

HOW TO CITE:

Ntuli TD, Sikeyi LL, Mongwe TH, Mkhari O, Coville NJ, Nxumalo EN, et al. From waste cooking oil to oxygen-rich onion-like nanocarbons for the removal of hexavalent chromium from aqueous solutions [supplementary material]. S Afr J Sci. 2023;119(9/10), Art. #14006. <https://doi.org/10.17159/sajs.2023/14006/suppl>

The experimental data were tested against the Lagergren pseudo-first-order (PFO)¹ and pseudo-second-order (PSO) kinetic models². The non-linear and linear forms of the PFO are represented by Supplementary equations 1 and 2, respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Supplementary equation 1}$$

$$\log(q_e - q_t) = \frac{k_1}{2.303} t + \log(q_e) \quad \text{Supplementary equation 2}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively; and k_1 (1/min) represents the rate constant of the PFO model.

The non-linear and linear forms of the PSO and the initial adsorption rate (h) proposed by Ho et al.² are presented by Supplementary equations 3, 4 and 5, respectively:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad \text{Supplementary equation 3}$$

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e^2} \quad \text{Supplementary equation 4}$$

$$h = k_2 = k_2 q_e^2 \quad \text{Supplementary equation 5}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively; and k_2 (g/mg x min) is the rate constant of the PSO model.

The experimental data were tested against the Langmuir³ and Freundlich⁴ isotherms to determine whether the adsorption process proceeded via monolayer or multilayer adsorption. The non-linear and linear forms of the Langmuir isotherm can be represented by Supplementary equations 6 and 7, respectively. The dimensionless separation factor R_L is represented by Supplementary equation 8.

$$q_e = \frac{Q_{max}^0 K_L C_e}{1 + K_L C_e} \quad \text{Supplementary equation 6}$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}^0}\right) C_e + \frac{1}{Q_{max}^0 K_L} \quad \text{Supplementary equation 7}$$

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Supplementary equation 8}$$

where Q_{max}^0 (mg/g) and q_e (mg/g) represent the maximum adsorption capacity for the Langmuir model and adsorption capacity for the experimental data at equilibrium, respectively; C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of the adsorbate; and K_L (L/mg) is the Langmuir equilibrium constant that is related to the affinity between the adsorbent and adsorbate.

The non-linear and linear forms of the Freundlich isotherms are represented by Supplementary equations 9 and 10, respectively:

$$q_e = K_F C_e^n \quad \text{Supplementary equation 9}$$

$$\log q_e = n \log C_e + \log K_F \quad \text{Supplementary equation 10}$$

where q_e (mg/g) is the amount of adsorbate uptake at equilibrium; K_F (mg/g)/(mg/L)ⁿ is the Freundlich constant; C_e (mg/L) is the concentration of the adsorbate at equilibrium; and n is the dimensionless Freundlich intensity parameter.

In the determination of the best model for the rate data we used the chi-squared (χ^2) and the coefficient of determination (R^2) using supplementary equations 11 and 12 respectively:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad \text{Supplementary equation 11}$$

$$R^2 = 1 - \frac{\sum (q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,mean})^2} \quad \text{Supplementary equation 12}$$

where $q_{e,exp}$ (mg/g) and $q_{e,cal}$ (mg/g) are the adsorption capacity of the experimental data and model, respectively; and $q_{e,mean}$ (mg/g) is the mean adsorption capacity of the $q_{e,exp}$ values.

The thermodynamic parameters were computed using Supplementary equations 13–17.

$$\Delta G^\circ = -RT \ln K_C \quad \text{Supplementary equation 13}$$

The equilibrium constant (K_C) was made dimensionless by multiplying the Langmuir constant (K_L) by 10^6 factor the density of the solution with the assumption that the density of pure water is 1.0 g/mL as shown by Supplementary equation 14

$$K_C = 10^6 K_L \quad \text{Supplementary equation 14}$$

Substitute Supplementary equation 14 into 15 to obtain Supplementary equation 16, then the relationship of the Gibbs energy change (ΔG°) to the enthalpy change (ΔH°) and the entropy change (ΔS°) can be described by Supplementary equation 16:

$$\Delta G^\circ = -RT \ln(10^6 K_L)$$

Supplementary equation 15

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

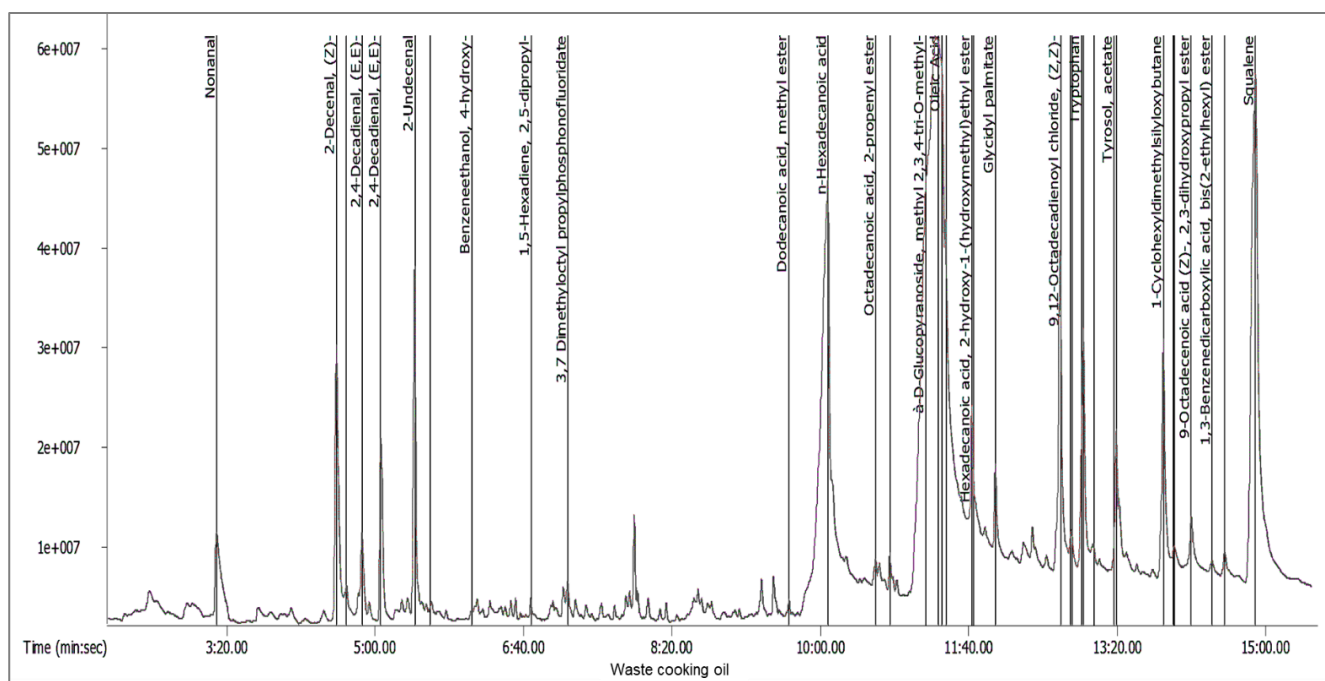
Supplementary equation 16

By substituting Supplementary equation 15 into 16, the van't Hoff equation can be obtained as shown by Supplementary equation 17:

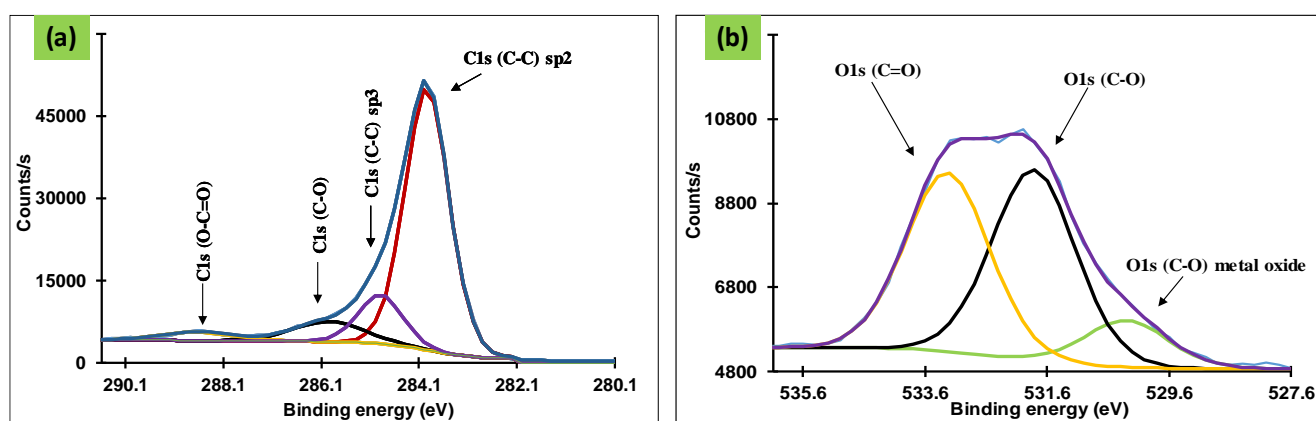
$$\ln(10^6 K_L) = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

Supplementary equation 17

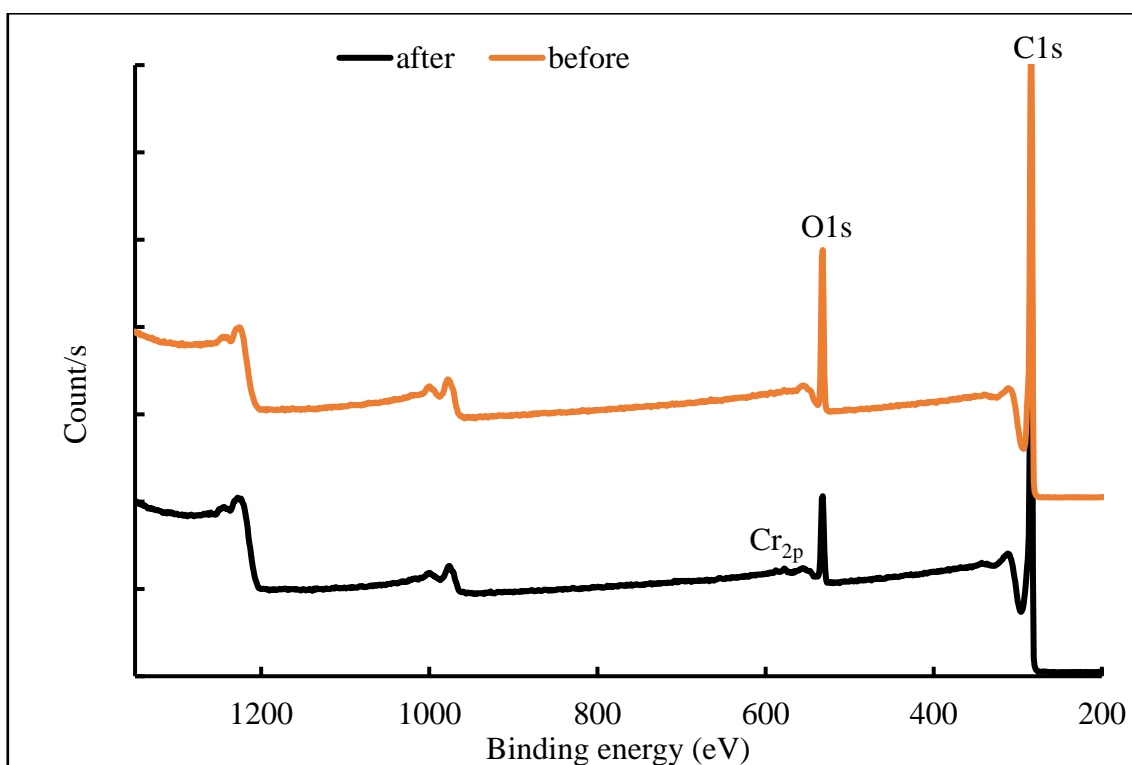
where T is the absolute temperature (K) and R is the universal gas constant (8.3144 J/mol x K). The (ΔG°) can be calculated from Supplementary equation 16, with (ΔH°) and (ΔS°) obtained from the slope and intercept, respectively, of the plot of $\ln K_c$ v/s $1/T$ from Supplementary equation 17.



Supplementary figure 1: Chromatogram for the waste cooking oil.



Supplementary figure 2: (a and b) The XPS spectra of OLNcs adsorbent for C1s and O1s peaks after adsorption of Cr.



Supplementary figure 3: The XPS survey spectra for the OLNCs before and after the removal of Cr(VI) ions.

Supplementary table 1: List of chemical compounds detected in different waste cooking oil

This study	Zayed et al. ⁵		Mannu et al. ⁶
Unknown waste cooking oil	Waste sunflower oil	Waste cotton	Unknown cooking oil
Oleic acid	Oleic acid	Oleic acid	
Hexadecenoic acid	Hexadecenoic acid	Hexadecenoic acid	
Palmitoleic acid	Palmitoleic acid	Palmitoleic acid	
9 -Octadecenoic acid (Z)-	9 -Octadecenoic acid (Z)-	9 -Octadecenoic acid (Z)-	
2-Pentanone	2-Pentacosanone		
2-Heptanone	2-Heptacosanone		2-Heptanone
Eicosatetraenoic acid	Eicosanoic acid		
Quinoline		Quinoline	
1-Cyclohexyldimethylsilyloxybutane		1Cyclohexyldimethylsiyoxybutane	
Nonanal			Nonanal
Cyclopropane			
9,12-Octadecadienoic acid (Z,Z)-			
Heptane			Heptane
Hexanoic acid			Hexanoic acid
2-Decenal, (E)-			2-Decenal, (E)-
Farnesene			Farnesene
2-Undecenal			2-Undecenal
2,4-Decadienal			2,4-Decadienal
2-Decenal, (E)-			2-Decenal, (E)-
Propanoic acid			Propanoic acid
2,4-Heptadienal			2,4-Heptadienal

Supplementary table 2: Peak ID and quantification

Adsorbent	Name	Peak BE	FWHM (eV)	Atomic %
OLNCs	C1s (C-C) sp2	284.2	1.4	41.9
	C1s (C-C) sp3	284.6	1.4	32.2
	C1s (C-O)	286.1	0.9	5.7
	C1s (C=O)	288.0	0.9	3.0
	C1s (O-C=O)	288.7	0.9	3.5
	O1s (Organic C-O)	531.7	1.4	6.9
	O1s (Organic C=O)	533.1	1.4	6.7
Cr-OLNCs	C1s (C-C) sp2	283.9	1.1	45.8
	C1s (C-C) sp3	284.9	1.1	25.7
	C1s (C-O)	286.3	1.3	9.1
	C1s (O-C=O)	288.6	1.3	6.2
	O1s (Organic C-O)	530.0	1.5	0.5
	O1s (Organic C-O)	531.9	1.4	6.4
	O1s (Organic C=O)	533.3	1.4	6.3

References

1. Lagergren S. Zur Theorie der Sogenannten Adsorption GelosterStoffe [On the theory of the so-called adsorption of gelatinous substances]. Kungliga Svenska Vetenskapsakademiens. Handl Band. 1898;24(4):1–39. German.
2. Ho YS, McKay G. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Can J Chem Eng. 1998;76(4):822–827. <https://doi.org/10.1002/cjce.5450760419>
3. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc. 1918;40(9):1361–1403. <https://doi.org/10.1021/ja02242a004>
4. Freundlich H. Über die Adorption in Lösungen [About adsorption in solutions]. Z PhysChem. 1906;57:385–471. German. <https://doi.org/10.1515/zpch-1907-5723>
5. Zayed MA, Abd El-Kareem MSM, Zaky NHS. Gas chromatography-mass spectrometry studies of waste vegetable mixed and pure used oils and its biodiesel products. J Pharm Appl Chem. 2017;3(2):109–116. <https://doi.org/10.18576/jpac/030204>
6. Mannu A, Vlahopoulou G, Urgeghe P, Ferro M, Del Caro A, Taras A, et al. Variation of the chemical composition of waste cooking oils upon bentonite filtration. Resources. 2019;8(2):1–15. <https://doi.org/10.3390/resources8020108>