Preparation of activated carbon from pine (*Pinus radiata*) sawdust by chemical activation with zinc chloride for wood dyes adsorption

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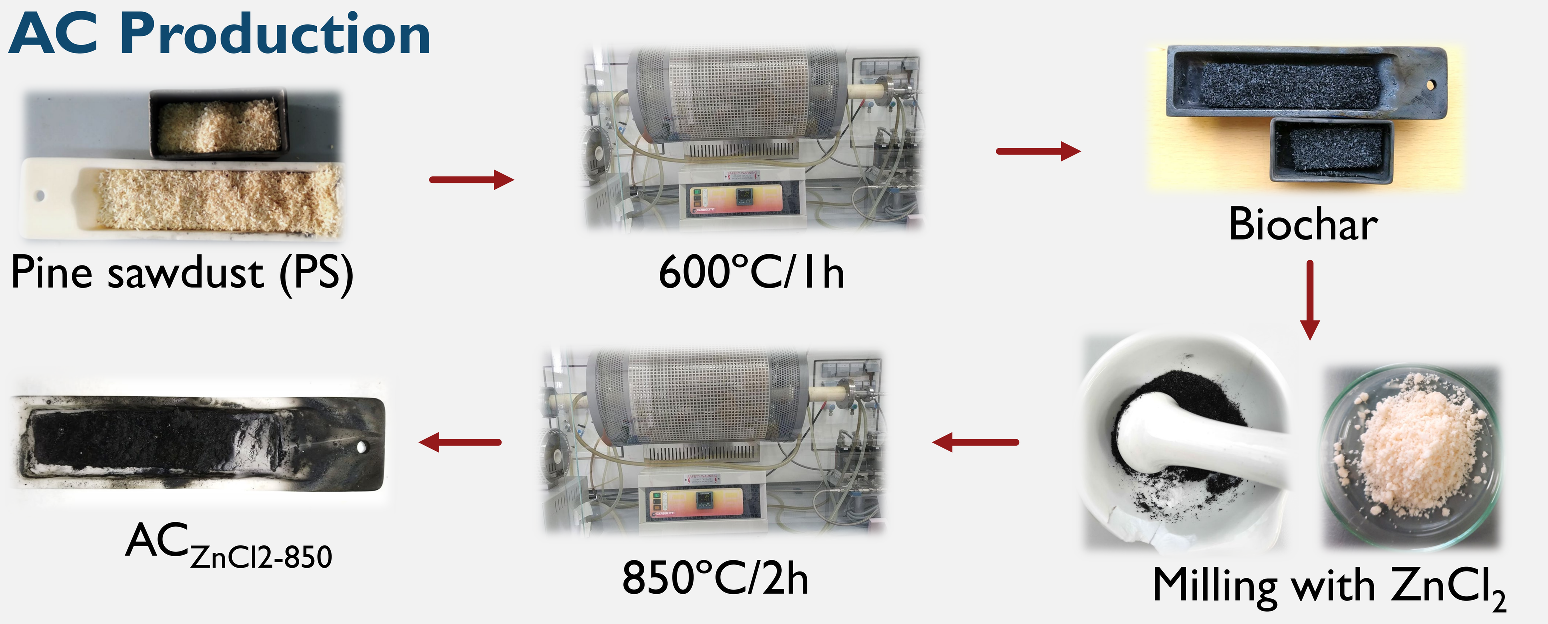
INTRODUCTION

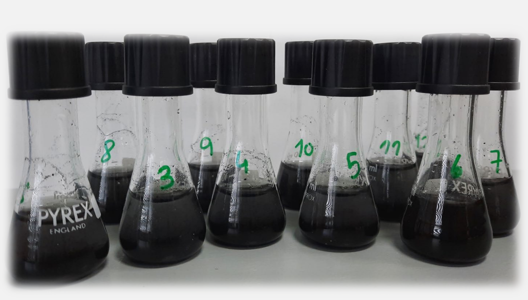
- **Water pollution** by contaminants, particularly **dyes** can generate serious problems in environment and human health.
- **Wastewater treatment** is essential, and **adsorption** has received special attention due to its simplicity, high efficiency, low cost and the possibility of reusing the adsorbent through its recovery and regeneration.
- **Activated carbons (AC)** present high porosity, surface area, physicochemical stability, mechanical strength, and surface reactivity and have been widely used but they present high cost and regeneration difficulty. Therefore, investigations have been focused on their production from natural, abundant, safe and low-cost precursors.
- ✓ Based on this scenario, the present study was focused on the **production and characterization of a novel activated carbon using pine (*Pinus radiata*) sawdust (PS)** from the wood industry as a precursor and on exploring the potential of the AC prepared with $ZnCl_2$ in the **adsorption of acid wood dyes (blue, red and black)** from aqueous solutions.

MATERIALS AND METHODS

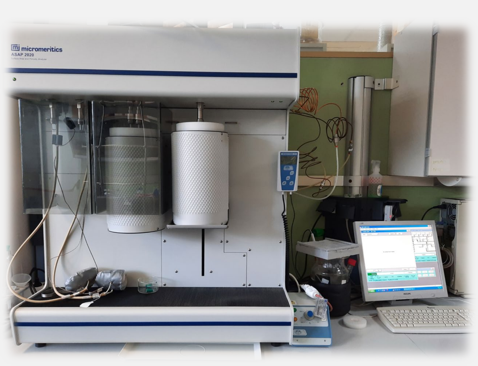
AC Production



Characterization



Point of Zero Charge



BET surface area and pore volume by ASAP 2020 sorption

Morphological characteristics and elemental composition by SEM-EDX

Adsorption experiments

210 rpm, 25°C

4000 rpm, 15min

λmax: 602 nm, 506 nm, 572 nm

$$\% Adsorption = (C_0 - C)/C_0 \times 100$$

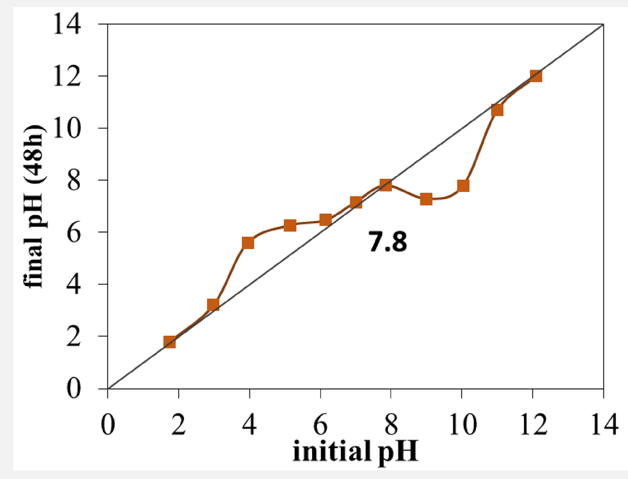
$$q = (C_0 - C)V/m$$

CONCLUSIONS

- A newly AC from PS with a reasonably good surface area can be prepared from dry chemical activation with $ZnCl_2$ as activating agent.
- The adsorption of blue, red and black wood dyes onto AC was very effective at low dye concentrations and the removal efficiency decreased with increasing the dye initial concentration.
- The pseudo-second order kinetic model was the most appropriate to describe dyes removal.

RESULTS AND DISCUSSION

AC Characterization

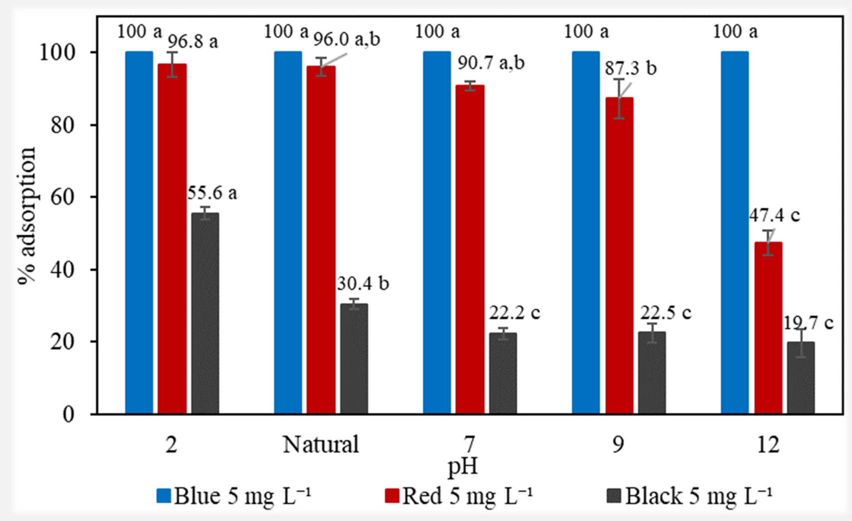


Determination of pH_{PZC} for $AC_{ZnCl2-850}$

Surface characterization of prepared AC

Parameters	$AC_{ZnCl2-850}$
BET surface area N_2 ($m^2\ g^{-1}$)	471.4
BET surface area CO_2 ($m^2\ g^{-1}$)	319.5
Total pore volume ($cm^3\ g^{-1}$)	0.26
Mesopore volume ($cm^3\ g^{-1}$)	0.02
Micropore volume ($cm^3\ g^{-1}$)	0.23
Average pore diameter (nm)	2.26

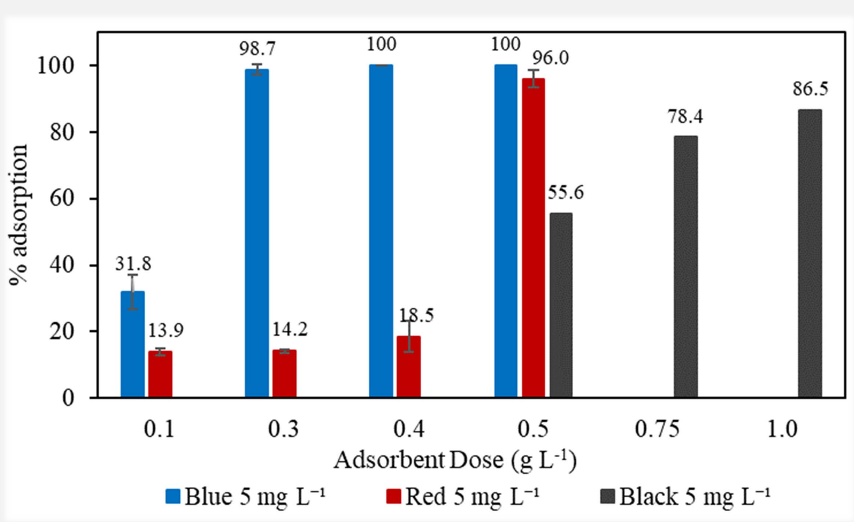
Effect of pH



- Total removal efficiency for blue and red dyes at 5 mg L^{-1}.
- Optimal pH value: **natural pH** for blue and red dyes and **pH 2** for black one.

Effect of pH (natural pH: 6.0, 5.1 and 4.8 for blue, red and black; 0.5 g L^{-1}; 48 h for blue and red; 6 h for the black.

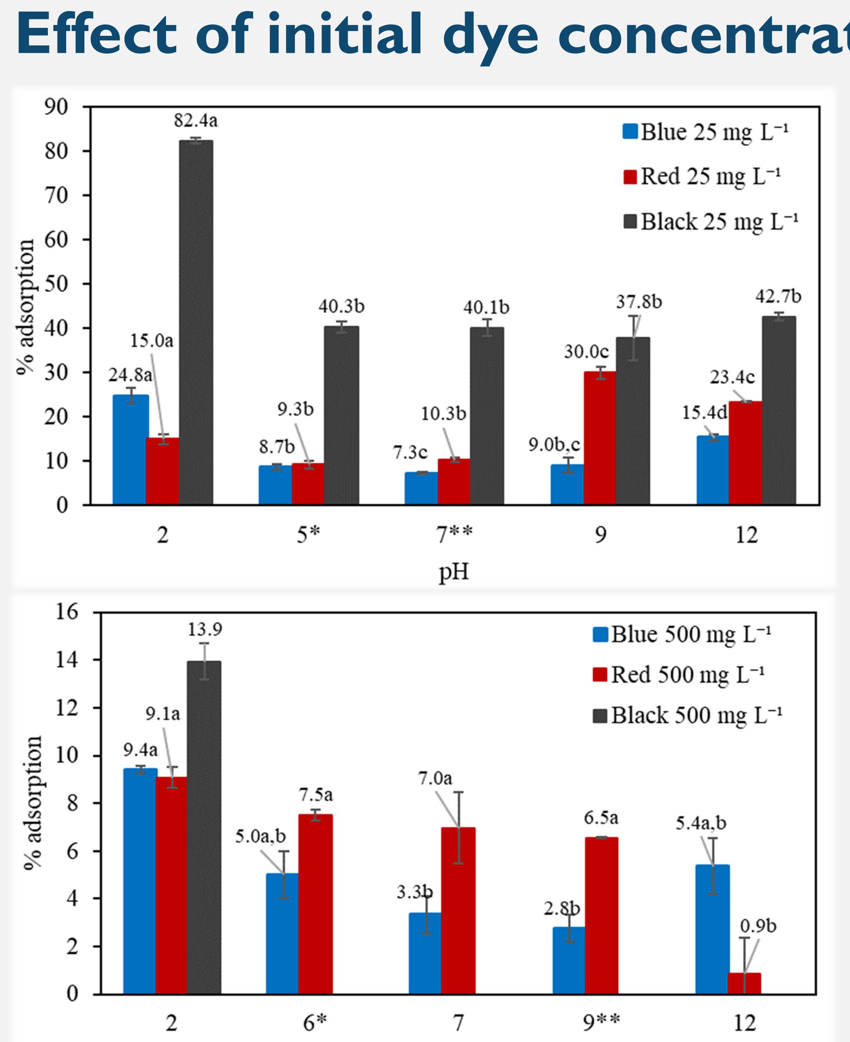
Effect of adsorbent dose



- Blue dye: 100% removal was maintained reducing adsorbent dose to 0.4 g L^{-1}.
- Red dye: almost complete removal only at 0.5 g L^{-1}.
- Black dye: 86.5% removal efficiency increasing the adsorbent up to 1.0 g L^{-1}

Effect of adsorbent dose (natural pH for blue and red and pH 2 for black; 48 h for blue and red; 6 h for the black.

Effect of initial dye concentration



Adsorption efficiency decreased with increasing dye concentration:

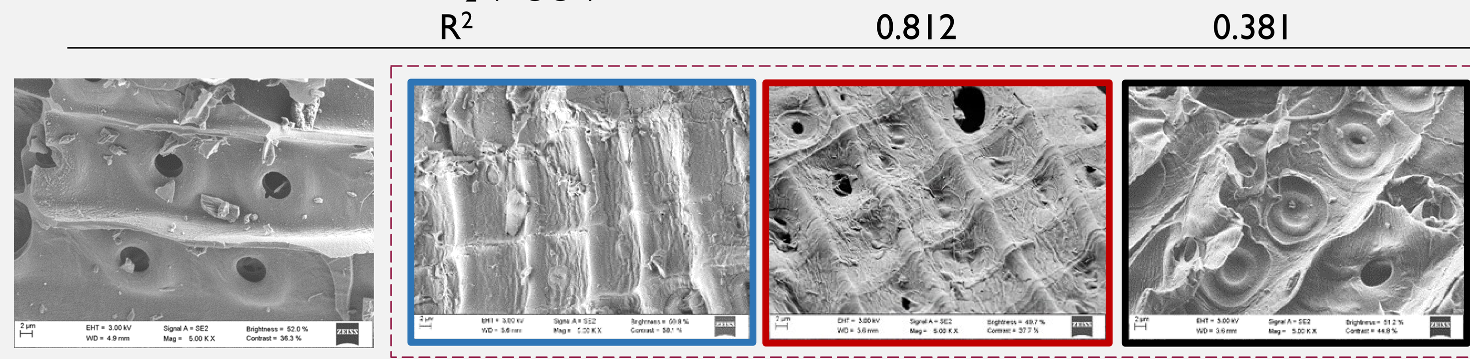
- Blue dye: at pH 2 the adsorption efficiency was 24.8% and 9.4% for 25 and 500 mg L^{-1}, respectively.
- Red dye: removal efficiency was 30% at pH 9 for 25 mg L^{-1} and 9.1% at pH 2 for 500 mg L^{-1}.
- Black dye: at pH 2 the adsorption efficiency was 82.4% and 13.9% for 25 and 500 mg L^{-1}, respectively.

Effect of initial dye concentration (natural pH at 25 mg L^{-1}: *5.1, **6.7 and *5.7; natural pH at 500 mg L^{-1}: *6.6, **9.0 for blue and red; 48 h for blue and red and 12 h for the black.

Kinetic data were best fitted to **pseudo-second order model**, which indicates a **chemisorption** mechanism and for the first stage data (1) were well fitted to **intraparticle diffusion**.

Pseudo-second order and intraparticle diffusion kinetic model parameters dye concentration: 5 mg L^{-1}, contact time: 48 h for blue and red dyes and 12 h for black dye).

Model	Parameter	Adsorption conditions: Blue 0.4 g L^{-1} natural pH	Red 0.5 g L^{-1} natural pH	Black 1.0 g L^{-1} pH= 2
Pseudo-second order	$q_{e,calc}$ (mg g^{-1})	13.12	9.33	4.77
	k_2 (g mg^{-1} min^{-1})	$1.92 \cdot 10^{-3}$	$1.17 \cdot 10^{-2}$	$2.44 \cdot 10^{-2}$
	R^2	0.999	0.999	1.000
Intraparticle diffusion	$k_{id,1}$ (mg g^{-1} $min^{-1/2}$)	1.02	0.83	0.69
	C_1 (mg g^{-1})	0.65	1.05	0.17
	R^2	0.934	0.876	0.937
	$k_{id,2}$ (mg g^{-1} $min^{-1/2}$)	$8.78 \cdot 10^{-2}$	$2.43 \cdot 10^{-2}$	$2.70 \cdot 10^{-2}$
	C_2 (mg g^{-1})	8.99	8.29	4.18
	R^2	0.812	0.381	0.584



Pores are occupied and it is observed a slight cover over the entire surface. EDX after adsorption confirmed the binding of dye molecules.

SEM images before and at high concentrations after adsorption.

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