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

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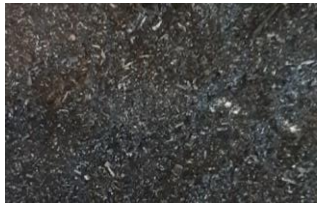
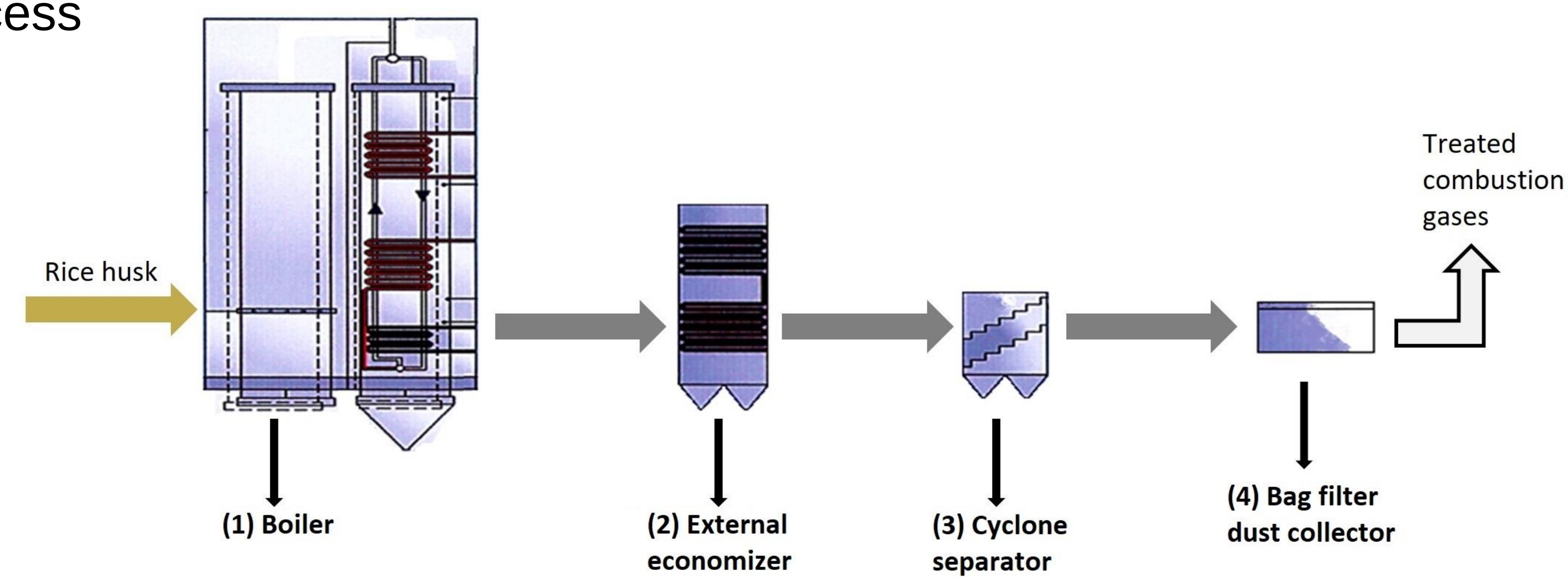
Rice husks

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



- Possible uses:
  - Silica production
  - Cement
  - Adsorbent

- Process



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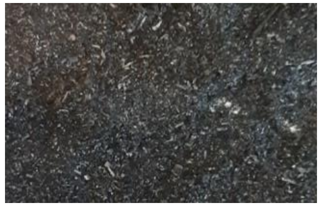

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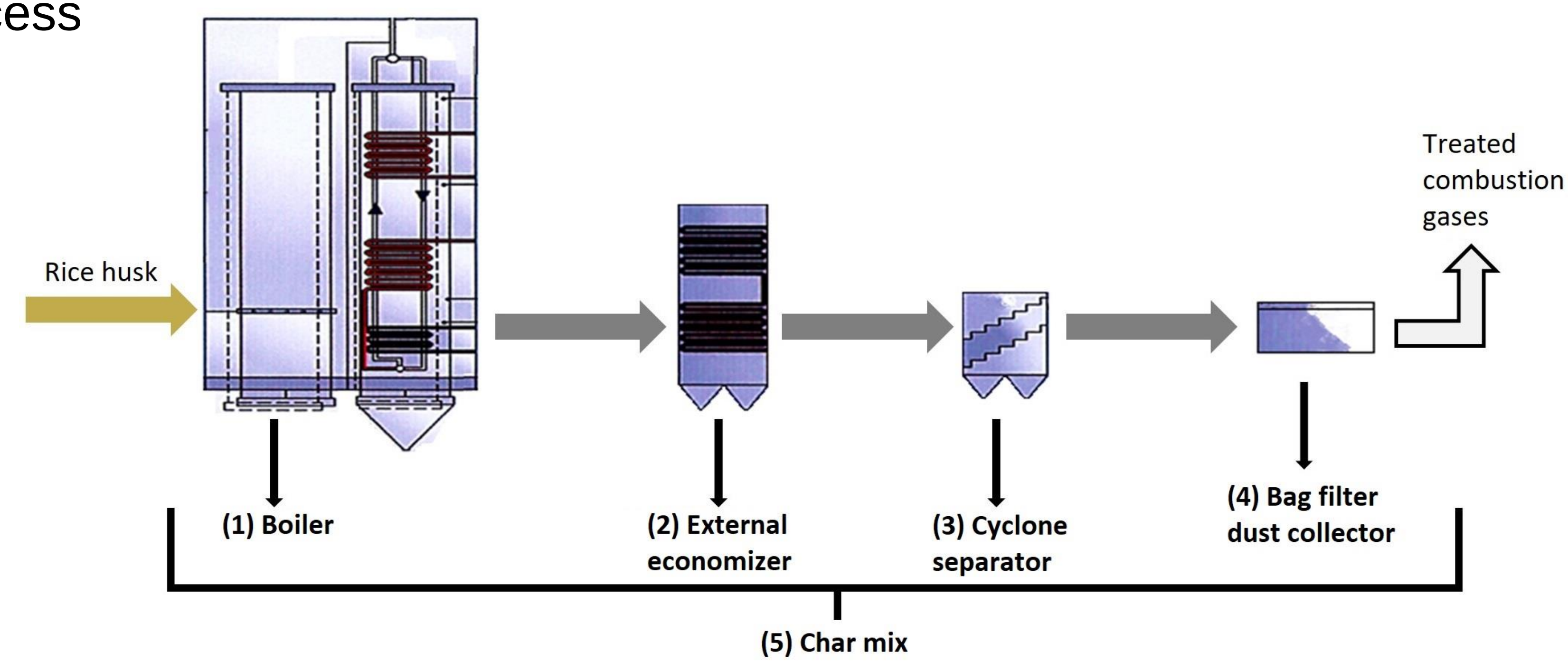


Aims and objectives

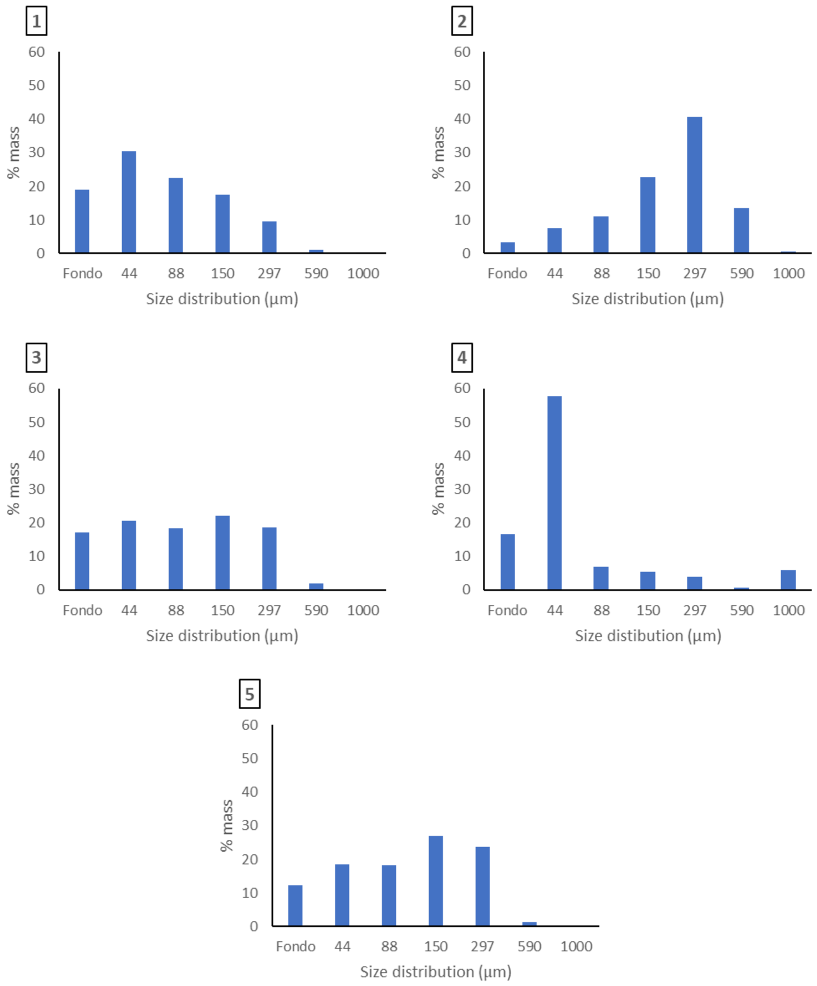
- Study the rice husk chars obtained in the industry as adsorbents to remove compounds from water
- Evaluate the use of the rice husk char in an adsorption reactor, and model its operation

Characterization of rice husk chars

Density

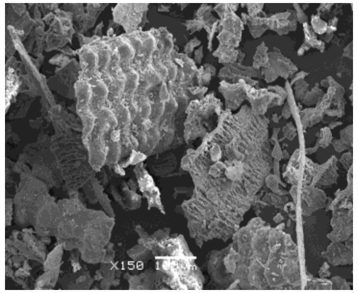
Char	Density (g/cm³)
Boiler (1)	0.37
Economizer (2)	0.15
Cyclone separator (3)	0.19
Bag filter (4)	0.21
Char mix (5)	0.19

Particle size distribution (µm)

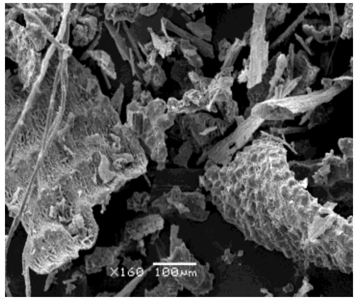


Scanning electron microscopy(SEM)

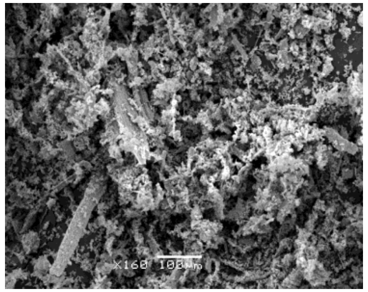
Boiler



Cyclone separator

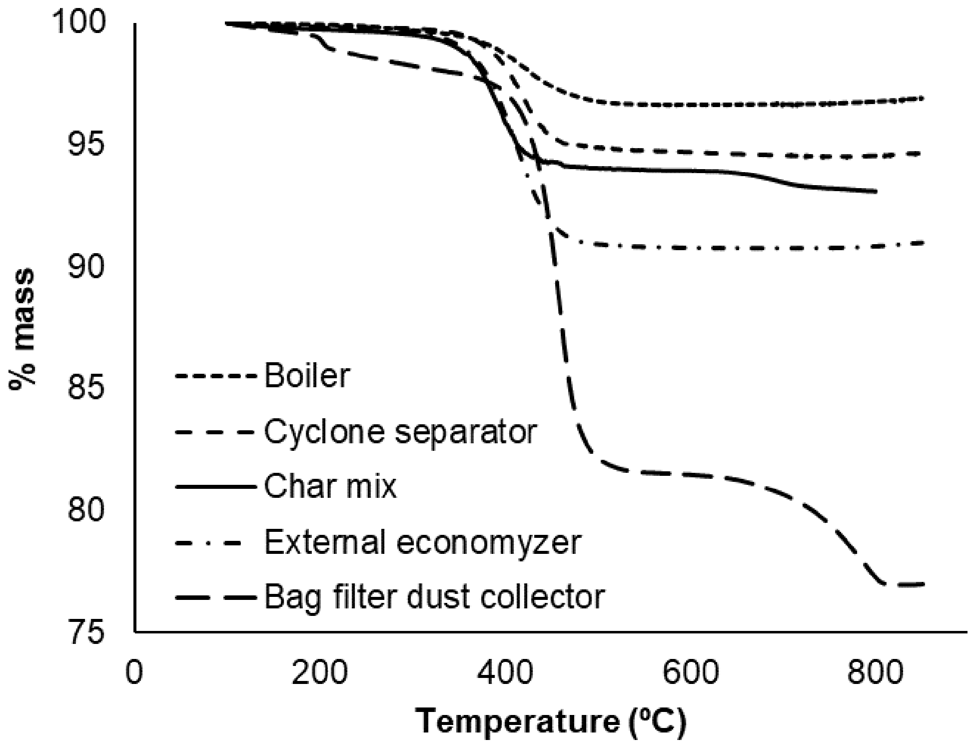


Bag filter



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

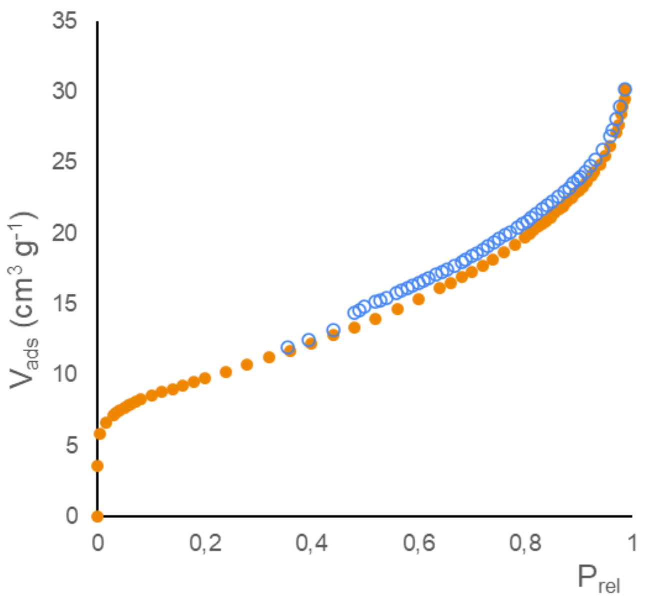
Elemental analysis

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

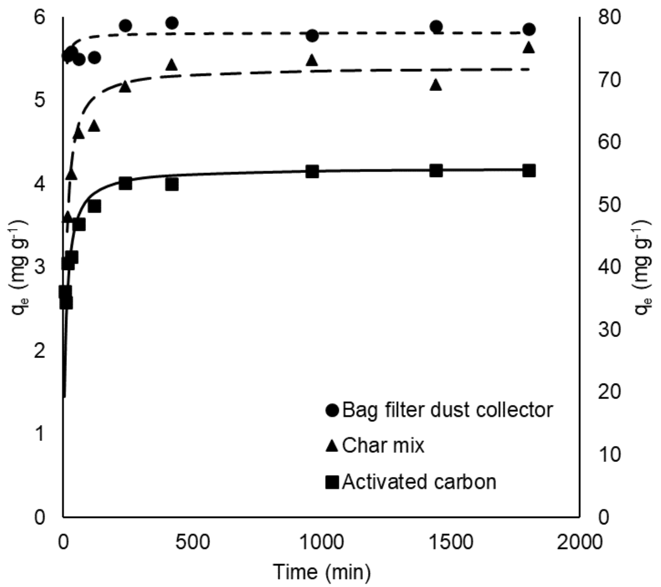
Phenol

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

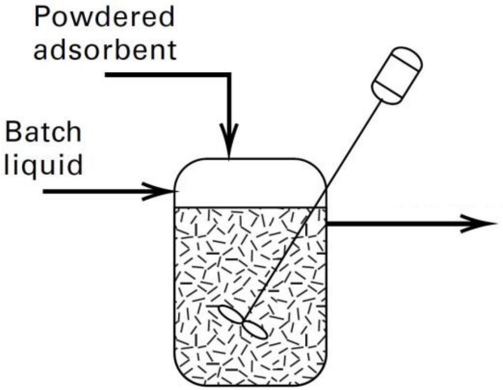
$$q(t) = \frac{q_e^2 \; k_2 \; t}{1 + q_e \; k_2 \; t}$$



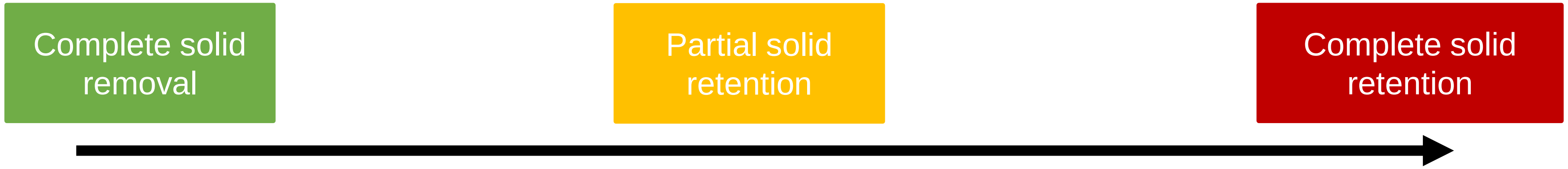
	C_0 (mg/L)	q_e (mg/g)	k_2 (g/mgmin)
Phenol			
Char mix	10	2.5	0.068
	20	2.79	0.0071
	50	5.52	0.013

* 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*

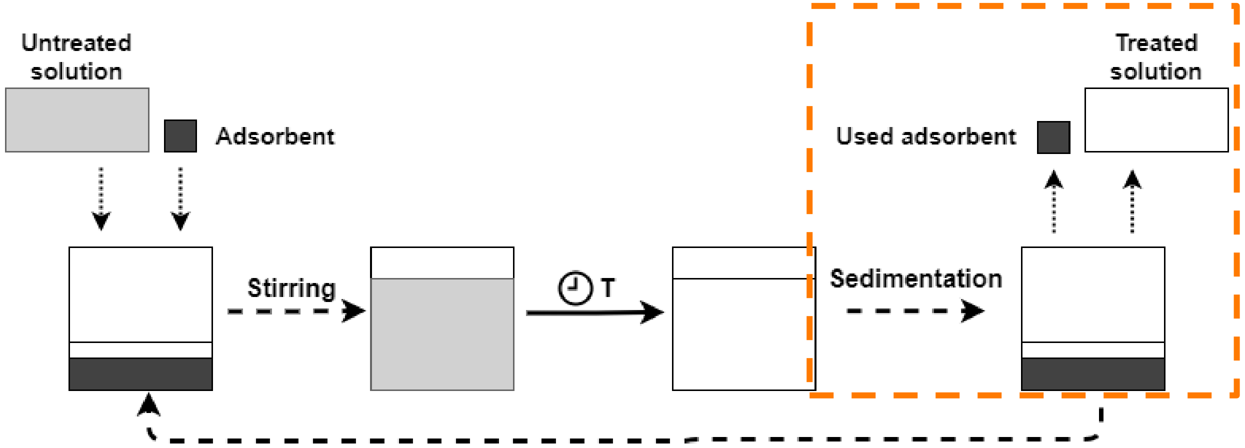


- ☑ Highest adsorption rate
- ☒ Underutilization of adsorbent capacity

- ☑ Maximum utilization of adsorbent
- ☒ Difficult to control

Parcially conserved batch (PCB)

Partial solid retention

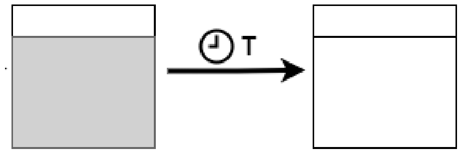


$$f_m = \frac{m_e}{m}$$ Fraction of adsorbent removed

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

Mathematical dynamic model

Cycle 1:



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

C_0: Initial concentration

$q(t)\frac{m}{V}$: Removed amount per volume at time *t*

Cycle 2:

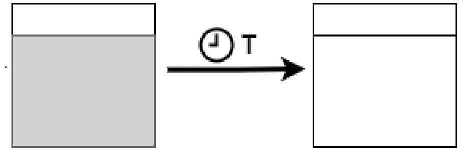
$$C_2(t) = \left(C_0 - q(T)\frac{m}{V}\right)(1 - f_V) + C_0 f_V - (q(t) - q(T))\frac{m}{V}(1 - f_m) - q(t - T)\frac{m}{V} f_m$$

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

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

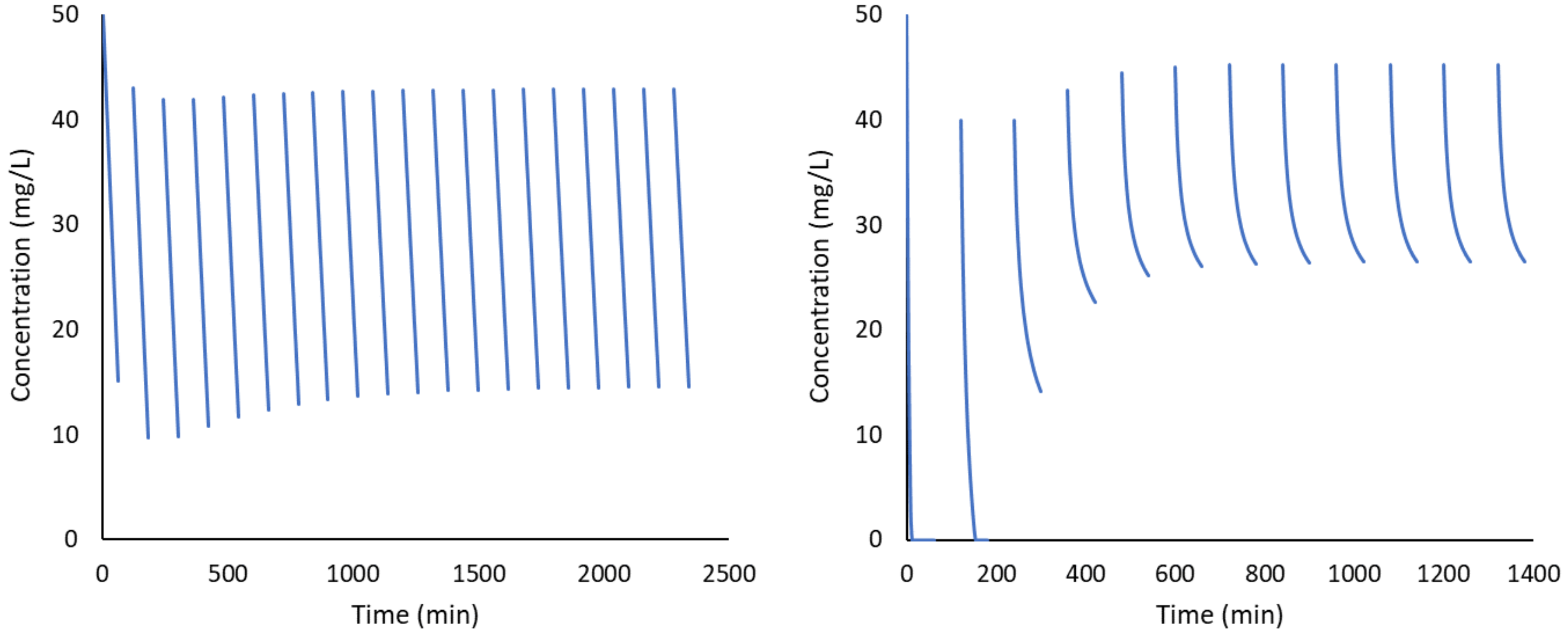
Cycle n:



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

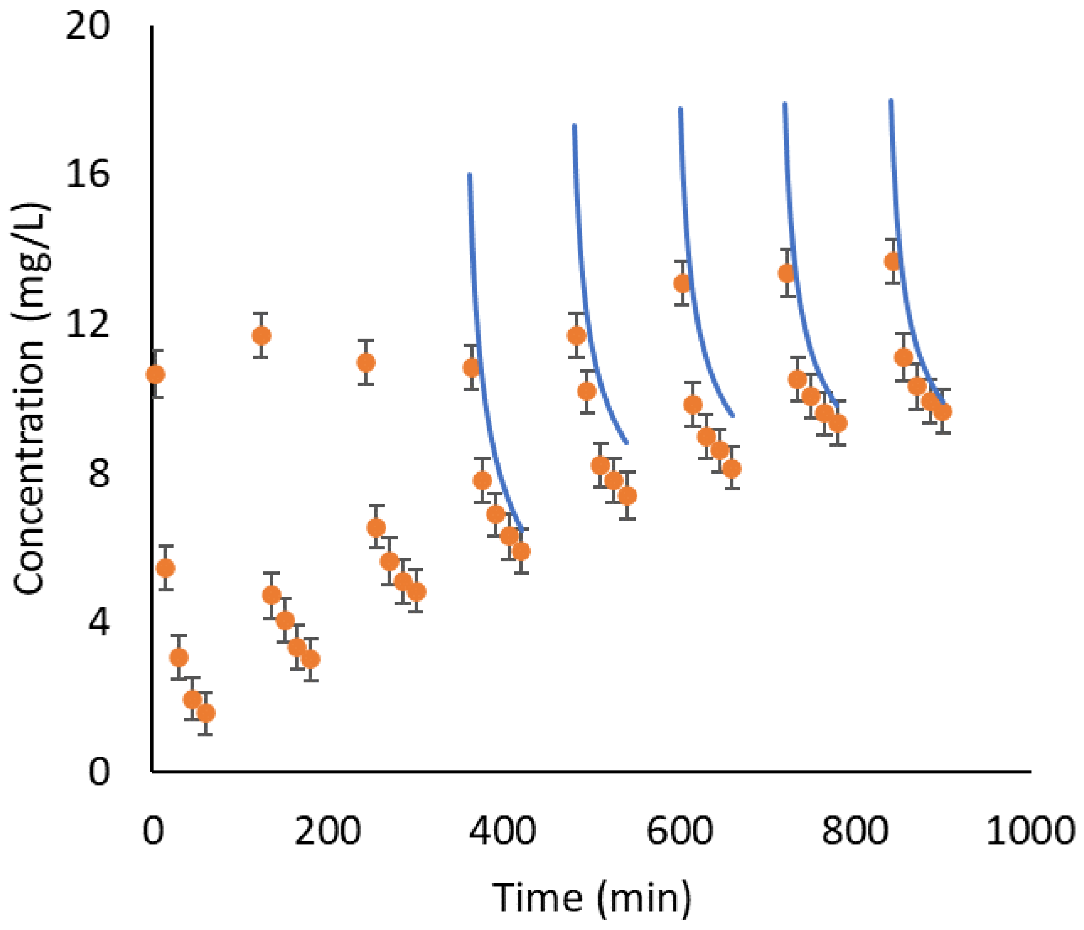
Mathematical dynamic model

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)

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

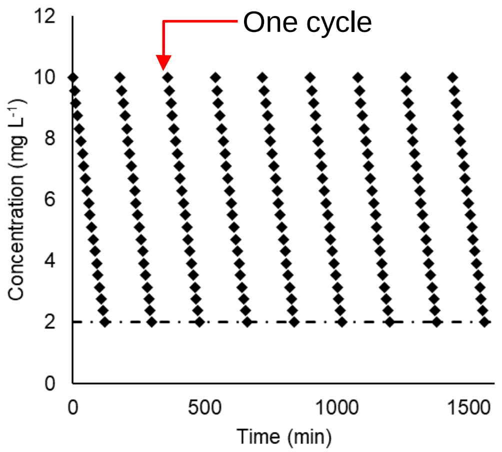
- Pseudo second order (PSO)

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

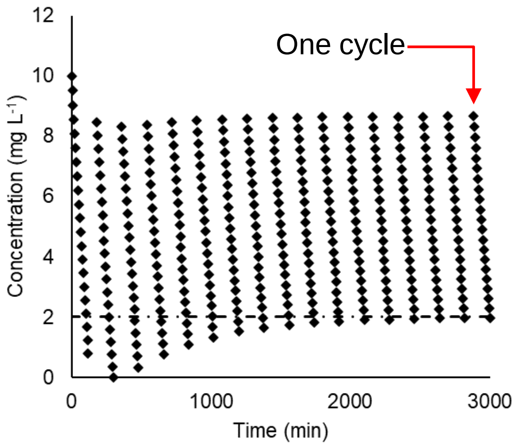
- Simulation: Calculate $C_{P,}$ knowing C_0, m, V, f_m, f_V, T
- Design of the PCBr: calculate reactor operating parameters (m, V, f_m, f_V, T) to obtain a set value for C_P

Comparing different operating modes

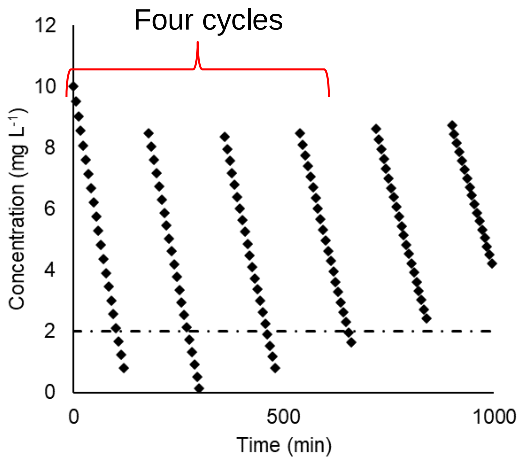
Complete solid removal



Partially conseved 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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