Electronic Supplementary Information

Carbonisation of a polymer made from sulfur and canola oil

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General considerations

Materials: The mercury standard to prepare the mercury solution was purchased from ARC (1000 mg/L, Matrix: 2% HNO₃). The granular activated charcoal was purchased from Sigma Aldrich (untreated, granular, 8-20 mesh) and used as revived. The powdered activated carbon (PAC) was purchased from ChemSupply and used as received. The PGW-150MP carbon was provided by Kuraray. HgCl₂ powder was purchased from ChemSupply.

The **50-poly-(S-***r***-canola) polymer** used for this experiment was synthesised as previously described by our laboratory by the direct copolymerisation of equal masses of sulfur and canola oil.¹ All characterisation data (¹H NMR, IR, TGA, DSC) was consistent with our previous reports.¹

Carbonisation of 50-poly-(S-*r***-canola)** was performed in a Carbolite Gero CWF 1200 furnace. The 50-poly-(S-*r*-canola) sample was heated to 600 °C using a 5 ° / minute heating rate. After the target temperature of 600 °C was reached the temperature was held for 30 minutes. Next, the oven was left to cool down naturally. The carbonised 50-poly-(S-*r*-canola) polymer generated is referred to as carbonised-**1**.

SEM and EDX images were obtained using a FEI Inspect F50 SEM fitted with a EDAX energy dispersive X-Ray detector. Samples were sputter coated with silver metal (20 nm thickness) before analysis.

Brunauer–Emmett–Teller (BET) surface areas were measured at 77.3 K using a Micromeritics TriStar II analyser and were determined from the N2 adsorption isotherms. The samples were prepared by adding between 40-100 mg of sample into the sample tube before the samples were put under vacuum using a VacPrep061 vacuum station for at least 24 hours.

Inductively Couple Plasma – Mass Spectroscopy (ICP-MS) was performed on a Perkin Elmer NexION 350D spectrometer fitted with an EIS SC2 D *X* autosampler. This technique was used for mixed-metal analysis.

Mercury analysis: CVAA was carried out by a commercial service. Briefly, aqueous samples were digested using bromine monochloride (BrCl) before Cold Vapour Atomic Absorption spectroscopic analysis using a method adapted from the following standard methods: APHA 3112 (USEPA 7471A & USEPA 1631 Rev E).

CHNS elemental analysis was performed by The Campbell Microanalytical Laboratory at the University of Otago in New Zealand.

Simultaneous Thermal Analysis (STA) was performed using a Perkin Elmer STA 8000 instrument. The sample was held at 40 °C for 4 minutes before the sample was heated to 800 °C at a rate of 10 °C / minute. This was done under nitrogen with a flow rate of 20 mL / minute.

Raman spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 40X objective (numerical aperture 0.40). Typical integration times for the Raman spectra were approximately 10 to 20 seconds. The grating used was 600 grooves/mm which gives a spectral resolution of approximately 3 to 4 wavenumbers. The current Activated carbon (AC) sample was analysed at multiple locations and hundreds of spectra were acquired not only to determine the level of disorder of the material but also to ascertain if any residual S₈ was present in the sample as the EDX indicated the element sulfur was present on the AC sheets. No S₈ was detected. For the commercial AC approximately 50 Raman spectra was collected per sample at multiple locations within each sample.

XPS (X-ray Photoelectron Spectroscopy)² was applied for determining the chemical and bond states of element of a sample surface. The apparatus was built by SPECS, which was operated in an ultra-high vacuum (UHV) condition at a base pressure of 10⁻¹⁰ mbar. A no-monochromatic X-ray source (12kV-200W) with a Mg anode was used for the measurements and survey and high-resolution scans were operated at a pass energy of 40eV and 10eV respectively and recorded. Spectra were calibrated based on identifying C-C sp3 species to 285.0 eV. The relative concentration of element was calculated by normalizing the individual element intensity to its atomic sensitive factor (ASF).

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance Eco diffractometer (Bragg-Brentano geometry) using Co-K α radiation (λ = 1.78897 Å). The Bragg angle (2 θ) was varied from 10° to 90° with a step size of 0.019°, measurement time of 0.6 s per step and sample rotation at 10 rpm. The samples were deposited onto a sample holder well before analysis

Synthesis and characterisation of 50-poly-(S-*r*-canola) (1)

50-poly-(S-*r*-canola) was prepared as previously described.¹ Briefly, sulfur (20.0 g) was added to a 250 mL round bottom flask and heated to 180 °C with stirring. Canola oil (20.0 g) was added over a period of 5 minutes, resulting in a two-phase mixture. The reaction was stirred vigorously and heated at 80 °C until the product solidifies (typically 20-30 minutes). The product was then removed from the flask and milled to provide particles <1 cm in diameter. This protocol typically provides a recovery of >98% polymer. Characterisation data was consistent with previously published data on this material.¹ ¹H NMR, IR, STA, XRD, and combustible analysis are shown below for reference:

The ¹H NMR of 50-poly-(S-*r*-canola) in pyridine-d5 was consistent with that previous reported:¹



The IR spectrum of 50-poly-(S-r-canola) was consistent with that previously reported:¹



The thermal analysis (STA) of 50-poly-(S-*r*-canola) was consistent with that previously reported:¹



XRD analysis of 50-poly-(S-*r*-canola) is consistent with that previously reported, displaying a broad peak for the polymer and distinct peaks for the free sulfur embedded in the polymer.¹



CHNS combustible analysis of 50-poly-(S-*r*-canola):

C: 42.0%; H: 6.5%; N: 0%; S: 48.4%

Synthesis of carbonised-1

The 50-poly-(S-*r*-canola) sample (100 g) was placed in a crucible and heated to 600 °C using a 5 ° / minute heating rate. The furnace was contained in a fume hood to remove off gases. After the target temperature of 600 °C was reached the temperature was held for 30 minutes. Next, the furnace was left to cool down. The carbonised 50-poly-(S-*r*-canola) polymer generated is referred to as carbonised-**1**. Three carbonisation cycles with 100 g of polymer-1 each were performed. The yield from the carbonisation of 300 g of polymer was 38.4 g. After that the carbon was roughly crushed up using mortar and pestle.



100 g of polymer-1 before (left) and after (right) carbonisation at 600 °C). The final product after it was ground up can be seen in the figure below



Ground up carbonised-1

Characterisation of carbonised-1

SEM and EDX analysis were used to characterise the size, shape, and surface composition of carbonised-1.



SEM image (left) of carbonised-1 and EDX elemental map (right)



CHNS analysis of carbonised-1

C: 65.5%; H: 1.6%; N: 0%; S: 16.0%

Brunauer-Emmett-Teller (BET) surface area analysis of carbonised-1

Nitrogen adsorption was measured three times for the carbonised-**1** sample. The desorption cycle could not be completed despite repeated attempts, so the surface area for carbonised-**1** was estimated using adsoption data only. The average surface area over four measurements was 111 m²/g. BET analysis for the commercial carbons on shown on the following page.



Representative isotherm plot of nitrogen adsorption and desorption

carbonised-1



BET isotherm plot for Kuraray PGW-150MP



BET isotherm plot for PAC (ChemSupply)



BET isotherm plot for GAC (Sigma Aldrich)



Representative isotherm plot of nitrogen adsorption and desorption

carbonised-1-0

Carbon	Surface Area (m ² /g)
Carbonised-1	111 ± 46
Carbonised-1-O	228 ± 45
PGW-150MP	1131 ± 136
PAC	742 ± 3
GAC	125 ± 12

Summary of BET surface areas of carbonised-1, PGW-150MP, PAC and GAC



SEM micrograph of the PGW-150MP carbon





EDX elemental map of the PGW-150MP carbon



SEM micrograph of the GAC (Sigma-Aldrich)



EDX elemental map of the GAC



SEM micrograph of the PAC (ChemSupply)





EDX elemental map of the PAC



Raman spectra of carbonised-1



Raman spectra of PGW-150MP



Raman spectra of the GAC



Raman spectra of the PAC



Raman spectra of elemental sulfur

XRD analysis of carbons



XRD spectrum of PAC (ChemSupply)



XRD spectrum of GAC (Sigma)



XRD spectrum of PGW-150MP



XRD spectrum of carbonised-1

XPS analysis of carbonised-1 and carbonised-1-O

For XPS analysis, the carbonised polymer samples were ground to a powder form and mounted on a sample holder. The high-resolution scans of C, O, S of the samples were recorded and fitted. The spectra of C and S are shown in (a) and (b). The normalized relative concentration of element, the relative intensity of C and S species are respectively exhibited in (c), (d) and (e).



a) and (b): Fitting of C and S spectra of two samples; (c): relative concentration of C, O and S; (d) and (e): relative intensity of C and S species of the samples

The fitting of C1s resulted in five individual peaks. The C-C sp3 was found and calibrated at 285.0 eV³ and a small peak with a full width half maximum (FWHM) of 1.0 eV at 284.0 \pm 0.15 eV was fitted,⁴⁻⁶ indicating a fraction of sp2 graphite species. C-S and C-O peaks were fitted at 286.7 \pm 0.15 eV.^{3,7} The peak levelling at 288.1 \pm 0.15 eV and 289.3 \pm 0.15 eV can be assigned to C=O⁸ and carboxyl⁹ groups. The fitting of S2p_{3/2} results in two distinguishable components. The one fitted at 164.1 \pm 0.15 eV is from C-S bonds in the carbon, while the other one fitted at 167.6 \pm 0.15 eV^{10,11} represents the high oxidation states of sulfur SO_x, such as sulfinates or sulfonates, as a consequence of the carbonization in air. Similar spectra and fitting were obtained for both carbonised-**1** and carbonised-**1-O**.

The relative surface concentration from (c) reveals a concentration of about 75% of C, 20% of O and nearly 4.6% S in both samples. Regarding the carbon in carbonised-**1** from (d), about 67.3 % is C-C, 5.1% is graphite sp2 and 12.8 % is C-S/C-O, while C=O and carboxyl are 7.3 % and 6.8 %. In Figure S13 (e), 95.4 % sulfur is bonded to carbon and 4.6% of the sulfur is presents as a higher oxidation state. The composition is similar in sample carbonized-**1-O**.

The chemical characterization of the two samples indicates no noticeable difference can be observed from the perspective of elemental distribution and chemical bonds.



Comparison of CHNS analysis of 50-poly-(S-*r*-canola), carbonised-**1**, PGW-150MP, GAC and PAC

Mercury removal from water

The same procedure was repeated for solutions of $Hg(NO_3)_2$ only, testing 2 more commercially available carbons (PAC and GAC), sonicated carbonised-1, carbonised-1-O as well as for a polymer-1 control. Mercury analysis was carried out using cold vapour atomic absorption spectroscopy (CVAA).

To prepare the sonicated carbonised-1 and carbonised-1-O, 500 mg of material and 100 mL of MilliQ water were combined in a 125 mL plastic tube and then sonicated using a Bueno Biotech BEM-900A Ultrasonic Homogeniser equipped with a Φ 12 probe. The settings of the ultrasonic homogeniser were set to a pulse of 2 seconds followed by a 5 second pause for a total time of 30 minutes. Further the power was set to 100% (900 W) and the temperature was capped at 60 °C. After that the carbon was vacuum filtered and dried under high vacuum overnight.



Non-sonicated carbonised-1



Sonicated carbonised-1

SEM micrographs of non-sonicated (left) and sonicated caronised-1 (right)



Graph of $Hg(NO_3)_2$ uptake of PGW-150MP, polymer-1, PAC, GAC, carbonised-1, sonicated carbonised-1 and carbonised-1-O over a time frame of 2 hours.

Kinetic analysis of mercury removal

To perform the kinetic analysis, the mass of mercury removed per gram of polymer was calculated using the concentrations of the heavy metal removal analysis of the carbon materials and their masses used. In order to fit the kinetic model to the dataset, pseudo-first order and pseudo second order kinetic models were used.^{12,13}

The linear equations of these kinetic models can be written as:

Pseudo-First Order (linear)

 $\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (eq. 1)^{12}$

Pseudo-Second Order (linear)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$$
(eq. 2)¹³

The pseudo-first order kinetic model equation can be rewritten in non-linearised form as:

Pseudo-First Order (non-linearised)

$$q_t = q_e (1 - e^{-k_1 t})$$
 (eq. 3)¹²

Pseudo-Second Order (non-linearised)

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \tag{eq. 4}$$

 q_e = mercury bound to the carbon substrate at equilibrium (mg mercury / g polymer) q_t = mercury bound to the carbon substrate at time t (mg mercury / g polymer) k_1 = rate constant of pseudo-first order kinetic model (hour⁻¹) k_2 = rate constant of pseudo-second order kinetic model (mg.g⁻¹.hour⁻¹) t = time (hours)



Pseudo-first order non-linear plot qt vs time for all carbon substrates used



Pseudo-second order non-linear plot q_t vs time for all carbon substrates used

Kinetic rate parameters of mercury sorption of the carbon substrates using non-linear models

Carbon Substrate	Rate constant (k)	q _e (expt.) (mg/g)	qe (calc.) (mg/g)	r ²
	$k_1 = 1.54 \pm 0.03 h^{-1}$	1.01	2.04 ± 0.01	1.000
GAC	$k_2 = 0.562 \pm 0.6 \text{ mg.g}^{-1}.\text{h}^{-1}$	1.94	2.64 ± 0.08	0.999
	$k_1 = 6.14 \pm 0.99 h^{-1}$	1 50	1.47 ± 0.02	0.998
PAC	$k_2 = 15.4 \pm 4.92 \text{ mg.g}^{-1}.\text{h}^{-1}$	1.50	1.51 ± 0.02	1.000
	$k_1 = 1.14 \pm 0.53 h^{-1}$	1.05	2.36 ± 0.46	0.927
Carbonised-1	$k_2 = 0.283 \pm 0.289 \text{ mg.g}^{-1}.\text{h}^{-1}$	1.95	$\textbf{3.29} \pm \textbf{1.05}$	0.923
	$k_1 = 36.8 \pm 3.61 h^{-1}$	0.00	$\textbf{2.32}\pm0.01$	0.999
PGW-150MP	$k_2 = 84.7 \pm 12.9 \text{ mg.g}^{-1}.\text{h}^{-1}$	2.33	2.34 ± 0.01	1.000
Seriested	$k_1 = 2.65 \pm 0.04 h^{-1}$	2.07	2.09 ± 0.01	1.000
carbonised-1	$k_2 = 1.55 \pm 0.23 \text{ mg.g}^{-1}.\text{h}^{-1}$	2.07	2.40 ± 0.06	0.998
corbonicod 4 O	$k_1 = 18.8 \pm 0.32 h^{-1}$	2.20	2.26 ± 0.01	1.000
k ₂ = 20.2 ± 3.26 mg.g ⁻¹ .h ⁻¹ 2.28	2.20	2.34 ± 0.03	0.996	

Isotherm adsorption of carbonised-1 and PGW-150MP

Isotherms of the carbonised-1 and PGW-15-MP were performed.

Firstly, a 1000 ppm Hg solution was made by dissolving 676.7 mg of HgCl₂ in a 500 mL volumetric flask in MilliQ water.

For the isotherm of the carbonised-**1**, 5 samples with different Hg concentrations (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm) and volumes of 20 mL were prepared in triplicate in plastic tubes. To each sample 100 μ g of carbonised-**1** was added. After that the samples were rotated at 25 RPM for 7 hours. Following that an aliquot of each sample was filtered using a 0.45 μ m nylon syringe filter and sent for analysis.

For the PGW-150MP isotherm, 5 samples with different Hg concentrations (50 ppm, 100 ppm, 200 ppm, 300 ppm, 400 ppm) and volumes of 20 mL were prepared in triplicate in plastic tubes. To each sample 20 mg of PGW-150MP was added. Following that the samples were rotated at 25 RPM for 7 hours. After that an aliquot of the samples were filtered using a 0.45 μ m nylon syringe filter and sent for analysis.

For the isotherm fitting the Langmuir model was used.

$$q_{eq} = \frac{Q_{max}K_LC_{eq}}{1 + K_LC_{eq}}$$



Adsorption isotherm of mercury onto samples of carbonised-**1** using Langmuir isotherm fitting (red line)



Adsorption isotherm of mercury onto samples of PGW-150MP using Langmuir isotherm fitting (red line)

Synthesis of carbonised-1-O

A glass dish was filled with 1.5 L of water. To that dish, 200 mL of oil (2 stroke motor oil) was added.



200 mL of 2 stroke oil in 1.5 L of water

Next, 100 g of polymer-1 was added to that oil / water mixture and left undisturbed for 8 minutes.



Oil and water mixture **a**) immediately after polymer-**1** was added **b**) after 8 minutes view from top and **c**) after 8 minutes view from side

Following that, the polymer was removed using a net. As previously reported, polymer-**1** was able to remove the oil from the water.¹⁴ The oil was removed by adding some of the oil-bearing polymer into a syringe and the plunger was pressed to squeezed the oil out of the polymer. Since the process was very slow, the remaining polymer and oil mixture was placed in a press to remove the oil. After using 200 mL of oil 160 mL were recovered. However, some of the oil has been lost during the recovery process or to the glassware and the press.



a) polymer removal with net b) remains of oil in water after polymer and oil removal

After the oil was removed from the polymer, the polymer was carbonised using the same protocol as described for the synthesis of carbonised-**1** shown above. Following the carbonisation, carbonised-**1-O** was sonicated using the same protocol as described for the synthesis of the sonicated carbonised-**1** shown further below.



a) Carbonised-1-O after being roughly crushed using mortar and pestle and b) carbonised-1-O after sonication

Characterisation of carbonised-1-O

SEM/EDX analysis was performed on the carbonised-1-0.



SEM micrograph of the carbonised-1-0



EDX elemental map of the carbonised-1-0



Raman spectra of carbonised-1-0



XRD spectrum of carbonised-1-0



CHNS analysis of caronised-1-0

C: 63.6%; H: 1.5%; N: 0%; S: 15.2%

BET analysis of carbonised-1-O of provided on page S13

Hg leaching from carbons

The following experiment was performed to investigate if Hg that was captured by carbonised-**1** is leached off again when exposed to acidic conditions. In this experiment all the available carbons were tested (carbonised-**1**, PGW-150MP, GAC, PAC). All experiments were performed in triplicate.

Firstly, 200 mg of each carbon was placed in separate 45 mL mercury solution (50 ppm) made form a 1000 ppm mercury standard in 2% HNO₃. After that all the samples were rotated at 25 RPM for 2 hours. After that, each sample was recovered by vacuum filtration and washed with 50 mL MilliQ water. Then, the samples were placed in 45 mL of a 5% HNO₃ solution and rotated at 25 RPM for 24 hours. Samples for Hg analysis were taken of each solution before adding the carbon and then after 2 hours Hg exposure in order to calculate the amount of mercury on the spent carbon sorbent. Samples were also taken immediately after adding the carbon to the nitric acid solution, and after the samples have been in the nitric acid solution for 24 hours. Samples to 7 mL, stabilised in 5% nitric acid. The samples were analysed by CVAAS. The results are summarised below.

-	
Sampla	Hg leached
Sample	(%)
Carbonised-1	5

Hg leached from spent carbon sorbents into 5% nitric acid:

Sample	(%)
Carbonised-1	5
Carbonised-1-O	9
PGW-150MP	22
GAC	32
PAC	28

Regeneration of carbonised-1 and carbonised-1-O after mercury sorption

First, spent sorbents were prepared with mercury bound to the carbon. All experiments were carried out in triplicate. To generate the spent sorbent, 1.000 g of either carbonised-1 or carbonised-1-O was placed in a 45 mL solution of 250 ppm Hg(NO₃)₂ and rotated for 24 hours. Following this time, the carbon samples were recovered by filtration and washed with 50 mL water and dried under vacuum. The concentration of the mercury solution after the incubation with carbon was measured by CVAA and used to determine the amount of mercury bound to each carbon sample:

Sample	Hg on carbon (mg)
Carbonised -1	8.9 ± 0.8
Carbonised-1-O	9.7 ± 1.1

Regeneration procedure: The spent sorbent (prepared above, bound to mercury) were placed in an open crucible and heated at a rate of 5 °C per minute up to 400 °C in a muffle furnace. The temperature was held at 400 °C for 30 minutes. The furnace was contained in a fume hood to extract any off gases. For larger scale, a mercury scrubber or retort is required for safe regeneration and capture of mercury.

XPS analysis of carbonised-1 and carbonised-1-O before and after regeneration



Mercury: XPS analysis was used to clearly detect mercury on the surface of spent carbonised-**1** and spent carbonised-**1-O**. After the regeneration procedure (400 °C, 30 minutes), no mercury could be detected by XPS.

Note that the signal for mercury at 101.6 eV +/- 0.2 eV corresponds to Hg^{2+.15}

XPS analysis before and after regeneration (continued)



Sulfur: XPS analysis of the spent carbonised-**1** and spent carbonised-**1-O** indicated there is no discernible change in the sulfur S2p signals after regeneration. These signals are the same observed for freshly prepared carbonised-**1** and carbonised-**1-O** (see page S22). These results indicate the sulfur species in the carbon are consistent throughout the mercury binding and regeneration process.



Carbon: XPS analysis of the spent carbonised-**1** and spent carbonised-**1-O** indicated there is no discernible change in the carbon C1s signal after the regeneration process.



XPS analysis before and after regeneration (continued)

XPS analysis of the spent carbonised-**1** and spent carbonised-**1-O** indicated and the regenerated carbon samples indicate minor changes in the relative amount of carbon, oxygen, and sulfur before and after regeneration. Mercury was removed during the regeneration.



XPS analysis of the spent carbonised-**1** and spent carbonised-**1-O** indicated the regenerated carbon samples undergo relatively minor changes in the carbon speciation after regeneration.

Combustible analysis of carbonised-1 and carbonised-1-O

The elemental composition of freshly prepared carbonised-**1** and carbonised-**1-O** are also provided for comparison. These results indicate the regeneration procedure does not substantially alter the elemental composition of the carbon.

Material	C (%)	S (%)	H (%)
Carbonised-1	65.5	16.0	1.6
Carbonised-1 regenerated	64.5	16.1	1.1
Carbonised-1-0	63.6	15.2	1.5
Carbonised-1-O regenerated	65.0	15.2	1.3

Mercury sorption of carbonised-1 and carbonised-1-O after regeneration

100 mg of sorbent was added to a 45 mL sample of 5 ppm $Hg(NO_3)_2$. The sample was mixed using an end-over-end mixer, sampling the water over a 2 hour period. The mercury concentration in the water was measured by CVAA. Triplicate measurements were made for each timepoint. The results are plotted below for carbonised-1 (freshly prepared), regenerated carbonised-1, carbonised-1-O (freshly prepared), and regenerated carbonised-1-O. While there are subtle variations in initial rate of mercury uptake for these samples, the mercury concentration at the end of the 2 hour period was essentially the same for all samples, with >99% of mercury removed from the water.



Heavy metal removal from aqueous solution (As, Cd, Hg, Pb)

This experiment was performed to assess the ability of carbonised-**1** to remove heavy metals from aqueous solution. Accordingly, five solutions containing a mixture of 5 ppm each of As₂O₅, Cd(NO₃)₂, Hg(NO₃)₂ and Pb(NO₃)₂ were prepared. All standards had an original concentration of 1000 ppm and were in a matrix of 2 % HNO₃. To make solutions with a concentration of only 5 ppm of As, Cd, Hg and Pd, 250 μ L of each standard was added to a 50 mL plastic tube and diluted to 45 mL using MilliQ water.

PGW-150MP had a particle size range from 150 μ m to 500 μ m. To have similar particle sizes for the S-activated carbon, the crushed carbon was sieved through a 500 μ m sieve.

To three 5 ppm heavy metal solutions, 100 mg of the sieved carbonised-**1** was added whereas 100 mg of the PGW-150MP carbon was added to another 3 heavy metal solutions. To the last solution no activated carbon was added as this solution acted as a control to monitor the metal concentration over time.

After the activated carbon was added to the 6 sample solutions, the samples were put on head over tail rotation at 25 RPM. Samples for ICP-MS were taken at 0, 0.5, 1, 1.5 and 2 hours after carbon addition.



Graph of percentage of heavy metals remaining in solution 2 hours after the addition of the commercial activated carbon compared the carbonised-1 carbon

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