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Removing Dissolved Silica from Waste Water with Catechol and Active Carbon

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Abstract

Fresh water scarcity is going to be a global great challenge in the near future because of the increasing population. Our water resources are limited and, hence, water treatment and recycling methods are the only alternatives for fresh water procurement in the upcoming decades. Water treatment and recycling methods serve to remove harmful or problematic constituents from ground, surface and waste waters prior to its consumption, industrial supply, or other uses. Scale formation in industrial and domestic installations is still an important problem during water treatment. In water treatment, silica scaling is a real and constant concern for plant operations.

The focus of this study is on the viability of using a combination of catechol and active carbon to remove dissolved silica from concentrated cooling tower water (CCTW). Various analytical methods, such as ICP-MS and UV-vis, were used to understand the structure-property relationship between the material and the silica removal results. UV-Vis indicates that catechol can react with silica ions and form a silica-catecholate complex. The speciation calculation of catechol and silica shows that catechol and silica bind in the pH range of 8 – 10; there is no evidence of linkage between them in neutral and acidic pHs. The silica removal results indicate that using ~4g/L of catechol and 10g/L active carbon removes up to 50% of the dissolved silica from the CCTW.

Acknowledgments

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Nomenclature

CCTW	Concentrated Cooling Tower Water
DOE	Department of Energy
HTC	Hydrotalcite
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
mg	milligrams
ml	milliliters
mmol	millimoles
ppm	parts per million
SNL	Sandia National Laboratories

1. INTRODUCTION

Silica has been labeled the most challenging constituent to be removed during water treatment as it can exist in the ground and surface water in form of various dissolved and particulate species.[1, 2] The limitation of silica solubility is the main reason behind the requirement of silica removal for many industrial applications and water treatment.[3] In the industrial applications, silica scales are formed on turbines, boilers, heat exchangers, and transfer pipes which can be the source of numerous problems such as formation of thin layer of silica scale on the surface of boiler tube and walls which disrupts the boiler function due to the very low thermal conductivity of the silica scale.[4, 5]

Silica, like carbon, has four covalent bonding sites and can form a very large number of potential molecules. Organic compounds containing a hydroxyl (R-OH) group can react with silica ions and forms the silica complex, such as alcohol.[6, 7] Another example is catechol, with the molecular formula $C_6H_4(OH)_2$, whose two –OH dangling bonds mimic those of alcohols (see Figure 1). Due to this doubled structural feature, catechol was chosen as a potential complexing agent for dissolved silica ions in aqueous solution. The assumed mechanism for silica complexation is: $R_1\text{-O-H} + \text{H-O-}R_2 \rightarrow H_2O + R_1\text{-O-}R_2$.

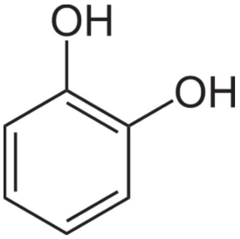

Figure 1. Catechol, molecular formula $C_6H_4(OH)_2$.

2. EXPERIMENTAL

Pure catechol solid from Fisher Scientific was used in this study. Concentrated cooling tower water (CCTW), was synthesized to mimic industrial waters. A baseline for CCTW solution was mixed to the relative ratios: (mmol/L) 0.41 $MgCl_2$ + 0.05 Na_2SO_4 + 0.62 $NaHCO_3$ + 1.0 $CaCl_2$ + 41.0 NaCl + 0.833 SiO_2. The initial pH of solution was adjusted by addition of 0.1 mol/L HCl or NaOH. In a typical silica removal test method, various amount of catechol (10-150 mg) was added into to a 50 ml solution of CCTW in 50 ml tube, to which 500 mg active carbon was added to the solution. The test tube was placed on shaker for 12 hours at room temperature. After shaking, the slurry (catechol/active carbon) was centrifuged, and the pH and silica concentration of supernatants were determined.

In an effort to understand the method of bonding between the silica and the catechol, separation UV-Vis experiments were performed using Varian UV-Visible Spectroscopy; 4 mg catechol was added to 10 ml of CCTW, and then 1 ml of the solution was transferred to the cuvette. The UV-Vis data was collected every minute for 8 minutes.

The effect of various organic solvents on the use of catechol for the extraction of silica via the formation of silica-catecholate complexes was studied. In particular, the extraction of silica was from the CCTW. In general, the extraction procedure was as follows: 500 mg catechol was added into a 25 ml solution of CCTW in a 50 ml tube; the pH solution was adjusted to 9 by the dropwise addition of 0.1 mol/L NaOH. Next, 25 ml of organic solvents added to the solution and then the test tube was placed on a shaker table for 12 hours at room temperature. The solvents tested included: such as benzene (C_6H_6), hexane (C_6H_{14}) and toluene (C_6H_5-CH_3). After shaking, the organic solvents were separated from the water, and the silica concentration of the remaining aqueous solution was determined.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the silica concentration in solution. The pH of the solution was measured with a Thermo Scientific pH meter. The speciation calculation was done separately with the PHREEQC program for 0.6 mM NaCl, 1.2 mM Si and 6 mM catechol.[8]

3. RESULTS AND DISCUSSION

3-1 Silica-Catechol Complex Formation

UV-Vis data was collected on mixed solution samples of catechol and CCTW water after given periods of time. The results show a peak at ~410 nm which can be assigned to the formation of silica and catechol complexes, growing over time. Hydrogen bonded complex involving Si-O-H-

-O-C linkage occur in aqueous system and on silica ions are described as a silica-catecholate complex.[6, 7, 9] It is suggested that silica-catecholate complex is formed with the silicon metal in center coordinated with three catechol ligands in an octahedral geometry.[7] (see Figure 2)

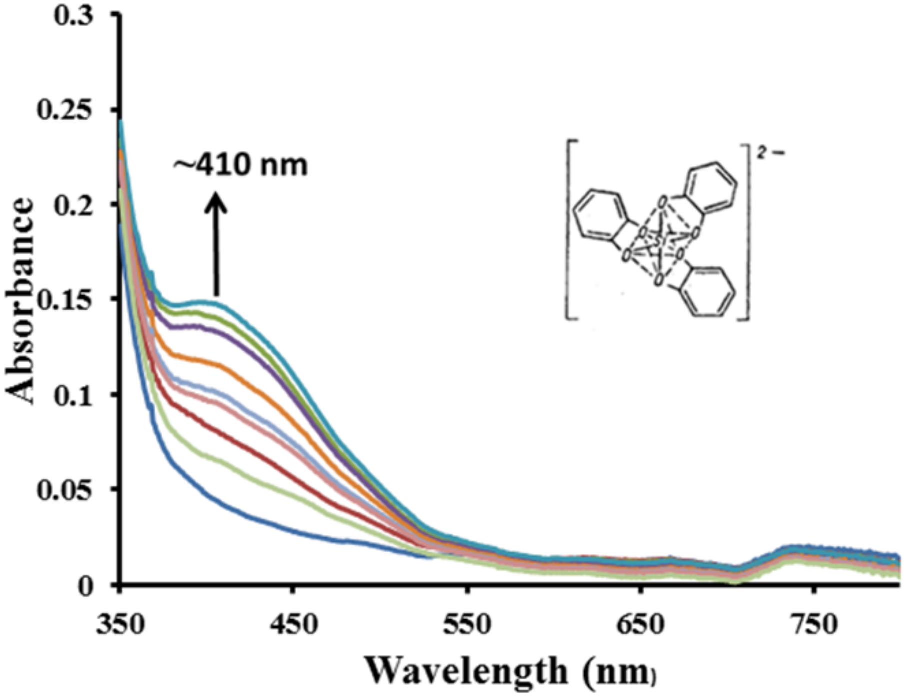

Figure 2. UV-Vis data of catechol (400 ppm) and silica (50 ppm), collected every minute for 8 minutes, showing formation of a silica-catecholate complex. (pH 9, temperature 25°C). Lower blue curve was taken at start of experiment and top curve taken after 8 minutes.

3-2 Effect of Different Solvents on Silica-Catecholate Complex Extraction

The use of catechol in organic solvents is a liquid-liquid extraction method for the removal of silica via the formation of silica-catecholate complexes. is an effective method of separating compounds having different solubilities in two immiscible liquids. The two liquids are typically water and a nonpolar organic solvent. Typically, polar compounds prefer the aqueous layer while nonpolar compounds are extracted into the organic layer.[10] The presence of benzene rings (nonpolar group) in the silica-catecholate complex (see insert in Figure 2) provides the possibility of removing silica from CCTW by using the liquid-liquid extraction method.

Therefore, the removal of silica from CCTW by using different organic solvents such as hexane, benzene and toluene was investigated. However, the results showed poor silica removal percentages, indicating that this is not an effective method. As seen in table 1, using solvents such as hexane and toluene results in only 5.1% and 8.7% removal of dissolved silica from CCTW, respectively. Furthermore, using benzene as an extraction solvent results in effectively no silica removal.

Table 1. Silica removal from the CCTW (50 ppm silica, 500 mg catechol, pH 9 and 25 ml solution) with varying organic extraction solvents (25 ml).

Extraction Solvents	Silica Removed
Benzene (C_6H_6)	0%
Hexane (C_6H_{14})	5.1%
Toluene (C_6H_5-CH_3)	8.7%

3-3 Effect of Catechol Concentration on Silica Removal

One concept for silica removal involves using the propensity of active carbon to sorb organic molecules. The non-hydroxide portions of the benzene ring attach to the high surface area of the activated carbon particles, while leaving the two hydroxide groups exposed to scavenge silica from solution. The percent silica removal from solution using varying catechol/active carbon concentrations (see Figure 3) was studied. The results indicate that using a slurry of ~4 g/L of catechol and ~10g/L active carbon removes up to 50% of the dissolved silica from the CCTW. While this shows the direct effect of hydroxides on the catechol binding to the silica ions in solution at higher pHs, there is a limit to the catechol's performance. This is particularly true when directly compared to the performance of hydrotalcites (HTC) as ion exchange materials for the removal of dissolved silica. Our ongoing studies show that using ~1.1 g/L HTC can effectively remove more than 95% of the dissolved silica from the CCTW.[11]

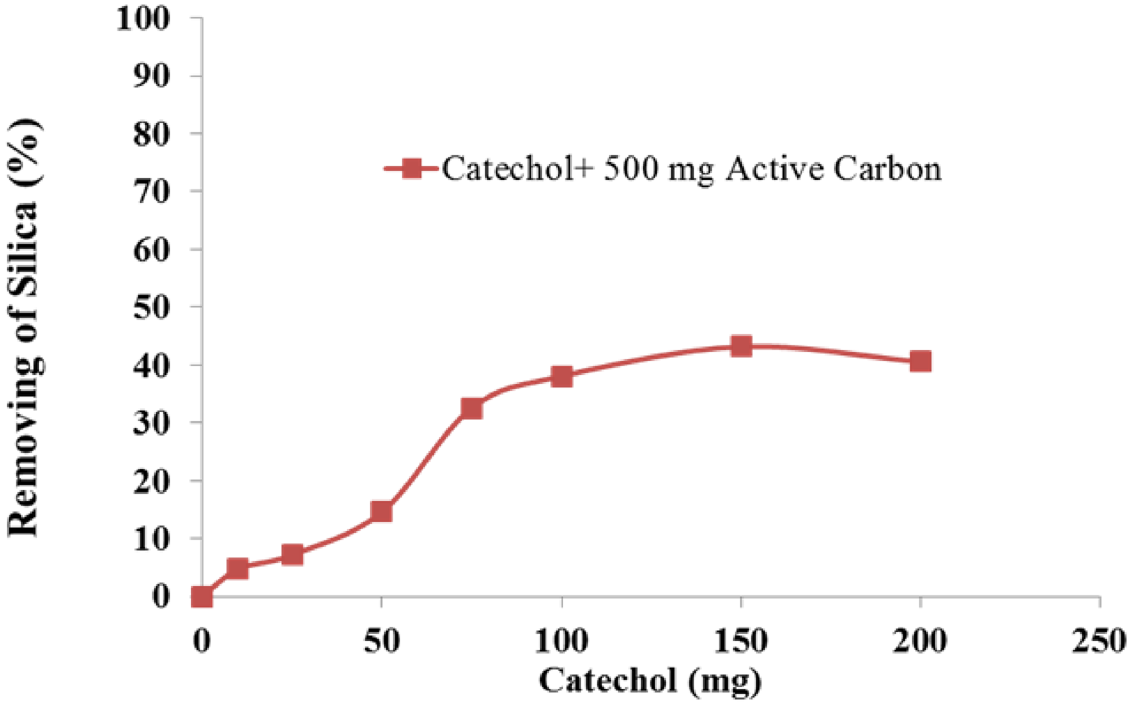

Figure 3. Silica removal from the CCTW (50 ppm silica, pH 9 and 50 ml solution) by catechol and active carbon.

3-4 Speciation Calculation of Catechol and Silica (pH effect)

Silica is highly pH dependent; ionic silica ($H_3SiO_4^-$) forms as the first dissociation of silicic acid (H_4SiO_4) occurs at pH ≥ 9.8. The speciation calculation of catechol and silica (see Figure 4) shows that they selectively bind in the pH region of 8 – 10; the silica ion is a stable sol in that region.[8] Data is presented of silica removal at 25°C as a function of pH (pH = 5, 7, 8, 9 and 10) with varying amounts of catechol present (and fixed amounts of activated carbon). See figure 5. Interestingly, the effect of lowering the pH results in a significant drop in silica removal performance. One explanation for this performance drop off is that in neutral to acidic pHs, the silica exists as a silica particulate. This does not afford an opportunity for strong hydrogen bonding between the –OH's of the catechol and a protonate acid site on the silica. As a result, the catechol cannot form the silica-catecholate complex needed for silica removal from solution.

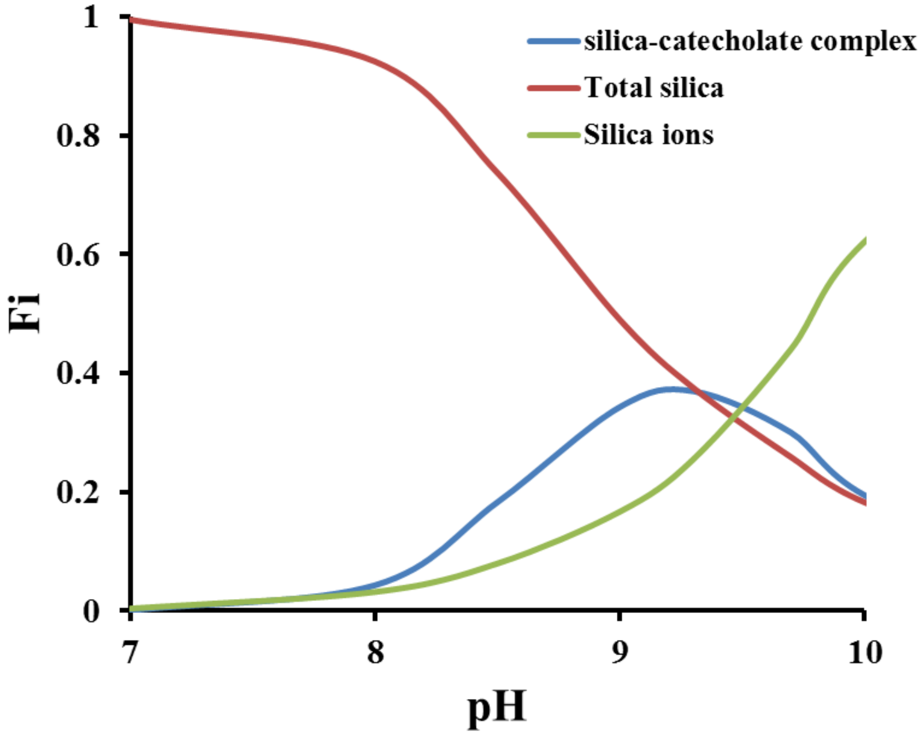

Figure 4. Distribution diagram F_i (-log h) in the H^+-$Si(OH)_4$-pyrocatechol system, as described in reference 8. F_i is defined as the ratio between Si in a species (eg., ionic silica) and total silica concentration.

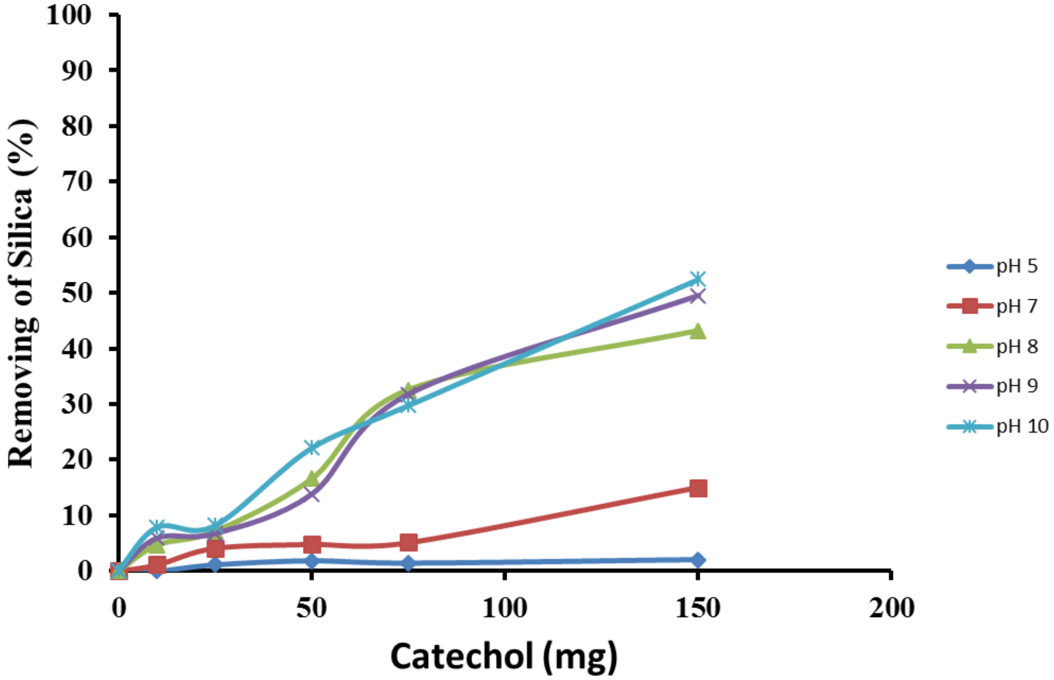

Figure 5. Silica removal as function of pH from the CCTW (50 ppm silica and 50 ml solution) by catechol and 500 mg (fixed amount) of active carbon

With this data, we are able to directly compare the silica removal ability of (200 mg) catechol versus that of (125 mg) hydrotalcite ion exchangers in 50ml CCTW solution at initial pH = 9. The maximum percent silica removal obtained with the catechol (in a slurry with activated carbon) is 50% and that is obtained in the pH range of 8-10. By comparison, our studies on HTC show that it can remove over 95% silica over a wide range of initial pH's (4-11).[11] See Table 2 for details.

Table 2. Catechol (200 mg catechol, 500 mg active carbon, 50 ppm silica, pH 9 and 50 ml CCTW solution) vs Hydrotalcite (125 mg HTC, 50 ppm silica, pH 9 and 50 ml CCTW solution)

	Hydrotalcite (HTC)	**Catechol**
Silica removal efficiency	~ 95 %	~ 50 %
Secondary pollution	Reduced; > 5 recycles for multiple reuse in silica removal	Yes, organic pollution from unreacted catechol; non-recyclable
Adding active carbon for silica removal	No	Yes
Effective pH	4-11	8-10

4. CONCLUSION

Thermoelectric power generation is the largest user of freshwater in the US, at *~500 billion gallons/day which is almost half of all water withdrawn daily*.[12] Replacement of that freshwater with purified oilfield produced waters, municipal or agricultural wastewaters, and subsurface brines is possible only if dissolved silica and calcite are prevented from forming mineral scales during the power generation process. Existing anti-scalant technology can already prevent calcite buildup. However, there is no low energy method for preventing silica scaling, thereby limiting the amount of impaired water recycling that can be achieved. Dissolved silica is ubiquitous in impaired waters, resistant to existing anti-scalants, and difficult to remove from power plant feedwaters.

Our research is focused on low energy, recyclable materials and processes that will effectively remove silica from produced and subsurface waters so that it can be reused in industrial applications. One of the class of materials studied for silica removal was catechol. Reported herein are the details from that study. Utilizing concentrated cooling tower water (CCTW), catechol shows the ability to remove up to 50% of the dissolved silica when utilized at basic pH's between 8 – 10. The assumed mechanism for silica complexation is:

$$R_1\text{-O-H} + \text{H-O-}R_2 \rightarrow H_2O + R_1\text{-O-}R_2.$$

Although this reaction formally shows no pH dependence it is likely that at an intermediate condition where both $H_4SiO_3^-$ and H_4SiO_4 are present in significant proportions is conducive to forming the complexed form of silica rather than only one of the dissolved silica species.

Furthermore, because a recyclable process is desired to reduce secondary environmental waste by the silica removal process (and avoid higher disposal costs to the process), the catechol removal of silica is not preferred. The catechol removal capability is low (maximum 50%). Additionally, it is lower than that for hydrotalcite (HTC) ion exchange materials also utilized in our studies.[11] (See Table 2)

The hydrotalcite,[11] which in contrast to the catechol / carbon mix tested here, operates by an anion exchange mechanism. Since silicic acid dissociates to anionic silica ($H_4SiO_3^-$) at pH ~ 9.5, it is not surprising that HTC is most effective in basic solutions, though tests down to 4.5 show a diminished ability to pick up silica at low pH (< 4; Table 2). The HTC process approaches 95% silica removal with recyclability of more than 5 cycles per batch of HTC. This minimizes the secondary waste produced in the process.

In conclusion, we have shown that catechol is a viable silica removal agent when mixed with activated charcoal. While it remains to be an optimized process, it does show that the potential exists for the use of properly hydroxide-functionalized molecules (eg., catechol) for correct recognition and complexation with silica, for silica's removal from waters.

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