UTILIZATION OF CHEMICALLY MODIFIED WALNUT SHELL FOR THE ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS

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Abstract

Due to intensive food production, the generation of agricultural waste leads to a significant environmental impact. Nuts, such as hazelnuts, walnuts, and pistachios, are produced in millions of tons annually, given their proven health benefits in human nutrition. However, their consumption implies separation of edible part from the shell, which remains as waste raw material. The shell makes up to 67% of the total weight of walnuts. In this research, the walnut shell was crushed and chemically modified (with 0.5 M citric acid) to investigate the potential of its application as an adsorbent for removing copper and zinc from water. Modified adsorbent material (particles <250 μm) led to the formation of ester bonds between citric acid and the lignocellulosic structure of the shell, which improved its adsorption properties. Characterization of the samples was performed by FTIR analysis, while structural changes were monitored by optical microscopy. Experiments were conducted at an initial metal concentration of 50 mg/L, where the metal removal rate was observed for three hours in a 50 mL solution with the addition of 1 g of adsorbent. The adsorption capacities of Zn^{2+} and Cu^{2+} by walnut shell were 0.082 mg/g and 0.143 mg/g, respectively. The kinetic studies of Zn^{2+} and Cu^{2+} adsorption onto modified walnut shells revealed that the pseudo-second-order (PSO) model best describes the adsorption kinetics of Zn^{2+} ($R^2 = 0.992$). At the same time, for Cu^{2+}, a slightly lower correlation was observed ($R^2 = 0.9423$). The Elovich model, which suggests possible chemisorption, also showed a high correlation, especially for Zn^{2+} ($R^2 = 0.9786$). Results indicated that the kinetics of Zn^{2+} and Cu^{2+} adsorption are initially very fast, then begin to stabilize at approximately 90 minutes of reaction. By the end of the experiment, at a contact time of 180 minutes, Cu^{2+} ion removal reaches approximately 70%, whereas Zn^{2+} adsorption efficiency is slightly lower, around 50%. This trend can be explained by the greater ability of Cu^{2+} ions to form stable complexes with functional groups on the adsorbent surface. Continued research will unveil the extensive possibilities of utilizing walnut shells in water purification processes, by reducing the health risks with heavy metal contamination.

Keywords: *agricultural waste, biosorption, chemical activation, copper, zinc, citric acid.*