Metal Ion Removal from Aqueous Solutions using NQSA-SC and TSC Chelating Resins

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Introduction

Heavy metal ions pose a threat to both the environment and human health. Due to increased contamination of water sources, different means of water remediation are being studied. Previous research has shown the use of thiosemicarbazones (TSC) and semicarbazones (SC) as an effective means of decreasing the concentration of metal ions in water.[1] These ligands create complexes with the heavy metals which can then be removed from the water. The structures of the NQSA-PTSC and PSC ligands used in this research are shown below:

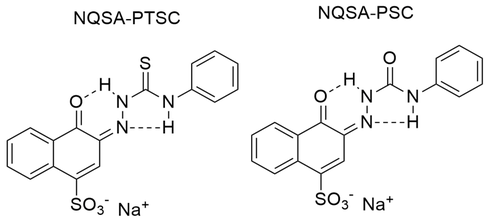

Figure 1. Comparison of NQSA-PTSC and PSC ligands

Experimental

- NQSA-PTSC and NQSA-SC ligands were synthesized by combining 1,2-napthoquinone-4-sulfonic acid (sodium salt) with 4-phenylthiosemicarbazide or 4-phenylsemicarbazide. The general synthesis of the ligand is shown in Figure 2.
- Ligands were gravity filtered and allowed to dry before using.
- Chelating resins were prepared at a 1% loading by mass by stirring the anion exchange resin with an aqueous solution of the ligand. The ion exchange process is shown in Figure 4.
- A pH 8 buffer was created using boric acid (H_3BO_3) and 0.1 M NaOH. The pH was determined to be 8.04.
- A stock solution ($2.7x10^5$ ppb) was created using cadmium chloride ($CdCl_2$) and diluted with pH 8.04 buffer
- Using the stock solution, a reaction solution ($1.7x10^4$ ppb) and calibration solutions (3000, 2250, 1500, 750, 15 ppb) were created by dilution with a pH 8.04 buffer
- Approximately 20-50 mg of the loaded resins were weighed out into small vials to study the adsorption of Cd^{2+} by a batch method.
- 1 mL of reaction solution was added to each vial at certain time increments to allow for an array of absorption times (15 min, 30 min, 1 hour, 2 hours, 4 hours).
- After the set absorption period, resins were syringe filtered from the solution.
- 0.75 mL of each filtered solution was placed in a 15 mL centrifuge tube and brought to a 5 mL volume using pH 8.04 buffer.
- The were analyzed using a PerkinElmer Avio 200 ICP-OES to determine the concentration of cadmium in solution.
- Dry weight distribution values (D_w) were calculated according to Equation 1 to determine the removal of cadmium from the solution.

Results

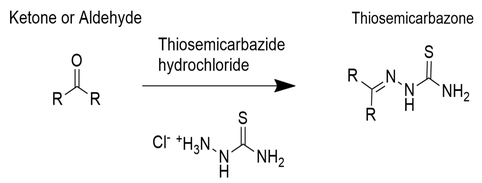

Figure 2: General Synthesis of TSC Ligands

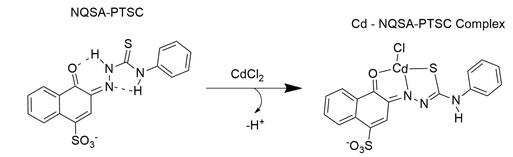

Figure 3: Formation of Cadmium-NQSA-PTSC Tridentate Metal-Ligand Complex

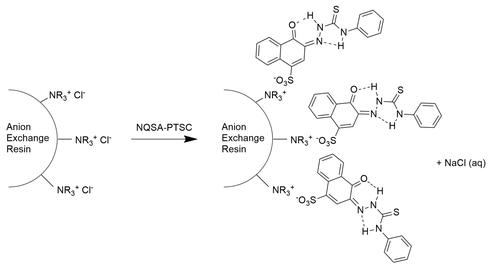

Figure 4: Synthesis of the chelating resins

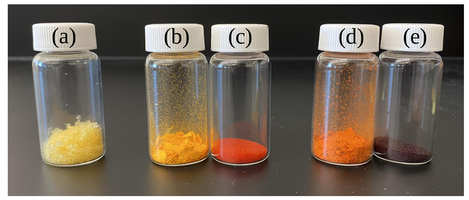

Figure 5: (a) Unmodified Resin, (b) NQSA-PSC Ligand, (c) NQSA-PSC Chelating Resin, (d) NQSA-PTSC Ligand, (e) NQSA-PTSC Chelating Resin

$$D_w = \frac{A_o - A_e}{A_e} * \frac{mL}{g}$$

A_o = Initial Cd^{2+} concentration
A_e = Concentration of Cd^{2+} in timed samples
mL = volume of Cd^{2+} solution used
g = mass of resin

Equation 1: Calculation of dry weight distribution (D_w) values

Table 1: Cadmium Concentration and D_w values for NQSA-PSC Chelating Resins

NQSA-PSC		
Time	Concentration Cd (ppb)	Distribution Value
15 min	13944	11.0
30 min	13441	8.60
1 hour	12910	13.5
2 hours	9081	22.3
4 hours	9236	29.0

Table 2: Cadmium Concentration and D_w values for NQSA-PTSC Chelating Resins

NQSA-PTSC		
Time	Concentration Cd (ppb)	Distribution Value
15 min	7049	46.8
30 min	3196	118
1 hour	1908	273
2 hours	1080	467
4 hours	776	665

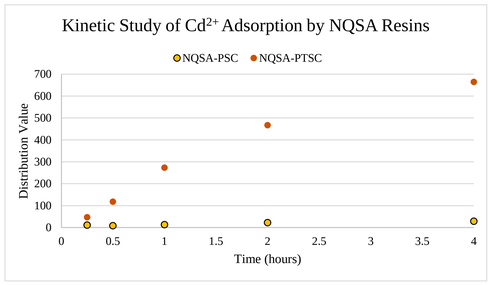

Figure 6: Kinetic Study of Adsorption of Cadmium by NQSA-PSC and NQSA-PTSC Chelating Resins

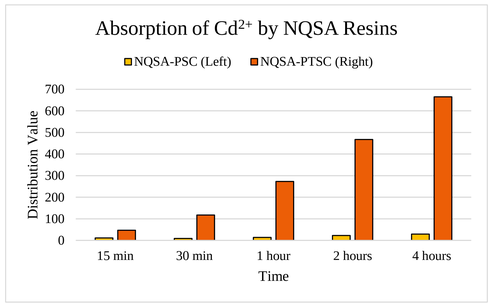

Figure 7: Comparison of Adsorption of Cadmium by NQSA-PSC and NQSA-PTSC Chelating Resins

Discussion

The ligands form a tridentate chelation system with the cadmium as shown in Figure 3. In the TSC ligand the sulfur atom is involved in the chelation of the metal ion, whereas the in SC ligand the oxygen atom is involved.

The loading of the ligand onto the resin causes a color change that can be observed visually as shown in figure 5.

It was found that the thiosemicarbazone chelating resin was more effective at removing the cadmium ions from the solution as shown by the higher D_w values for this resin. According to hard-soft acid base theory, this is due to the sulfur atom being a softer base forming a strong attraction to the cadmium, which is a soft acid. The semicarbazone chelating resin did not adsorb much cadmium from solution due to the presence of the oxygen, which is a hard base, in place of the sulfur in the ligand structure.

The kinetic study showed that the adsorption of cadmium from the solution did not greatly increase after about 1 hour of contact with the NQSA-PSC resin, while the NQSA-PTSC continued to increase up to the maximum time studied of four hours. Longer time studies can be conducted to determine the time required to reach maximum adsorption of the metal from solution by the resin.

Future Work

- A cerium(III) solution will be tested with both ligands using the same process as the cadmium.
- Different loading percentages of the resins can be studied to determine the best loading on absorptivity of the metal ion from solution.
- An array of pH buffers can be used to see effects of pH on ligand efficiency.

References

[1] Crook, Amanda J. et. Al., Thiosemicarbazone and Semicarbazone Chelating Resins and Their Potential Use in Environmental Applications. *Separation Science and Technology.* 2012, 47:14-15, 2225-2229, DOI: 10.1080/01496395.2012.697524 (Accessed August 2021)

[2] Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N. Toxicity, Mechanism and Health Effects of Some Heavy Metals. Interdisciplinary Toxicology 2014, 7 (2), 60–72. https://doi.org/10.2478/intox-2014-0009. (Accessed August 2021)

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