

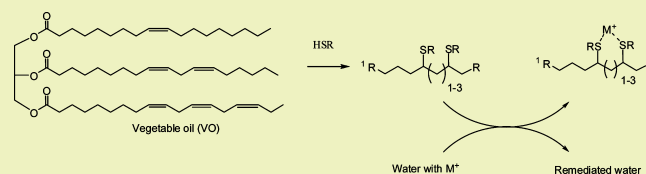
# Thioether-Functionalized Vegetable Oils: Metal-Absorbing Biobased Ligands

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**ABSTRACT:** Vegetable oils containing thioether groups have been synthesized and used to effectively remove heavy metal ions from aqueous solution. The use of thioether-functionalized corn oil (TF-corn oil) and thioether-functionalized canola oil (TF-canola oil) were both effective in the extraction of  $\text{Ag}^+$  from a 600 ppm aqueous silver nitrate solution. The TF-corn oil reduced the observed silver in solution to a level below the detection limit, whereas the TF-canola oil was only able to remove slightly over 50% of the concentration. A study of the absorption rate is also reported, where both the TF-corn oil and the TF-canola oil removed the  $\text{Ag}^+$  rapidly, at nearly the same rate. Preliminary results suggest that the efficacy and capacity of silver removal relates directly to the fatty acid composition of the oil precursor.

**KEYWORDS:** Remediation, Thiolated oil, Vegetable oil derivative, Metal Chelate, Vegetable oil ligand, Thioether sulfide, Ligand



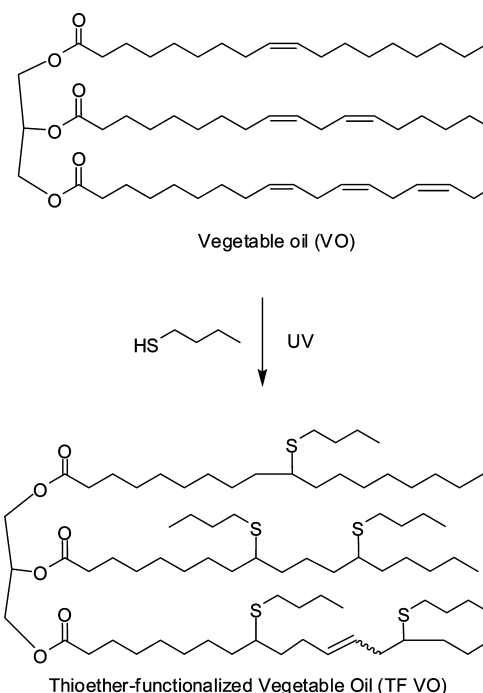
## INTRODUCTION

Water availability and purity is an extremely important topic in the world today and is anticipated to be of even greater future importance due to population growth.<sup>1</sup> Unfortunately, modern society has caused the contamination of water with toxic elements such as arsenic, lead, mercury, cadmium, chromium, and selenium, which stem from the mining of metals and coal, manufacturing, and other sources.<sup>2</sup> The ability to remove heavy elements is an important research topic where the use of metal-binding ligands, particularly sulfur-based systems, such as thiophenols<sup>3–7</sup> and thioether<sup>8,9</sup> donors, have been useful approaches.

Vegetable oils, shown in Scheme 1, have a triacylglycerol structure with a glycerol backbone connected to a varied distribution of three long-chain fatty acids via ester linkages. The hydrocarbon chains of the structure are lipophilic and immiscible with water or lower alcohols. The ester groups and internal double bonds give ample routes for modification.<sup>10</sup> However, despite the wide variety of reported vegetable oil derivatives,<sup>11–18</sup> there is no demonstrated use of any of these compounds for the extraction of metal ions from water. The use of vegetable oils as a base material from which to build a simple ligand system is an approach to a biobased metal ion removal system. Through simple chemical modifications, ligand-pendant oils can be derived that are effective in partitioning heavy metal ions from water into an organic layer.

Herein, a new technological use of ligand-modified vegetable oils, useful for a broad realm of applications encompassing metal coordination, is reported. The extraction of  $\text{Ag}^+$  ion from a water solution is used as an example model for the remediation of water contaminated by heavy metals. This ion system is an ideal model as it possesses similar “softness” to many harmful metals, is readily detected at very low

## Scheme 1. Synthesis of TF-Vegetable Oil, an Illustrative Fatty Ester Composition



concentrations, and also allows convenient sample preparation without the creation of hazardous solutions. The extracting oil,

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thioether-functionalized vegetable oil (TF-VO), has been previously synthesized and its composition thoroughly characterized.<sup>19</sup> The two TF-VOs described in this work were originally evaluated as superior lubricity additives.<sup>20</sup> The synthesis (Scheme 1), a one-step thiol-ene addition of thiols to double bonds, yields thioethers<sup>9</sup> that possess soft sulfur moieties that exhibit strong binding affinity for soft metals, such as the heavy metal elements. Thiol-ene methodology works also with heteroatom substituted thiols.<sup>21</sup> Hence, a wealth of possible pendant chains of variable length, with or without additional donor atoms, can be designed beyond the simple *n*-butyl chain described herein.

The concept of utilizing vegetable oils as starting materials is inviting because several agriculturally derived crops exhibit unique fatty acid distributions that can be exploited to design a variety of metal coordination affinities. The resultant ligand structures possible are thereby imprinted mainly by the crop source.

## EXPERIMENTAL SECTION

**Materials.** Corn and canola oils used in this study were obtained from a local retailer. Thioether functionalized (TF) corn and canola oils were produced by reacting them with excess butanethiol using a UV light according to literature methods.<sup>19</sup> Purification was done by distillation instead of the chromatography employed in the literature method.<sup>19</sup> Elemental analyses show sulfur content of 9.7% for TF-corn oil and 10% for TF-canola oil. Silver nitrate was obtained from Sigma Aldrich (St. Louis, MO). Analytical standards were obtained from Spex Certiprep (Metuchen, NJ). The water used for the samples was purified by reverse osmosis.

**Silver Extraction Procedures.** Extractions were run by two different bench-scale methods. In the experiments for capacity determination, samples of 1 mL of ~600 ppm silver nitrate solution were added to samples of TF-VO ranging in mass from 0.004 to 0.104 g. A micro stir bar was added, and the foil-wrapped reaction vials were placed in a Pierce Reacti-therm (Rockford, IL) 9-place stirring block and allowed to stir for 11 d to ensure equilibration between the Ag<sup>+</sup> solution and the TF-VO. Aliquots of the aqueous layer were taken and analyzed on a Perkin-Elmer Optima 7000DV inductively coupled plasma spectroscope (Waltham, MA) at 328.068 nm.

In the rate of extraction experiments, 3 mL of stock solution was added to 0.3 g of oil. These samples were vortexed for 1 min and then foil wrapped. Aliquots were taken at appropriate time periods with a pipet and analyzed as above.

## RESULTS AND DISCUSSION

**Synthesized Products.** Through the reaction process outlined in Scheme 1, it is evident that the composition of acyl chains of the starting material determines the oil's potential for conversion to the ligand-modified system. The saturated fatty chains have no active reaction site, while the monounsaturated (oleic), diunsaturated (linoleic), and triunsaturated (linolenic) have one, two, and three sites, respectively. The characterization in earlier work<sup>19</sup> demonstrated that, under the reaction conditions employed here, there is no preference of thiol molecule incorporation into a specific double bond type. Therefore, the fatty chain composition of the starting oil will be projected onto the product TF-VO. The differences in the three unsaturated components—28%, 56%, and 1% in corn oil and 63%, 19%, and 9% in canola oil—show the possibility of producing TF-VOs with similar sulfur content yet different structure. For example, TF-canola oil has ~65% of its chains incorporating one thioether group but only ~20% incorporating two. TF-corn oil has a different distribution, 39% with one and 37% with two thioether groups.

**Comparison of Extraction Performance of Vegetable Oil and TF-VO.** Ag<sup>+</sup> Extractions with TF-VO: Capacity Experiments. The capacities for Ag<sup>+</sup> absorption by corn oil, TF-corn oil, and TF-canola oil were evaluated by determining how much silver could be removed from a stock solution at extraction times over 72 h. The data, shown in Table 1, displays

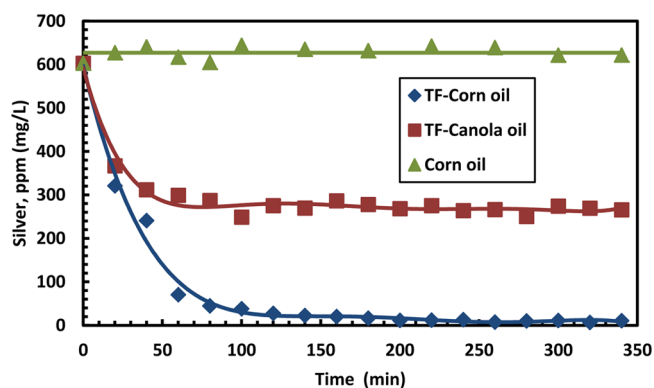
**Table 1.** Concentration of Ag<sup>+</sup> Detected in Aqueous Solution After Extraction with Specified Amount of TF-VO or Ordinary Corn Oil, Using the Capacity Method

corn oil		TF-corn oil		TF-canola oil	
oil (g)	[Ag] (ppm)	oil (g)	[Ag] (ppm) <sup>a</sup>	oil (g)	[Ag] (ppm)
0	600	0	600	0	600
0.0074	604	0.0023	549	0.0037	510
0.0285	627	0.0338	134	0.0317	311
0.0476	608	0.0480	58	0.0484	251
0.0761	615	0.0723	ND	0.0802	208
0.1057	604	0.1006	ND	0.1040	235

<sup>a</sup>ND = below detection limit of 0.5 ppm.

several interesting trends. First, corn oil with no added ligands showed essentially no ability to remove the Ag<sup>+</sup> from the aqueous solution. Second, TF-corn oil is able to decrease the silver concentration in the water below the detection limit. Finally, TF-canola oil was also effective but much less effective than the TF-corn oil. For example, when 0.07–0.08 g of the TF-VO was used, all of the Ag<sup>+</sup> detectable was extracted in the TF-corn oil system (0.83 wt % Ag<sup>+</sup> absorbed), but 34% was left (208 ppm) by TF-canola oil (0.49 wt % Ag<sup>+</sup> absorbed). Apparently, the key difference is that while TF-canola was saturated with Ag<sup>+</sup>, TF-corn was not. Even more telling is that the TF-canola oil system with even more oil, 0.1 g, was no more effective than the system with lower amounts of TF-corn oil. The data also supports that the Ag<sup>+</sup> capacity and Ag<sup>+</sup> concentration are interrelated through an equilibrium; hence, TF-corn excels particularly as aqueous Ag<sup>+</sup> concentration decreases.

**Ag<sup>+</sup> Extractions with TF-VO: Rate of Extraction Experiments.** As in the capacity experiments, three oil systems were tested in the extraction of Ag<sup>+</sup>: ordinary corn oil, TF-corn oil, and TF-canola oil. The data in Figure 1 show that both of the TF-VOs can remove the Ag<sup>+</sup> in a relatively short time. In the TF-corn oil, more than 90% of the Ag<sup>+</sup> was removed from the water within 80 min. The TF-canola oil also reached its



**Figure 1.** Observed Ag<sup>+</sup> concentration of aliquots of a solution stirred with TF-VO and ordinary corn oil using the rate of extraction method.

maximum absorption, just over 50% of the silver, in roughly the same time frame. As before, essentially no capacity for metal absorption was noticed for the corn oil, which also serves as a control experiment for the system in general. In other words, no experimental artifact caused the observed decrease in the concentration of  $\text{Ag}^+$ .

The bench-scale experiments conducted in this work were done primarily to demonstrate the concept and advantages of employing a biobased methodology, with respect to conventional industrial processes. The influence of process, stirring, and extraction conditions that may be encountered in larger scale processes will need to be determined to optimize the use of TF-VO in extracting heavy metals, such as  $\text{Ag}^+$ , from aqueous streams under industrial conditions. This work will be the focus of future studies scaling up the process.

**Absorption Differences.** The data show that the modification of the double bonds into thioether groups gives the capability for extraction of metal ions from the aqueous solution as both of the TF-VO samples removed appreciable  $\text{Ag}^+$ , with efficiencies between 69 and >99%. The TF-corn oil exhibited metal-removal capacities comparable to more elaborate ligand systems, such as the thiocrown,<sup>8,22</sup> which contains poly dentate thioether ring structures.

The significantly higher efficacy of TF-corn oil relative to TF-canola oil was achieved even though the sulfur content of the oils, by weight, was essentially the same. Also, the  $\text{Ag}^+$  capacity of TF-corn oil remains high even as the silver concentration approaches single digit values. The system can be analyzed with the equilibrium absorption constant model shown in Scheme 2.

#### Scheme 2. Equation of an Equilibrium Absorption Constant for TF-VO with $\text{Ag}^+$



From the data presented in Table 1, taking the point where 0.048 g of oil was used, the ratio of  $\text{Ag}^+$  (captured in the oil) /  $\text{Ag}^+$  (still observed in solution) is a metric that compares the system efficiency. The TF-corn oil has a ratio of 542/58, whereas TF-canola oil has a ratio of 349/251, i.e., 9.3 vs 1.4, showing TF-corn oil to be ~6.6 times more effective under these conditions. At this stage, there is no sufficient evidence to decide unambiguously on the best-performing structure(s) and how to maximize their content in the product. However, a couple of broad generalizations are implied. First, TF-canola oil had more mono-thioether chains, yet lower absorption, indicating that this is a less effective binding motif. TF-corn oil had more dithioether chains, so there is the possibility of a strong binding chelate effect. TF-canola oil actually has more trithioether chains but does not seem to gain additional adsorption beyond dithioether chains from them. Finally, the TF-corn oil also has many more chains that contain both one thioether and an unreacted double bond. It is possible that a synergistic bidentate hemi-labile type complex in which both a double bond and sulfur coordinate to the metal is stronger than a monodentate sulfur coordination. Further effects, such as the number of sulfur atoms on neighboring chains, are also possible but beyond the scope of this report. However, even just from the data presented here, there is a strong inference that multiple-chain fatty acid unsaturations can imprint higher levels of multi-dentate thioether and/or hemi-labile chains when thiolated, which should translate to appreciably higher  $\text{Ag}^+$  binding capacities. As such, more highly unsaturated TF-oils, such as

linseed oil could increase capacity beyond the current benchmark of ~2 wt %  $\text{Ag}^+$  or  $\text{S}/\text{Ag}^+ = \sim 15$ . In summary, chemical modification of vegetable oils represents an inexpensive and convenient way to utilize an agriculturally based approach to solve a serious problem relating to heavy metal pollution and water purification.

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##### Notes

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