight at room temperature (20 ± 5 °C) to reach adsorption equilibrium.

Experimental

Adsorption of Hg(II) on kaolinite

- For adsorption in the presence of organic acid ligands (OA), the suspensions were spiked with oxalate or cysteine (OA in solution: 1.0 mM).
- The suspensions were centrifuged (3000 rpm/15 min).
- The supernatants were acidified for Hg(II) analysis.
- The remaining solid portions were collected for desorption experiments.
- All adsorption experiments were done in duplicate.

Experimental

Desorption of Hg(II) on kaolinite

- Kaolinite solids with adsorbed Hg(II) were mixed with 100 mL MQ-H_2O and 200 μL 5 M $NaNO_3$ plus oxalate or cysteine.
- Suspension was stirred magnetically and purged with N_2.
- Temperature was maintained at 298 K or as desired.
- At desired time intervals, an aliquot of the suspension tested was sampled and filtered (0.45 μm) for Hg analysis.
- All desorption experiments were done in duplicate.

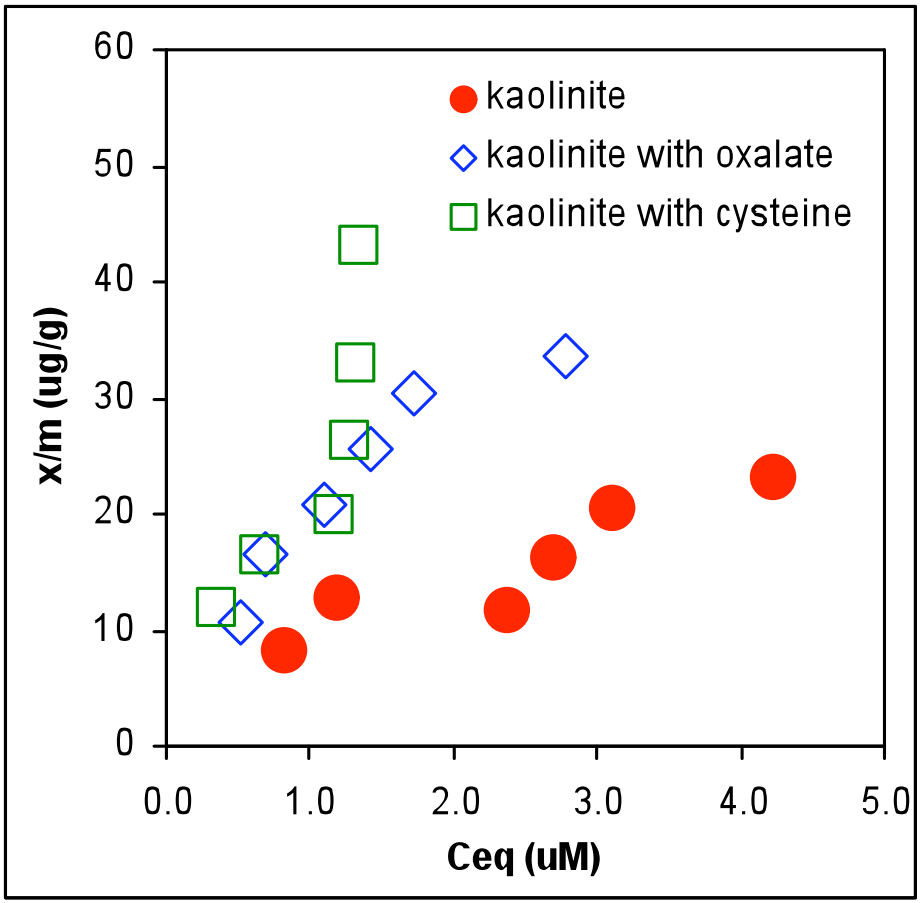
Experimental

Analyses and Measurements

- Hg(II) was analyzed by a spectroscopic method using dithizone
- The pH was measured using a Thermo Orion pH meter with a combination pH electrode.

Results and Discussion

Adsorption of Hg(II) on Kaolinite



- More adsorption in the presence of Ox or Cys.

The effect of Ox and Cys seems similar at low initial concentrations of Hg(II).

The effect of Cys seems greater than Ox at high initial concentrations of Hg(II) (the role of thio-group)

pH = 5.5
OA: 1.0 mM

Results and Discussion

Adsorption of Hg(II) on Kaolinite

- Potential particle surface available for adsorption of Hg(II)

(1) Original mineral surface

Aluminol surface: >Al-O^- (or >Al-OH, pH dependent)
Silanol surface: >Si-O^- (or >Si-OH, pH dependent)

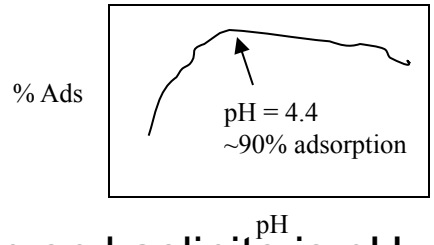
(2) Modified mineral surface

Aluminol-Ox surface complex: >Al-$OOCCOO^-$
Silanol-Ox surface complex: >Si-$OOCCOO^-$

Aluminol-Cys surface complex: >Al-OOC-CH(NH_3^+)-CH_2SH
Silanol-Cys surface complex: >Si-OOC-CH(NH_3^+)-CH_2SH

Results and Discussion

Adsorption of Hg(II) on Kaolinite



According to Sarkar et al. (2000)*

- In the absence of other ligands, Hg(II) adsorption on kaolinite is pH-dependent with an adsorption edge (pH_{max} = 4.4);
- Adsorption results from formation of inner-sphere surface complex with $Hg(OH)_2^0$ and outer-sphere surface complex with $HgOH^+$;
- Hg(II) is mainly adsorbed by silanol surface group as $>SiO^-$-$HgOH^+$ and $>SiOHg(OH)_2^-$, both dominant at low pH, but $>SiOHg(OH)_2^-$ dominant at high pH;
- $Hg(OH)_2^0$ is the major adsorbate;
- only ~15% of adsorption is associated with aluminol surface functional group as $>AlO^-$-$HgOH^+$ at pH 3-6.

*Sarkar, D. Essington, M.E., and Misra, K.C. Adsorption of mercury(II) by kaolinite. Soil Sci. Soc. Am. J. 64, 1968-1975, 2000.

Results and Discussion

Adsorption of Hg(II) on Kaolinite

- Hypothesis to account for adsorption of Hg(II) on kaolinite

Surface reaction in the absence of Ox or Cys:

Silanol surface: $>Si\text{-}O^- + Hg(II)$ (Sarkar et al., 2000)

Surface reaction in the presence of Ox:

Aluminol-Ox surface complex: $>Al\text{-}OOCCOO^- + Hg(II)$
Silanol-Ox surface complex: $>Si\text{-}OOCCOO^- + Hg(II)$
Silanol surface: $>Si\text{-}O^- + Hg(II)$

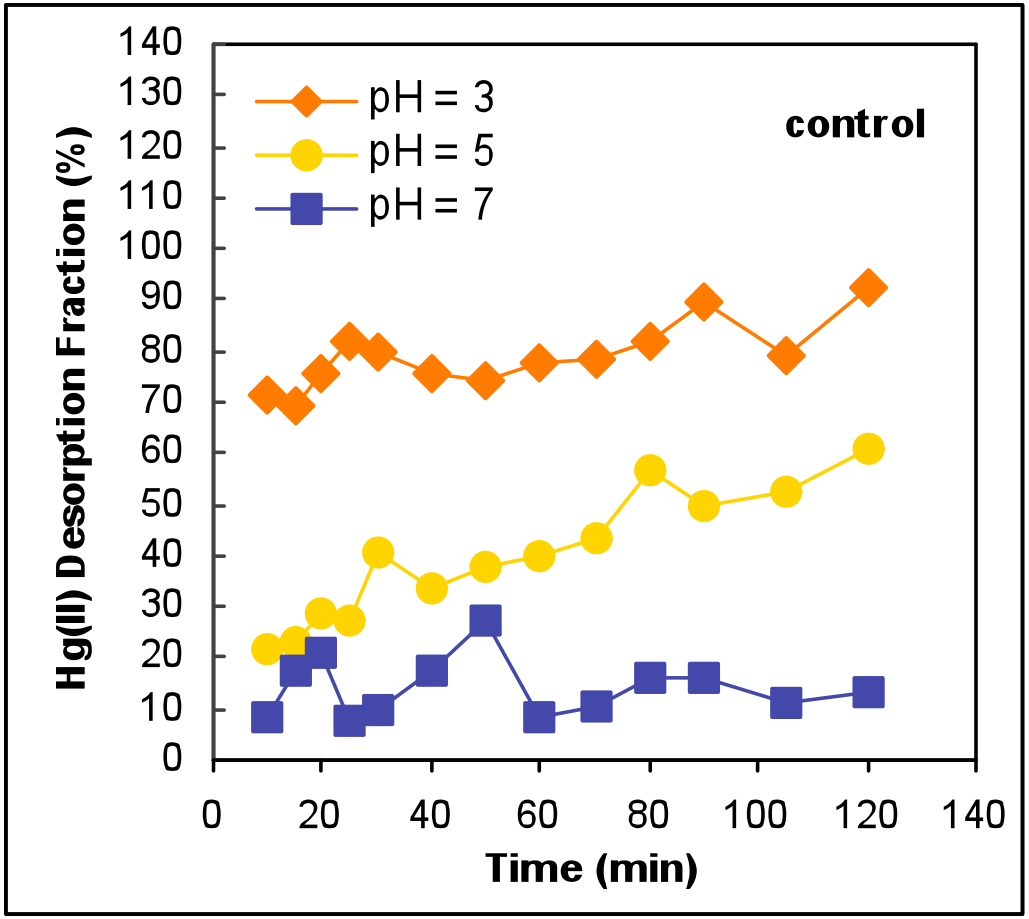
Surface reaction in the presence of Cys:

Aluminol-Cys surface complex: $>Al\text{-}OOC\text{-}CH(NH_2)\text{-}CH_2SH + Hg(II)$
Silanol-Cys surface complex: $>Si\text{-}OOC\text{-}CH(NH_2)\text{-}CH_2SH + Hg(II)$
Silanol surface: $>Si\text{-}O^- + Hg(II)$

In the presence of Ox or Cys, ternary surface complex may be involved.

Results and Discussion

Desorption of Hg(II) on Kaolinite: pH



- Desorption is rapid at pH 3, but increases with time gradually at pH 5.

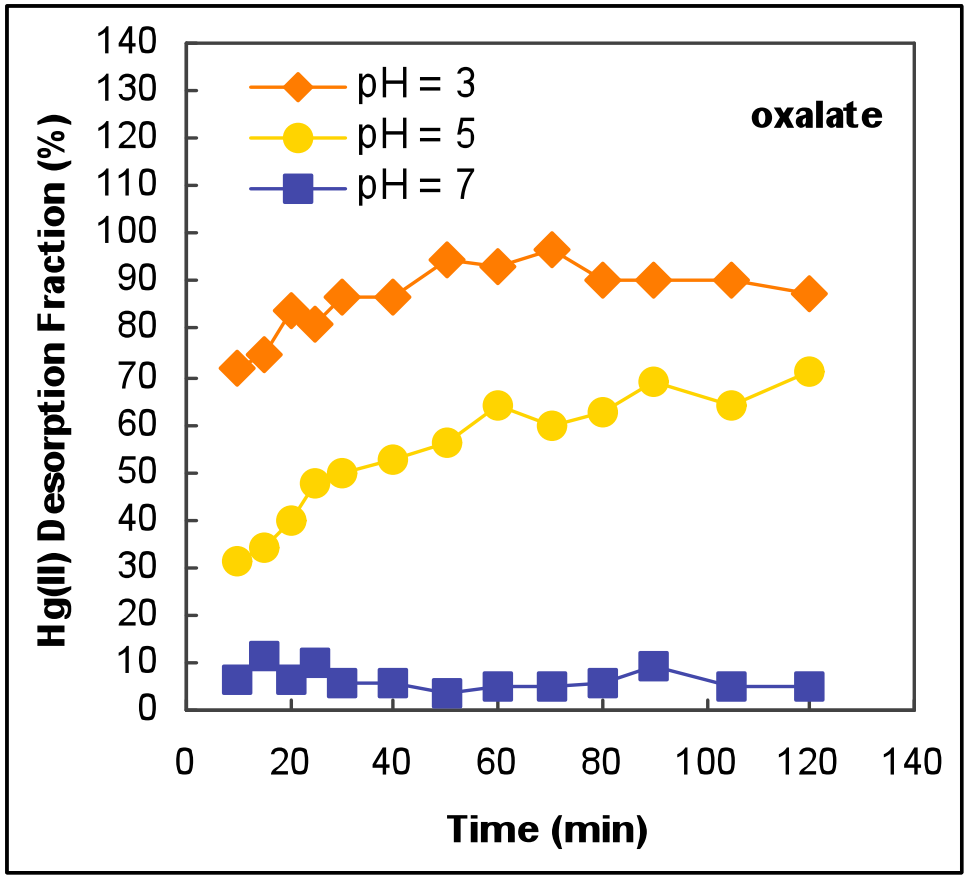
  Small desorption at pH 7.

  The trends seem to be consistent with features of Hg(II) adsorption on kaolinite as described by Sarkar et al. (2000).

SD: pH 3: 5.5% (0.3 – 9.9%)
pH 5: 7.8% (0.7 – 13.2%)
pH 7: 7.6% (0.2 – 14.7%)

Results and Discussion

Desorption in the Presence of Oxalate: pH



- Desorption of Hg(II) in the presence of Ox is similar to the case in the absence of Ox.

This suggests that Ox in the solution does not enhance the desorption significantly.

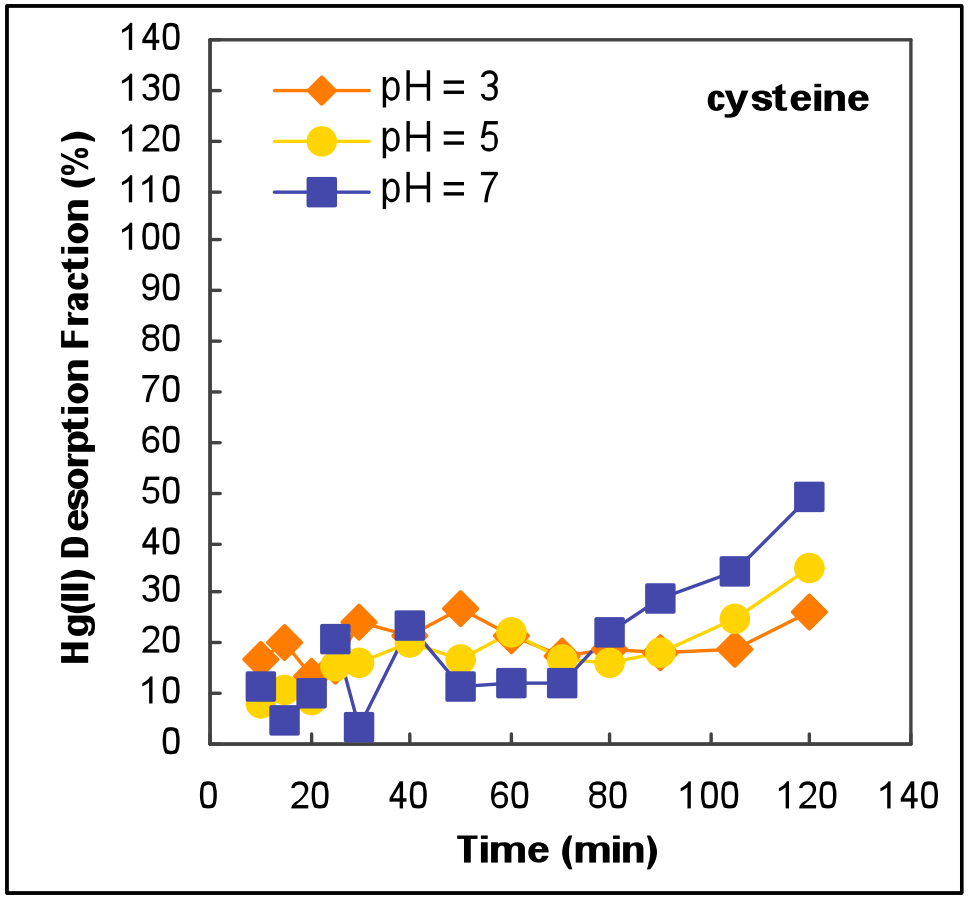
This is consistent with that Ox has a low affinity for Hg(II).

Ox: 1 mM

SD: pH 3: 4.5% (0.3 – 11.9%)
pH 5: 8.1% (0.1 – 18.0%)
pH 7: 6.8% (0.6 – 13.5%)

Results and Discussion

Desorption in the Presence of Cysteine: pH



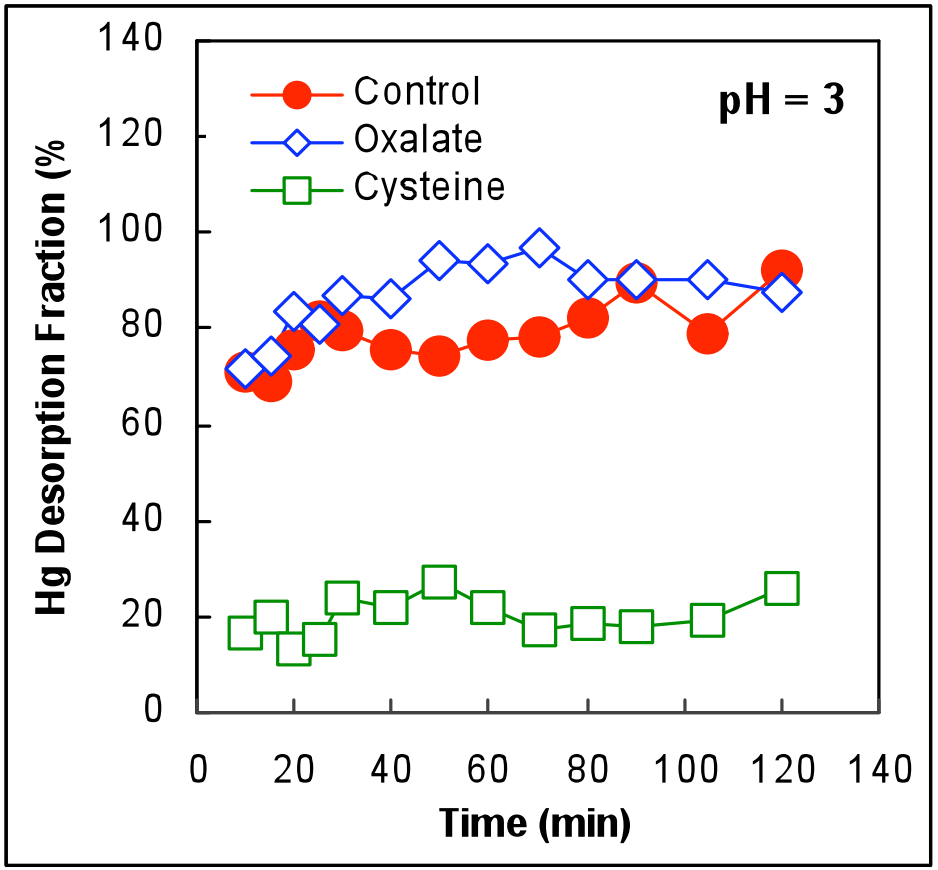
- Desorption in the presence of Cys at all pHs tested is low and slow, but gradually increases with time after ~80 min.
- Since Hg(II) desorption is rapid, during desorption, Cys may be adsorbed; then Hg(II) may be re-adsorbed via the ternary surface complex.

Cys: 1 mM

SD: pH 3:16.4% (0.7 –26%)
pH 5: 12.8% (4.8 – 25.2%)
pH 7: 5.6% (0.7 – 14.2%)

Results and Discussion

Effect of Organic Ligand on Desorption: A Comparison



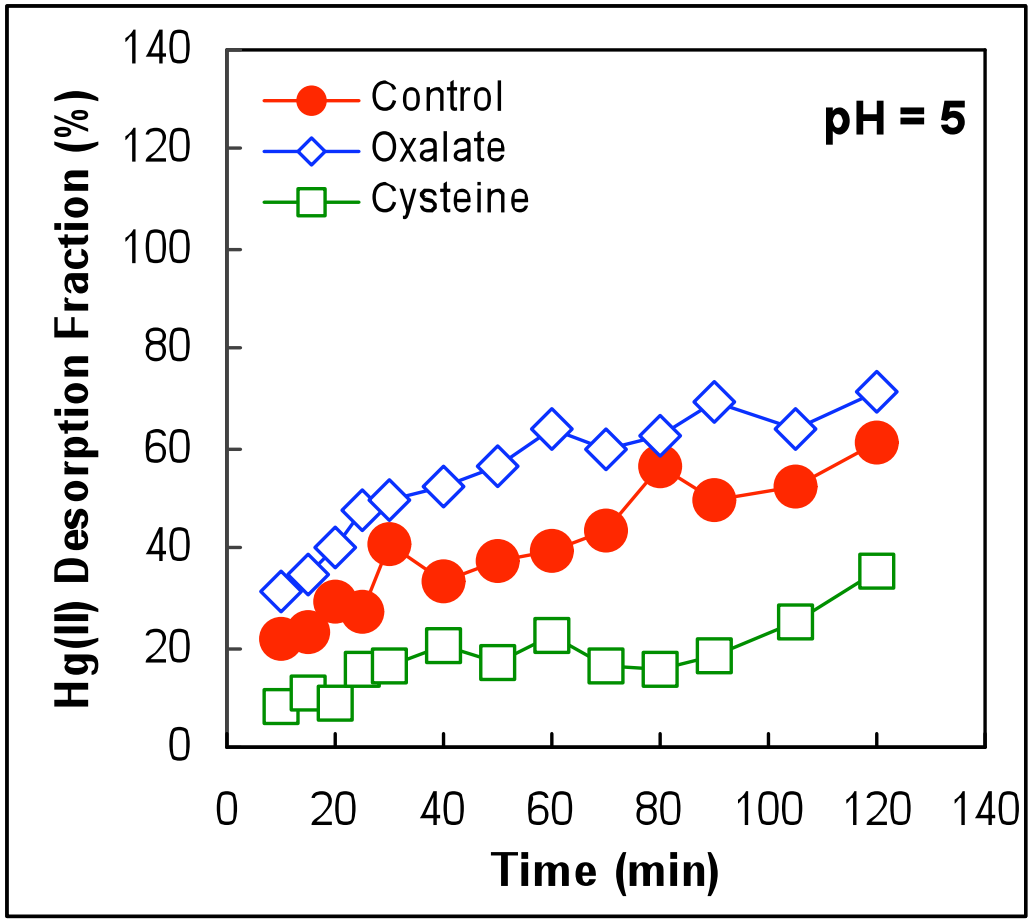
- At pH 3, Ox has no significant effect on Hg(II) desorption.

  But, Cys inhibits desorption ultimately.

Ox and Cys: 1 mM

Results and Discussion

Effect of Organic Ligand on Desorption: A Comparison



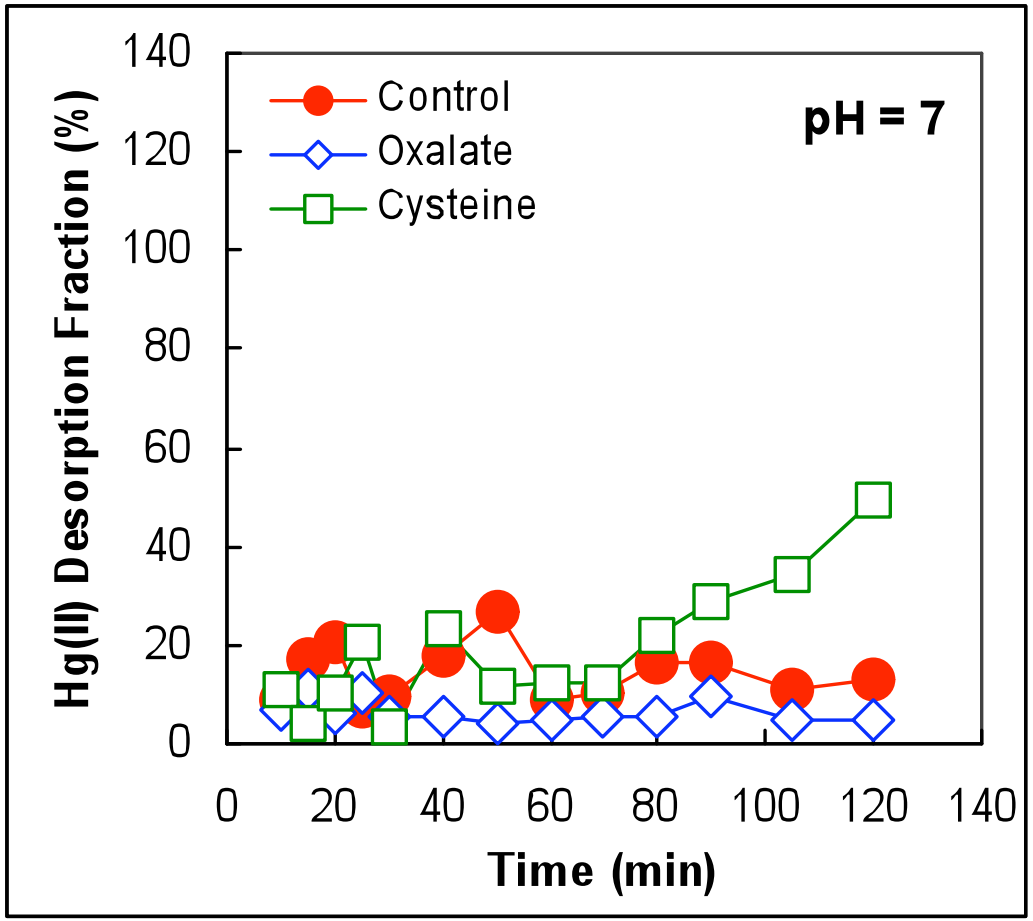
- At pH 5, Hg(II) desorption decreases. Ox does not appear to enhance the desorption significantly, if any.

  Cys still clearly inhibits Hg(II) desorption.

Ox and Cys: 1 mM

Results and Discussion

Effect of Organic Ligand on Desorption: A Comparison



- At pH 7, Hg(II) desorption decreases significantly. Ox clearly does not enhance Hg(II) desorption

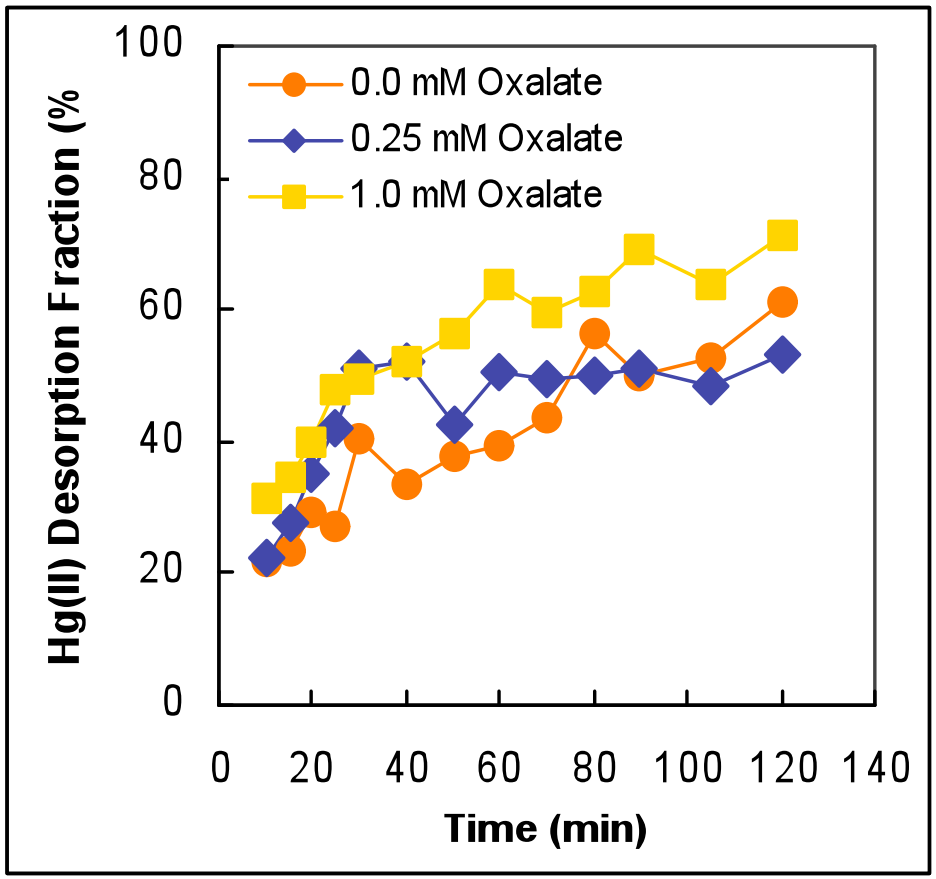
Interestingly, Cys appears to be able to enhance desorption after ~ 80 min.

There could be a kinetic competition for Hg(II) between Cys on particle and Cys in solution.

Ox and Cys: 1 mM

Results and Discussion

Desorption in the Presence of Oxalate: Concentration



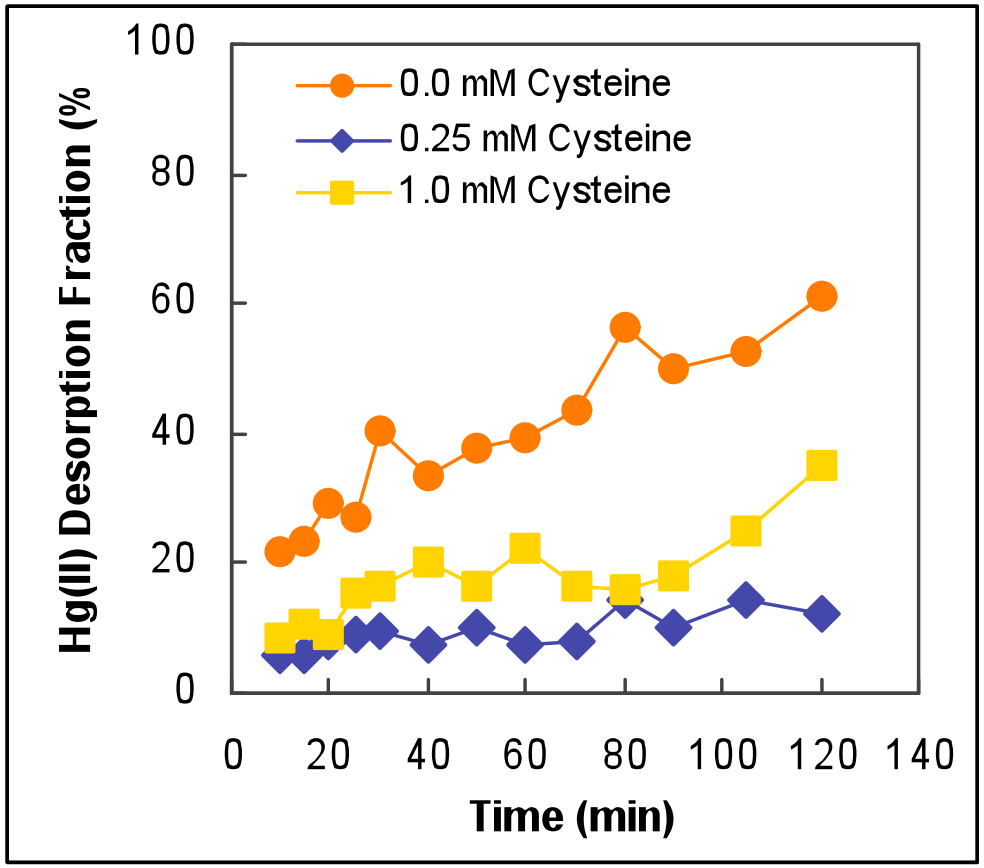
- This shows that Ox has no significant effect on Hg(II) desorption at the two concentrations of Ox.

pH = 5.5

SD: 0.0 mM: 8.7% (0.7 –19%)
0.25 mM: 19.4% (10.3 – 29.6%)
1.0 mM: 8.1% (0.1 – 18%)

Results and Discussion

Desorption in the Presence of Cysteine: Concentration



- This shows that the effect of Cys on the Hg(II) desorption seems concentration-dependent.

  At the higher level of Cys, there is more Cys present in the solution without being adsorbed. The Cys in solution can then enhance the Hg(II) desorption.

pH = 5.5

SD: 0.0 mM: 8.7% (0.7 –19%)
0.25 mM: 3.7% (0.04 – 15%)
1.0 mM: 12.8% (4.8 – 25.2%)

Conclusions

Major Conclusions from This Study

- Desorption of Hg(II) on kaolinite is pH-dependent. At pH < 4.4, the desorption is rapid kinetically and high quantitatively.
- Generally, oxalate has little effect on desorption of Hg(II) on kaolinite, although it appears to be able to enhance Hg(II) adsorption on kaolinite.
- Generally, cysteine can inhibit Hg(II) desorption. But, its effect is kinetically dependent. After ~ 1.5 hour, Cys can desorb Hg(II) slowly, but Ox still has no effect under the same conditions.
- It is likely that Hg(II) tends to stay on particles in the presence of organic ligands with carboxylic group, but can be desorbed slowly in the presence of organic ligands with thio- group.

Acknowledgments

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