

Mercury sorbents made by inverse vulcanization of sustainable triglycerides: the plant oil structure influences the rate of mercury removal from water

Alfred D. Tikoalu, Nicholas A. Lundquist, Justin M. Chalker*

Institute for Nanoscale Science and Technology, Flinders University, Bedford Park, South Australia, 5042, Australia

KEYWORDS: inverse vulcanization, mercury, plant oils, polymer, sulfur, triglycerides

ABSTRACT: High sulfur content polymers were prepared through the copolymerization of sustainable triglycerides and sulfur. The products of the so-called “inverse vulcanization” contain 50% sulfur by mass and were evaluated in the removal of inorganic and alkylmercury compounds from water. The structurally distinct triglycerides found in canola oil, castor oil, and rice bran oil were all examined as co-monomers in the inverse vulcanization reaction to determine how each influences the rate and capacity of mercury uptake. It was found that the high percentage of hydroxylated ricinoleic acid in castor oil improves both wetting and the rate of uptake of mercury(II) chloride into the polymer, in comparison to the polymers made from canola oil and rice bran oil. For the castor oil, the initial rate of uptake of mercury(II) chloride was more than three times the initial rate of uptake of the canola oil polymer, with a mercury removal efficiency exceeding 99.99%. The affinity of the castor oil polymer for HgCl_2 was also excellent, with a distribution coefficient (K_d) on the order of 10^6 mL/g. In contrast, the polymer made from the inverse vulcanization of canola oil and sulfur had an initial rate of uptake more than twice the rate of the castor oil copolymer in experiments involving sorption of the mercury-based fungicide 2-methoxyethylmercury chloride (MEMC). In addition to kinetics, sorption isotherms were obtained for all polymer sorbents and fit to both Langmuir and Freundlich isotherm models. In terms of sustainability, this work advances the use of renewable monomers such as triglycerides sourced from plants and inexpensive industrial byproducts such as sulfur to make affordable mercury-binding materials.

INTRODUCTION

Mercury pollution is a persistent threat to the environment and human health.¹⁻⁵ Mercury emissions originate from a variety of sectors, but pollution from artisanal gold mining⁶ and coal combustion⁷ are especially problematic, with the majority of anthropogenic mercury emissions originating from these activities.⁸ With the Minamata Convention recently coming into force,⁹ there is an urgent need to develop cost-effective measures for stemming mercury pollution. Indeed there has been extensive work on mercury decontamination of air, water and soil,¹⁰ including the development of high performance sorbents based on activated carbon¹¹ and other porous materials.¹² Nevertheless, these materials are often not suitable in developing nations because of prohibitive cost, limited scale, or difficulty in deployment. And while mercury sorbents based on abundant bio-based materials have been reported,¹³ their performance in mercury capture is often limited in rate, selectivity and capacity. Thus, there remains a need for sustainable and low-cost mercury sorbents that can be easily prepared and deployed in areas with limited economic resources. To address this need, polymeric sorbents for mercury made from elemental sulfur and renewable plant oils have emerged as attractive materials.¹⁴⁻²¹ The plant-derived monomers are renewable and there is a surfeit of sulfur produced during petroleum refining, so these polymers can be prepared sustainably and on a large scale.^{22,23} These high sulfur content polymers, prepared by “inverse vulcanization,”²⁴⁻²⁷ have been shown to be effective in the capture of mercury metal, mercury gas, inorganic mercury, organic mercury and mercury bound to humic mat-

ter.¹⁵ In a recent report from our laboratory, we specifically employed canola oil or even used cooking oil in the polymerization so that the resulting mercury sorbent would be made from inexpensive and sustainable starting materials.^{15,28} We have since explored this polymer system in a variety of environmentally-focused applications including oil spill remediation,²² metal sorption,^{15,29} water filtration,²³ and controlled-release fertilisers.³⁰ Additionally, methods to tune the thermal and mechanical properties of these polymers have recently been explored to further increase their versatility.³¹ In this study, we investigate the inverse vulcanization of two additional plant oils—rice bran oil and castor oil—and compare their mercury sorption performance in aqueous media to the original canola oil and sulfur copolymer (Figure 1).

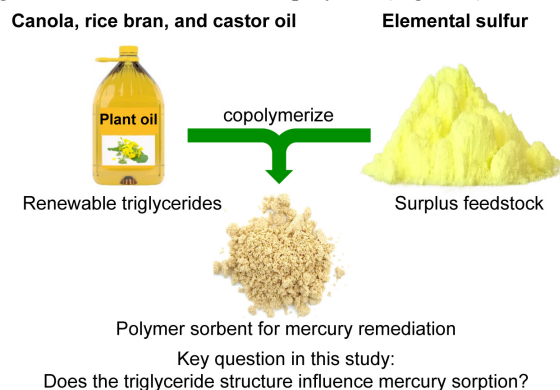


Figure 1. Plant-derived triglycerides can be copolymerized with elemental sulfur to form sustainable, low-cost mercury sorbents.

The hypothesis at the outset of the study was that the hydroxylated triglyceride in castor oil would improve wetting and mass transfer of aqueous mercury to the polymer (Figure 2). It was also of interest to determine if the rice bran oil—with its greater unsaturation from high linoleic acid content—would affect mercury sorption. More generally, our goal was to apply inverse vulcanization to other renewable triglycerides that are widely available so that they could be used in environmentally beneficial applications.^{26,27}

RESULTS AND DISCUSSION

POLYMER SYNTHESIS AND CHARACTERIZATION

The composition of the three plant oil triglycerides was first analyzed to determine the identity and quantity of the unsaturated components. To do this analysis, the triglyceride was reacted with sodium methoxide in methanol to produce glycerol and the corresponding fatty acid methyl ester (Supporting Information S3). The methyl esters were extracted into ethyl acetate and then characterized further by infrared and ¹H NMR spectroscopy and GC-MS (Supporting Information S3-S7). The canola oil triglyceride used in this study contained oleic acid (74%) and linoleic acid (18%) as the major constituents (Figure 2). Rice bran oil also contained oleic acid as the major component of the triglyceride (46%), but had greater amount of linoleic acid (30%) and palmitic acid (21%). Castor oil, in contrast, is structurally distinct in that 92% of the triglyceride is comprised of ricinoleic acid (Figure 2).

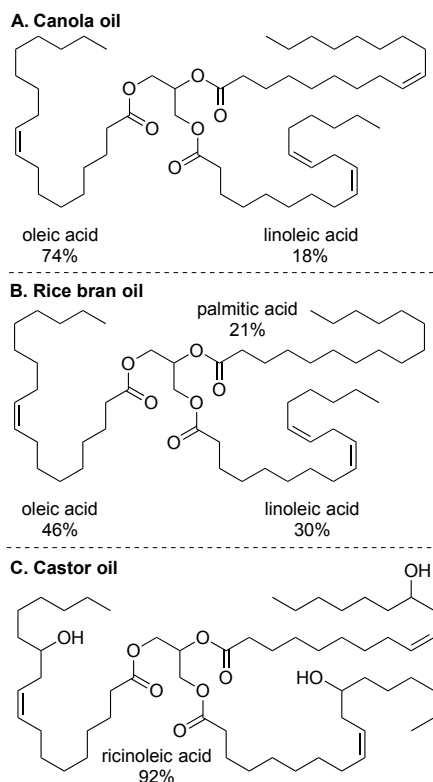


Figure 2. The fatty acid compositions in the plant-derived triglycerides canola oil, rice bran oil and castor oil were determined by GC-MS after transesterification to the methyl ester (Supporting Information S5). The major fatty acid components are shown. These triglycerides were used as monomers for inverse vulcanization with subsequent testing as mercury sorbents.

Determining the structural differences of these triglycerides is important because the degree of unsaturation might affect the crosslink density in the polymer. Furthermore, the hydroxyl groups in the castor oil triglyceride might facilitate wetting and mass transfer of contaminated water to the polymer surface. There is also the possibility that these hydroxyl groups could also bind to mercury.

With the composition of the triglycerides known, each was subject to copolymerization with sulfur (Supporting Information S8-S9). First, the triglyceride was added to an enamelled cast iron reactor and heated to 170 °C, with mixing imparted from an overhead stirrer. An equal mass of sulfur was then added to the heated triglyceride at such a rate that the reaction temperature did not drop below 159 °C—the temperature at which sulfur undergoes ring-opening polymerization.²⁴ After the addition of sulfur, the reaction mixture is two-phases with the molten sulfur as the higher density phase on the bottom of the reactor and the oil on the top. At this stage the reaction temperature was increased to 175 °C. Sodium chloride was then added to the reaction mixture, serving as a porogen that could be removed after polymerization to provide a higher surface area polymer.^{15,22} After the addition of sodium chloride, the reaction mixture solidifies after 12 minutes for canola oil, 25 minutes for rice bran oil, and 21 minutes for castor oil (for a 30 gram polymerization). The polymer-salt composite was then removed from the reactor, ground to small particles (0.2-10 mm diameter) and then washed repeatedly in water to remove the sodium chloride. After drying the polymer in air, the isolated yields for all polymers were typically between 84-97%. The final product presented as a soft, rubbery solid varying in color from brown (copolymers made from the inverse vulcanization of canola oil and rice bran oil) to yellow/tan (copolymer made from inverse vulcanization of castor oil) (Scheme 1). Subsequently, these polymers will be referred to by the following names: poly(S-*r*-Canola), poly(S-*r*-Rice Bran), and poly(S-*r*-Castor). This nomenclature is adapted from Pyun's conventions for preparing random (*r*) copolymers from sulfur (S) and a polyene (the triglyceride).^{24,32}

Spectroscopic characterization of the copolymers revealed reaction of the triglyceride alkenes, as expected for inverse vulcanization (Supporting Information S10-S13). In the infrared spectrum, for instance, the C-H sp^2 stretch at 3010 cm^{-1} clearly observed in the triglyceride (Figure 3A) is absent in all of the copolymers (Figure 3B). The IR spectrum for poly(S-*r*-Castor) also contained a broad OH stretch between 3550 and 3200 cm^{-1} , indicating that the hydroxyl groups of the ricinoleic acid component of the castor oil triglyceride were unaltered by the polymerization. ¹H-NMR spectroscopy of the copolymers in deuterated pyridine was used to quantify the consumption of alkenes. This analysis was achieved by comparing the ratio of the integrated signal of the alkenes to terminal methyl group in the triglyceride for both the unreacted triglyceride and the polymer (Supporting Information S11-S13). For poly(S-*r*-Canola), 86% of the alkenes were consumed and for poly(S-*r*-Rice Bran), 93% of the alkenes had reacted. In contrast, poly(S-*r*-castor) reached its gel point at a lower alkene conversion, with only 77% of the alkenes consumed in the inverse vulcanization.

Scheme 1. Inverse vulcanization of plant-derived triglycerides. A. Equal masses of sulfur and a triglyceride were copolymerized at 175 °C in the presence of a sodium chloride porogen. The reaction was removed from the heat upon vitrification (12-25 minutes). The sodium chloride (70% of the mass of the reaction mixture) was then removed by a water wash. B. Digital image of the copolymers prepared from each triglyceride and an equal mass of sulfur. The image was obtained after grinding, washing, and drying the polymer particles (0.2 to 10 mm).

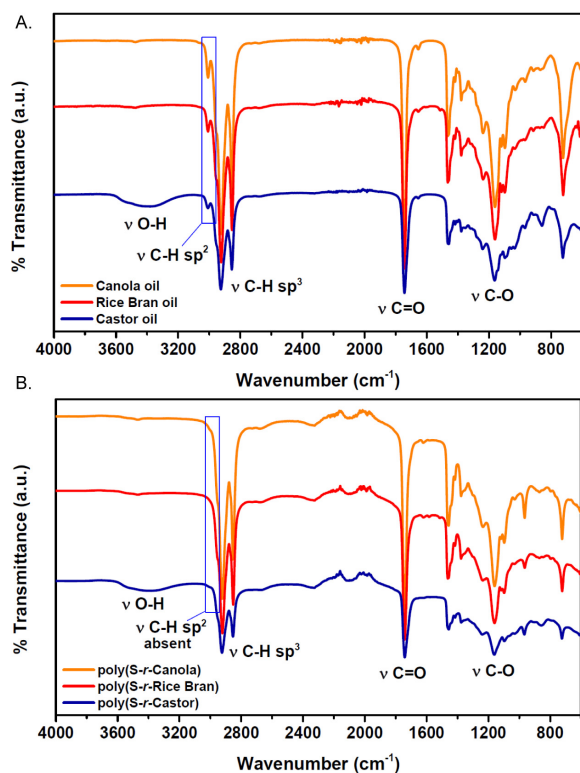
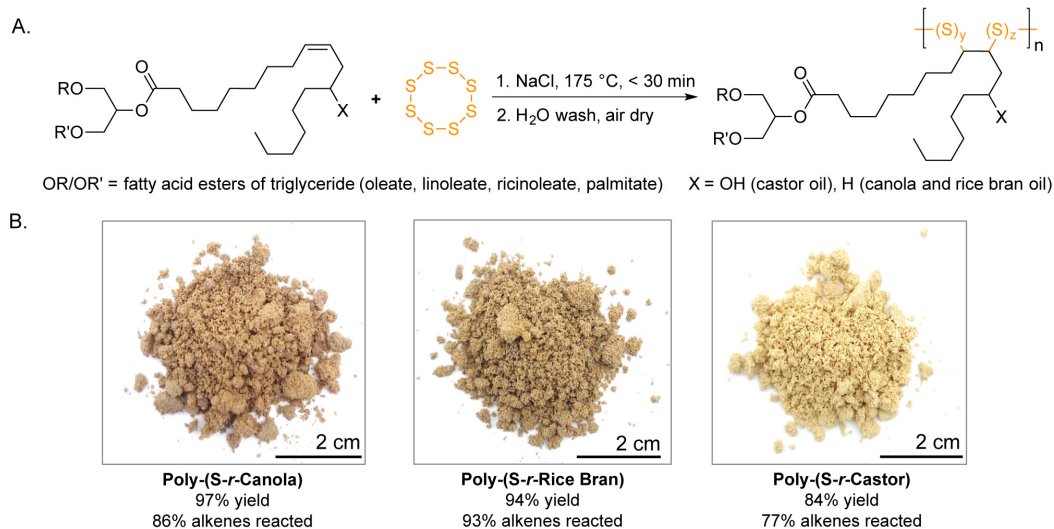


Figure 3. A. FTIR spectra of the triglyceride monomers. B. FTIR spectra of the copolymer formed after inverse vulcanization of the triglyceride. The castor oil and corresponding polymer display the expected OH stretch from the ricinoleic acid. The alkene C-H stretch is absent in the polymer IR spectrum, consistent with reaction at the triglyceride olefin.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy were next used to analyze both the surface and cross-sections of the copolymers (Figure 4 and Supporting Information S14-S15). On the surface of these polymers, crys-

tals of unreacted sulfur were typically observed, as previously noted by our previous work on poly(S-r-Canola) and also the work of Theato on related polymers.^{15,33} The free sulfur was particularly prevalent for poly(S-r-Castor) (Figure 4A), which did indeed contain a higher percentage of unreacted sulfur (20 wt%) as determined by DSC (see below). However, SEM and EDS analysis of a cross-section of the bulk polymer showed a smooth, sulfur rich polymer with only small regions of crystalline sulfur (Figure 4B and 4C).

Thermogravimetric analysis (TGA) of the sulfur polymers showed two major mass losses (Figure 5 and Supporting Information S16-S17). The first mass loss at 230 °C was due to the thermal decomposition of free sulfur and the weak S-S bonds in the polymer backbone, as previously described for related polymers.^{15,33} The second mass loss at 325 °C is attributed to the remaining triglyceride domain and C-S bond cleavage in the polymer.

Differential Scanning Calorimetry (DSC) revealed an endotherm between 100 and 130 °C, which corresponds to the transition of sulfur from an orthorhombic to monoclinic crystalline state and then melting and conversion to liquid sulfur (Figure 6).³⁴ An estimation of free, non-polymeric sulfur content was made by integrating the area of these endothermic peaks after constructing a standard curve with crystalline S₈ standards (Supporting Information S18-S19). Consistent with the higher amounts of crystalline sulfur observed by SEM (Figure 4A), poly(S-r-Castor) contained the most free sulfur (20 wt%). Poly(S-r-Canola) and poly(S-r-Rice Bran) were found to contain 12 wt% and 14 wt% of free sulfur, respectively.

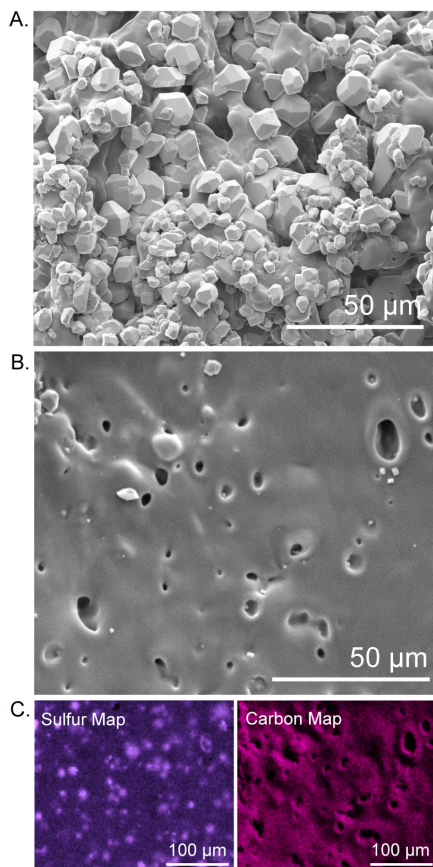


Figure 4. A. An SEM micrograph of the surface of the poly(S-*r*-Castor) polymer, revealing sulfur crystals on the surface of the polymer. B. An SEM micrograph of a cross section of the same material, indicating a smooth surface of the bulk sulfur-triglyceride copolymer. C. EDS mapping of the cross section revealed high sulfur and carbon content in the bulk polymer. Additional SEM micrographs and EDS analysis for all three copolymers are provided in the Supporting Information (S14-S15).

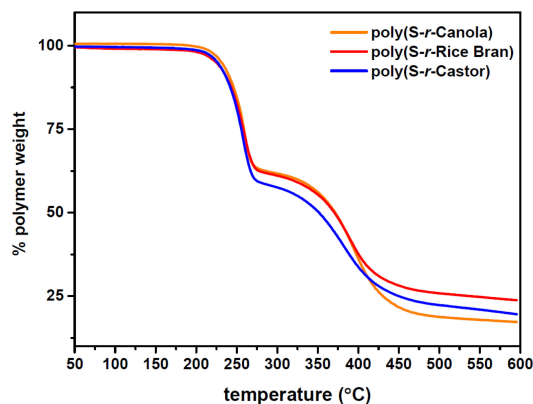


Figure 5. Thermogravimetric Analysis (TGA) of the sulfur polymers. Two mass losses are observed in the thermal decomposition of all polymers, consistent with previous reports on related materials.^{15,33} The first mass loss corresponds to extrusion of sulfur (as SO₂, for instance) following scission and reaction of weak S-S bonds. The second mass loss corresponds to any remaining organic matter and other sulfurized material.

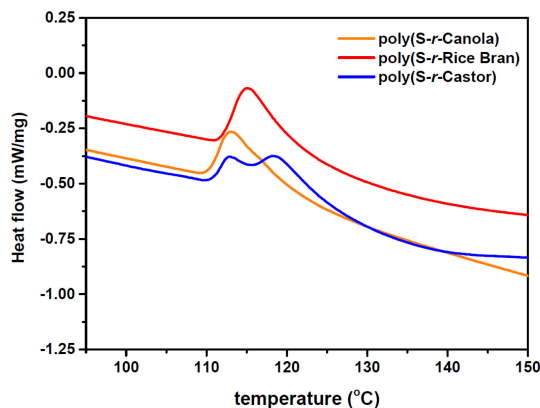


Figure 6. Differential Scanning Calorimetry (DSC) of the sulfur polymer at the range of sulfur endotherm peak. Integration of these transitions was used to estimate the amount of unreacted residual sulfur in the copolymers (Supporting Information S18-S19).

While the free sulfur content of these polymers has not precluded their use as oil spill sorbents,²² new cathode materials,³³ support for activated carbon for organic micropollutant remediation,²³ and components of fertilisers,^{30,35} the amount of free sulfur might affect the performance in mercury sorption. Accordingly, poly(S-*r*-Canola), poly(S-*r*-Rice Bran), poly(S-*r*-Castor), and elemental sulfur were all evaluated next in their removal of inorganic and organic mercury from water.

MERCURY SORPTION STUDIES

Poly(S-*r*-Canola), poly(S-*r*-Rice Bran), and poly(S-*r*-Castor) were tested in the sorption of two types of aqueous mercury solutions: HgCl₂ and 2-methoxyethylmercury chloride (MEMC). The former is a common model for inorganic mercury contamination and the latter is an organomercury compound still used widely as a fungicide by sugarcane, potato and rice growers.^{15,36} Because MEMC dip and spray solutions are released directly and intentionally into the environment, it is important to have methods to treat runoff or spent solutions of the fungicide. In the sorption experiments, one gram of each powdered polymer (particle size <5.0 mm) was added to a plastic centrifuge tube. All experiments were done in triplicate and elemental sulfur was used as a control sorbent for comparison to the sulfur polymers. Next, the solution of mercury was added: 20 mL of HgCl₂ solution (107 ppm) or 20 mL of the MEMC solution (130 ppm – near the working concentration of the fungicide). The concentrations of these mercury stock solutions were determined by cold vapor atomic absorption (CVAA) spectroscopy. The samples were capped and then rotated at 25 rpm on an end-over-end mixer at 20 °C. Aliquots of 0.5 mL were sampled from each tube at 1, 2, 4, 6, and 24 hours and analyzed by CVAA spectroscopy (Supporting Information S20-S22).

The mercury concentrations at equilibrium (24 hour treatment) were first used to assess each sorbent's affinity for the heavy metal. Accordingly, the distribution coefficient (K_d) was calculated using Equation 1, where C_i is the initial mercury concentration and C_f is the final mercury concentration (mg/L), respectively; V is the volume of mercury solution (mL) and m is the mass of the sorbent used in the experiment (g):^{37,38}

$$K_d = \frac{(C_i - C_f)}{C_f} \times \frac{V}{m} \quad \text{Eq. 1}$$

For HgCl₂ sorption, the poly(*S-r-Castor*) sorbent had the highest calculated K_d of 2.0×10^6 mL/g. The K_d for poly(*S-r-Canola*) was lower at 3.4×10^2 mL/g and the K_d for poly(*S-r-Rice Bran*) was 1.49×10^5 mL/g. High performance and commercial mercury sorbents typically have a $K_d > 10^5$ mL/g for Hg(II),^{37,38} so the affinity for inorganic mercury is very good for these polymer sorbents. In particular, the affinity of poly(*S-r-Castor*) for HgCl₂ is particularly excellent, as its K_d is on the same order of some recently reported high performing porous sorbents.³⁸ This result is particularly striking when considering that the poly(*S-r-Castor*) sorbent is prepared in a single chemical step from inexpensive and sustainable castor oil and sulfur. It is also worth noting the elemental sulfur had a far lower affinity for the HgCl₂ ($K_d = 0.39 \times 10^1$ mL/g), indicating the polymeric sulfur sorbents are far superior in their affinity for inorganic mercury (Figure 7). This result also indicates that the polysulfides in the polymer, rather than any residual free sulfur, are responsible for the high mercury affinity. For MEMC sorption, the K_d values were lower than those for HgCl₂. The poly(*S-r-Castor*) still exhibited the highest affinity, with a K_d value of 1.3×10^3 mL/g. The K_d values of Poly(*S-r-Canola*) and poly(*S-r-Rice Bran*) for MEMC were both on the order of 10^2 mL/g. This result indicates that it is important for a sorbent to be evaluated against multiple types of mercury, as the affinities can vary with mercury speciation. Again, elemental sulfur had a very low affinity for MEMC and removed essentially no mercury from solution after 24 hours (Figure 7C).

To determine the equilibrium sorption capacity, q_e (mg/g), of the sulfur polymer sorbents, the following mass balance equation was used (Equation 2).³⁹

$$q_e = (C_0 - C_e) \times \frac{V}{m_s} \quad \text{Eq. 2}$$

where C_0 and C_e are the initial and the equilibrium concentration (mg/L), respectively, V is the volume of mercury solution (L) and m_s is the amount of the sorbent used in the experiment (g). It was found that all three polymer sorbents had a similar equilibrium uptake of HgCl₂: 2.02 mg/g for poly(*S-r-Canola*), 2.13 mg/g for poly(*S-r-Rice Bran*), and 2.13 mg/g for poly(*S-r-Castor*). For MEMC, these sorption capacities were 2.23 mg/g for poly(*S-r-Canola*), 2.19 mg/g for poly(*S-r-Rice Bran*), and 2.56 mg/g for poly(*S-r-Castor*).

The mercury removal efficiency (R) was obtained using Equation 3, where C_0 is the initial mercury concentration in solution and C_t is the mercury concentration at time t .

$$R (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad \text{Eq. 3}$$

The mercury removal efficiency over the first hour is graphed in Figure 7A and over 24 hours in Figures 7B and 7C. Notably, the poly(*S-r-Castor*) sorbent was the most efficient, removing 94% of the HgCl₂ in one hour and >99.99% over 24 hours (reducing 107 ppm HgCl₂ to 1.1 ppb HgCl₂). Interestingly, poly(*S-r-Canola*) was the most efficient of the sorbents in the first hour of MEMC capture with 65% removal efficiency (Figure 7A). However, after 24 hours of treatment, the poly(*S-r-Castor*) was still superior with 99% removal efficiency over this time (reducing 130 ppm MEMC to 194 ppb).

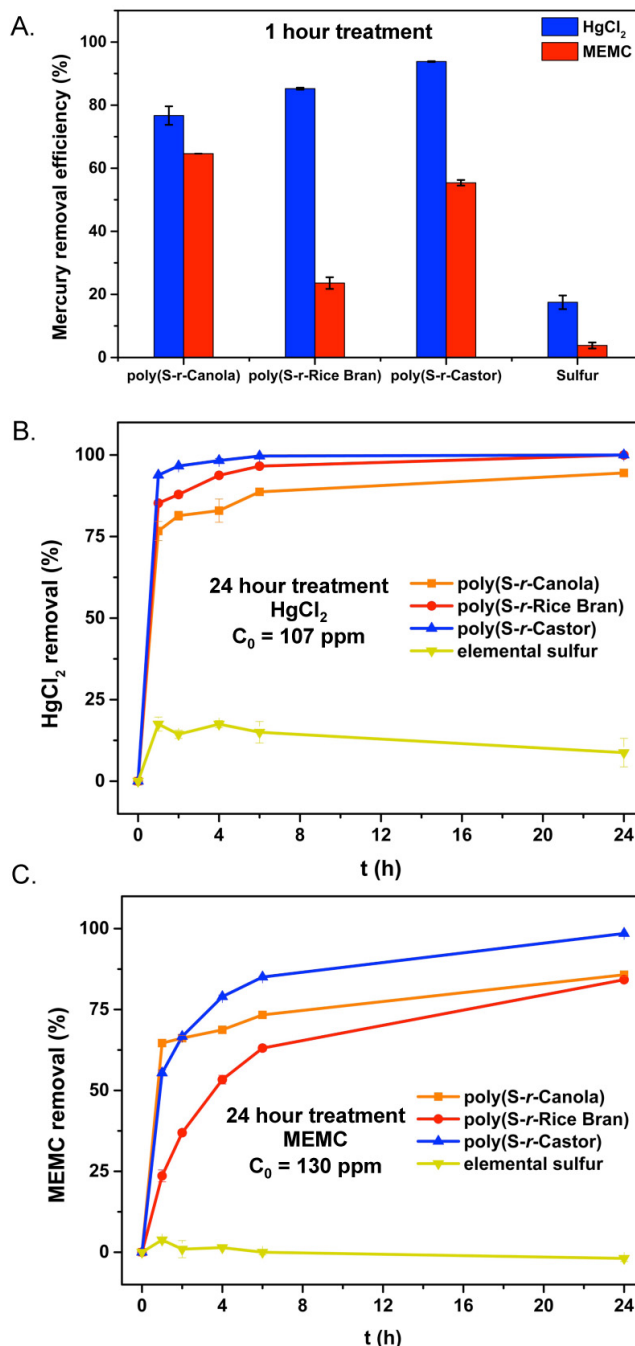


Figure 7. Removal of mercury from water using polymers made from sulfur and triglycerides. All experiments were carried out at 20 °C using 1.0 g of the polymer in 20 mL of the aqueous solution of mercury (either 107 ppm of HgCl₂ or 130 ppm of 2-methoxyethylmercury chloride, MEMC). A. Mercury removal efficiency after 1 hour. B. Percentage of HgCl₂ removed over 24 hours. C. Percentage of MEMC removed over 24 hours.

The kinetics of the mercury sorption were investigated further using both a Lagergren pseudo-first order kinetic model (Equation 4)^{40,41} and also a pseudo-second order kinetic model (Equation 5).^{41,42}

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Eq. 4}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \text{Eq. 5}$$

Here q_t is the amount of absorbed mercury per sorbent (mg/g) at time t , and q_e is this value at equilibrium. The parameters k_1 and k_2 are the pseudo-first order and pseudo-second order rate constants, respectively. These parameters, for both models, were evaluated by non-linear regression analysis using OriginPro 9.0 software. The resulting models are plotted in Figure 8 for both HgCl₂ and MEMC sorption, with the raw data set and additional modeling details provided in the Supplementary Information (S16-S21). The calculated parameters and the accuracies of fit (r^2) are compiled in Table 1. Additionally, initial rates of sorption (H , mg/g•h) were calculated according to Equation 6.⁴²

$$H = k_2 q_e^2 \quad \text{Eq. 6}$$

As shown in Table 1, r^2 values for both non-linear kinetic equations were close to unity, showing good fitting between the experimental data and model. Analysis using linear kinetic equations was also carried out (Supporting Information S23-S24), but the fit of the non-linear analysis (Supporting Information S25-S26) was superior and therefore presented here. Additionally, it is clear that the pseudo-second order model better describes the kinetics of sorption with generally higher r^2 , which is thought to be consistent with a chemisorption process.⁴² Indeed we have shown previously that polymers prepared by inverse vulcanization are indeed *reactive* sorbents that do not merely bind to mercury, but participate in redox processes that generate mercury sulfide species on the surface of the polymer.^{14,15}

In the kinetic analysis, several interesting results were revealed. First, poly(S-*r*-Castor) had a higher initial rate of uptake of HgCl₂ (~3 fold faster in the pseudo-second order model) than both poly(S-*r*-Canola) and poly(S-*r*-Rice Bran). This may reflect the ability of the poly(S-*r*-Castor) polymer to wet more efficiently and therefore improve mass transfer of the mercury. Indeed, the poly(S-*r*-Castor) was found to take up more water per mass over 1 hour (448 ± 11 mg/g) than either poly(S-*r*-Canola) (299 ± 7 mg/g) or poly(S-*r*-Rice Bran) (248 ± 4 mg/g) (Supporting Information S27). In MEMC sorption, poly(S-*r*-Canola) had superior initial rates of uptake (6.5 mg/g•h) in comparison to poly(S-*r*-Castor) (2.86 mg/g•h) and poly(S-*r*-Rice Bran) (0.8 mg/g•h). As seen in Figure 7, however, poly(S-*r*-Castor) still displayed the best mercury removal efficiency when the system reached equilibrium.

Next, Langmuir and Freundlich isotherm models were used to describe the sorption process for HgCl₂ (Supporting Information S28-S31).⁴³ The Langmuir model is based on Equation 7, where q_m is the maximum sorption capacity (mg/g) and K_L is a Langmuir isotherm constant (L/mg).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Eq. 7}$$

The Freundlich isotherm model is based on Equation 8

$$q_e = K_F C_e^n \quad \text{Eq. 8}$$

where K_F is a Freundlich isotherm constant and n is a dimensionless constant related to sorption intensity.⁴³ For both models, q_e and C_e are the corresponding sorption capacity (mg/g) and the concentration of mercury solution at equilibrium, respectively. Sorption isotherm data was obtained by submerging 50 mg of the powdered sulfur polymers in separate polypropylene plastic vials containing 20 mL of a HgCl₂ solution and mixing for 24 hours at 15 °C in an end-over-end mixer. Separate experiments were carried out for mercury concentrations of 0.5, 1, 5, 10, 50, and 100 mg/L. The concentration of mercury left in the solution after the sorption was determined by CVAA. The sorption data was then analyzed by non-linear regression using OriginPro 9.0 software. Model parameters are summarized in Table 2, along with the r^2 values and root mean square error (RMSE). The isotherm curves are shown in Figure 8.

In the modeling, it was revealed that the Freundlich model was a better fit than the Langmuir model for all three polymer sorbents (Table 2 and Figure 8). This may reflect the heterogeneous nature of the sorbents.⁴³ Nonetheless, important information can be gleaned from both models. From the Langmuir isotherm data, a dimensionless separation factor (R_L) can be calculated (Supporting Information S30) and used to determine if the sorption process is favorable: the sorption process is favorable when $0 < R_L < 1$ and it is unfavorable when $R_L > 1$.⁴³ In this study, all sulfur polymer sorbents have separation factors between 0 and 1, indicating that the mercury sorption process is favorable (S24). Additionally, the Langmuir equilibrium constant (K_L) values for all sulfur polymer sorbents indicate a strong affinity towards mercury(II) chloride, as expected for a sorbent with high sulfur content. It is also important to note that the Langmuir model indicated that the maximum capacity of the three sorbents were all similar at 8.99 mg/g for Poly(S-*r*-Canola), 10.99 mg/g for Poly(S-*r*-Rice Bran), and 8.15 mg/g for Poly(S-*r*-Castor). It should be noted that these capacities are related to amount of active sites available for mercury binding on the surface of the polymer. By increasing the surface area of these polymer materials (by foaming or preparing the polymers on a high surface area support, for instance), an increase in capacity is likely possible—a strategy that has been validated for other polymers made by inverse vulcanization.²¹ Finally, from the Freundlich model, the sorption intensity parameter (n) can be used to assess if the metal uptake is favorable. Values >1 reflect a favorable process and indeed all the sorbents analyzed displayed sorption intensity parameters of $n > 2$ (Table 2).

CONCLUSIONS

Three polymers were prepared by the direct copolymerization of sulfur and renewable triglycerides (canola oil, castor oil, and rice bran oil). These polymers were then evaluated as low-cost sorbents for mercury removal from water. It was found that the copolymer made from sulfur and castor oil was the fastest in uptake of inorganic mercury. This rate enhancement was attributed to the hydroxylated ricinoleic acid content, which increased wettability. The hydroxyl group may also participate in mercury chelation with the sulfur groups in the sorbent. The polymer made from sulfur and canola oil, in contrast, was the fastest in the uptake of MEMC. These results indicate that it is not only the sulfur that is important in these

sorbents, but also the comonomer. The subtle difference in sorption performance can help guide the deployment of these sorbents in mercury remediation, while also providing flexibility in the specific triglyceride used to make the polymer. More generally, this study demonstrates how renewable and surplus feedstocks (triglycerides and sulfur, respectively) can be converted in a single step into new, low-cost sorbents for the remediation of mercury.

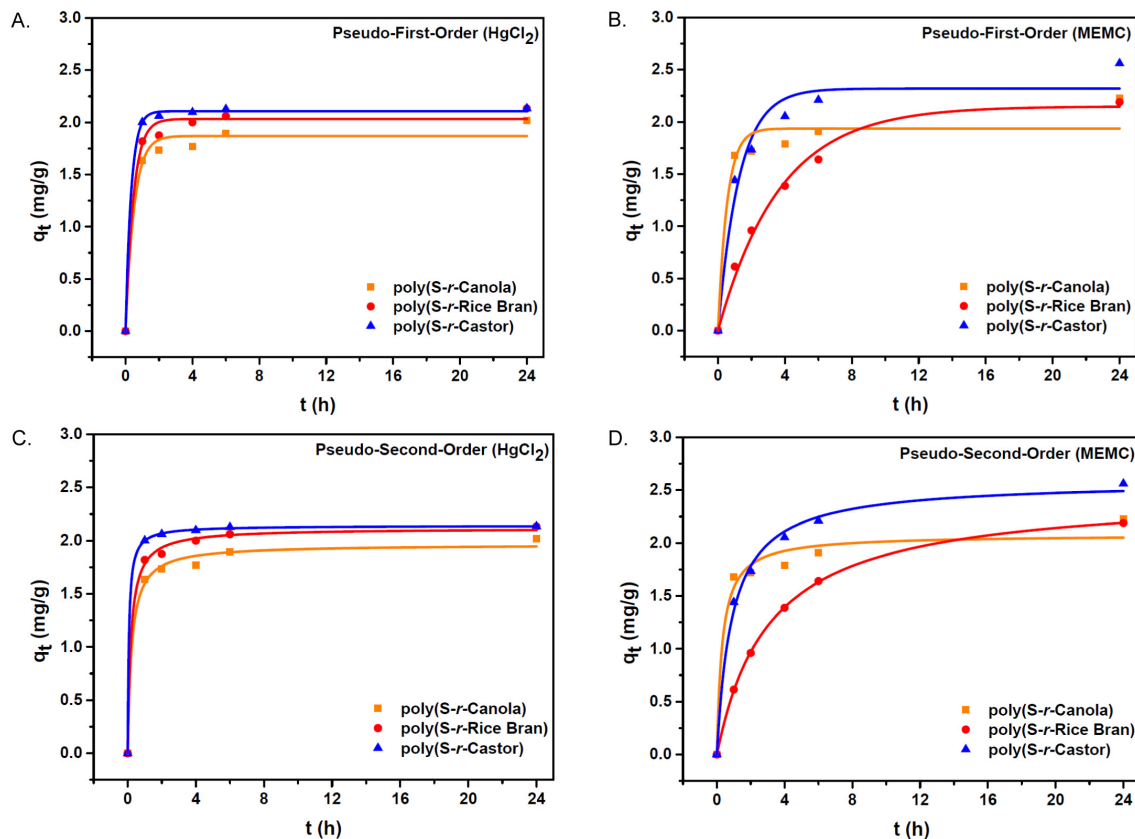


Figure 8. Kinetic models for mercury sorption. A. Pseudo-first-order non-linear model for HgCl_2 sorption. B. Pseudo-first-order non-linear model for MEMC sorption. C. Pseudo-second-order model for HgCl_2 sorption. D. Pseudo-second-order model for MEMC sorption. Parameters for the model are listed in Table 1.

Table 1. Pseudo-first-order and pseudo-second-order kinetic parameters obtained by using non-linear equation for mercury sorption.

Sulfur polymer	Mercury species	q_e (exp) (mg/g)	Pseudo-first order model			Pseudo-second order model			
			k_1 (h^{-1})	q_e (calc) (mg/g)	r^2	k_2 ($\text{g}/\text{mg}\cdot\text{h}$)	q_e (calc) (mg/g)	r^2	Initial rate uptake (H) ($\text{mg}/\text{g}\cdot\text{h}$)
Poly(S-r-Canola)	HgCl_2	2.02	1.97	1.87	0.9851	2.22	1.96	0.9947	8.55
	MEMC	2.23	1.82	1.94	0.9549	1.51	2.08	0.9769	6.53
Poly(S-r-Rice Bran)	HgCl_2	2.13	2.12	2.03	0.9912	2.51	2.12	0.9980	11.25
	MEMC	2.19	0.27	2.15	0.9917	0.13	2.47	0.9999	0.80
Poly(S-r-Castor)	HgCl_2	2.13	2.95	2.11	0.9992	6.54	2.14	0.9999	29.97
	MEMC	2.56	0.79	2.32	0.9666	0.43	2.59	0.9955	2.86

Table 2 Sorption isotherm parameters of Langmuir and Freundlich models for mercury(II) chloride sorption by sulfur polymer sorbents

Isotherm Model	Sulfur polymer	Parameter	Unit	Value	Standard error (SE)	r ²	RMSE
Langmuir	Poly(S-r-Canola)	q _m	mg/g	8.99	1.83	0.9517	0.70
		K _L	L/mg	0.04	0.03		
	Poly(S-r-Rice Bran)	q _m	mg/g	10.99	1.94	0.9554	0.88
		K _L	L/mg	0.06	0.04		
	Poly(S-r-Castor)	q _m	mg/g	8.15	1.08	0.9146	1.11
		K _L	L/mg	0.22	0.16		
Freundlich	Poly(S-r-Canola)	K _F	(mg/g)(L/mg) ^{1/n}	1.10	0.18	0.9897	0.33
		n	-	2.36	0.23		
	Poly(S-r-Rice Bran)	K _F	(mg/g)(L/mg) ^{1/n}	1.75	0.35	0.9836	0.54
		n	-	2.63	0.35		
	Poly(S-r-Castor)	K _F	(mg/g)(L/mg) ^{1/n}	2.38	0.37	0.9795	0.54
		n	-	3.51	0.49		

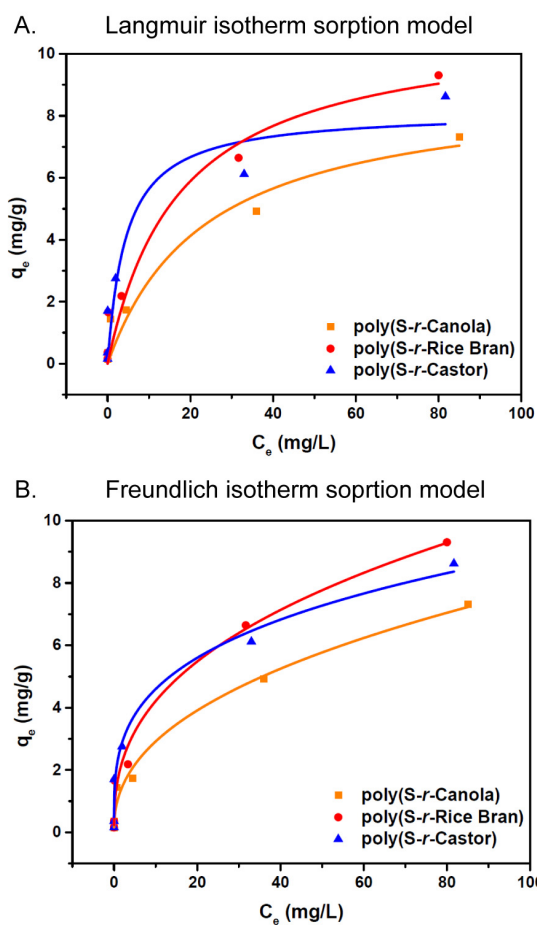


Figure 8. A. Non-linear fitting of the Langmuir isotherm model for HgCl₂ sorption. B. Non-linear fitting of Freundlich isotherm model for HgCl₂ sorption. Model parameters are listed in Table 2.

ASSOCIATED CONTENT

Supporting Information. Full experimental details including polymer synthesis and characterization, mercury sorption protocols, and modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* justin.chalker@flinders.edu.au

ACKNOWLEDGMENT

The authors acknowledge financial support from Clean Earth Technologies, Flinders University, the AMP Foundation (J.M.C.), and an Australia Awards (A.D.T.). The authors also thank Dr Louisa Esdaile for assistance in polymer synthesis and Dr Jonathan Campbell and Dr Jason Gascooke for technical assistance in polymer characterization.

CONFLICT OF INTEREST

J.M.C. is an inventor on a patent covering synthesis and applications of polymers made from sulfur and plant oils, including the polymers described in this study. This patent is assigned to Clean Earth Technologies.

REFERENCES

- (1) Boening, D. W. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere* **2000**, *40*, 1335-1351.
- (2) Scheuhammer, A. M.; Meyer, M. W.; Sandheinrich, M. B.; Murray, M. W. Effects of Environmental Methylmercury on the Health of Wild Birds, Mammals, and Fish. *Ambio* **2007**, *36*, 12-18.
- (3) Bose-O'Reilly, S.; Lettmeier, B.; Gothe, R. M.; Beinhoff, C.; Siebert, U.; Drasch, G. Mercury as a serious health hazard for children in gold mining areas. *Environ. Res.* **2008**, *107*, 89-97.
- (4) Park, J.-D.; Zheng, W. Human Exposure and Health Effects of Inorganic and Elemental Mercury. *J. Prev. Med. Public Health* **2012**, *45*, 344-352.

- (5) Tchounwou, P. B.; Ayensu, W. K.; Ninashvili, N.; Sutton, D. Environmental Exposure to Mercury and Its Toxicopathologic Implications for Public Health. *Environ. Toxicol.* **2003**, *18*, 149-175.
- (6) Esdaile, L. J.; Chalker, J. M. The Mercury Problem in Artisanal and Small-Scale Gold Mining. *Chem. Eur. J.* **2018**, *24*, 6905-6916.
- (7) Zhao, S.; Pudasainee, D.; Duan, Y.; Gupta, R.; Liu, M.; Lu, J. A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. *Prog. Energy Combust. Sci.* **2019**, *73*, 26-64.
- (8) UN Environment. Global Mercury Assessment 2018. <https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018>
- (9) Minamata Convention on Mercury, United Nations Environmental Programme. <http://www.mercuryconvention.org>.
- (10) Wang, J.; Feng, X.; Anderson, C. W. N.; Xing, Y.; Shang, L. Remediation of mercury contaminated sites – A review. *J. Hazard. Mater.* **2012**, *221-222*, 1-18.
- (11) Shewchuk, S. R.; Azargohar, R.; Dalai, A. K. Elemental Mercury Capture Using Activated Carbon: A Review. *J. Environ. Anal. Toxicol.* **2016**, *6*, 379.
- (12) Sun, D. T.; Peng, L.; Reeder, W. S.; Moosavi, S. M.; Tiana, D.; Britt, D. K.; Oveisi, E.; Queen, W. L. Rapid, Selective Heavy Metal Removal from Water by a Metal–Organic Framework/Polydopamine Composite. *ACS Cent. Sci.* **2018**, *4*, 349-356.
- (13) Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D. A Review of Potentially Low-Cost Sorbents for Heavy Metals. *Wat. Res.* **1999**, *33*, 2469-2479.
- (14) Crockett, M. P.; Evans, A. M.; Worthington, M. J. H.; Albuquerque, I. S.; Slattery, A. D.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Bernardes, G. J. L.; Chalker, J. M. Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil. *Angew. Chem. Int. Ed.* **2016**, *55*, 1714-1718.
- (15) Worthington, M. J. H.; Kucera, R. L.; Albuquerque, I. S.; Gibson, C. T.; Sibley, A.; Slattery, A. D.; Campbell, J. A.; Alboaiji, S. F. K.; Muller, K. A.; Young, J.; Adamson, N.; Gascooke, J. R.; Jampaiah, D.; Sabri, Y. M.; Bhargava, S. K.; Ippolito, S. J.; Lewis, D. A.; Quinton, J. S.; Ellis, A. V.; Johs, A.; Bernardes, G. J. L.; Chalker, J. M. Laying Waste to Mercury: Inexpensive Sorbents Made from Sulfur and Recycled Cooking Oils. *Chem. Eur. J.* **2017**, *23*, 16219 – 16230.
- (16) Hasell, T.; Parker, D. J.; Jones, H. A.; McAllister, T.; Howdle, S. M. Porous inverse vulcanised polymers for mercury capture. *Chem. Commun.* **2016**, *52*, 5383-5386.
- (17) Thielke, M. W.; Bultema, L. A.; Brauer, D. D.; Richter, B.; Fischer, M.; Theato, P. Rapid Mercury(II) Removal by Electrospun Sulfur Copolymers. *Polymers* **2016**, *8*, 266.
- (18) Akay, S.; Kayan, B.; Kalderis, D.; Arslan, M.; Yagci, Y.; Kiskan, B. Poly(benzoxazine-co-sulfur): An efficient sorbent for mercury removal from aqueous solution. *J. Appl. Polym. Sci.* **2017**, *134*, n/a.
- (19) Parker, D. J.; Jones, H. A.; Petcher, S.; Cervini, L.; Griffin, J. M.; Akhtar, R.; Hasell, T. Low cost and renewable sulfur-polymers by inverse vulcanization, and their potential for mercury capture. *J. Mater. Chem. A* **2017**, *5*, 11682-11692.
- (20) Abraham, A. M.; Kumar, S. V.; Alhassan, S. M. Porous sulphur copolymer for gas-phase mercury removal and thermal insulation. *Chem. Eng. J.* **2018**, *332*, 1-7.
- (21) Wu, X.; Smith, J. A.; Petcher, S.; Zhang, B.; Parker, D. J.; Griffin, J. M.; Hasell, T. Catalytic inverse vulcanization. *Nat. Commun.* **2019**, *10*, 647.
- (22) Worthington, M. J. H.; Shearer, C. J.; Esdaile, L. J.; Campbell, J. A.; Gibson, C. T.; Legg, S. K.; Yin, Y.; Nicholas A. Lundquist; Gascooke, J. R.; Albuquerque, I. S.; Shapter, J. G.; Andersson, G. G.; Lewis, D. A.; Bernardes, G. J. L.; Chalker, J. M. Sustainable Polysulfides for Oil Spill Remediation: Repurposing Industrial Waste for Environmental Benefit. *Adv. Sustainable Syst.* **2018**, 1800024.
- (23) Lundquist, N. A.; Sweetman, M. J.; Scroggie, K. R.; Worthington, M. J. H.; Esdaile, L. J.; Alboaiji, S. F. K.; Plush, S. E.; Hayball, J. D.; Chalker, J. M. Polymer Supported Carbon for Safe and Effective Remediation of PFOA- and PFOS-Contaminated Water. *ACS Sustainable Chem. Eng.* **2019**, *7*, 11044-11049.
- (24) Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; Somogyi, Á.; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J. The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nat. Chem.* **2013**, *5*, 518.
- (25) Zhang, Y.; Glass, R. S.; Char, K.; Pyun, J. Recent advances in the polymerization of elemental sulphur, inverse vulcanization and methods to obtain functional Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs). *Polym. Chem.* **2019**, *10*, 4078-4105.
- (26) Worthington, M. J. H.; Kucera, R. L.; Chalker, J. M. Green chemistry and polymers made from sulfur. *Green Chem.* **2017**, *19*, 2748-2761.
- (27) Chalker, J. M.; Worthington, M. J. H.; Lundquist, N. A.; Esdaile, L. J. Synthesis and Applications of Polymers Made by Inverse Vulcanization. *Top. Curr. Chem.* **2019**, *377*, 16.
- (28) Worthington, M. J. H.; Chalker, J. M. Mercury Adsorbent Material and Uses Thereof. WO 2017181217. Priority Application AU 2016-901470, April 20 2016.
- (29) Lundquist, N. A.; Worthington, M. J. H.; Adamson, N.; Gibson, C. T.; Johnston, M. R.; Ellis, A. V.; Chalker, J. M. Polysulfides made from re-purposed waste are sustainable materials for removing iron from water. *RSC Adv.* **2018**, *8*, 1232-1236.
- (30) Mann, M.; Kruger, J. E.; Andari, F.; McErlean, J.; Gascooke, J. R.; Smith, J. A.; Worthington, M. J. H.; McKinley, C. C. C.; Campbell, J. A.; Lewis, D. A.; Hasell, T.; Perkins, M. V.; Chalker, J. M. Sulfur polymer composites as controlled-release fertilizers. *Org. Biomol. Chem.* **2019**, *17*, 1929-1936.
- (31) Smith, J. A.; Green, S. J.; Petcher, S.; Parker, D. J.; Zhang, B.; Worthington, M. J. H.; Wu, X.; Kelly, C. A.; Baker, T.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Jenkins, M. J.; Willcock, H.; Chalker, J. M.; Hasell, T. Crosslinker Copolymerization for Property Control in Inverse Vulcanization. *Chem. Eur. J.* **2019**, *25*, 10433-10440.
- (32) For additional considerations in the nomenclature of these so-called Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs), the reader is referred to a recent and detailed discussion by Pyun and co-workers (Reference 25).
- (33) Hoeffling, A.; Lee, Y. J.; Theato, P. Sulfur-Based Polymer Composites from Vegetable Oils and Elemental Sulfur: A Sustainable Active Material for Li-S Batteries. *Macromol. Chem. Phys.* **2017**, *218*, 1600303.
- (34) Wręczycki, J.; Bieliński, D. M.; Anyszka, R. Sulfur/Organic Copolymers as Curing Agents for Rubber. *Polymers* **2018**, *10*, 870.
- (35) Valle, S. F.; Giroto, A. S.; Klatic, R.; Guimarães, G. G. F.; Ribeiro, C. Sulfur Fertilizer Based on Inverse Vulcanization Process with Soybean Oil. *Polym. Degrad. Stab.* **2019**.
- (36) Kathryn, L. M.; Andrew, H. B.; Craig, H.; Andrew, P. N. Insecticides and a fungicide affect multiple coral life stages. *Mar. Ecol. Prog. Ser.* **2007**, *330*, 127-137.
- (37) Shin, Y.; Fryxell, G. E.; Um, W.; Parker, K.; Mattigod, S. V.; Skaggs, R. Sulfur-Functionalized Mesoporous Carbon. *Adv. Func. Mater.* **2007**, *17*, 2897-2901.
- (38) Li, B.; Zhang, Y.; Ma, D.; Shi, Z.; Ma, S. Mercury nano-trap for effective and efficient removal of mercury(II) from aqueous solution. *Nat. Commun.* **2014**, *5*, 5537.
- (39) Ho, Y.-S.; Wang, C.-C. Sorption equilibrium of mercury onto ground-up tree fern. *J. Hazard. Mater.* **2008**, *156*, 398-404.
- (40) Lagergren, S. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar* **1898**, *24*, 1-39.
- (41) Simonin, J.-P. On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chemical Engineering Journal* **2016**, *300*, 254-263.
- (42) Ho, Y.-S. Review of second-order models for adsorption systems. *J. Hazard. Mater.* **2006**, *136*, 681-689.
- (43) Foo, K. Y.; Hameed, B. H. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **2010**, *156*, 2-10.

The copolymerization of sulfur and renewable triglycerides provides low-cost materials that are effective at removing mercury from water. In this study it was found that the hydroxylated triglyceride in castor oil improves wetting and the rate of Hg^{2+} uptake.

