# Valorization of rice husk chars as adsorbent: characterization and utilization in a novel reactor operating mode

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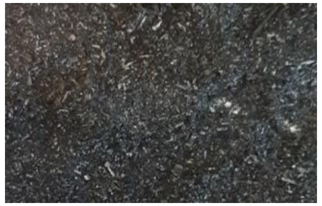
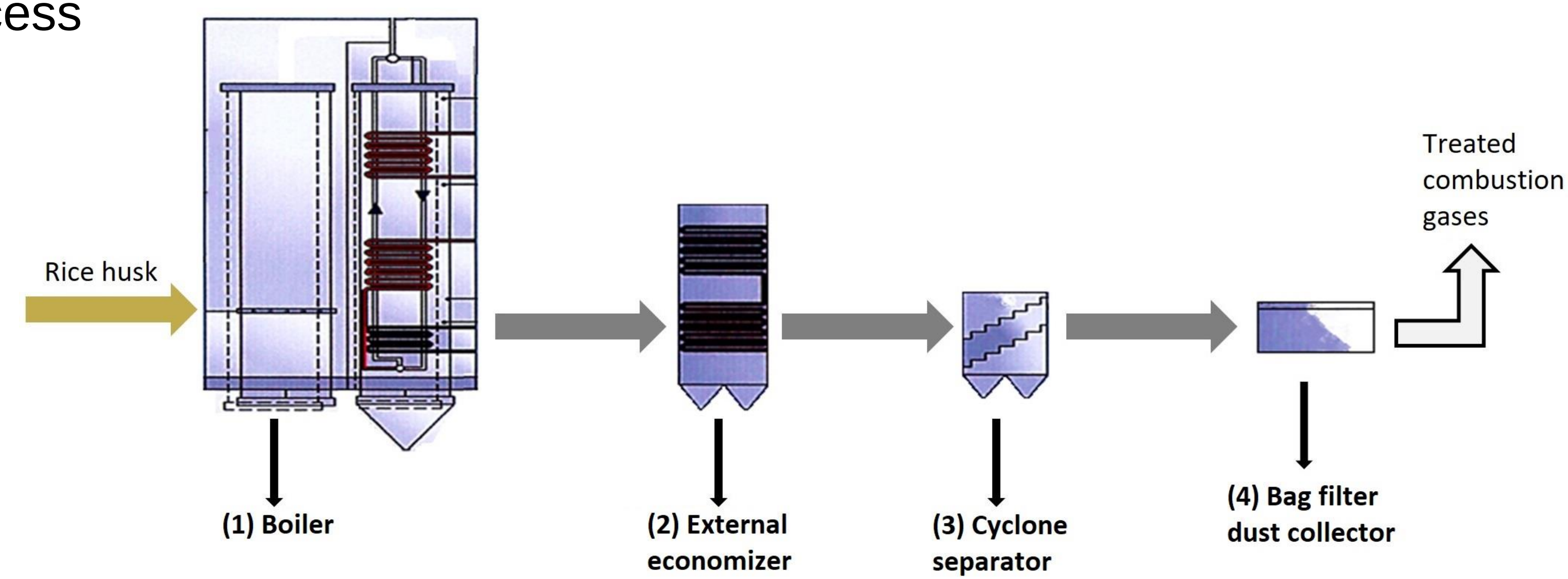
# Rice husks

- Rice husks are incinerated to produce energy and steam
- Problem: Rice husk char



- Possible uses:
  - Silica production
  - Cement
  - Adsorbent

- Process



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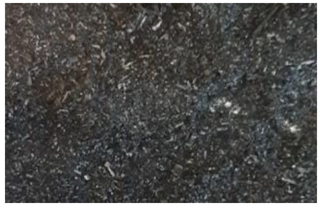

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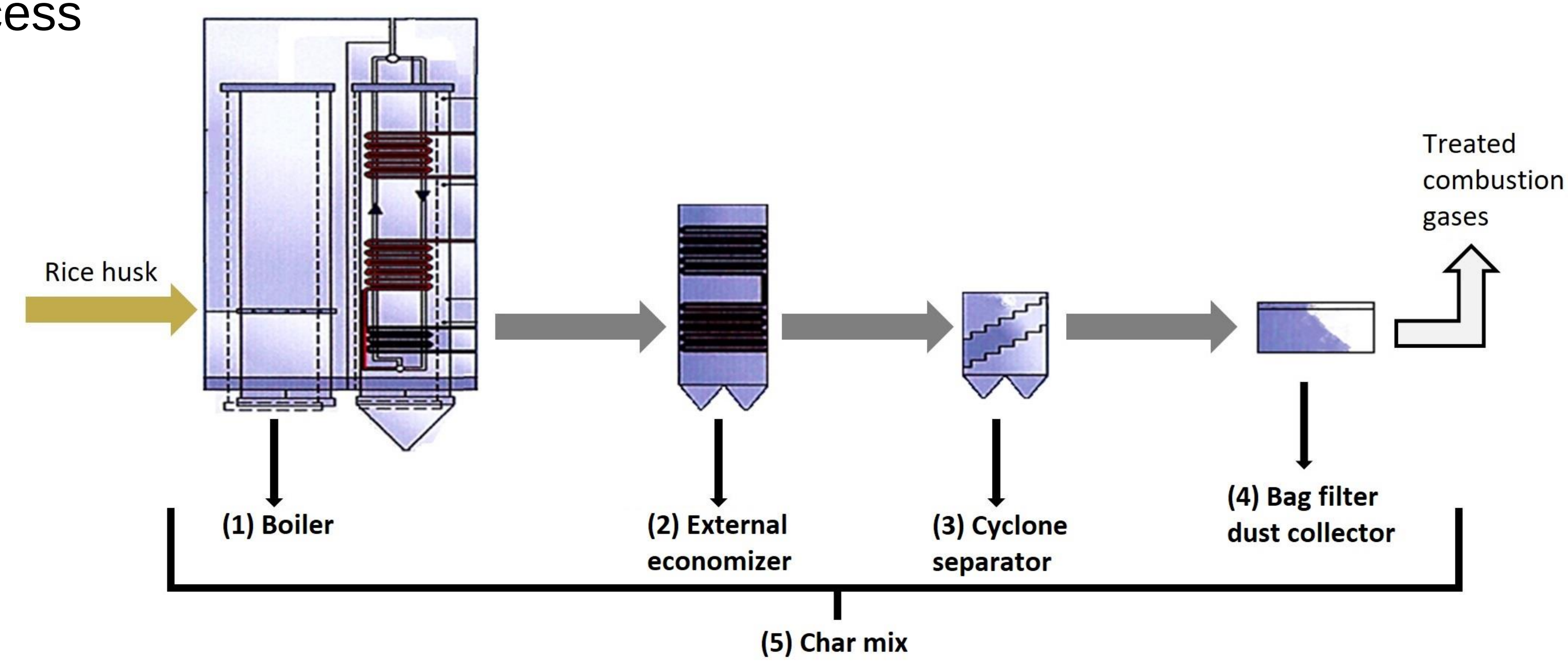


# Aims and objectives

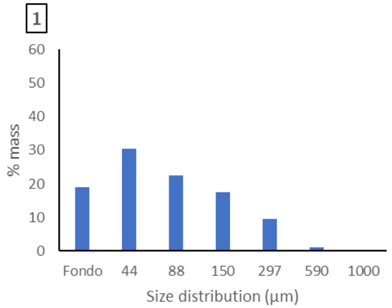
- Study the rice husk chars obtained in the industry as adsorbents to remove compounds from water
- Evaluate the use of the rice husk char in an adsorption reactor, and model its operation

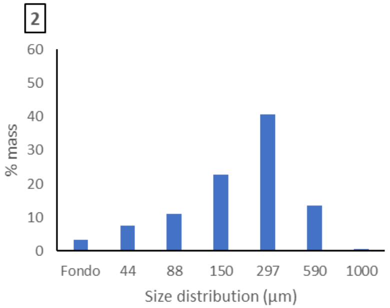
# Characterization of rice husk chars

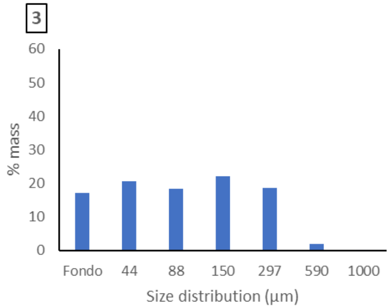
## Density

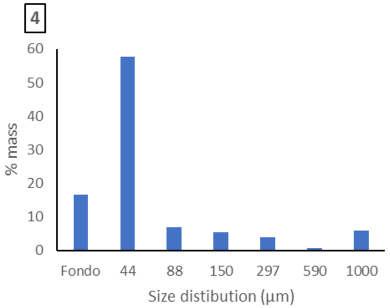
| Char | Density (g/cm³) |
|---|---|
| Boiler (1) | 0.37 |
| Economizer (2) | 0.15 |
| Cyclone separator (3) | 0.19 |
| Bag filter (4) | 0.21 |
| Char mix (5) | 0.19 |

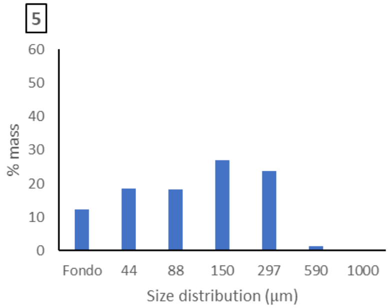
## Particle size distribution (µm)



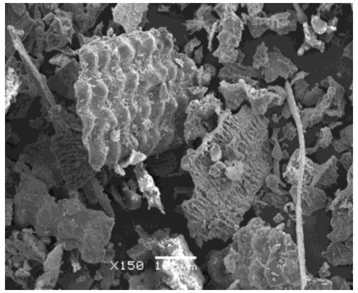



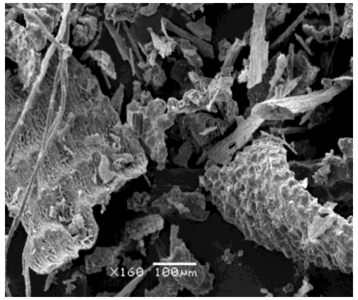




## Scanning electron microscopy(SEM)

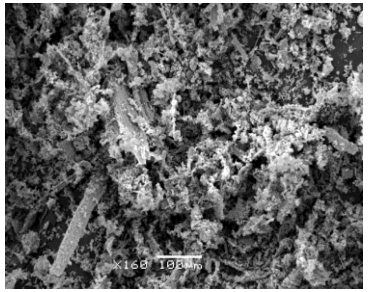
Boiler



Cyclone separator

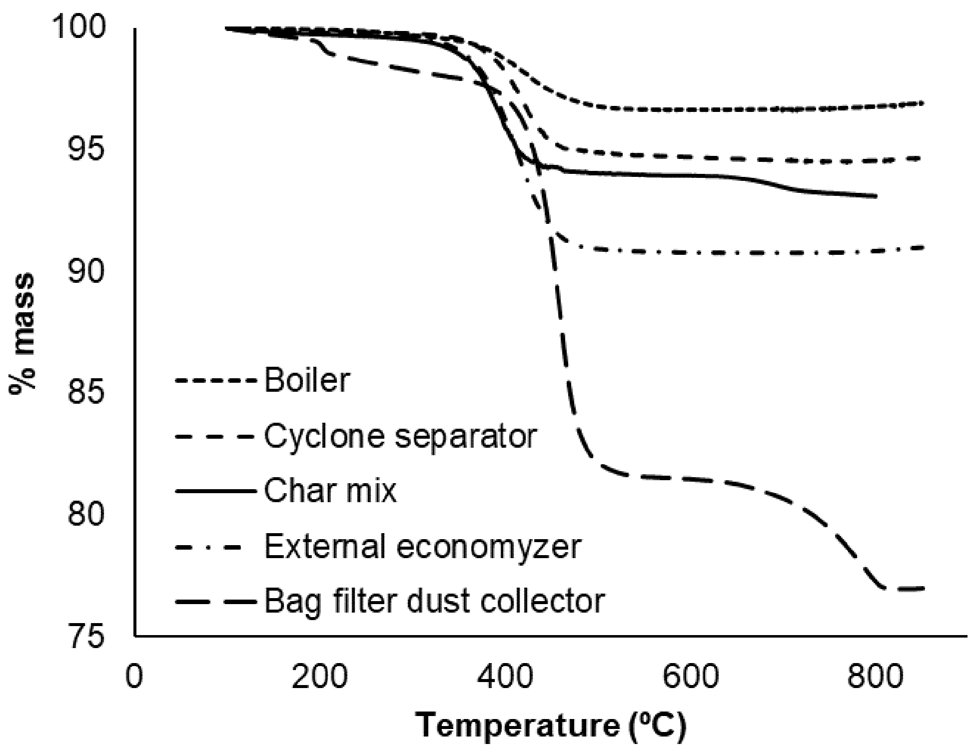


Bag filter



# Characterization of rice husk chars

Termogravimetric analysis




Energy dispersive spectroscopy (EDS)

| Char | % C | % O | % Si | % Others |
|---|---|---|---|---|
| **Boiler** | 1.7 | 43 | 40 | 15.3 |
| **Economizer** | 2.7 | 39 | 42 | 16.3 |
| **Cyclone separator** | 0.3 | 37 | 49 | 13.7 |
| **Bag filter** | 17 | 35 | 22 | 26 |
| **Char mix** | n/d | 44 | 43 | 13 |

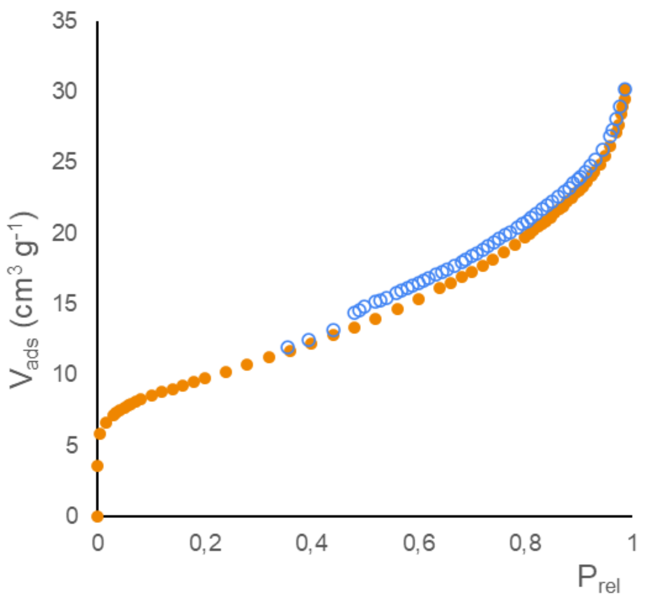
Elemental analysis

| Char | % N | % C | % H | % S |
|---|---|---|---|---|
| **Boiler** | 0.00 | 2.84 | 0.58 | 0.00 |
| **Economizer** | 0.00 | 7.59 | 0.79 | 0.00 |
| **Cyclone separator** | 0.00 | 5.56 | 0.67 | 0.00 |
| **Bag filter** | 0.09 | 17.02 | 0.83 | 0.76 |
| **Char mix** | 0.00 | 5.89 | 0.60 | 0.30 |

% mass

# Characterization of rice husk chars

BET area and pore volume




| Char | BET area ($m^2$ / g) | Microporous volume ($cm^3$ / g) | Total pore volumen ($cm^3$ / g) |
|---|---|---|---|
| **Boiler** | 11 | 0.0048 | 0.018 |
| **Economizer** | 56 | 0.011 | 0.055 |
| **Cyclone separator** | 54 | 0.01 | 0.06 |
| **Bag filter** | 45 | 0.071 | 0.075 |
| **Char mix** | 35 | 0.003 | 0.045 |

X-ray diffraction (XRD)

| Char | $SiO_2$ |
|---|---|
| **Boiler** | Crystalline |
| **Economizer** | Amorphous |
| **Cyclone separator** | Amorphous |
| **Bag filter** | Amorphous |
| **Char mix** | Amorphous |

# Adsorption capacity / Adsorption kinetics

## Methylene blue

Initial concentration: 10 – 250 mg/L
Char: 100 mg
Volume: 50 mL

| Char | $q_{max}$ (mg/g) |
|---|---|
| Boiler | 10.6 |
| Economizer | 42.4 |
| Cyclone separator | 28.2 |
| Bag filter | 56.5 |
| Char mix | 34.9 |
| Activated carbon | 126.9 |
| Rice husk char (*) | 246 |

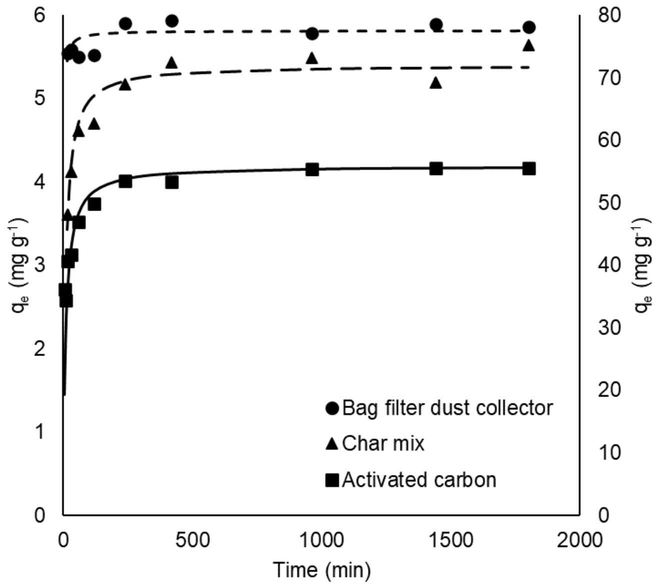
## Phenol

Initial concentration: 10 –1000 mg/L
Char: 100 mg
Volume: 50 mL

| Char | $q_{max}$ (mg/g) |
|---|---|
| Bag filter | 13.4 |
| Char mix | 8.3 |
| Activated carbon | 102 |

## Pseudo second order model

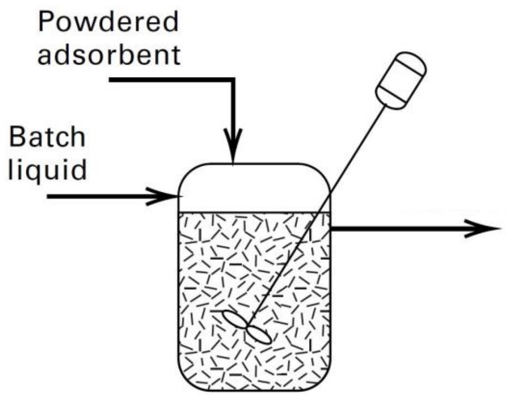
$$q(t) = \frac{q_e^2\ k_2\ t}{1 + q_e\ k_2\ t}$$




| | $C_0$ (mg/L) | $q_e$ (mg/g) | $k_2$ (g/mgmin) |
|---|---|---|---|
| *Phenol* | | | |
| Char mix | 10 | 2.5 | 0.068 |
| | 20 | 2.79 | 0.0071 |
| | 50 | 5.52 | 0.013 |

* Lacuesta, J., *et al*. (2020). Rice Husk Bio-Chars as Adsorbent for Methylene Blue and Ethinylestradiol from Water. *Journal of Renewable Materials*, *8*(3), 275.

# Stirred tank adsorption reactors-batch mode




Seader *et al* (2011), *Separation Process Principles*

Complete solid removal → Partial solid retention → Complete solid retention

☑ Highest adsorption rate

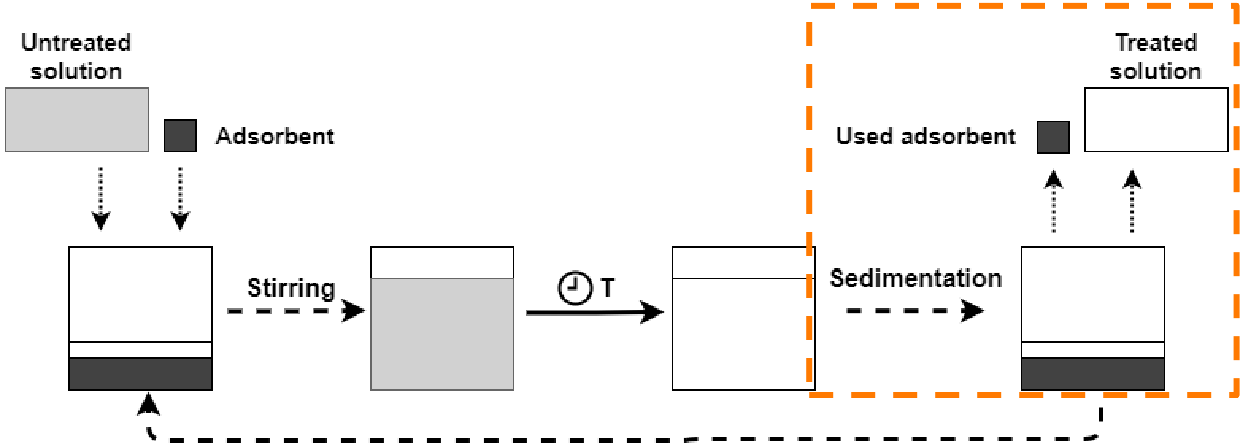
☒ Underutilization of adsorbent capacity

☑ Maximum utilization of adsorbent

☒ Difficult to control

# Parcially conserved batch (PCB)

Partial solid retention

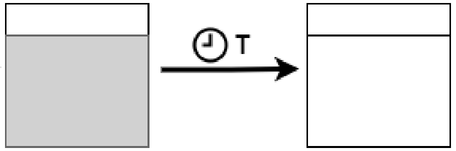



$$f_m = \frac{m_e}{m}$$ Fraction of adsorbent removed

$$f_V = \frac{V_e}{V}$$ Fraction of liquid removed

# Mathematical dynamic model

Cycle 1:




$$C_1(t) = C_0 - q(t)\frac{m}{V}$$

Removed amount per volume at time *t*

Initial concentration

Cycle 2:

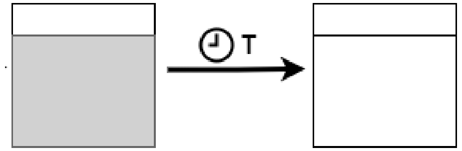
$$C_2(t) = \left(C_0 - q(T)\frac{m}{V}\right)(1 - f_V) + C_0 f_V - (q(t) - q(T))\frac{m}{V}(1 - f_m) - q(t - T)\frac{m}{V} f_m$$

$$C_2(t) = \left(C_0 - q(T)\frac{m}{V}\right)\widehat{f_V} + C_0 f_V - (q(t) - q(T))\frac{m}{V}\widehat{f_m} - q(t - T)\frac{m}{V} f_m$$

| Parameters | |
|---|---|
| $C_0$ | Initial concentration of the solution (mg/L) |
| $m$ | Adsorbent mass (g) |
| $V$ | Reactor volumen (L) |
| $m_e$ | Adsorbent mass removed each cycle (g) |
| $V_e$ | Treated solution volumen removed from the reactor each cycle (L) |
| $\widehat{f_V}$ | $1 - f_V$ |
| $\widehat{f_m}$ | $1 - f_m$ |
| **Variables** | |
| $q(t)$ | Amount adsorbed at time t (mg/g) |
| $C_i(t)$ | Compound concentration inside the reactor during cycle *i* at time t (mg/L) |

# Mathematical dynamic model

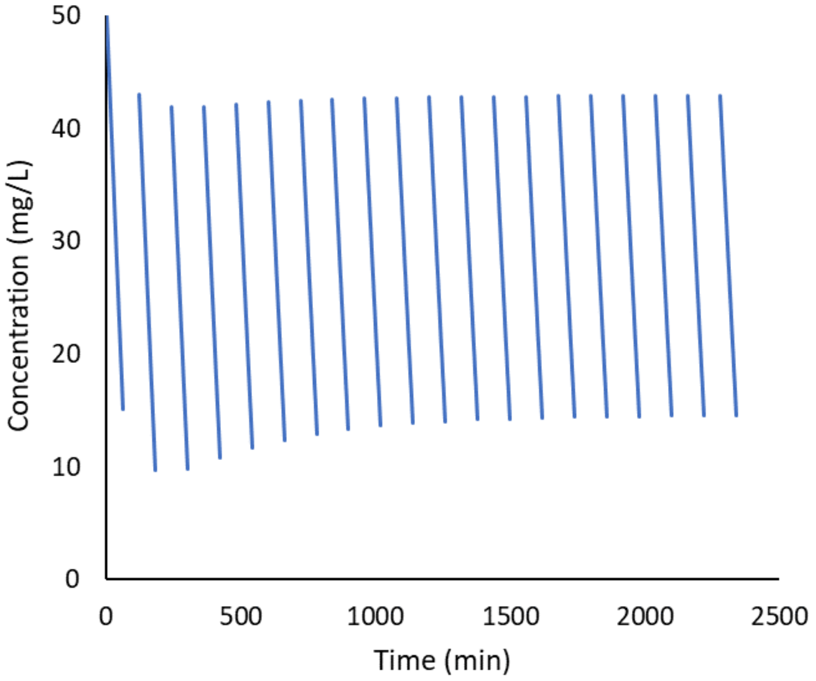
Cycle n:

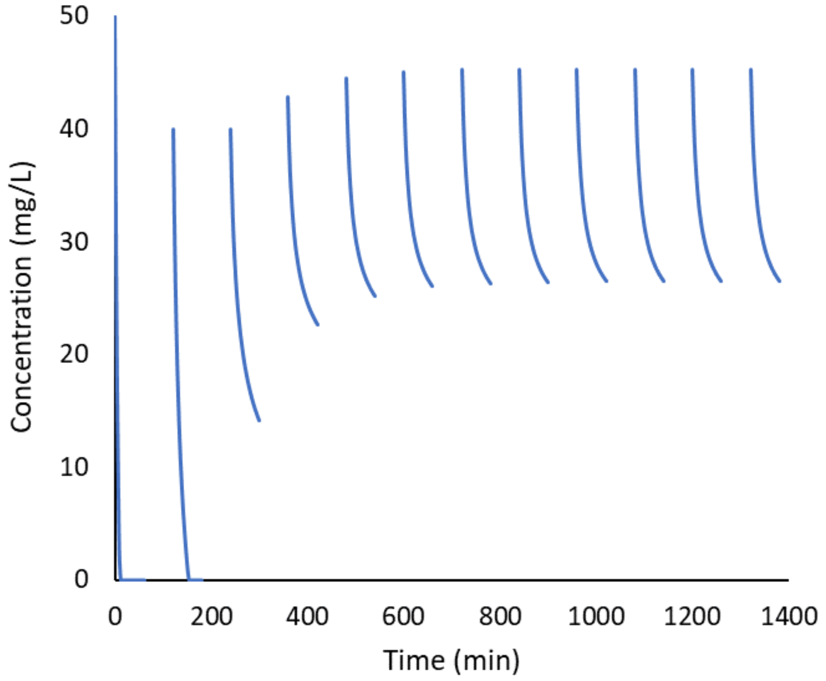



$$
\begin{aligned}
C_n(t) = {} & C_0 \widehat{f_V}^{\,n-1} + C_0 f_V \sum_{j=0}^{n-2} \widehat{f_V}^{\,j} - q(T)\frac{m}{V}\left(\widehat{f_V} - \widehat{f_m}\right)\left(\widehat{f_V}^{\,n-2} + f_m \sum_{j=0}^{n-3} \widehat{f_V}^{\,j}\right) \\
& - q(2T)\frac{m}{V}\left(\widehat{f_V} - \widehat{f_m}\right)\widehat{f_m}\left(\widehat{f_V}^{\,n-3} + f_m \sum_{j=0}^{n-4} \widehat{f_V}^{\,j}\right) \\
& - q(3T)\frac{m}{V}\left(\widehat{f_V} - \widehat{f_m}\right)\widehat{f_m}^{\,2}\left(\widehat{f_V}^{\,n-4} + f_m \sum_{j=0}^{n-5} \widehat{f_V}^{\,j}\right) \\
& - \cdots - q((n-1)T)\frac{m}{V}\left(\widehat{f_V} - \widehat{f_m}\right)\widehat{f_m}^{\,n-2} \\
& - q(t)\frac{m}{V}\widehat{f_m}^{\,n-1} - q(t-T)\frac{m}{V} f_m \widehat{f_m}^{\,n-2} - q(t-2T)\frac{m}{V} f_m \widehat{f_m}^{\,n-3} \\
& - \cdots - q(t-(n-1)T)\frac{m}{V} f_m
\end{aligned}
$$

# Mathematical dynamic model

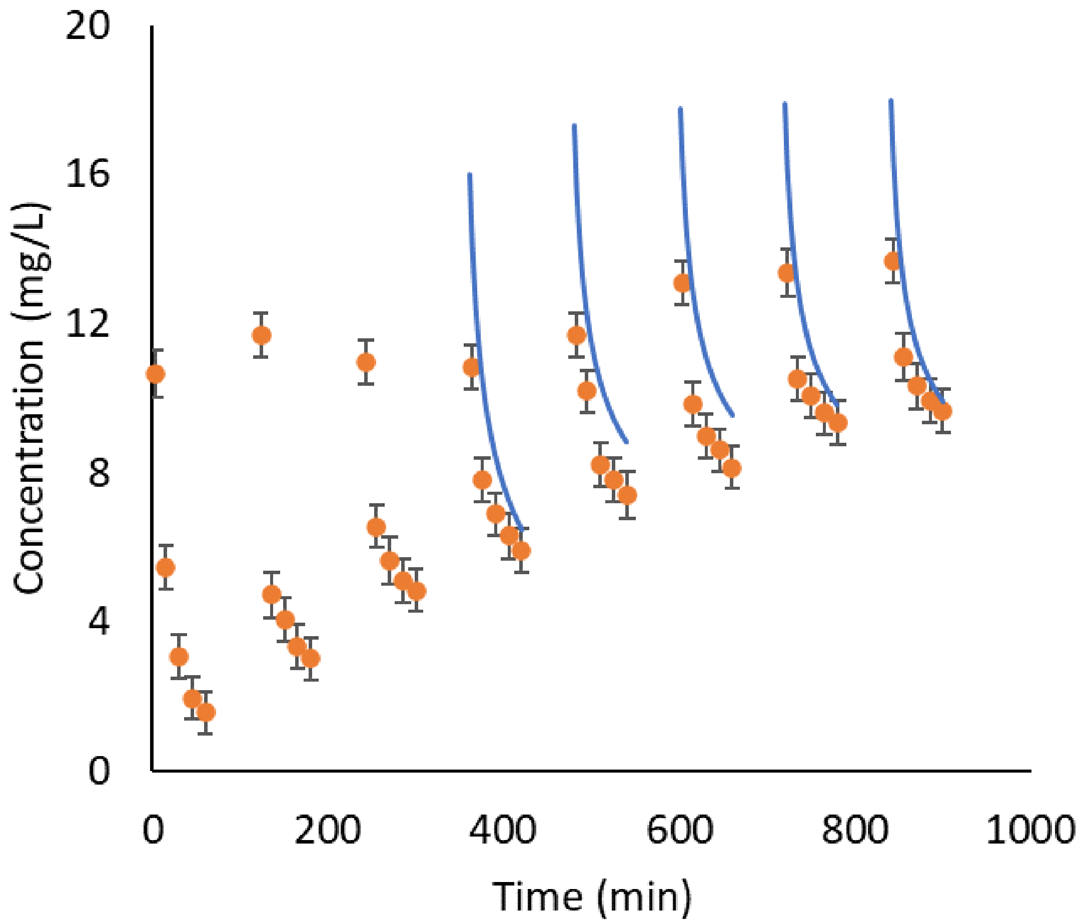
Considering the two most common adsorption kinetic models (pseudo first order -left- and pseudo second order -right-), the concentration inside the reactor is presented:




After several cycles the concentration at the end of each cycle does not change

# Lab scale experiment



# Periodic final concentration ($C_p$)

- Pseudo first order (PFO)

$$C_p(T) = C_0 - \frac{m\, f_m\, q_e(e^{kT} - 1)}{V\, f_V e^{kT} + f_m - 1}$$

- Pseudo second order (PSO)

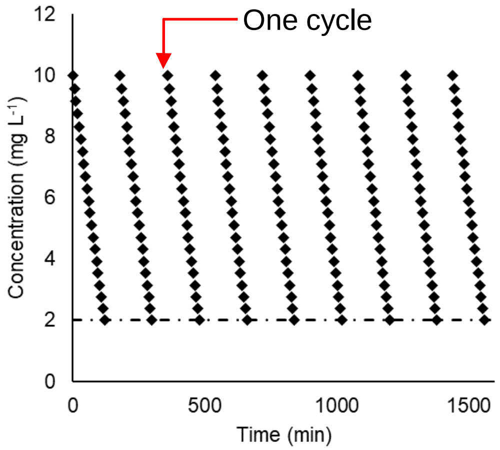
$$C_P(T) = C_o - \frac{m\, f_m^2}{V f_V} \sum_{j=1}^{\infty} \left[ \frac{q_e^2 kjT}{1 + q_e kjT} (1 - f_m)^{j-1} \right]$$

- Simulation: Calculate $C_{P,}$ knowing $C_0$, $m$, $V$, $f_m$, $f_V$, $T$

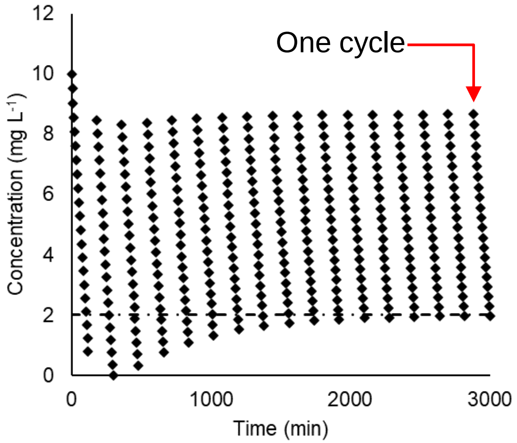
- Design of the PCBr: calculate reactor operating parameters ($m$, $V$, $f_m$, $f_V$, $T$) to obtain a set value for $C_P$

# Comparing different operating modes

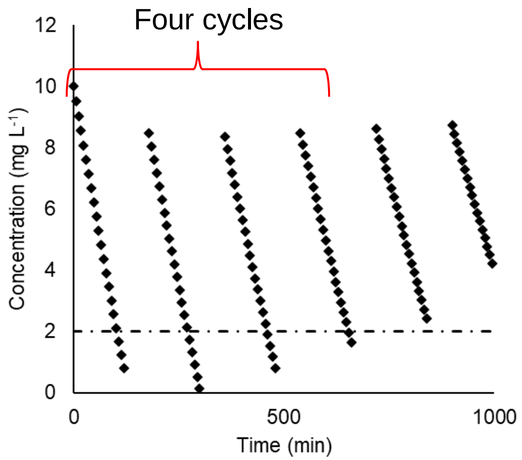
Complete solid removal




Partially consevred batch




Complete solid retention




| | Complete solid removal | Partially conserved batch | Complete solid retention |
|---|---|---|---|
| Initial adsorbent mass (kg) | 63 | 72.6 (calculated using $C_p$ equation) | 72.6 |
| Adsorbent added (kg) | 63 (one cycle) | 14.5 (one cycle) | 72.6 (four cycles) |
| Adsorbent mass added per unit of treated water (kg $m^{-3}$) | 0.420 | 0.116 | 0.145 |

| | | | |
|---|---|---|---|
| $f_V$ | 1 | 5/6 | 5/6 |
| $f_M$ | 1 | 1/5 | 0 |

V= 150 m3
T= 2 h

# Conclusions

- Rice husk chars have different adsorption properties depending where they are generated

- Rice husk chars can be used to remove compounds from water

- The proposed reactor operation allows to better control the adsorption process, and can reduce the adsorbent mass used

# Thank you for your attention!

**ACKNOWLEDGEMENT**

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