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

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A problem that has persisted over the years and has attracted the attention of many researchers is water pollution. With the huge expansion of industrialization (such as textile, wood, rubber and dye industries) the amount of untreated wastewaters that are discharged into streams and water bodies also increased. Among the wastewater contaminants, particularly dyes can generate serious problems in human health due to their toxicity, mutagenicity, and carcinogenicity even at low concentrations. Moreover, they are highly resistant to light, aerobic digestion and oxidizing agents due to their chemical stability. Therefore, wastewater treatment is essential and various technologies have been employed for dye removal such as electrocoagulation, photocatalytic, oxidative and biochemical degradation and adsorption. Adsorption has received special attention due to its simplicity, high efficiency, including the treatment of concentrated dye effluents, low cost and the possibility of reusing the adsorbent through its recovery and regeneration (Agarwal *et al*, 2016; Piriya *et al*, 2021).

Adsorption on activated carbons (AC) has been widely used for dye removal due to their high porosity and surface area. However, due to their high cost and regeneration difficulty, numerous investigations have focused on their production from natural and low-cost precursors (Chikri *et al*, 2020). Thus, pine sawdust, a byproduct from the wood industry, can be used as a good precursor due to its availability, abundance and low-cost. Additionally, the type of activation agent will strongly influence the properties of the activated carbon (Heidarinejad *et al*, 2020). Among the most used activating chemical agents such as $ZnCl_2$, KOH, H_3PO_4 and K_2CO_3, which present an enhanced effect on carbon surface area and porosity (Agarwal *et al*, 2016), $ZnCl_2$ stands out as an excellent activating agent, however with limited use in the food and pharmaceutical industries due to possible health problems (Heidarinejad *et al*, 2020; Piriya *et al*, 2021).

Based on this scenario, the present study was focused on the production of a novel activated carbon using pine (*Pinus radiata*) sawdust, provided by a regional sawmill (Lugo, Spain) as precursor and exploring the $ZnCl_2$ role as activating agent on the adsorption of acid wood dyes.

Thereby, pine sawdust, after being dried and sieved (0.5 - 1 mm), was carbonized in a horizontal tubular furnace at 600°C for 1 h under a nitrogen atmosphere. Thereafter, the biochar produced was mixed with $ZnCl_2$ at a weight ratio of 1:4 and activated at 850°C for 2 h under a nitrogen atmosphere ($AC_{ZnCl2\text{-}850}$). Finally, the obtained material was washed with HCl 0.1M and distilled water and dried overnight at 105°C (Eleri *et al*, 2020).

$AC_{ZnCl2\text{-}850}$ was characterized by the point of zero charge (pH_{PZC} = 7.8), BET surface area, N_2 and CO_2 sorption isotherms and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) before and after adsorption.

To optimize adsorption process, experiments were performed at different pH (2, natural pH, 7, 9 and 12), initial dye concentration (5 and 500 mg L^{-1}) and adsorbent dose (0.1 - 0.5 g L^{-1}) to study the removal of acid blue (Blue for wood AGN-270%), red (Red for wood GRA-200%) and black (Black Hispalan M-RN-140%) industrial wood dyes by the $AC_{ZnCl2\text{-}850}$ prepared. Natural pH is 5.1, 6.0 and 6.2 for aqueous blue, black and red dyes solutions at 5 mg L^{-1}, respectively.

Activated carbon produced has a surface area of 471.4 m^2 g^{-1} and meso and micropore volumes of 0.024 and 0.232 cm^3 g^{-1}, respectively. pH effect was evaluated at an initial dye concentration of 5 mg L^{-1}, an adsorbent dose of 0.5 g L^{-1} and a contact time of 48 h to assure equilibrium, except for the black dye that was not stable for times greater than 6 h as determined in a previous work (unpublished). Figure 1 shows that the total removal of the blue dye was achieved at all pH values. For the red dye the highest removal was obtained at pH from 2 (96.8%) to the natural pH (96.0%) but decreased when pH was increased from 7 to 12. Regarding the black colorant, the removal percentages were much lower than those for the red and blue ones. The greatest elimination was achieved at pH = 2 (55.6%) and progressively fell by increasing pH from 2 to 12. Possibly, the improvement of dye adsorption at pH lower than pH_{PZC} is because the AC surface is positively charged and adsorption of acid dye anions increases through electrostatic attraction (Piriya *et al*, 2021). For the blue and red dyes that showed high removal efficiencies at natural pH and 5 mg L^{-1}, the influence of the adsorbent dose was analysed. Particularly for the blue colorant, a 100% removal percentage was maintained by reducing the dose from 0.5 to 0.4 g L^{-1}, but there was a significant decrease to 31.8% when the adsorbent dose was lowered to 0.1 g L^{-1}.

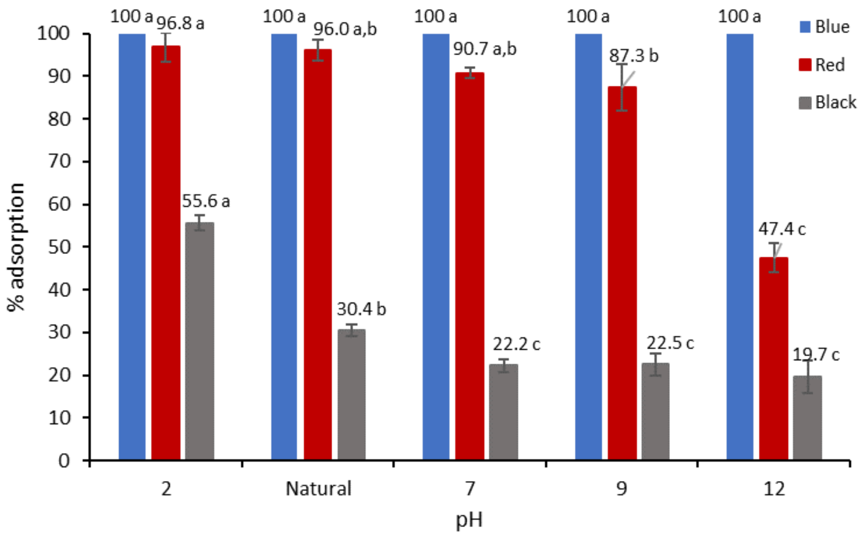

Figure 1. Effect of pH on adsorption of blue, red and black wood dyes onto $AC_{ZnCl2-850}$ (dye concentration: 5 mg L^{-1}, adsorbent dose: 0.5 g L^{-1}, contact time: 48 h for blue and red dyes and 6 h for black dye, temperature: 25 °C, agitation speed: 210 rpm). For each dye different letters indicate significant differences ($p \leq 0.05$) between samples.

Additionally, impact of pH became more evident with the increase of the initial dye concentration to 500 mg L^{-1} since, generally, caused a decrease in the dye adsorption percentage. For instance, for the blue dye that was completely removed at 5 mg L^{-1} at all pH values, at 500 mg L^{-1} and pH = 2 the maximum efficiency attained was 9.4%. Finally, kinetic studies were performed at the best operational conditions for each dye and experimental data were best fitted to the pseudo-second order kinetic model.

SEM-EDX images before and after adsorption demonstrated the presence of dyes on the $AC_{ZnCl2-850}$ surface.

Results shown demonstrate the potential of pine (*Pinus radiata*) sawdust to produce activated carbons with capacity of removing dyes from aqueous solutions. The activated carbon prepared showed high efficiency for the removal of blue and red wood yes but limited for the black one. Moreover, initial dye concentration, adsorbent dose and pH were found to have a significant influence on dye removal. Thus, further work will be focused on investigating the carbon activation process with the aim of optimizing the dye removal process.

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