

## Carbonisation of a polymer made from sulfur and canola oil

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**A polymer made from equal masses of sulfur and canola oil was carbonised at 600 °C for 30 minutes. The resulting material exhibited improved uptake of mercury from water compared to the parent polymer. The carbonisation could also be done after using the polymer to clean up oil spills, which surprisingly improved mercury uptake to levels rivaling high performance commercial carbons.**

Mercury is a toxic heavy metal encountered in a variety of sectors including gold mining, oil and gas refining, and coal combustion.<sup>1, 2</sup> Mercury is known to bioaccumulate in aquatic organisms, so cost-effective remediation of contaminated water is particularly important.<sup>3</sup> Because sulfur binds strongly to mercury, sulfur-rich materials are attractive mercury sorbents.<sup>4-6</sup> Recently, polymers prepared by *inverse vulcanisation*<sup>7</sup> have also been the subject of intense interest in this context of mercury remediation.<sup>8-13</sup> In this unique polymerisation, elemental sulfur is reacted directly with an unsaturated crosslinker (typically an alkene or polyene) to generate polysulfide materials with high sulfur content.<sup>14-16</sup> Such polysulfides have shown great promise in mercury remediation, particularly due to the low-cost and sustainability of the starting materials,<sup>17</sup> and scalability.<sup>8, 18</sup> However, the rate of mercury uptake from water by these polymers is often slow, thereby hindering continuous water purification processes. To improve mercury sorption kinetics, a number of methods for increasing the surface area of the polymers have been reported such as foaming,<sup>19</sup> porogen introduction,<sup>10-12, 20</sup> electrospinning,<sup>21</sup> or coating high surface area substrates such as silica gel.<sup>13, 22</sup> Despite these important advances, there is a pressing need for a simple, direct and scalable method for preparing high-sulfur content materials for mercury sorption.

In this study, we report a carbonisation method to improve the mercury uptake of polymers made by inverse vulcanisation. The goal was to develop a process that was as simple as possible and to test the hypothesis that the sulfur-functionalised carbon is as effective as commercial activated carbon in mercury

remediation—even if the sulfurised carbon has a lower surface area. The Hasell laboratory has pioneered the synthesis of porous carbon materials from polymers made by inverse vulcanisation,<sup>23, 24</sup> but we note that the present study is distinct in that the polymer used as the precursor can be manufactured on multi-tonne scale<sup>8</sup> and the carbon product is graphitic and low in porosity (<250 m<sup>2</sup>/g). The carbonisation process reported here also benefits from not requiring activating agents, multiple steps, or gaseous reagents.<sup>25, 26</sup> The sulfur source in the polymer is also convenient in comparison to other preparations of sulfurised carbons that require hazardous reagents such as nitric and sulfuric acid,<sup>27</sup> H<sub>2</sub>S and SO<sub>2</sub>,<sup>28</sup> or solvent processing of solutions of elemental sulfur in CS<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub>.<sup>29</sup> Additionally, the temperature of the carbonisation process reported here (600 °C) is also lower than typical activated carbon preparations, so it is more energy efficient. The carbon product also has different types of binding sites for mercury, distinguishing it from typical porous activated carbons.



**Figure 1.** A sulfur-rich graphitic carbon was prepared from a sustainable polymer made by the direct copolymerisation of sulfur and canola oil.

First, the base polymer was prepared as previously described by the our laboratory.<sup>10, 18</sup> In short, equal masses of canola oil and elemental sulfur were reacted directly together at 180 °C for 30 minutes. After the reaction reaches its gel point, the resulting polymer can be isolated as a friable rubber (Figure 1 and S5-S6).<sup>10</sup> No porogen was used in this preparation and the polymer was used directly as isolated for carbonisation experiments. We refer to this polymer as 50-poly(S-r-canola)<sup>11</sup> or polymer 1.

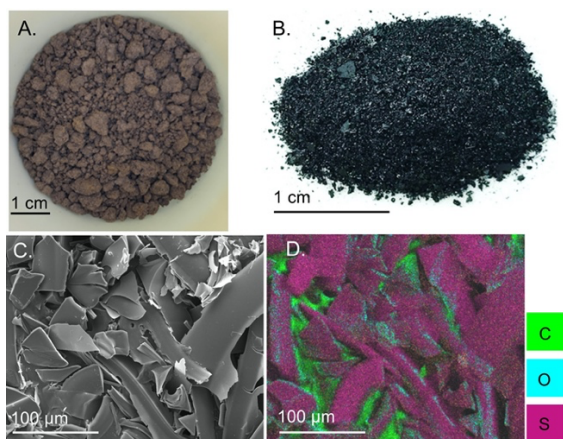
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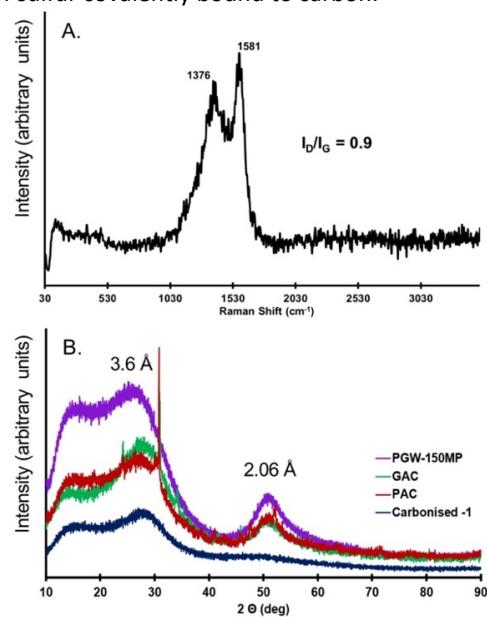
**Figure 2.** A. 100 g of 50-poly(*S-r*-canola) polymer (**1**) before carbonisation. B. Carbonised-**1** after removal from crucible and coarse crushing with a mortar and pestle. C. SEM micrograph of carbonised-**1**. D. EDX elemental map of carbonised-**1**

Thermogravimetric analysis (TGA) of 50-poly(*S-r*-canola) revealed that an 88% weight loss occurs before 500 °C and only 4 % between 500 and 800 °C (S6). Hence, it was expected that carbonisation at 600 °C should result in an incomplete combustion and yield a carbon material. This hypothesis was tested in a muffle furnace by placing 100 g of the 50-poly(*S-r*-canola) polymer in a 1.1 L Al<sub>2</sub>O<sub>3</sub> crucible and heating it at a rate of 5 °C/min to 600 °C in an atmosphere of air, and then holding the final temperature for 30 minutes (S7). This procedure was repeated three times, so characterisation could be carried out in triplicate to assess reproducibility. The carbonised 50-poly(*S-r*-canola) polymer, referred to here as carbonised-**1**, was obtained in an average yield of 38 g from 300 g of the 50-poly(*S-r*-canola) polymer precursor, which is the approximate mass expected based on the TGA analysis. The carbon material presents as a brittle black solid, that can be pulverised by mortar and pestle into a powder. Although scrubbing of SO<sub>2</sub> would be required for larger amounts of carbonised-**1**, scrubbing technologies are readily available that convert the flue gas to sulfate,<sup>30, 31</sup> sulfuric acid,<sup>32</sup> or sulfur.<sup>33</sup> In the case of recovering sulfur, this would regenerate the monomer that was used in the original polymer synthesis.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopic (EDX) imaging revealed that the material is made up of carbon sheets with a high content of sulfur on the surface (Figure 2 and S8). (The carbon imaged in Figure 2D is from the carbon tape used to mount the sample; carbonised-**1** presents primarily as a sulfur-rich material on its surface). To further characterise carbonised-**1**, combustible CHNS analysis was performed, revealing a composition of carbon (65.5%), sulfur (16.0%) and hydrogen (1.6%) (S8). This is a reasonably high level of sulfur for a carbon material, especially considering the high levels on the surface of the carbon. For comparison, previous reports of sulfurised carbon have described sulfur content of 4% as high<sup>34</sup> and that even for carbons with higher sulfur content, the reactive sulfur on the *surface* of the sorbent is especially important for mercury sorption.<sup>35</sup>

In order to determine the surface area of the carbonised-**1**, surface area analysis was performed using Brunauer-Emmett-Teller (BET) analysis (S9-S13). BET analysis was also performed on three commercially available carbons: powdered activated carbon PGW-150MP (PAC, Kuraray), a second powdered activated carbon (PAC, ChemSupply Australia) and a granular activated charcoal (C2889 8-20 mesh, Merck). The powdered activated carbons had the highest surface area, with the Kuraray PGW-150MP having a surface area of 1131 m<sup>2</sup>/g and the ChemSupply PAC having a surface area of 742 m<sup>2</sup>/g. SEM analysis confirmed the porous structure of these commercial carbons (S14-S16). In contrast, the granular activated charcoal and carbonised-**1** had a lower surface area of 125 m<sup>2</sup>/g and 111 m<sup>2</sup>/g, respectively.

To gain insight into the structure of carbonised-**1**, Raman analysis was performed (Figure 3A and S17-S19). The intensity and positions of Raman peaks can provide important structural information for the carbon samples. The G peak between 1560 to 1600 cm<sup>-1</sup> is associated with a vibrational mode of sp<sup>2</sup>-hybridized graphene planes. The D peak at 1300 to 1400 cm<sup>-1</sup> is the band associated with defects and correlated with the degree of disorder in the graphitic structure.<sup>36</sup> The ratio of D band to G band peak intensities, I<sub>D</sub>/I<sub>G</sub>, has been used to probe the level of disorder and to indicate the relative degree of functionalisation of carbon materials.<sup>37</sup> For carbonised-**1**, I<sub>D</sub>/I<sub>G</sub> was 0.9 and all three commercial carbons examined had an I<sub>D</sub>/I<sub>G</sub> value of 1.2. We attribute this difference to the non-porous graphitic nature of carbonised-**1**, and the highly porous commercial carbons. Additional Raman analysis of carbonised-**1** was carried out over multiple areas with hundreds of spectra collected. Importantly, there was no evidence of S<sub>8</sub> or polysulfides present, so the sulfur content detected by EDX and combustible analysis is likely to be associated with shorter chains of sulfur covalently bound to carbon.



**Figure 3.** A. Raman spectrum of carbonised-**1**. B. XRD spectra of powdered activated carbon (PAC, PGW-150MP, Kuraray), granular activated charcoal (GAC, Merck), PAC (ChemSupply) and carbonised-**1**.

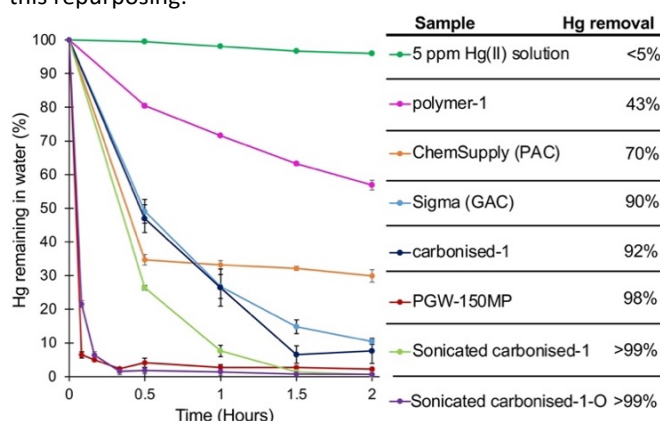
The powder XRD pattern showed that carbonised-1 is of low crystallinity with a broad reflection at  $d = 3.6 \text{ \AA}$  which corresponds to the van der Waals contact between graphite-like sheets (Figure 3B and S20-S21). The reflection is also present in the XRD patterns of commercial activated carbons, however these commercial carbons also show a broad reflection at  $d = 2.06 \text{ \AA}$  which corresponds to the 101 reflection of graphite-2H (Figure 3B). The lack of the  $2.06 \text{ \AA}$  reflection in carbonised-1 may indicate it has a highly disordered stacking sequence. High resolution XPS of carbonised-1 was also consistent with a sulfurised graphitic structure, with evidence for C-S functional groups on the surface of the material (S22).

With the sulfur-rich carbon in hand, we hypothesised that the sulfur functionality would impart affinity for mercury. This was investigated by adding 100 mg of the carbonised-1 to a 45 mL solution of mercury nitrate in water (5 ppm in mercury) and agitating using an end-over-end mixer. For comparison, 100 mg of commercially available activated carbons were added to separate 45 mL samples of the 5 ppm  $\text{Hg}^{2+}$  solutions. These carbons were selected for evaluation based on their commercial availability and use in water purification.<sup>38</sup> Carbonised-1 was sieved to a size of 150–500  $\mu\text{m}$  before mercury removal was tested and the commercial carbons were used as received. To investigate if sonication changes the mercury removal properties of carbonised-1, 500 mg of material was sonicated in 100 mL water using an ultrasonic probe. While the sonication was used primarily to homogenise the carbon, we thought it might generate finer carbon particles with greater surface area (S24). All experiments were completed in triplicate and mercury concentration was monitored by Cold Vapour Atomic Absorption Spectroscopy (CVAAS) over 2 hours.

As shown in Figure 4, carbonised-1 was faster in mercury uptake than the polymer from which it was made, removing 99% of the mercury in less than 2 hours. In contrast 50-poly(*S-r*-canola) only removed 43% of mercury over the same period of time. Additionally, carbonised-1 performed better than 2 of the 3 activated carbons, and was comparable to the highest performing commercial PAC tested in this study (Kurraray PGW-150MP). Interestingly, it was found that homogenising carbonised-1 by sonication significantly improved the rate of mercury uptake. Because carbonised-1 has a lower surface area than the Kurraray PGW-150MP, we attribute the high performance of carbonised-1 to its high sulfur content which creates distinct binding sites compared to the non-sulfurised carbon. Because the Kurraray PGW-150MP is an order of magnitude greater in surface area than carbonised-1, this suggests that the sulfur functionality is very important for the rate of mercury uptake and that a highly porous structure, while beneficial, is not necessary for effective mercury sorption. Additional kinetic analysis was carried out on this sorption data and fit to both a pseudo-first order model and a pseudo-second order model (S25-S28). For carbonised-1,  $k_1 = 1.14 \text{ h}^{-1}$  and  $k_2 = 0.3 \text{ mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  for the first and second order models, respectively. For the sonicated carbonised-1 the rate constants were  $k_1 = 2.7 \text{ h}^{-1}$  and  $k_2 = 1.6 \text{ mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  for the first and second order models, respectively. To determine the capacity of mercury uptake for carbonised-1, isotherms were constructed

and fitted to the Langmuir model (S29-S30). The mercury capacity of carbonised-1 was determined to be 1.1 mg/g and the PGW-150MP carbon achieved a capacity of 9.7 mg/g. Given that the surface area of carbonised-1 is approximately 10 times lower than that of PGW-150MP, carbonised-1 shows a similar capacity of mercury relative to the active surface area.

Next, we considered carbonisation as a method to extend the lifetime of sulfur polymer 1. The polymer was therefore used first as a sorbent for oil spills, as previously described.<sup>18</sup> The oil was then recovered by compression and the polymer, with residual oil on its surface, was carbonised (S31-S32). The product (carbonised-1-O) was largely indistinguishable to carbonised-1 according to SEM, EDX, Raman, XRD, and combustibility analysis (S33-S35). However, the surface area (228  $\text{m}^2/\text{g}$ ) was approximately double that of carbonised-1, possibly due to combustion of the residual oil and concomitant foaming (S13). When carbonised-1-O was sonicated and tested in mercury sorption, this extra surface area improved the rate of mercury uptake 7-fold relative to carbonised-1 (Figure 4). This experiment demonstrates that carbonisation can be used to repurpose polymer 1 as a mercury sorbent after use as an oil spill sorbent, and that superior mercury sorption can result from this repurposing.



**Figure 4.** Mercury sorption over 2 hours after the addition of 100 mg of sorbent to a 45 mL sample of 5 ppm  $\text{Hg}(\text{NO}_3)_2$ . The sonicated carbonised-1-O (made from the repurposed oil sorbent) removed the most mercury and was comparable in rate to the best performing commercial carbon tested.

Next, mercury leaching from the sorbents was examined (S35). Carbonised-1 likely binds to mercury through its sulfur functionality, while Kurraray PGW-150MP does not have sulfur or nitrogen based on combustibility analysis (S23), so its mercury binding is driven by a physisorption process. We hypothesised that this difference might lead to differences in leaching for these sorbents. To prepare the spent sorbent, each carbon (200 mg) was added to 45 mL of a 50 ppm  $\text{Hg}(\text{NO}_3)_2$ . Each sample was prepared in triplicate. All samples were then rotated at 25 RPM for 2 hours to bind mercury to the sorbent. The concentration of mercury in the solution was measured to calculate the amount of mercury bound to each carbon. Next, each sample was isolated by filtration and washed with 50 mL deionised water. Analysis of the wash solution indicated that no mercury was leached from the carbon with this brief washing procedure. In the leaching experiment, the spent carbons were placed in 45

mL of a 5% HNO<sub>3</sub> solution and rotated at 25 RPM for 24 hours. The solutions were then analysed for leached mercury using CVAAS, with 32% of mercury leached from the granular activated charcoal, 28% leached from the ChemSupply PAC, and 22% leached from Kurraray's PGW-150MP PAC. In contrast, only 5% of the bound mercury leached from carbonised-1 and 9% from carbonised-1-O (S35). This result indicates the importance of the sulfur in binding and adhering mercury, with far less leaching observed after prolonged incubation in highly acidic water. This bodes well for the safety in recovery, storage, transport, and disposal of the sorbent in comparison to non-sulfurised carbon.

Finally, regeneration of carbonised-1 and carbonised-1-O was tested (S36). By simply returning the spent carbon to a furnace and heating at 400 °C for 30 minutes, the bound mercury was reduced and volatilised, providing a regenerated carbon sorbent. For larger scale processing, established mercury recovery units and retorts could be used for this procedure. XPS analysis clearly revealed mercury on the spent carbon sorbents, but no mercury could be detected on the regenerated carbons (S36). XPS and combustible analysis also indicated essentially no change in the elemental composition of the sorbent after regeneration (S37-S39). The regenerated carbons also performed well in the removal of Hg<sup>2+</sup> from water: 100 mg of the regenerated carbons removed >99% of mercury from a 45 mL solution of 5 ppm Hg<sup>2+</sup> solution over 2 hours (S39). In this way, carbonised-1 and carbonised-1-O can be used repeatedly in mercury remediation.

### Conflict of interest

J.M.C. is an inventor on a patent assigned to Clean Earth Technologies that covers the synthesis and applications of the polymer used in this study (WO2017181217).

### Notes and references

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