# A comparative study on the performance of a polymeric resin and activated carbon for the adsorptive removal of diclofenac from water

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• Introduction
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• Results and Discussion
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# *Introduction*

**Analytical techniques confirmed the presence of ECs in natural waters**

**Pharmaceuticals are an especially worrying class**

**STPs non efficient in the removal of ECs**

**Water Framework Directive** *(2000/60/EC)* → **first list of priority substances**

↓

**Commission Proposal** *(31-1-2012)* → **regarding priority substances in the field of water policy**

↓

**Directive 2013/39/EU** → **diclofenac** **E2** **EE2**

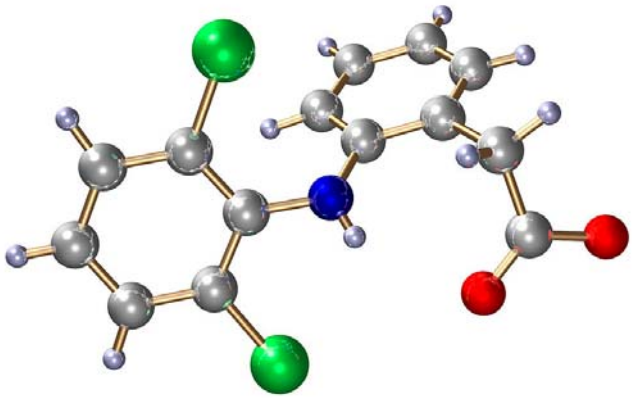
## *The aim of the work*

Study the **adsorptive removal of diclofenac** from ultrapure and waste water and to compare the adsorption kinetics and capacity of two types of adsorbents, namely a **polymeric resin** and **activated carbon**.

## *Main novelty*

Consider **adsorption from wastewater**, since most of the published works report adsorption results from ultrapure or distilled water.

# Adsorbent materials



***Diclofenac sodium (adsorbate)***

***Activated carbons***

GPP20
WP270

***Polymeric resin***

Sepabeads SP207

| Adsorbent | GPP20 | Pulsorb WP270 | Sepabeads SP207 |
|---|---|---|---|
| Matrix | Coal based activated carbon | Coal based steam activated carbon | Styrene and DVD copolymer |
| Colour | Black carbon | Black carbon | Yellowish opaque beads |
| Specific surface area ($m^2g^{-1}$) | 725 | 1050 | 630 |
| Mean particle diameter (mm) | 0.04 | 0.03 | 0.4 |

# Wastewater

**Secondary effluent from the STP of León (Spain)**

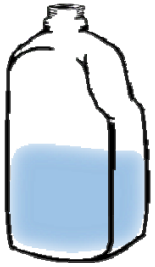
| pH | Conductivity ($\mu S\ cm^{-1}$) | TSS ($mg\ L^{-1}$) | $BOD_5$ ($mg\ L^{-1}$) | COD ($mg\ L^{-1}$) | NTK ($mg\ L^{-1}$) | $N\text{-}NH_4$ ($mg\ L^{-1}$) | $N\text{-}NO_3$ ($mg\ L^{-1}$) | $N\text{-}NO_2$ ($mg\ L^{-1}$) | Total $P\text{-}PO_4$ ($mg\ L^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 7.8±0.2 | 612±3 | 22±1 | 21±2 | 47±3 | 17±2 | 13.10±0.42 | 1.73±0.18 | 0.48±0.09 | 1.75±0.13 |

# Adsorption experiments

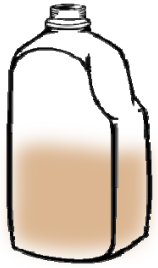
***Adsorption kinetic experiments*** ⟹ Time necessary to attain equilibrium ($t_{eq}$)

***Equilibrium experiments*** ⟹ Adsorption isotherm

**ultrapure water**

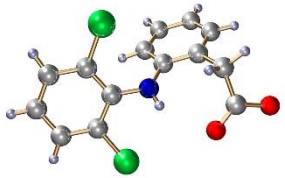


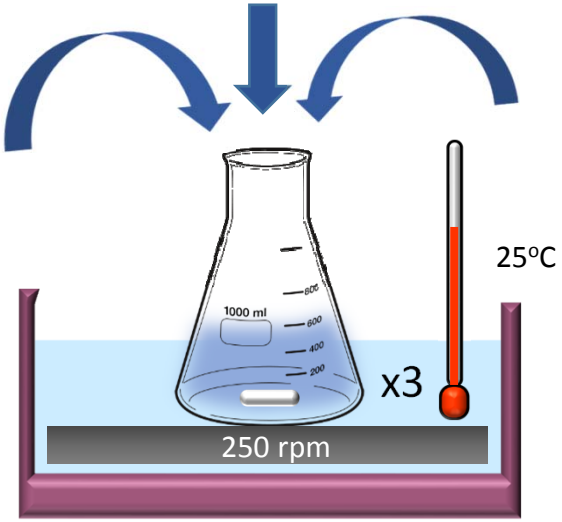
**or**



**wastewater**

**diclofenac sodium**






**activated carbon**

**or**

**polymeric resin**

**CONTROL –**

# Kinetic experiments

Analyse $C_t$ at different times

Mass balance → $q_t = (C_o - C_t)\frac{V}{W}$

Determine $q_t$ at different times

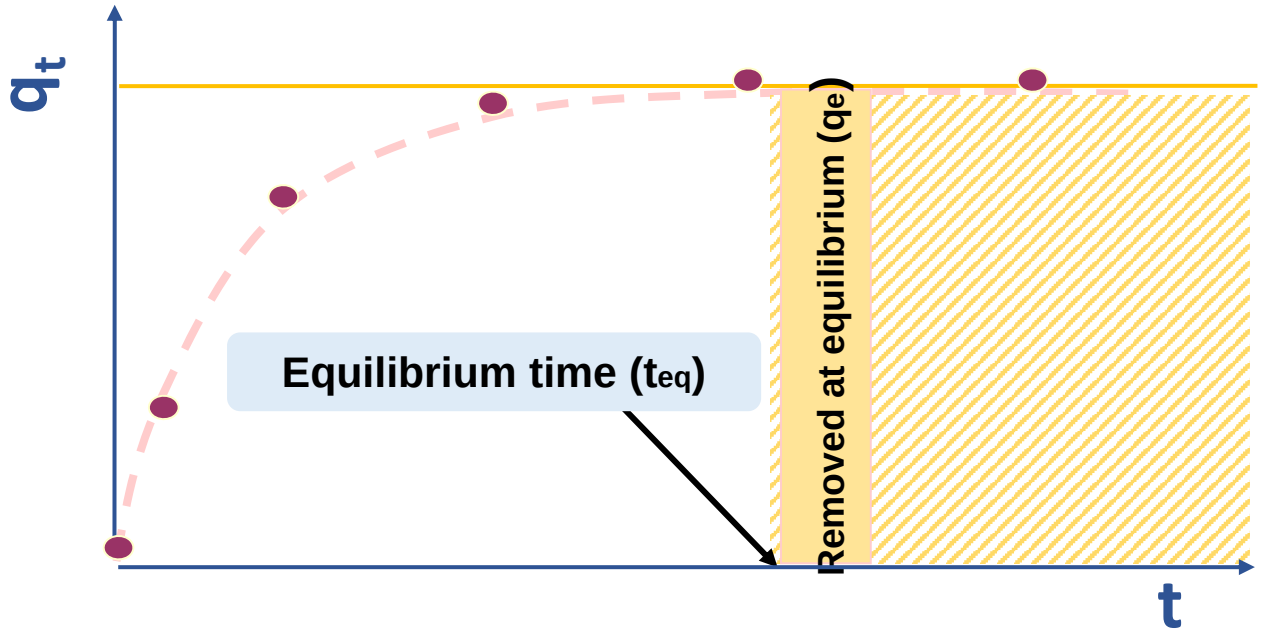
Kinetic curves →

***Pseudo first-order***

$$q_t = q_e(1 - e^{-k_1 t})$$

***Pseudo second-order***

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$



# Equilibrium experiments

Analyse $C_e$ at different masses of adsorbent

Mass balance ⟹ $q_e = (C_0 - C_e)\frac{V}{W}$

Determine $q_e$ at different masses

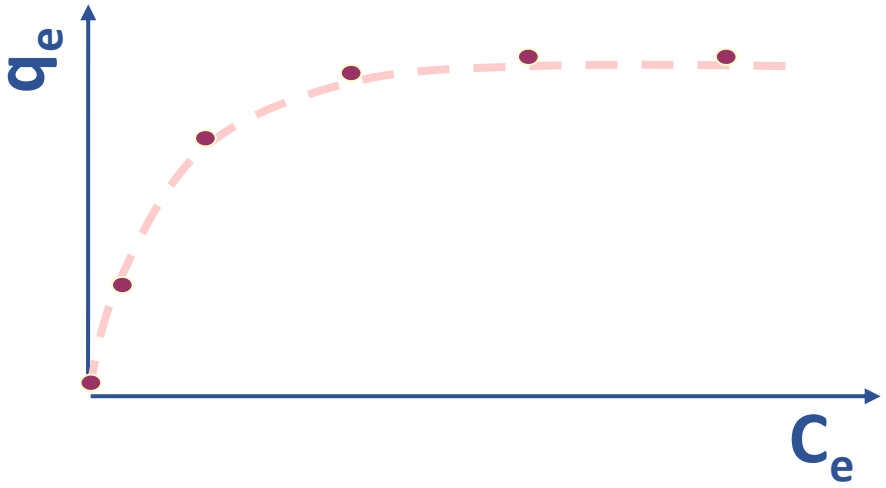
Adsorption isotherms ⟹

***Freundlich isotherm***

$$q_e = K_F C_e^{1/n}$$

***Langmuir isotherm***

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$




***Langmuir-Freundlich isotherm***

$$q_e = \frac{Q_m K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}}$$

# Results and Discussion

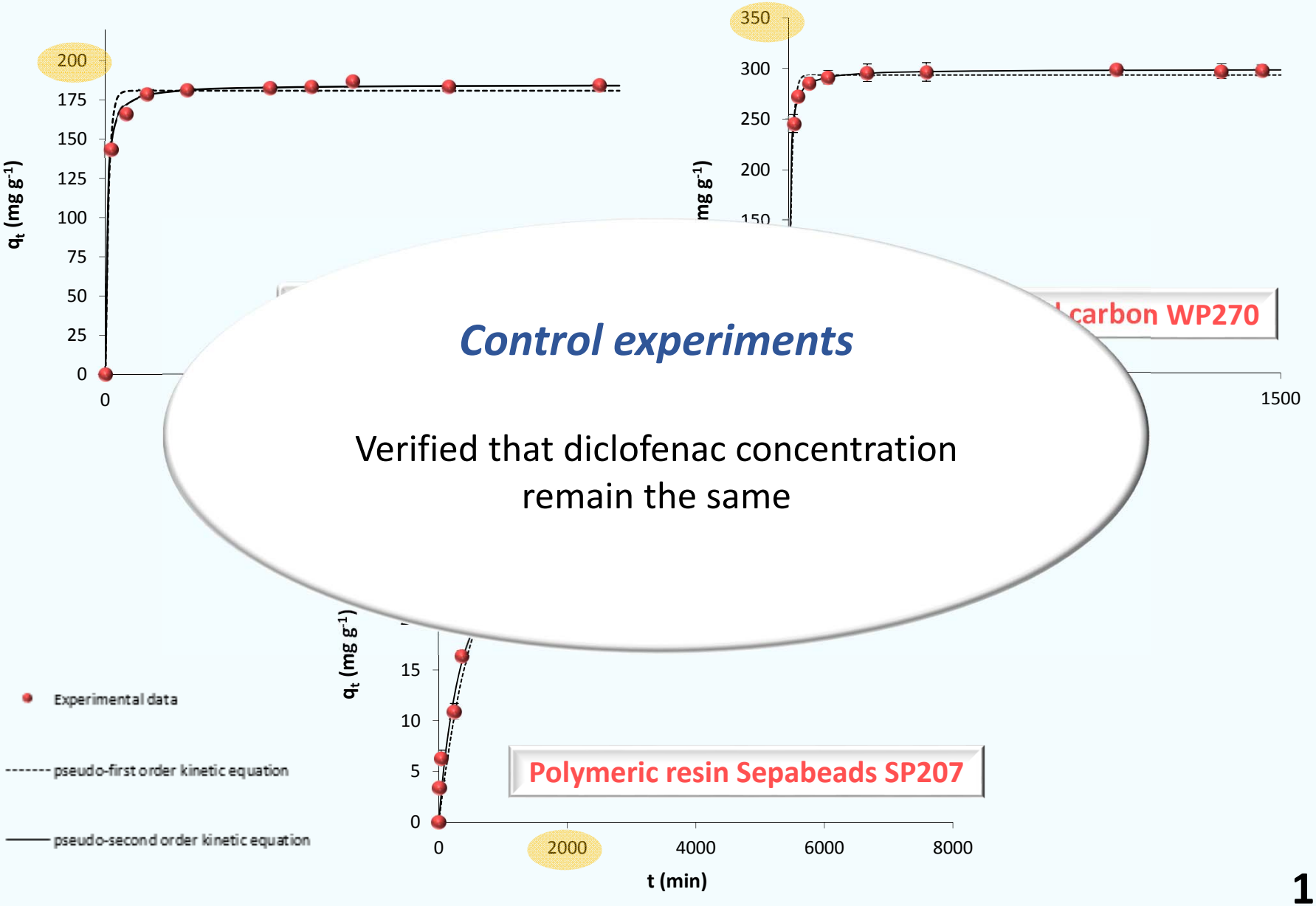
***Kinetic results*** *on the adsorptive removal of diclofenac from:*

- Ultrapure water
- Wastewater

***Equilibrium results*** *on the adsorptive removal of diclofenac from*:

- Ultrapure water
- Wastewater

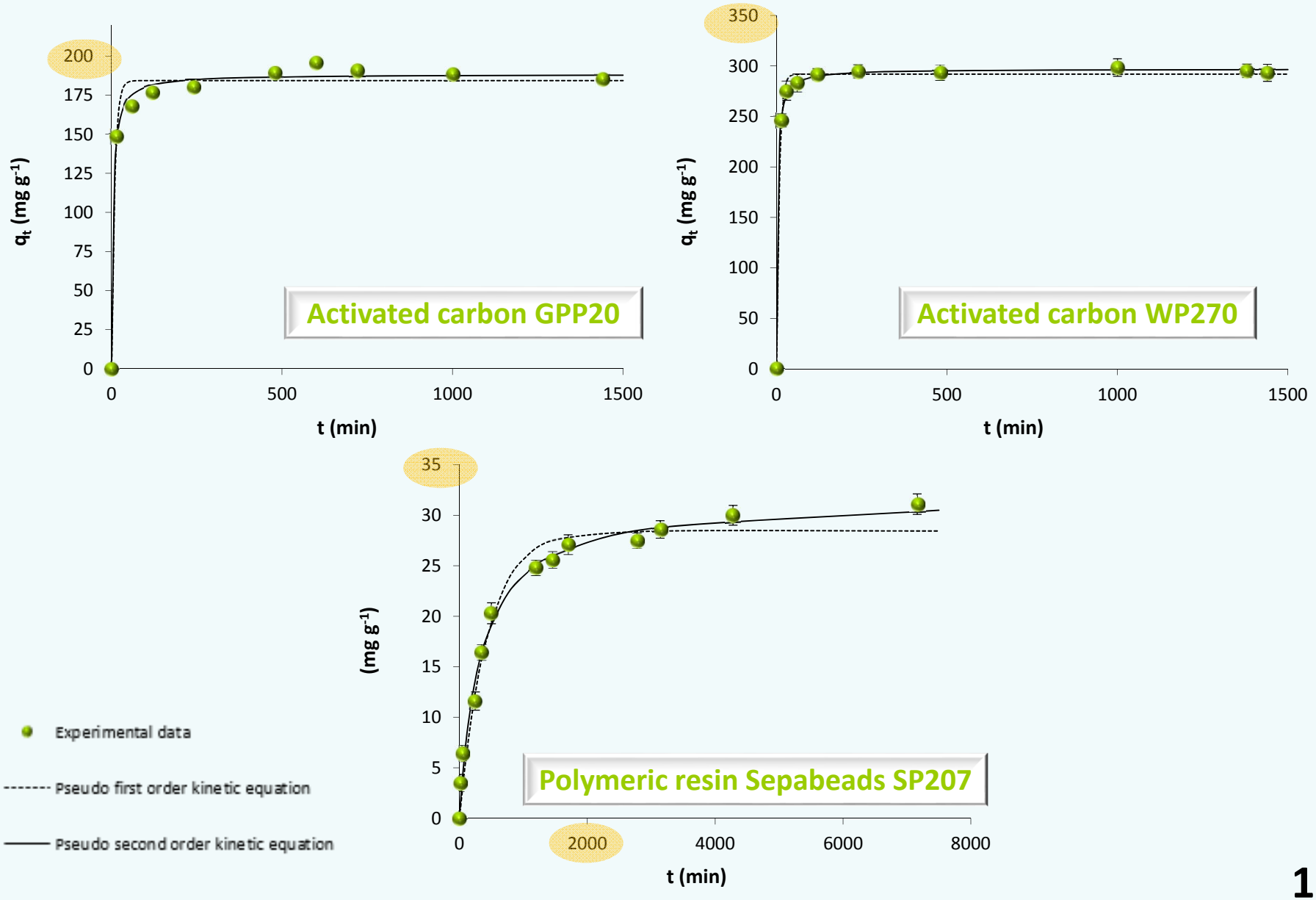
# Kinetic results from ultrapure water




## Control experiments

Verified that diclofenac concentration remain the same

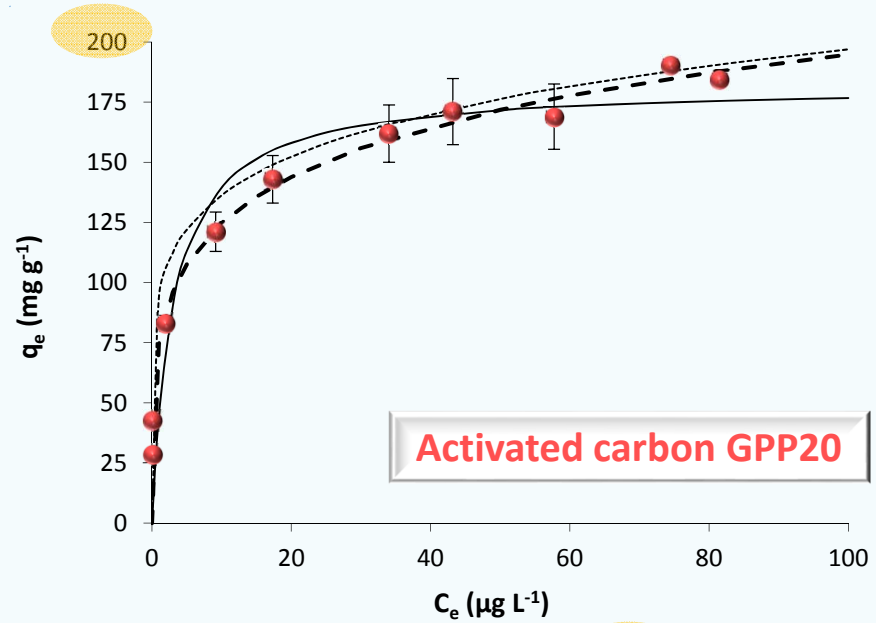
# Kinetic results from wastewater

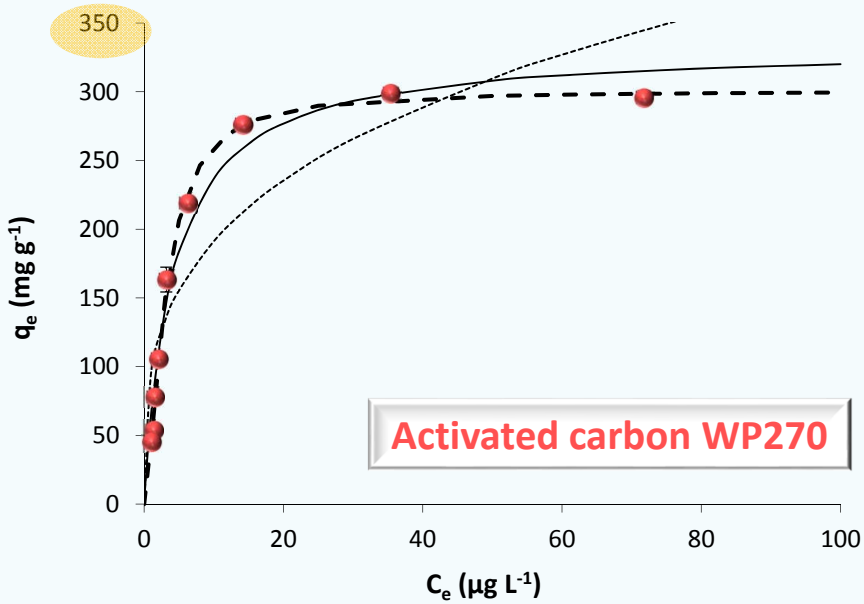


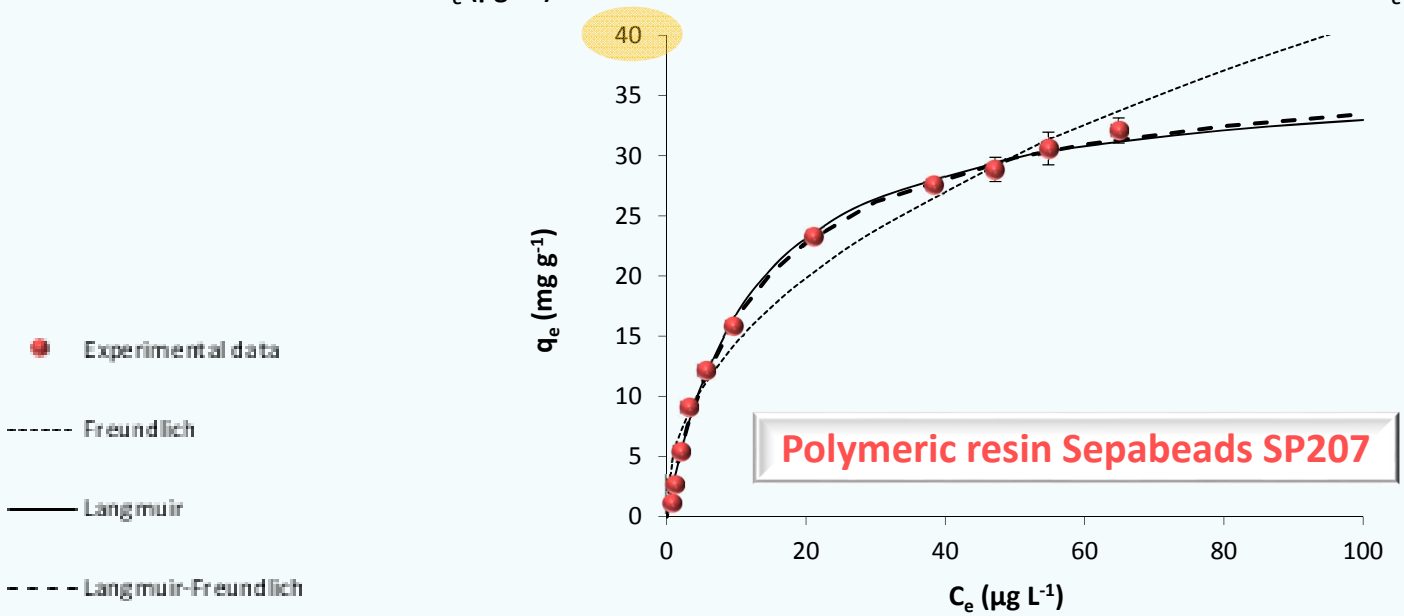
# Kinetic parameters

| | | GPP20 | | WP270 | | SP207 | |
|---|---|---|---|---|---|---|---|
| | | UPW | WW | UPW | WW | UPW | WW |
| *pseudo-first order* | $k_1$ (min$^{-1}$) | 0.104 ± 0.011 | 0.108 ± 0.015 | 0.115 ± 0.008 | 0.119 ± 0.007 | 0.0017 ± 0.0002 | 0.0023 ± 0.0003 |
| | $q_e$ (mg g$^{-1}$) | 180.90 ± 2.13 | 184.40 ± 2.96 | 293.50 ± 2.27 | 291.90 ± 1.89 | 30.64 ± 0.83 | 28.45 ± 0.84 |
| | $R^2$ | 0.9903 | 0.9820 | 0.996 | 0.9972 | 0.9734 | 0.9692 |
| | $S_{xy}$ | 5.99 | 8.33 | 6.16 | 5.14 | 1.92 | 1.98 |
| *pseudo-second order* | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.00119 ± 0.00010 | 0.00118 ± 0.00020 | 0.00106 ± 0.00003 | 0.00117 ± 0.00008 | **0.00007 ± 0.000009** | **0.00010 ± 0.00001** |
| | $q_e$ (mg g$^{-1}$) | 188.70 ± 1.01 | 188.40 ± 2.09 | 299.1 ± 0.45 | 296.90 ± 1.09 | 33.94 ± 0.83 | 31.83 ± 0.92 |
| | $R^2$ | **0.9983** | **0.9930** | **0.9999** | **0.9993** | **0.9869** | **0.9835** |
| | $S_{xy}$ | **2.50** | **5.22** | **1.06** | **2.58** | **1.35** | **1.45** |

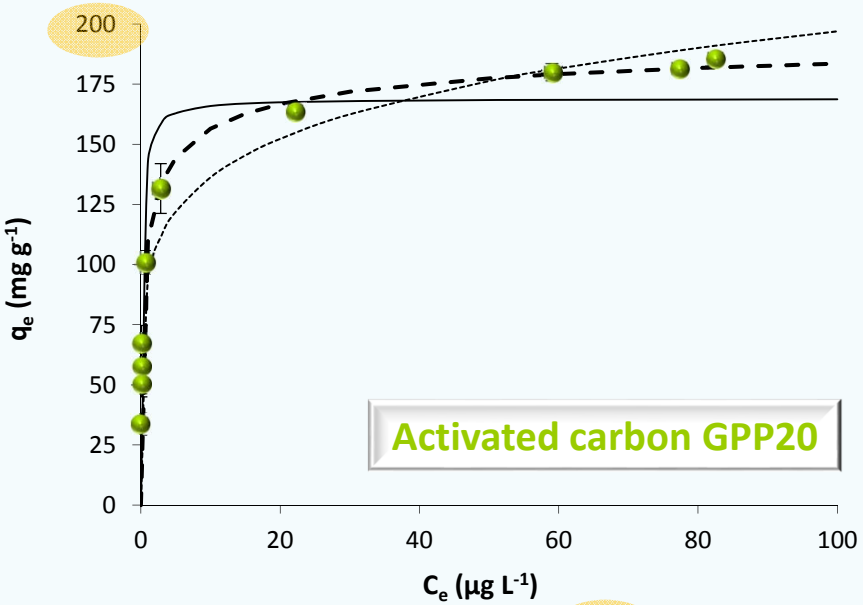
# Equilibrium results from ultrapure water

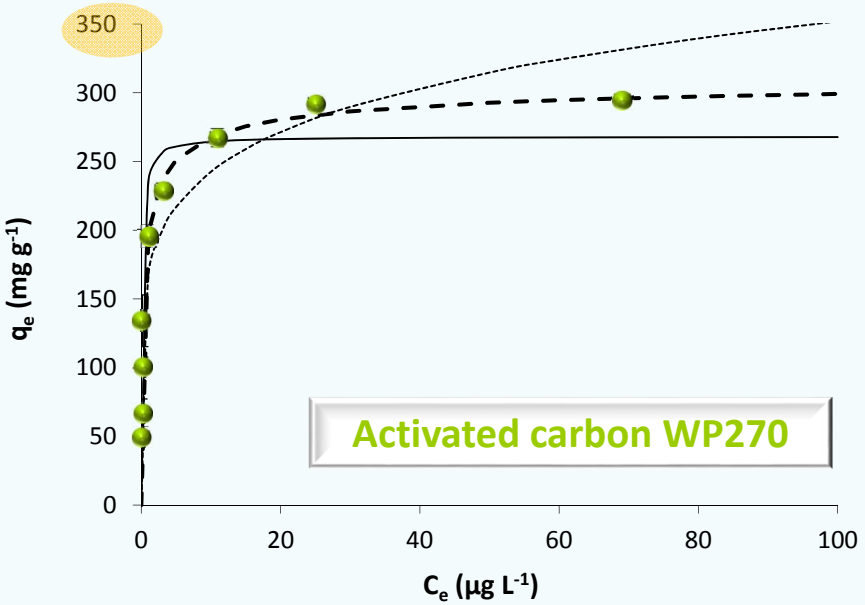


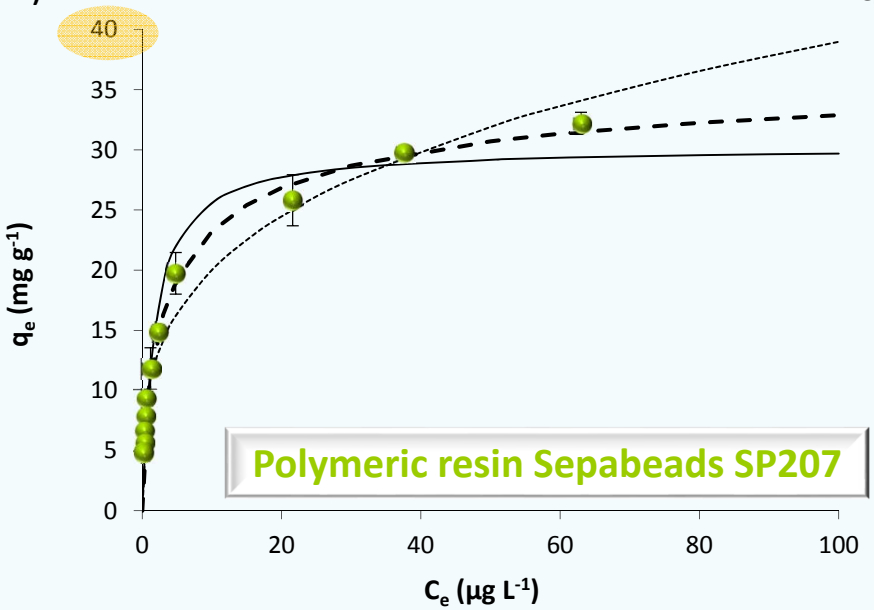



# Equilibrium results from wastewater




Experimental data

Freundlich

Langmuir

Langmuir-Freundlich

# Equilibrium parameters

| | | GPP20 | | WP270 | | SP207 | |
|---|---|---|---|---|---|---|---|
| | | UPW | WW | UPW | WW | UPW | WW |
| *Freunlich* | $K_F$ [mg $g^{-1}$ (mg $L^{-1}$)$^{-1/n}$] | 74.53 ± 2.73 | 94.30 ± 5.39 | 96.07 ± 19.17 | 167.20 ± 12.05 | 5.12 ± 0.70 | 10.28 ± 0.63 |
| | *n* | 4.689 ± 0.214 | 6.252 ± 0.598 | 3.343 ± 0.678 | 6.186 ± 0.8822 | 2.212 ± 0.182 | 3.454 ± 0.225 |
| | $R^2$ | 0.9932 | 0.9540 | 0.8116 | 0.9074 | 0.9728 | 0.9689 |
| | $S_{yx}$ | 5.14 | 13.72 | 48.62 | 31.30 | 2.04 | 1.85 |
| *Langmuir* | $Q_m$ (mg $g^{-1}$) | 182.10 ± 11.06 | 169.00 ± 8.10 | 333.00 ± 15.82 | 268.10 ± 12.78 | 36.90 ± 0.86 | 30.23 ± 1.19 |
| | $K_L$(L $mg^{-1}$) | 0.327 ± 0138 | 5.334 ± 1.440 | 0.246 ± 0.038 | 7.157 ± 1.890 | 0.084 ± 0.006 | 0.551 ± 0.078 |
| | $R^2$ | 0.9019 | 0.9252 | 0.9712 | 0.9371 | 0.9959 | 0.9695 |
| | $S_{yx}$ | 19.57 | 17.49 | 19.02 | 25.79 | 0.89 | 1.84 |
| *Langmuir-Freundlich* | $Q_m$ (mg $g^{-1}$) | 445.50 ± 254.70 | 202.60 ± 12.59 | 300.80 ± 5.17 | 315.00 ± 18.64 | **38.63 ± 2.59** | **37.94 ± 2.31** |
| | $K_{LF}$ [mg $g^{-1}$ (mg $L^{-1}$)$^{-1/n}$] | 0.158 ± 0.086 | 1.198 ± 0.259 | 0.182 ± 0.015 | 1.698 ± 0.422 | **0.087 ± 0.008** | **0.385 ± 0.038** |
| | *n* | 3.670 ± 0.495 | 2.208 ± 0.302 | 0.646 ± 0.038 | 1.912 ± 0.261 | 1.070 ± 0.092 | 1.628 ± 0.126 |
| | $R^2$ | **0.9952** | **0.9896** | **0.9969** | **0.9868** | **0.9962** | **0.9953** |
| | $S_{yx}$ | **4.62** | **6.98** | **6.72** | **12.78** | **0.81** | **0.76** |

# Conclusions

- Adsorption kinetics of diclofenac onto activated carbons and polymeric resin was described by the pseudo second-order kinetic model and no differences were determined between ultrapure and waste water respect $k_2$ parameter.

- The three parameter Langmuir-Freundlich isotherm fitted equilibrium adsorption results onto the three adsorbent materials and no differences were determined between ultrapure or wastewater in the $Q_m$ parameter.

- Steeper isotherms were obtained in wastewater than ultrapure water, which points to an increased affinity for diclofenac in wastewater for all the adsorbents.

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