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## REMOVAL OF PHARMACEUTICAL COMPOUNDS FROM WATER USING WALNUT SHELL-BASED BIOADSORBENTS

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### **Introduction**

Pharmaceutical residues are increasingly recognized as contaminants of emerging concern in aquatic environments due to their persistence, low biodegradability, and potential toxic effects even at trace concentrations. Global studies have reported frequent detection of antibiotics, antiepileptics, NSAIDs, and psychoactive compounds in rivers, lakes, and treated effluents. Carbamazepine, a widely used antiepileptic drug, is especially problematic due to its stability and poor removal efficiency in conventional wastewater treatment plants (WWTPs), which are not specifically designed to eliminate organic micropollutants.

In the context of Romania, national studies addressing pharmaceutical pollution are scarce, and sustainable removal methods remain underexplored. Given the urgent need for cost-effective, low-impact technologies aligned with circular economy principles, adsorption using bio-based materials represents a promising strategy. Walnut shells, an abundant agricultural by-product, have shown potential as eco-friendly adsorbents due to their low cost, availability, and modifiable surface properties.

This study investigates the use of walnut shell bio-adsorbents for the removal of carbamazepine from aqueous solutions. The influence of operational parameters such as pH, contact time, adsorbent dose, and initial pollutant concentration was assessed, with DOC (dissolved organic carbon) analysis used as the quantification method. The findings aim to support the development of sustainable, decentralized water treatment solutions using biomass waste.

### **Materials and methods**

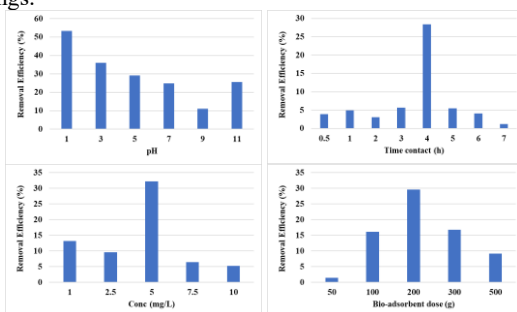
Carbamazepine (CBZ) analytical standard was used to prepare stock solutions in ultrapure water. Bio-adsorbents were prepared from ground walnut shells, washed and dried, with low intrinsic DOC content. Batch adsorption experiments were conducted at room temperature in 250 mL Erlenmeyer flasks, each containing 100 mL of CBZ solution. The effects of pH (adjusted from 1 to 11 using HCl or NaOH), contact time (30 min to 8 h), initial CBZ concentration (1–10 mg/L), and adsorbent dose (50–500 mg) were investigated. Samples were filtered before DOC analysis using a Total Organic Carbon analyser (TOC-LCPN, Shimadzu). Each condition was tested in duplicate, and average values were reported. CBZ removal

efficiency (%) was calculated based on initial and final DOC concentrations, assuming CBZ was the dominant DOC contributor.

### Results and conclusions

The removal efficiency of carbamazepine varied significantly with pH, adsorbent dose, and contact time (Figure 1). The most favorable pH for CBZ adsorption was pH 1, where removal efficiency reached 53%. This suggests increased electrostatic interaction or protonation favoring adsorption at highly acidic conditions. At neutral and alkaline pH values, adsorption efficiency decreased markedly.

Contact time influenced CBZ removal, with maximum efficiency (30%) recorded after 4 hours. Beyond this time, no significant increase was observed, suggesting adsorption equilibrium. Regarding initial CBZ concentration, the highest removal (32.2%) was observed at 5 mg/L, while lower or higher concentrations yielded poorer performance (e.g., 13.2% at 1 mg/L, 5.23% at 10 mg/L). This nonlinear behavior may be attributed to adsorbent saturation or diffusion limitations at high pollutant loadings.



**Figure 1.** Carbamazepine removal efficiency under different experimental conditions using walnut shell-based bioadsorbents: (a) effect of solution pH (range: 1–11); (b) effect of contact time (0.5–8 h); (c) effect of initial carbamazepine concentration (1–10 mg/L); (d) effect of adsorbent dosage (50–500 mg).

Adsorbent dosage also played a key role: 200 mg provided optimal performance (30% removal), whereas both lower (50 mg = 1.5%) and higher doses (300–500 mg) led to reduced efficiencies (9–17%). This may result from particle agglomeration or reduced active surface availability at higher solid concentrations.

In summary, walnut shell bio-adsorbents demonstrated moderate removal potential for carbamazepine under acidic conditions and optimized operational parameters. Although removal was partial, the method offers a low-cost, low-impact alternative for polishing steps in wastewater treatment. Further functionalization of bio-adsorbents and integration into hybrid treatment systems could enhance performance for real-world applications.