Removal of copper from aqueous solutions by biosorption onto pine sawdust

C. I. Orozco, M. S. Freire, D. Gómez-Díaz, J. González-Álvarez*

Department of Chemical Engineering, School of Engineering,
Universidade de Santiago de Compostela, Santiago de Compostela, 15782, Spain
*(Email: julia.gonzalez@usc.es)

Background

- **Copper** is among the most abundant heavy metals in wastewaters discharged in Europe [1].

Heavy metals are a serious ecology problem:
- ✓ mutagenic and carcinogenic effects
- ✓ high toxicity in trace concentrations
- ✓ non-biodegradability
- ✓ accumulation in the food chain

- Actual technologies to remove heavy metals (precipitation, ion exchange, etc.) have several limitations: high cost or energy requirements, low efficiency for concentrations below 100 mg/L… [2]
- Adsorption with conventional adsorbents is one of the most effective processes. Nowadays, research is focused in biosorbents derived from natural materials with low-cost and high adsorption capacity.

- ***Pinus radiata* sawdust (PS)** is a renewable and promising adsorbent cheaper than activated carbons. Some studies have reported good results using pine sawdust for pollutants removal [3]. Moreover, it is one of the most abundant wastes in Spanish wood industries [4].

Objectives

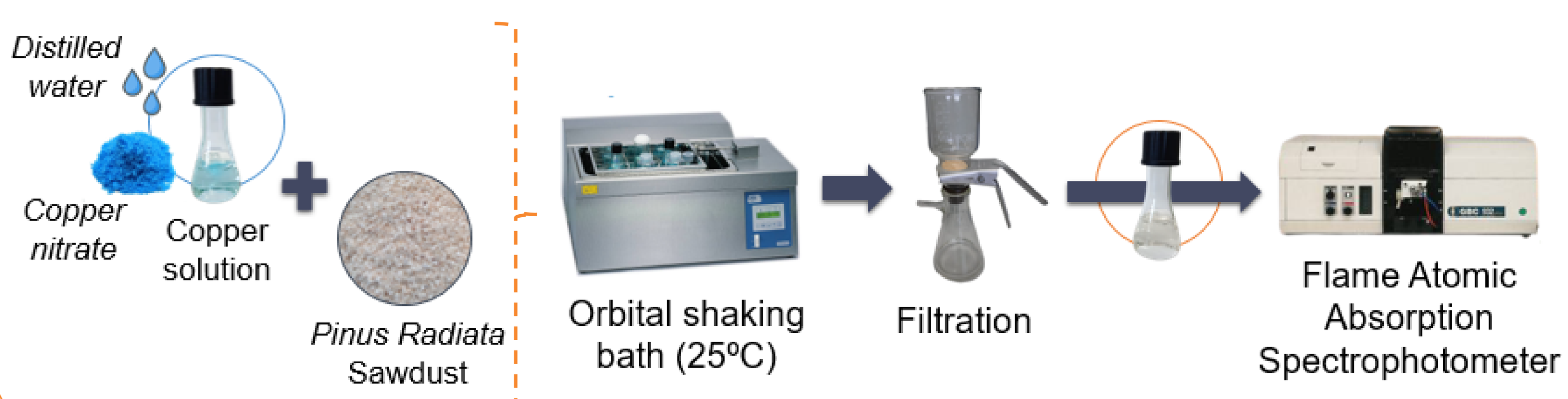
Verify if untreated ***Pinus radiata*** sawdust is a good adsorbent for the removal of Cu^{+2} from aqueous solutions studying the influence of different variables:

- Contact time
- Adsorbent dose (1 - 50 g/L)
- Initial metal ion concentration (5 - 300 mg/L)
- pH (2 - 8)

Methods

ADSORBENT PREPARATION — PS was provided by a regional sawmill (Lugo, Spain), sun-dried for 24 h and sieved between 0.5 and 1 mm

BATCH ADSORPTION EXPERIMENTS



CALCULATIONS

$$\text{Adsorption efficiency } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad q_t\ (mg/g) = \frac{(C_0 - C_t)}{m} \times V$$

CHARACTERIZATION OF ADSORBENT MATERIAL

Table Inductively Coupled Plasma (ICP) results in mg/kg

Pine species	Fe	Al	As	Cd	Pb	Co	Cu	Cr	Mn	Zn	Ni
Pinus radiata (this study)	552.6	43.6	0.02	0.03	0.2	0.1	1.0	0.2	111.6	11.5	0.2
Pinus pinaster (wood stem)	29,375.0	5,884.4	3.8	0.9	13.4	17.1	926.3	109.4	9,750.0	1,250.0	37.5
Pinus pinaster (bark stem)	9,794.0	8,231.2	3.0	2.1	0.4	26.3	85.1	8.5	7,239.0	1,618.1	21.3

PS shows a low metal concentration

There is no interference by PS metals in the adsorption process

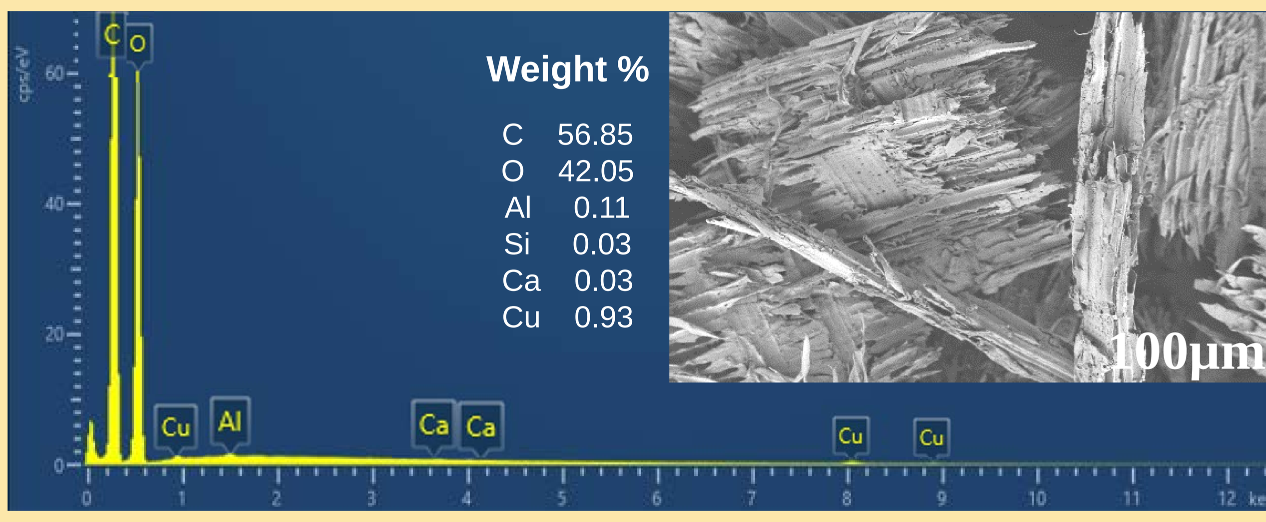


Fig. SEM-EDX of sawdust after copper adsorption (Co: 45 mg/L, adsorbent dose: 12.5 g/L, pH: 7, contact time: 2h)

Cu adsorption was demonstrated by SEM-EDX

Adsorbent surface became rougher after Cu adsorption

Results

EFFECT OF CONTACT TIME

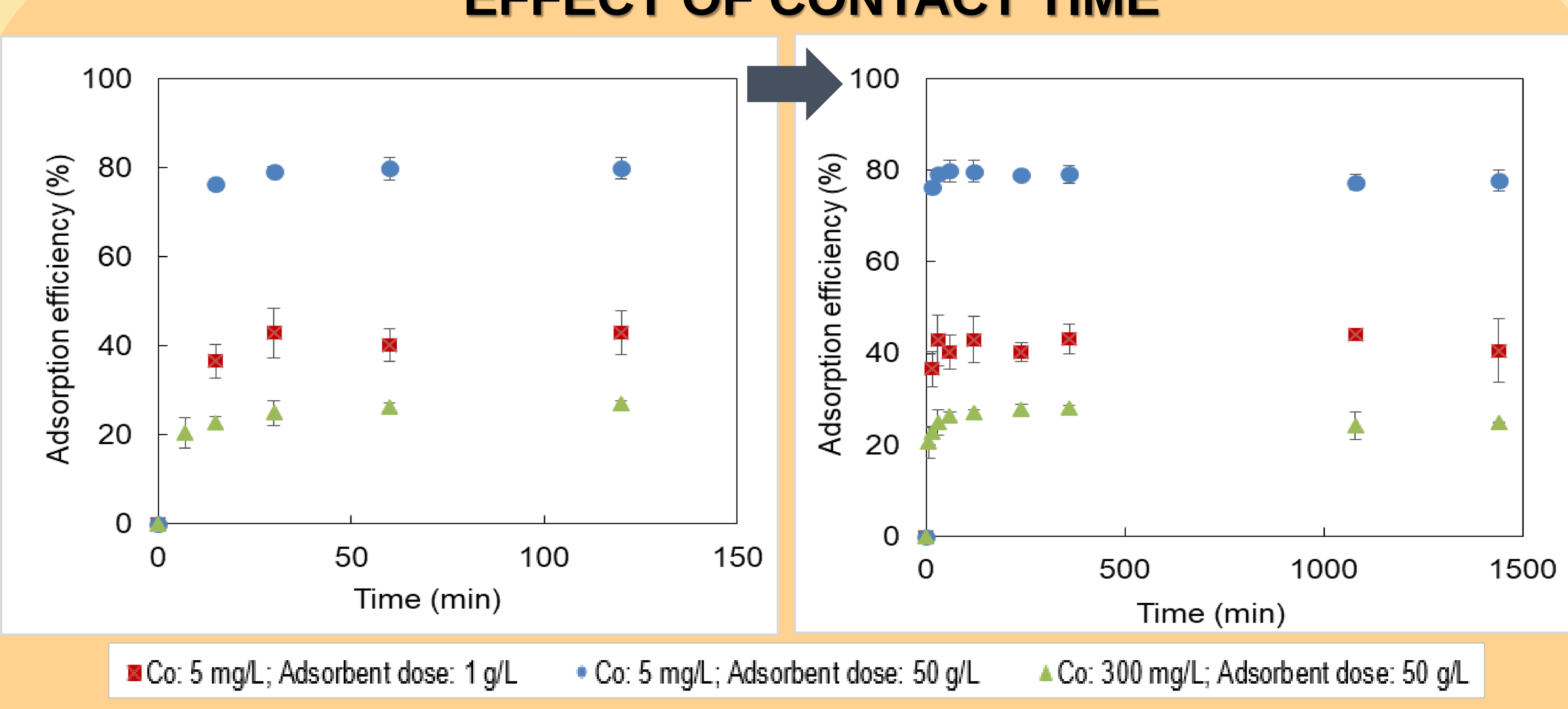


Fig. Effect of contact time on Cu^{+2} adsorption efficiency at natural pH in the first 2 hours (a) and 24 hours (b)

Equilibrium conditions were attained in 2 h in all cases

High adsorption rates in the first minutes are due to the large surface area available and to the high metal concentration still not adsorbed which favors mass transfer

EFFECT OF PH

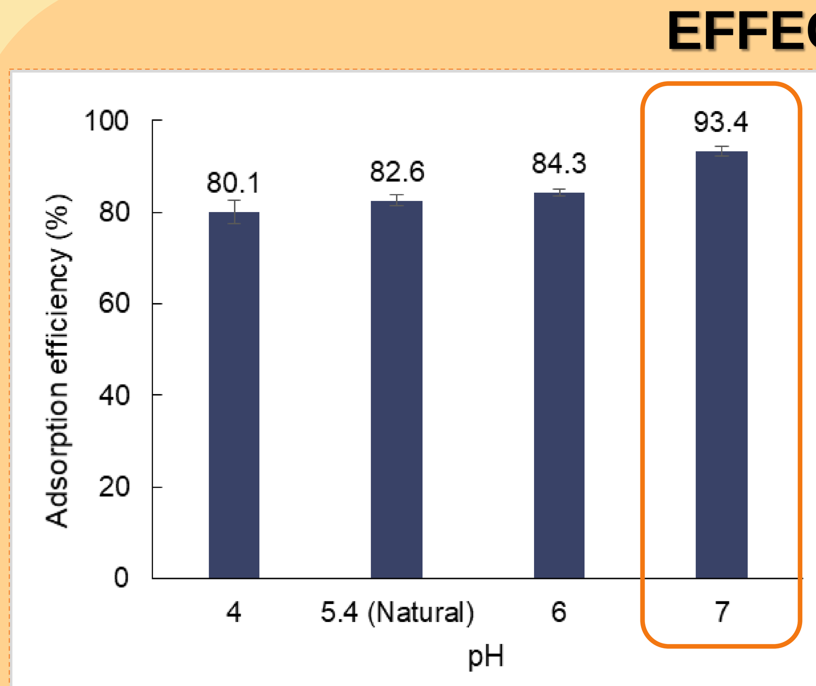


Fig. Effect of pH on Cu^{+2} adsorption efficiency (Co: 5 mg Cu^{+2}/L, adsorbent dose: 5 g/L, contact time: 2h)

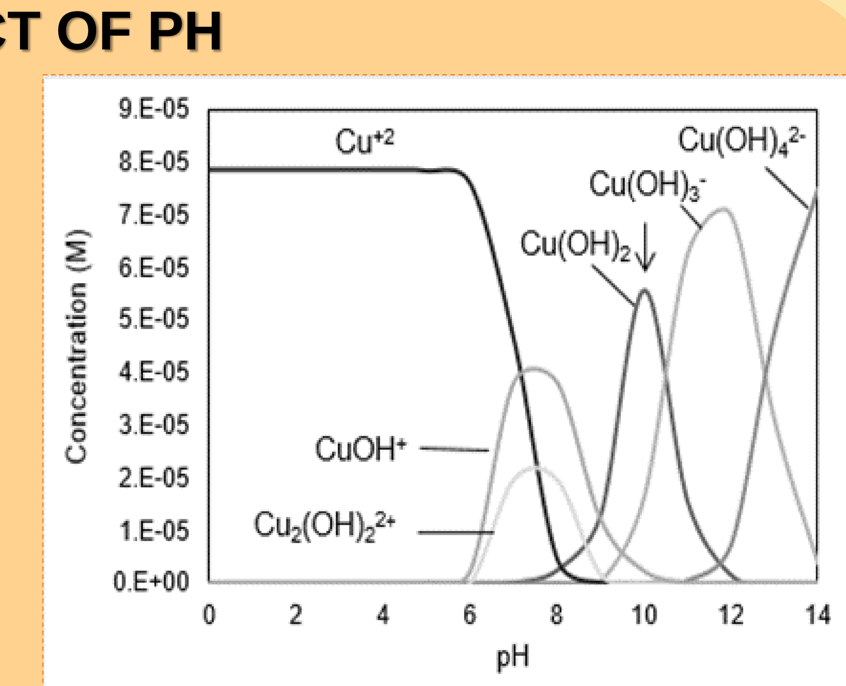


Fig. Copper speciation diagrams of 5 mg Cu^{+2}/L in MINTEQ 3.0 software

At **pH > pH_{PZC} (4.8)**, the PS surface is **negatively charged**, which favors the electrostatic attraction with copper ions

$Cu(OH)^+$ and **$Cu(OH)_2$** (pH 6-7) reach the PS pores easier than Cu+2 (pH<5) due to their smaller size

EFFECT OF ADSORBENT DOSE

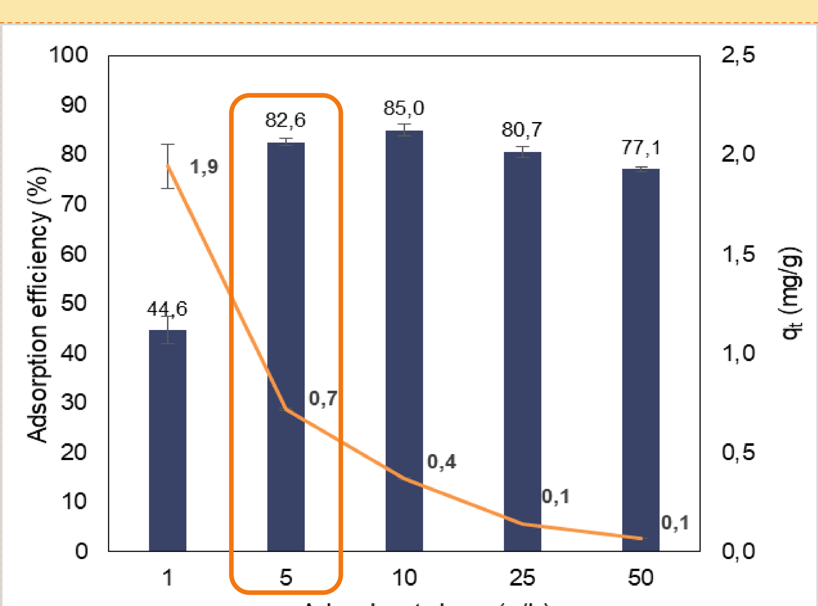


Fig. Effect of pine sawdust dose on Cu^{+2} adsorption efficiency (Co: 5 mg Cu^{+2}/L, natural pH, contact time: 2h)

Metal removal increases with increasing the adsorbent dose from 1 to 10 g/L due to the higher availability of binding sites

The decrease from 10 to 50 g/L is attributed to an available surface area decrease due to overlapping adsorption sites or particle interactions

EFFECT OF INITIAL METAL CONCENTRATION

The adsorption efficiency decreases with increasing the metal initial concentration due to adsorbent saturation

KINETIC STUDIES

Table Parameters and correlation coefficients for adsorption of copper on pine sawdust

Initial concentration C_0 (mg/L)	Adsorbent dose (g/L)	q_e exp (mg/g)[(a)]	Pseudo first-order			Pseudo second-order		
			k_1 (min^{-1})	q_e calc (mg/g) [(b)]	R^2	k_2 (g mg^{-1} min^{-1})	q_e calc (mg/g) [(b)]	R^2
5	1	1.63	$9\cdot10^{-4}$	$9.7\cdot10^{-2}$	0.19	0.15	1.63	0.99
	50	$7.4\cdot10^{-2}$	$5\cdot10^{-4}$	$9\cdot10^{-4}$	0.16	5.38	$7.2\cdot10^{-2}$	0.99
300	1	3.69	$1.4\cdot10^{-2}$	3.31	0.27	$4.7\cdot10^{-3}$	3.66	0.99
	50	1.68	$5\cdot10^{-4}$	0.27	0.07	$5.5\cdot10^{-2}$	1.52	0.99

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

Kinetic data for Cu^{+2} removal are satisfactorily fitted to the **pseudo-second-order model,** which is related with chemical sorption

Conclusions

Pine sawdust is a promising efficient, renewable and economic adsorbent for metal removal. Moreover, its use is an alternative for its management and valorization

Best removal efficiency (93.4%) was obtained at pH=7 with an adsorbent dose of 5 g/L, 2 h of contact time and an initial concentration of 5 mg Cu^{+2}/L

References

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[4] CIF Lourizan. Pino insigne. https://lourizan.xunta.gal/pino-insigne (2017). Accessed March 31, 2022

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