# Supplementary Materials

## Removal of the Water Pollutant Ciprofloxacin Using Biodegradable Sorbent Polymers Obtained from Polysaccharides

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**Fernando Hernandez-Mateo** [1,2,3]**,F. Javier Lopez-Jaramillo** [1,2,3,]***** **and Francisco Santoyo-Gonzalez** [1,2,3,]*****

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*  Correspondence: fjljara@ugr.es (F.J.L.-J.); fsantoyo@ugr.es (F.S.-G.)
†  Current address: Institute for Advanced Chemistry of Catalonia, CSIC, 08034 Barcelona, Spain.
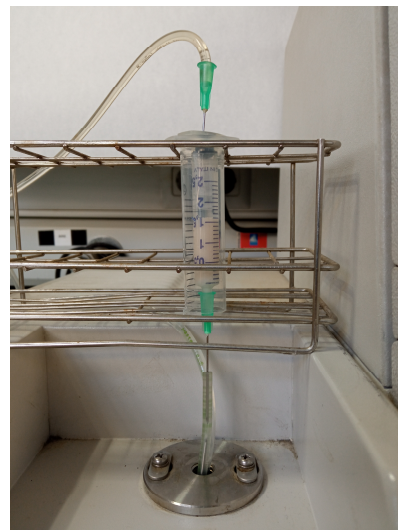
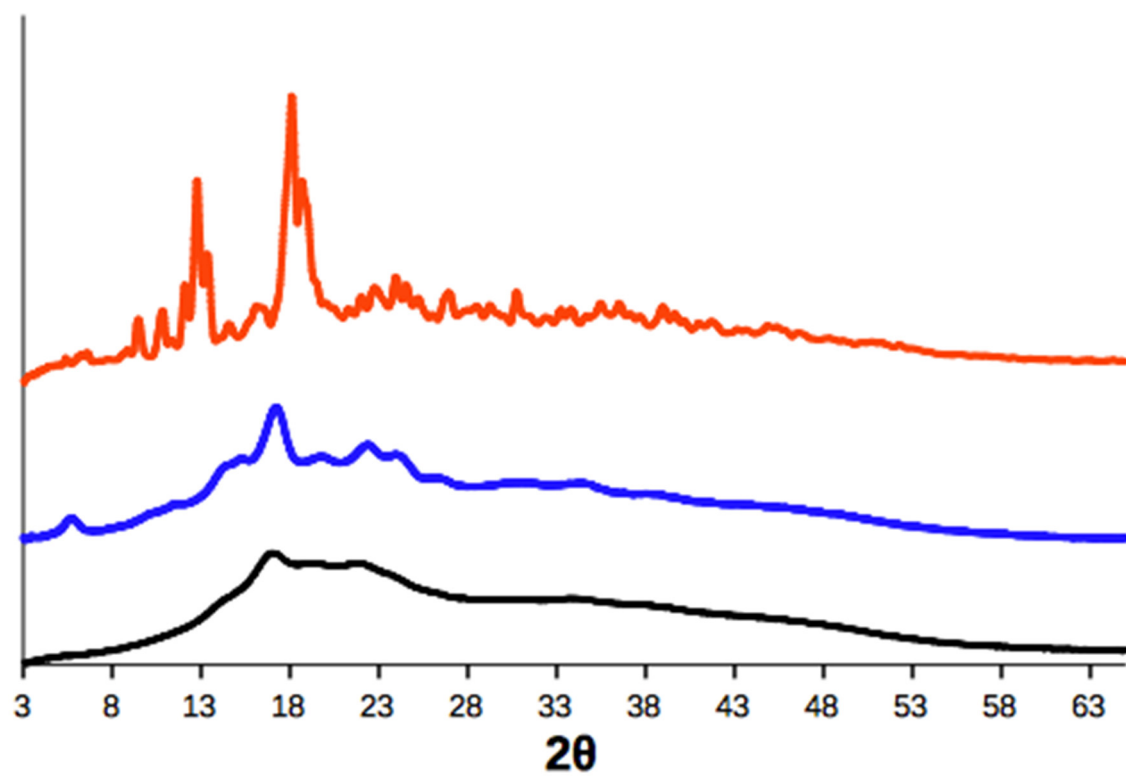**Figure. S1**. (a) General setting for the fixed bed studies with **pSt**. (b) Detail of the **pSt** packing.

**Figure. S2.** DRX of the starting material β-CD (red) St (blue) and Dx (black) showing the d-spacing of some peaks.
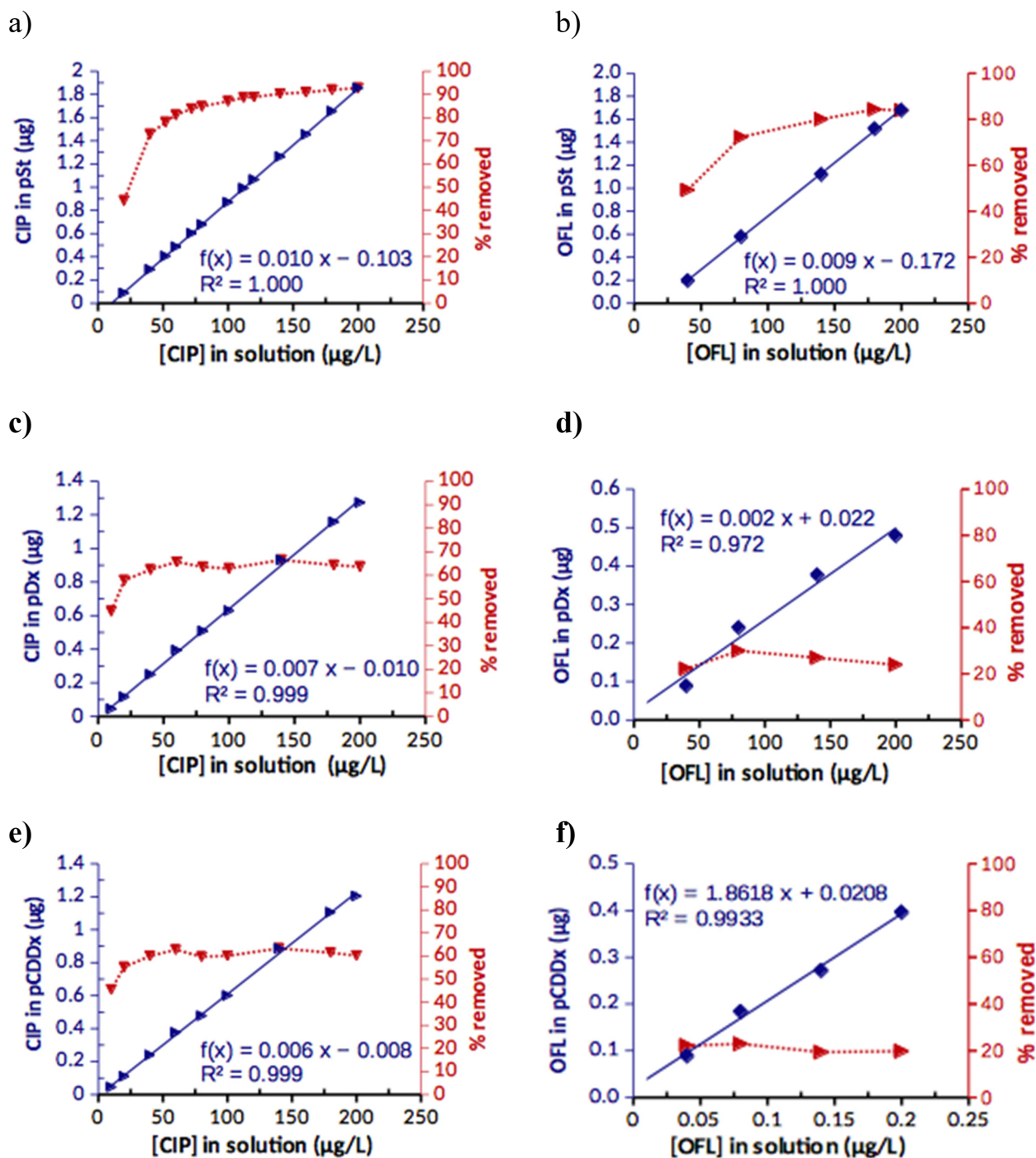
a)

b)

c)

d)

e)

f)

**Figure. S3.** Characterization of the polymers **pSt** (a & b), **pDx** (c & d) and **pCD-Dx** (e & f) as sorbent for CIP (a, c, e) and OFL (b, d, f). In blue, amount retained by the polymer and in red the percentage removed from the solution as a function of the initial concentration of quinolone.
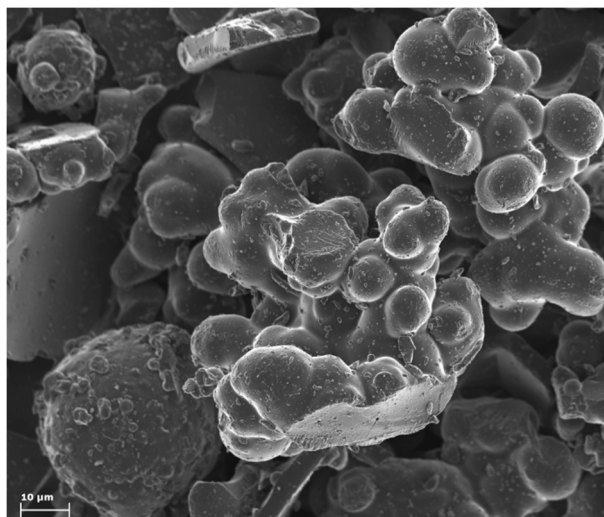
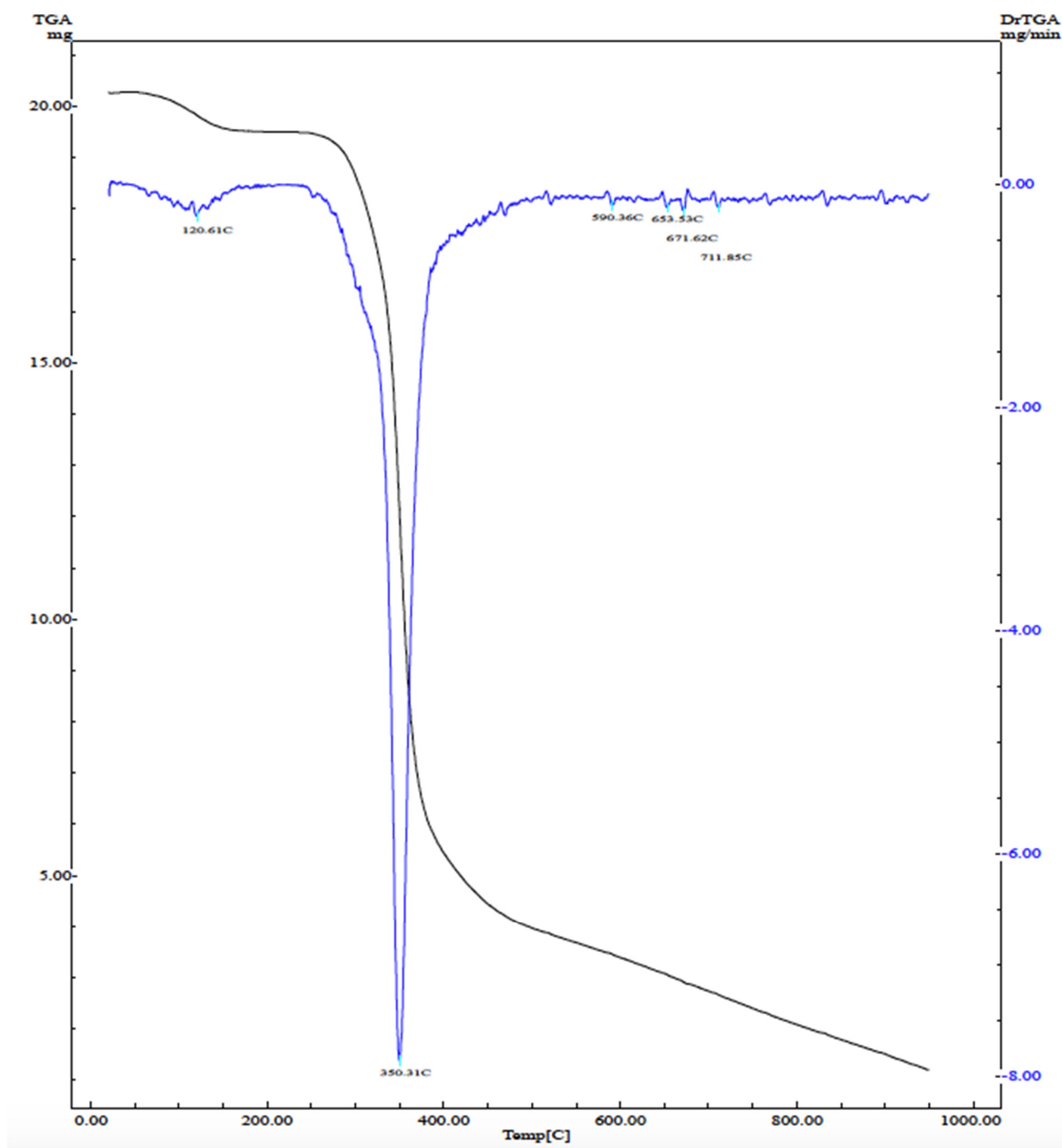**Figure. S4.** SEM micrograph of **pCD-Dx** at 10.00 K x.

**Figure. S5** Derivative TGA of **pSt**. In black is shown the evolution of the mass of the sample as a function of the temperature and in blue the first derivative
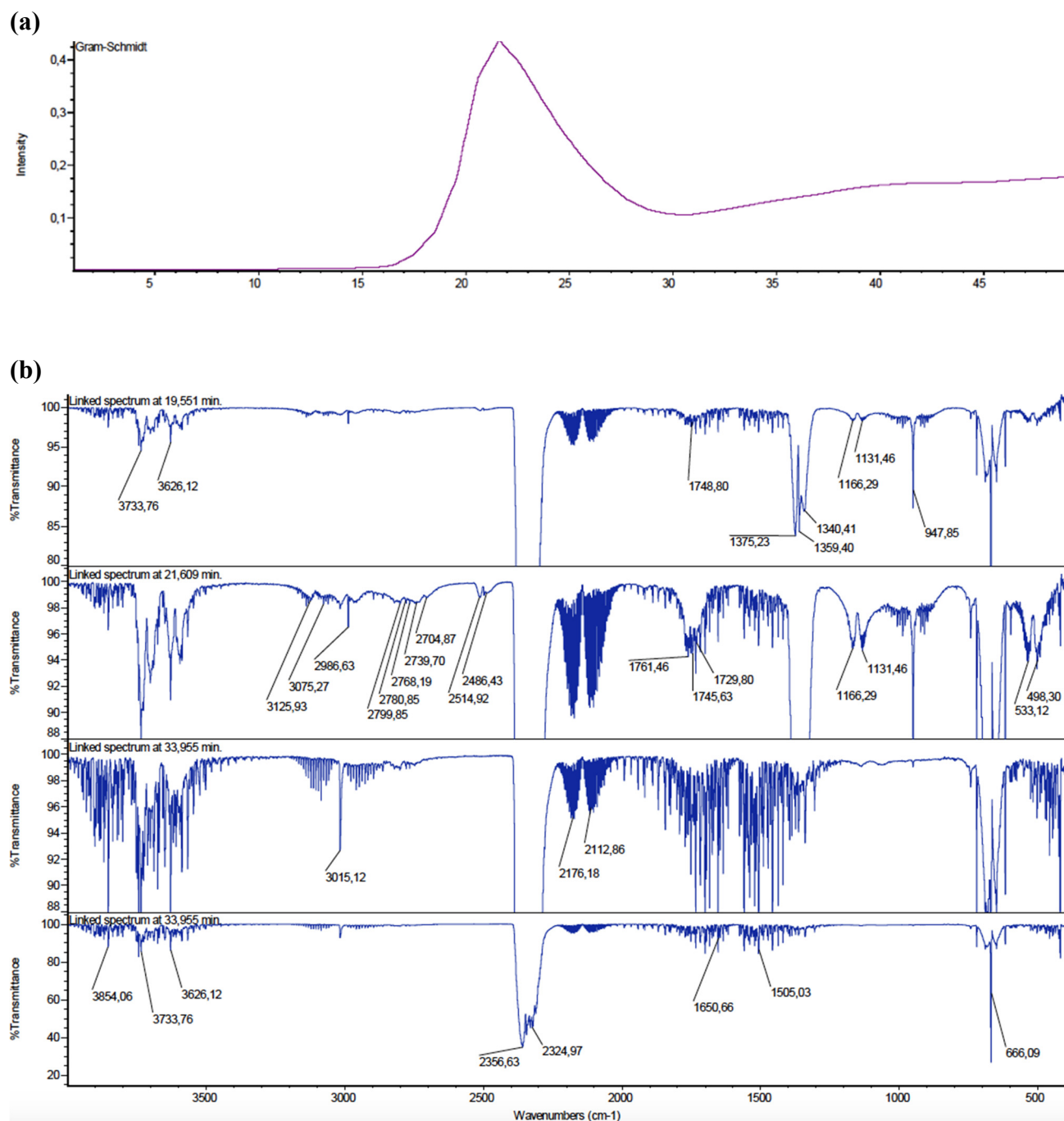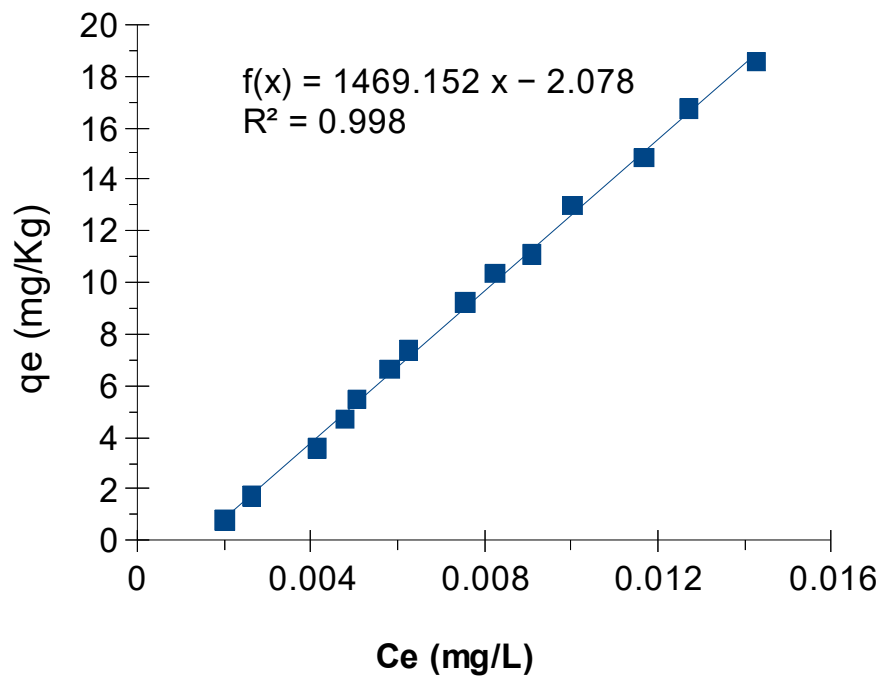
**(a)**



**(b)**



**Figure. S6.** IR-TGA of **pSt**. (a) Gram-Schmidt. (b) Most representative signals at three single time points 19.6 min, 21.6 min and 34.0 min. The delay between the TG and the FTIR detector is from 4 to 5 min.

(a)

f(x) = 1469.152 x − 2.078
R² = 0.998

qe (mg/Kg)

Ce (mg/L)

(b)

f(x) = 405.050 x − 0.485
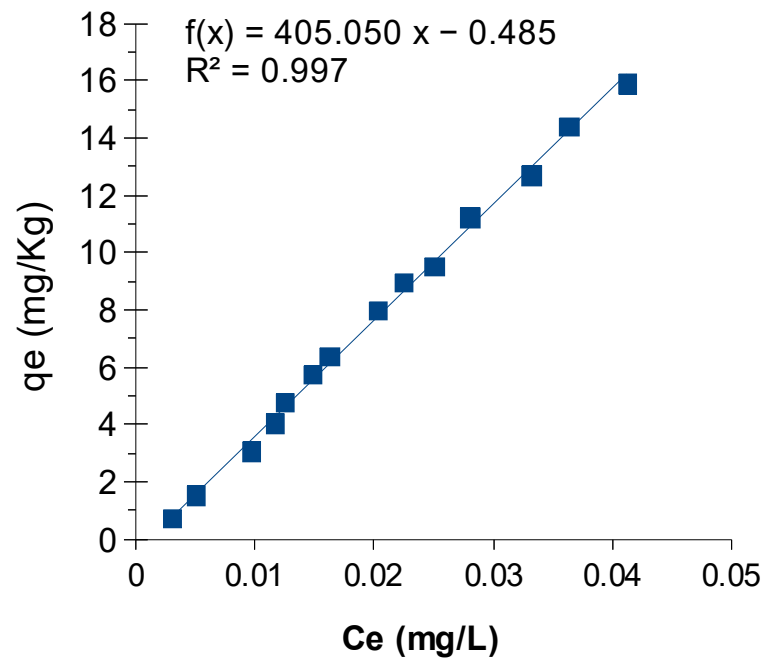R² = 0.997

qe (mg/Kg)

Ce (mg/L)

**Figure. S7.** Estimation of the sorption coefficient of CIP (a) and OFL (b) on **pSt**.
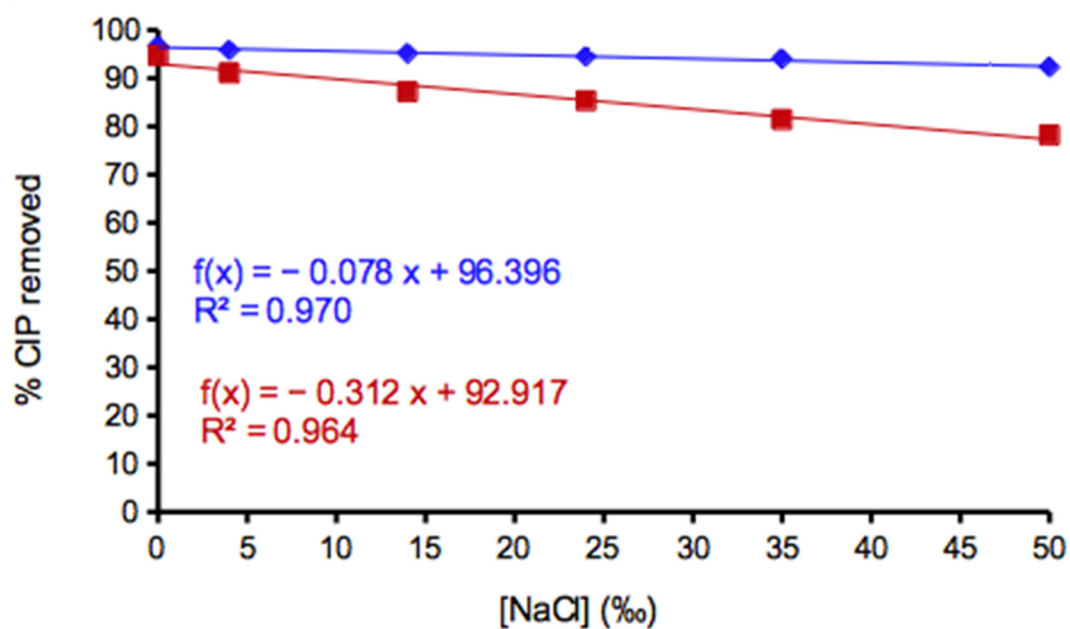
**Figure. S8.** Negative effect of the salinity on the sorption of CIP on **pSt** (red) and improvement of the performance by buffering to pH 8 (blue)

(a)
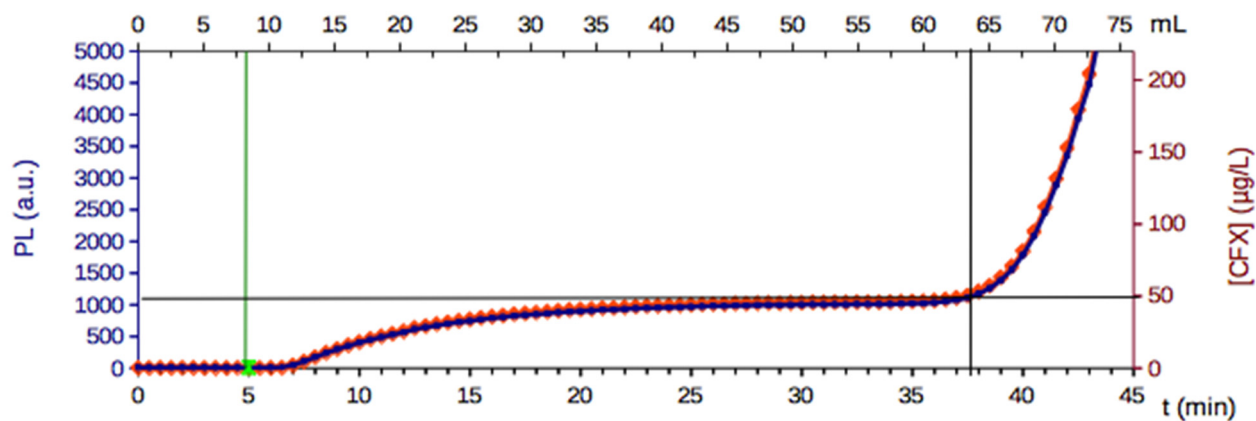


(b)
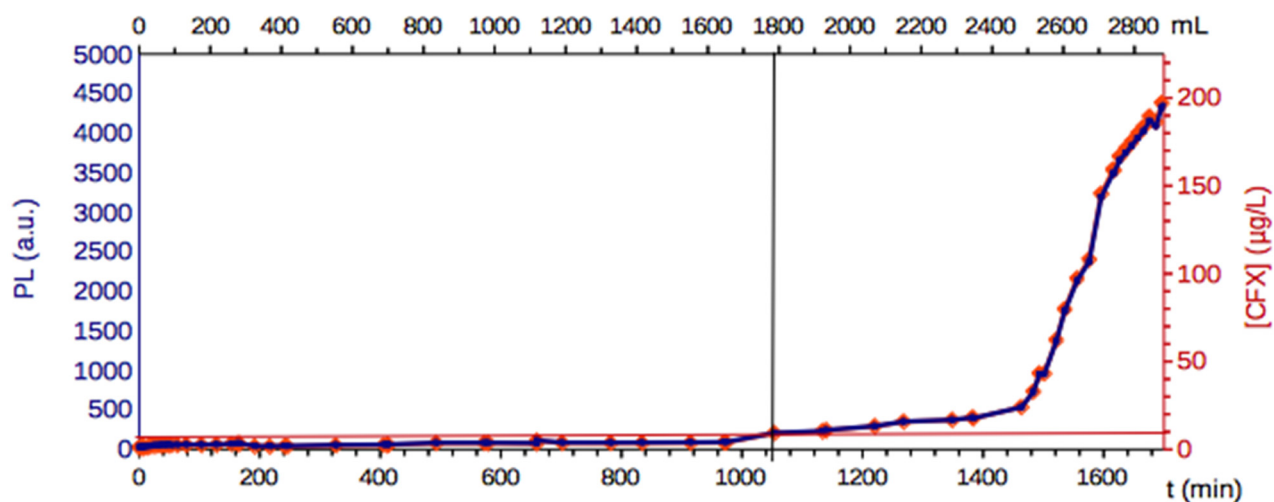


**Figure. S9.** Fixed bed studies of the sorption of CIP on **pSt**. Photoluminescence (arbitrary units, in blue) and concentration of CIP (µg/L, in red) of a solution of 10 mg/L (a) and 200 µg/L (b) flown through the regenerated **pSt** (0.5 g) packed into a 2.5 mL syringe. The green line in (a) marks the inition of pumping the solution of CIP.

**Table S1**. Equations of the isotherm model assayed for the fitting of the experimental sorption data as defined by ISOT_calc [31,43].

| Isotherm (# parameters) | Equation ($q_e$ = ...) | Parameter definition [43] |
|---|---|---|
| Langmuir (2) | $S_T \dfrac{K_L \cdot C_e}{1 + K_L \cdot C_e}$ | $S_T$ is maximum adsorption capacity <br> $K_L$ is affinity constant |
| Freundlich (2) | $K_F \cdot C_e^N$ | $K_F$ is adsorption potential <br> $N$ is strength constant associated to heterogeneity (for homogenous systems N=1) |
| Temkin (2) | $k_1 \cdot \ln(C_e) + k_2$ | $k_1$ and $k_2$ are constants of Temkin isotherm and $k_1$ is related to sorption heat |
| Vieth-Sladek (3) | $K_D \cdot C_e + \dfrac{S_T \cdot b \cdot C_e}{1 + b \cdot C_e}$ | $K_D$ and $b$ are Vieth-Sladek constants <br> $S_T$ is the maximum adsorption capacity |
| Redlich-Peterson (3) | $S_T \dfrac{k \cdot C_e}{1 + (k \cdot C_e)^N}$ | $S_T$ is maximum adsorption capacity <br> $k$ is related to constants of Redlich-Peterson model <br> $N$ ranges from 0 to 1 |
| 2-sites Langmuir (4) | $\dfrac{S_{T1} \cdot k_1 \cdot C_e}{1 + k_1 \cdot C_e} + \dfrac{S_{T2} \cdot k_2 \cdot C_e}{1 + k_2 \cdot C_e}$ | $S_{T1}$ and $S_{T2}$ are the maximum adsorption capacity for sites 1 and 2 <br> $K_1$ and $K_2$ are affinity constant for sites 1 and 2 |

**Table S2.** Elemental analysis of cross-linked polymers. Results are expressed as means ± SD(n = 3)

|         | pSt              | pDx              | pCD-Dx           |
|---------|------------------|------------------|------------------|
| **% C** | $41.04 \pm 1.387$ | $39.77 \pm 0.381$ | $40.13 \pm 0.255$ |
| **% H** | $7.45 \pm 0.236$  | $7.49 \pm 0.307$  | $7.81 \pm 0.116$  |
| **% S** | $7.16 \pm 0.453$  | $7.40 \pm 0.080$  | $7.51 \pm 0.163$  |

**Table S3.** Isotherm models that fail the non-linear fitting of the sorption of CIP and OFL on **pSt**.

| | Langmuir | Vieth-Sladek | Redlich-Petrson | 2 sites Langmuir |
|---|---|---|---|---|
| **CIP-pSt** | $S_T$=1.033x10$^3$ *r.s.d. (%)=1.6x10$^3$* $K_L$=1.119x10$^{-0}$ *r.s.d. (%)=1.6x10$^3$* *MWSE=4.82x10$^{-2}$* | $K_D$=1.144x10$^3$ *r.s.d. (%)=7.7x10$^0$* $S_T$=1.000x10$^{-1}$ *r.s.d. (%)=2.6x10$^6$* b=1.000x10$^0$ *r.s.d. (%)=2.6x10$^6$* *MWSE=4.71x10$^{-2}$* | $S_T$=2.619x10$^3$ *r .s.d. (%)=1.8x10$^6$* K=8.733x10$^{-1}$ *r.s.d. (%)=1.8x10$^6$* N=1.000x10$^0$ *r.s.d. (%)=2.6x10$^6$* *MWSE=4.71x10$^{-2}$* | $S_{T1}$=1.038x10$^3$ *r.s.d. (%)=1.8x10$^3$* $K_{L1}$=1.114x10$^0$ *r.s.d. (%)=1.8X10$^3$* $S_{T2}$=1.020x10$^3$ *r.s.d. (%)=2.7x10$^6$* $K_{L2}$=1.114x10$^{-3}$ *r.s.d. (%)=2.7x10$^6$* *MWSE=4.82x10$^{-2}$* |
| **OFL-pSt** | $S_T$=5.468x10$^5$ *r.s.d. (%)=1.2x10$^5$* $K_L$=6.381x10$^{-4}$ *r.s.d. (%)=1.2x10$^5$* *MWSE=1.29x10$^{-2}$* | $K_D$=3.666x10$^2$ *r.s.d. (%)=4.3x10$^0$* $S_T$=1.000x10$^0$ *r.s.d. (%)=1.3x10$^6$* b=1.000x10$^0$ *r.s.d. (%)=1.3x10$^6$* *MWSE=1.14x10$^{-2}$* | $S_T$=1.023x10$^3$ *r.s.d. (%)=8.9x10$^5$* K=7.164x10$^{-1}$ *r.s.d. (%)=8.9x10$^5$* N=1.000x10$^{-0}$ *r.s.d. (%)=1.3x10$^6$* *MWSE=1.14x10$^{-2}$* | $S_{T1}$=5.605x10$^5$ *r.s.d. (%)=5.1x10$^5$* $K_{L1}$=6.540x10$^{-4}$ *r.s.d. (%)=5.1X10$^5$* $S_{T2}$=5.468x10$^3$ *r.s.d. (%)=1.3x10$^6$* $K_{L2}$=6.381x10$^{-4}$ *r.s.d. (%)=1.3x10$^6$* *MWSE=1.14x10$^{-2}$* |

References

31. Beltrán, J.L.; Pignatello, J.J.; Teixidó, M. ISOT_Calc: A Versatile Tool for Parameter Estimation in Sorption Isotherms. *Comput. Geosci.* **2016**, *94*, 11–17. https://doi.org/10.1016/j.cageo.2016.04.008.
43. Majd, M.M.; Kordzadeh-Kermani, V.; Ghalandari, V.; Askari, A.; Sillanpää, M. Adsorption Isotherm Models: A Comprehensive and Systematic Review (2010−2020). *Sci. Total Environ.* **2022**, *812*, 151334. https://doi.org/10.1016/j.scitotenv.2021.151334.