

1 *Supporting Information*

2 **Porous carrageenan-derived carbons for efficient**
 3 **ciprofloxacin removal from water**

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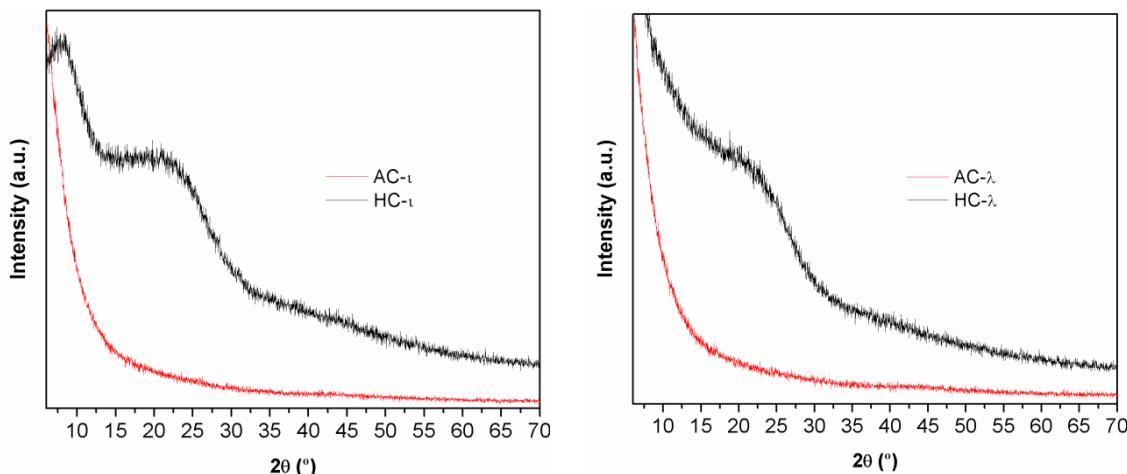
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13 **A. Characterization of carbon materials**



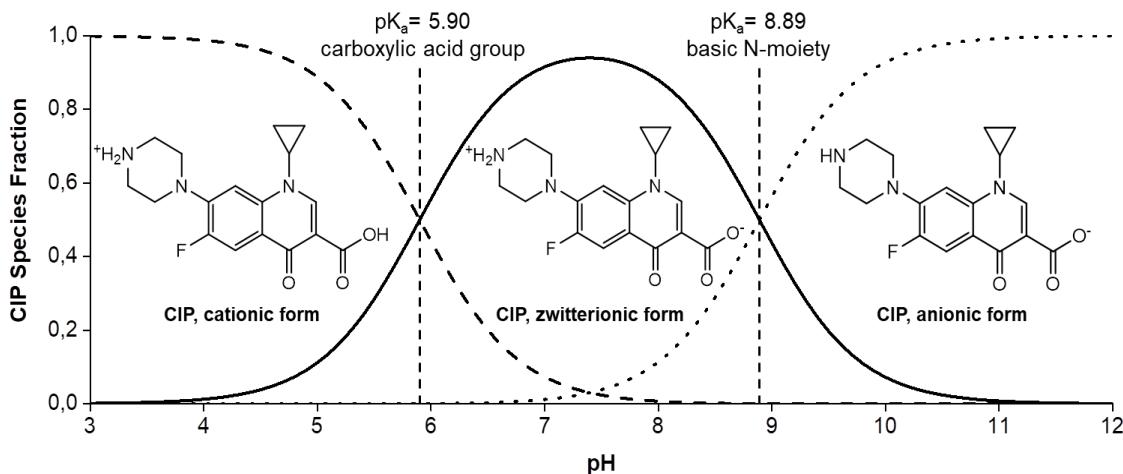
14 **Figure S1.** Powder XRD pattern of carrageenan (ι - and λ -type; left and right, respectively) derived
 15 carbons before (HC) and after activation (AC).

16 **Table S1.** Selected infrared bands (cm^{-1}) for the materials and respective assignments^a.

Assignment	Hydrothermal carbons			Activated carbons		
	HC- κ	HC- ι	HC- λ	AC- κ	AC- ι	AC- λ
v(O-H)	3273 (vs)	3221 (vs)	3315 (vs)	--	--	--
v(C-H) aliphatic	2926 (s) 2879 (s)	2922 (s) 2879 (s)	2926 (s) 2879 (s)	--	--	--
v(C=O)	1693 (s)	1695 (s)	1695 (s)	--	--	--
v(C=C)	1606 (vs)	1606 (vs)	1606 (vs)	1560-1520 (vs)	1560-1520 (vs)	1560-1520 (m)
aromatic	1290 (vs)	1292 (vs)	1298 (vs)	--	--	--
C-H aromatic	798 (s)	798 (s)	798 (s)	--	--	--

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^a vs – very strong; s – strong; m – medium; v – stretching vibration; δ – deformation vibration

18 **B. CIP Adsorption Modelling**19 **Figure S2.** Speciation of CIP [1,2]20 **Table S2.** Isotherm models and parameters [3–6].

Model	Equation (non-linear form)	Parameters
Langmuir	$q_e = \frac{q_L K_L C_e}{1 + K_L C_e}$	q_L is the monolayer adsorption capacity (mg.g^{-1}) K_L is the Langmuir isotherm constant (L.mg^{-1}), related to the affinity of binding sites.
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K_F is the Freundlich constant ($\text{mg}^{(1-1/n)} \cdot \text{L}^{(1/n)} \cdot \text{g}^{-1}$) $1/n$ is the heterogeneity factor; n is usually between 1 and 10 (dimensionless)
Sips	$q_e = \frac{N_T a C_e^m}{1 + a C_e^m}$	N_T is the total number of binding sites (mg.g^{-1}) a is related to the median binding affinity k ($a=k^m$) m is the heterogeneous index (dimensionless, $0 < m < 1$)

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22 **Table S3.** Kinetic models and parameters. q_t and q_e (mg.g^{-1}) are the adsorption capacity at time t and 23 equilibrium time, respectively [7,8].

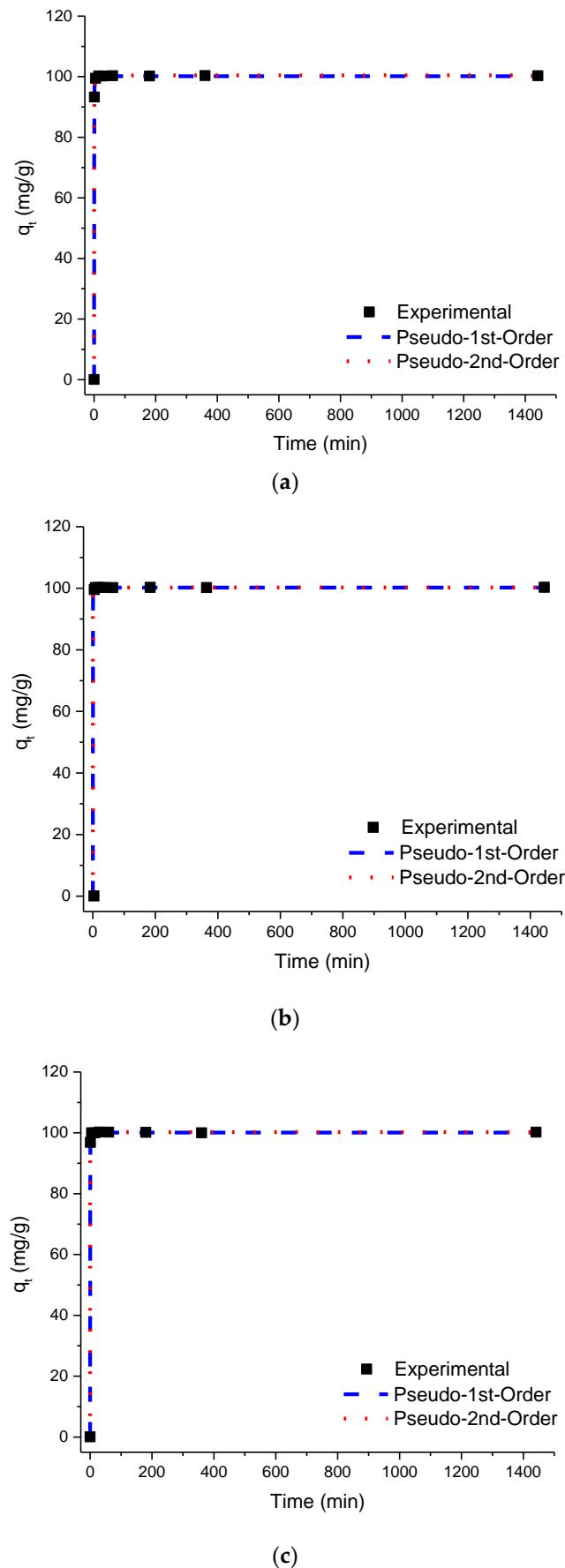
Model	Equation (non-linear form)	Parameters
Pseudo 1 st order	$q_t = q_e(1 - e^{-k_1 t})$	k_1 - equilibrium rate constant of pseudo 1 st order adsorption (min^{-1}).
Pseudo 2 nd order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	k_2 - equilibrium rate constant of pseudo 2 nd order adsorption ($\text{g.mg}^{-1} \cdot \text{min}^{-1}$).

24

25 The goodness of the fittings was determined based on the calculation of the correlation
26 coefficient (R^2) (S1) and Chi-square test value (χ^2) (S2), expressed by the following equations
27 respectively:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (\text{S1}) \quad \chi^2 = \sum_{i=1}^n \frac{(y_i - \hat{y}_i)^2}{\hat{y}_i} \quad (\text{S2})$$

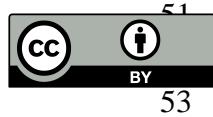
28 where y_i and \hat{y}_i are the experimental and model predicted values respectively, \bar{y} is the mean of the
29 experimental data and n is the sample size.



30 **Figure S3.** Time profile of CIP adsorption capacity over 24h and corresponding kinetic model fitting
31 using pseudo 1st and pseudo 2nd order equations: AC- κ (a), AC- ι (b), AC- λ (c).

32 References

- 33 1. Carmosini, N.; Lee, L.S. Chemosphere Ciprofloxacin sorption by dissolved organic carbon from
34 reference and bio-waste materials. *Chemosphere* **2009**, *77*, 813–820,
35 doi:10.1016/j.chemosphere.2009.08.003.
- 36 2. Drakopoulos, A.I.; Ioannou, P.C. Spectrofluorimetric study of the acid-base equilibria and complexation
37 behavior of the fluoroquinolone antibiotics ofloxacin, norfloxacin, ciprofloxacin and pefloxacin in
38 aqueous solution. *Anal. Chim. Acta* **1997**, *354*, 197–204.
- 39 3. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*
40 **1918**, *40*, 1361–1403, doi:10.1021/ja02242a004.
- 41 4. Freundlich, H. Concerning Adsorption in Solutions. Zeitschrift fur physikalische chemie-stochiometrie
42 und verwandtschaftslehre. *Phys. Chem.* **1906**, *57*, 385–470.
- 43 5. Sips, R. On the structure of a catalyst surface. *J. Chem. Phys.* **1948**, *16*, 490–495, doi:10.1007/978-1-4614-
44 5836-4_45.
- 45 6. Umpleby, R.J.; Baxter, S.C.; Chen, Y.; Shah, R.N.; Shimizu, K.D. Characterization of Molecularly
46 Imprinted Polymers with the Langmuir-Freundlich Isotherm. *Anal. Chem.* **2001**, *73*, 4584–4591.
- 47 7. Lagergren, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska
48 Vetenskapsakademiens. *Handlingar* **1989**, *24*, 1–39.
- 49 8. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–
50 465, doi:10.1016/S0032-9592(98)00112-5.



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