Removal of copper from aqueous solutions by biosorption onto pine sawdust

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In the past decades, the fast growth of the industrial activity has promoted the discharge of pollutants in the surface and groundwater. Heavy metals can be distinguished from other pollutants for their serious implications on the environment and human health. These kinds of pollutants are not only a serious ecology problem for their high toxicity in trace concentration but also due to their non-biodegradability, accumulation in the food chain, and mutagenic and carcinogenic effects (World Health Organization, 2006). In response to these adverse effects, governments have implemented diverse regulations and standards to limit heavy metal discharges. However, most industries have problems to achieve those limits due to the actual technologies to remove heavy metals from wastewaters, such as precipitation, ion exchange, membrane separation, etc., that have several difficulties and limitations. These include high costs, high reagent usage or energy requirements and low efficiency for heavy metals concentrations below 100 mg/L (Centro Común de Investigación, 2016). Nevertheless, adsorption arises as one of the most low-cost and effective methods. Activated carbons are the most widely used adsorbents but their high production cost and difficult regeneration have caused the search for cheaper and more eco-friendly options (Sahmoune and Yeddou, 2016). From a wide range of adsorbents, waste biomass meets those requirements and its use as adsorbent provides an alternative for its valorization.

Pinus radiata is one of the coniferous species most widely spread across northern Spain and large quantities of wastes are generated from its industrial processing. Particularly, pine sawdust is a promising adsorbent that is widely available (Meez *et al*, 2021) and this work aims to investigate the feasibility of using *Pinus radiata* sawdust (PS) without any pre-treatment for the removal of Cu^{2+} from wastewaters.

PS was provided by a regional sawmill (Lugo, Spain). It was sun dried for 24 h (moisture content 10% dry basis) and subsequently, sieved to a fraction between 0.5 and 1 mm. In previous studies, the point of zero charge ($pH_{PZC} = 4.8$) and BET surface area (0.36 ± 0.01 m^2/g) were determined.

Batch adsorption experiments were performed by placing 50 mL of a metal solution and the appropriate amount of adsorbent according to the dose selected in an orbital shaking bath at 25ºC and 100 rpm. After reaching the target contact time, the samples were vacuum filtered and the residual Cu^{+2} concentration was determined by atomic absorption spectrophotometry. The effect of the most relevant variables for adsorption was investigated: pH (2-8), Cu^{+2} initial concentration (5-300 mg/L), adsorbent dose (1-50 g/L), and contact time (till equilibrium).

Firstly, the effect of the contact time at the natural pH (5.4) was studied for a 5 mg/L copper initial concentration and adsorbent dose of 1 g/L. The results shown in Fig. 1 demonstrated that adsorption was relatively fast achieving a 36% adsorption rate in only 15 min and equilibrium conditions (42%) were attained between the first 30 min and 1 h. For a Cu^{+2} concentration of 5 mg/L and 50 g/L adsorbent, the equilibrium adsorption rate rose to 80% also in 1 h. However, lower equilibrium adsorption efficiencies were recorded for the experiments carried out with a copper initial concentration of 300 mg/L, 26% for an adsorbent dose of 50 g/L at 1h. Kinetic data for Cu^{+2} removal by PS were satisfactorily fitted to the pseudo-second-order model, which means that the adsorption process can be described by a chemical sorption mechanism.

In a second stage, the effect of the adsorbent dose (1, 5, 10, 25, and 50 g/L) was studied for a 5 mg/L copper initial concentration, which led to the best results in the contact time study. At 5 g/L an equilibrium adsorption rate of 82.6% was reached which was not significantly improved by further increasing the adsorbent dose. For this reason, 5 g/L was the dose selected to continue the experimentation.

Although in the kinetic experiments a high concentration was tested (300 mg/L) to ensure that the regulation standards (Centro Común de Investigación, 2016) can be achieved, concentrations below 5 mg/L (1 and 2.5 mg/L) were also essayed. The best adsorption rate (90.9%) was achieved at 1 mg/L demonstrating that reducing initial concentration has a good effect on adsorption.

Finally, the effect of pH (2, 4, natural (5.4), 6, 7, 8) was investigated for a 5 mg/L Cu^{+2} solution and 5 g/L of pine sawdust. It was proved that adsorption rate increases with pH (Fig. 2) except for pH=8 at which precipitation occurs. Also, it is remarkable that there was no adsorption at pH=2. Therefore, pH=7 was selected as the optimal reaching a 93.4% adsorption rate. At pH higher than pH_{PZC}, the sawdust surface is negatively charged which favours the electrostatic attraction between Cu^{2+} and PS surface and explains the improvement observed. On the contrary, at $pH < pH_{PZC}$, the surface is positively charged, therefore repulsion could exist (Wu *et al*, 2014).

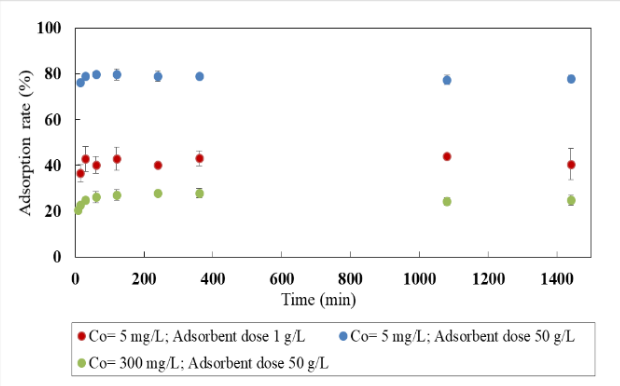

Figure 1: Effect of contact time on Cu^{2+} adsorption rate (Co: 5-300 mg Cu^{+2}/L, 1-50 g/L adsorbent dose, natural pH)

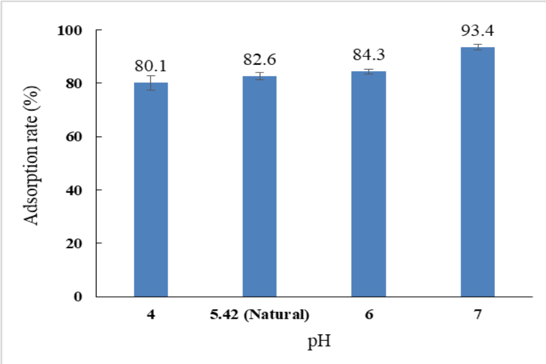

Figure 2: Effect of pH on Cu^{2+} adsorption rate (Co: 5 mg Cu^{+2}/L, 5 g/L adsorbent dose, contact time: 2h)

Pinus radiata sawdust has demonstrated to be a good adsorbent for the removal of Cu^{2+} from aqueous solutions under selected operational conditions. This process may be used to comply with the limitations imposed on the discharge of industrial wastewater containing Cu^{2+}, while at the same time being a way of managing and valorizing pine sawdust.

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Centro Común de Investigación, Instituto de Prospectiva Tecnológica, Delgado Sancho, L., Roudier, S., Brinkmann, T., et al. (2016). Best available techniques (BAT) reference document for common waste water and waste gas treatment/management systems in the chemical sector: Industrial Emissions Directive 2010/75/EU (integrated pollution prevention and control). Publications Office. https://data.europa.eu/doi/10.2791/37535

Meez, E., Rahdar, A., and Kyzas, G. Z. (2021). Sawdust for the Removal of Heavy Metals from Water: A Review. *Molecules, 26* (14), 4318. https://doi.org/10.3390/molecules26144318

Sahmoune, M.N. and Yeddou, A.R. (2016). Potential of sawdust materials for the removal of dyes and heavy metals: examination of isotherms and kinetics. New pub: Balaban, 57 (50), 24019-24034. https://doi.org/10.1080/19443994.2015.1135824

World Health Organization (2006). *Guías para la calidad del agua potable*, vol. 1, 3° ed., Spain: World Health Organization. ISBN 9243544608

Wu, Q., Chen, J., Clark, M. and Yu, Y. (2014). Adsorption of copper to different biogenic oyster shell structures. *Applied Surface Science*, 311, 264-272. https://doi.org/10.1016/j.apsusc.2014.05.054