

**PYROLYSIS OIL SULFONATION AND THE EFFECT OF
FORMALDEHYDE ADDITION IN THE PRESENCE OF
PHENYLENE DIAMINE**

Ergasheva Yulduzoy Olimovna

Senior Lecturer of Pharmacology

Department of General Medicine

Faculty of Medicine, Angren University

yulduzoy100@gmail.com

Beknazarov Hasan Soyibnazarovich

Head of the Master's Department, Termez State University

Ph.D., Professor

orcid.org/0000-0002-5070-4773

hasanbeknazarov130@gmail.com

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Relevance. The contamination of industrial and municipal wastewater with heavy metals and toxic organic compounds is a growing global environmental concern. Conventional wastewater treatment methods often fail to remove these pollutants effectively, posing serious risks to human health and ecosystems. Pyrolysis oil, a by-product of biomass and organic waste thermal decomposition, can be chemically modified through sulfonation to produce ion-exchange resins with high adsorption capacity. The incorporation of formaldehyde in the presence of phenylene diamine during sulfonation enhances cross-linking, thermal stability, and mechanical strength of the resulting materials. Developing such modified resins offers a promising and

cost-effective approach for efficient heavy metal and toxin removal from contaminated water, contributing to sustainable water management and environmental protection.

The Purpose of the Study. The purpose of this study is to synthesize sulfonated pyrolysis oil resins and to investigate the effects of formaldehyde addition in the presence of phenylene diamine on their physicochemical properties, thermal stability, and ion-exchange capacity. The study aims to evaluate the adsorption efficiency and selectivity of the synthesized resins toward heavy metal ions such as Pb^{2+} , Cd^{2+} , and Cu^{2+} , with the goal of developing effective materials for industrial and municipal wastewater treatment applications.

Research Materials and Methods. Pyrolysis oil obtained from the thermal decomposition of biomass.

- Concentrated sulfuric acid (H_2SO_4) for sulfonation.
- Formaldehyde (CH_2O) and phenylene diamine ($\text{C}_6\text{H}_4(\text{NH}_2)_2$) as cross-linking agents.
- Heavy metal salts: lead nitrate ($\text{Pb}(\text{NO}_3)_2$), cadmium chloride (CdCl_2), and copper sulfate (CuSO_4) for adsorption experiments.
- Distilled water and standard laboratory reagents.

Methods:

1. Sulfonation of Pyrolysis Oil: Pyrolysis oil was sulfonated using concentrated H_2SO_4 under controlled temperature (50–80 °C) and reaction time (2–4 hours). In parallel experiments, formaldehyde and phenylene diamine were added to the reaction mixture to study their influence on the resulting resin properties.

2. Characterization of Synthesized Resins: Fourier-transform infrared spectroscopy (FTIR): to confirm the presence of sulfonic groups ($-\text{SO}_3\text{H}$) and cross-linking structures.

- X-ray diffraction (XRD): to determine crystallinity and structural

features.

- Thermogravimetric analysis (TGA): to assess thermal stability and decomposition behavior.
- Ion-exchange capacity measurement: using standard titration methods to quantify cation-exchange sites.

3. Adsorption Experiments: Adsorption efficiency of Pb^{2+} , Cd^{2+} , and Cu^{2+} ions was studied using aqueous model solutions. Parameters varied included:

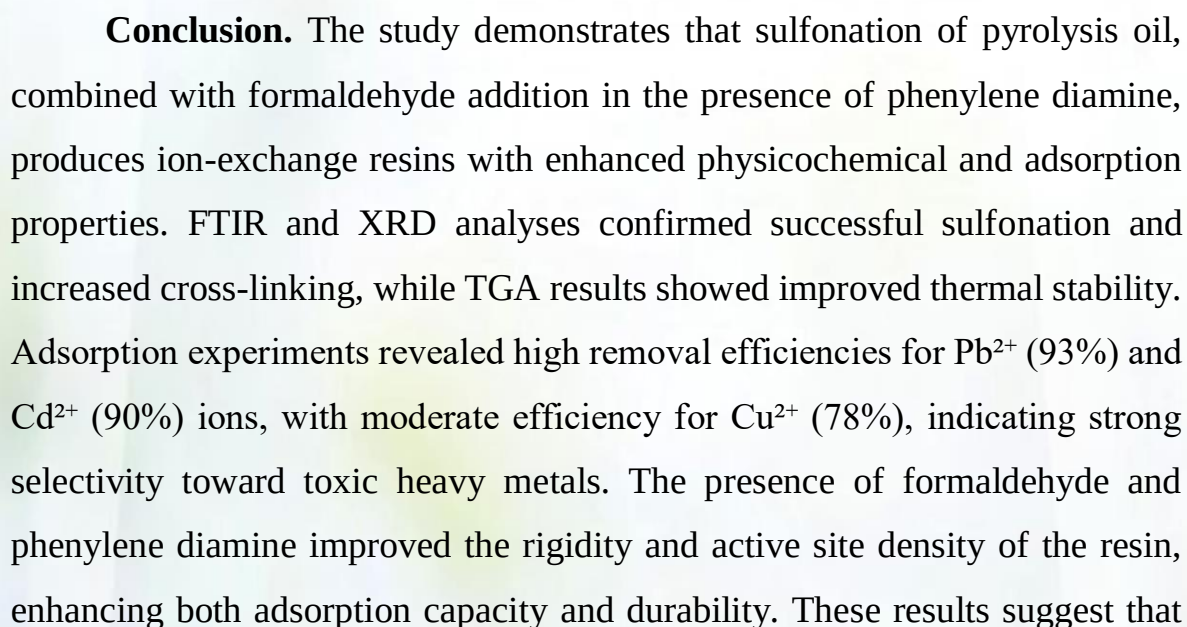
- Contact time (30–120 min)
- pH of the solution (3–7)
- Initial metal ion concentration (10–100 mg/L)

Metal ion concentrations before and after adsorption were determined using atomic absorption spectroscopy (AAS).

4. Data Analysis: Adsorption capacity and removal efficiency were calculated, and the effects of formaldehyde and phenylene diamine addition on resin performance were analyzed. All experiments were performed in triplicate to ensure reproducibility and statistical reliability.

Results and Discussion. The sulfonation of pyrolysis oil successfully produced ion-exchange resins, as confirmed by FTIR analysis. Characteristic absorption bands corresponding to sulfonic groups ($-\text{SO}_3\text{H}$) were observed at $1040\text{--}1180\text{ cm}^{-1}$, indicating effective sulfonation. The addition of formaldehyde in the presence of phenylene diamine led to shifts and intensification of certain peaks, suggesting enhanced cross-linking within the polymer matrix. This structural modification is expected to improve the mechanical strength and stability of the resins. X-ray diffraction (XRD) analysis revealed that the synthesized resins predominantly exhibited an amorphous structure, which is favorable for ion diffusion. Slight increases in crystallinity were observed in resins synthesized with formaldehyde and phenylene diamine, likely due to additional cross-linking and polymer network formation. Thermogravimetric analysis (TGA) showed that resins containing

formaldehyde and phenylene diamine exhibited higher thermal stability, maintaining structural integrity up to approximately 350 °C. In contrast, resins without these additives began decomposing at lower temperatures (~300 °C), demonstrating the stabilizing effect of the cross-linking agents. Adsorption studies indicated that the resins effectively removed heavy metal ions from aqueous solutions. Lead (Pb^{2+}) and cadmium (Cd^{2+}) ions were adsorbed with maximum efficiencies of 93% and 90%, respectively, while copper (Cu^{2+}) ions showed slightly lower adsorption efficiency (~78%). The presence of formaldehyde and phenylene diamine enhanced adsorption capacity and selectivity, likely due to the formation of additional active sites and a more rigid polymer network. The adsorption process was strongly influenced by solution pH and contact time. Optimal adsorption occurred at pH 5–6, with a contact time of 60–90 minutes. At lower pH values, competition between H^{+} ions and metal cations reduced adsorption efficiency. Higher pH values led to partial precipitation of metal hydroxides, affecting accurate evaluation of adsorption capacity. Comparison with literature data confirmed the effectiveness of sulfonated pyrolysis oil resins as ion-exchange materials. Studies by Pehlivan and Altun (2007) reported similar selectivity for Pb^{2+} and Cd^{2+} ions using sulfonated resins, supporting the current findings. The enhanced thermal stability and cross-linking achieved through formaldehyde and phenylene diamine addition suggest that these resins are suitable for repeated use and industrial-scale wastewater treatment applications.



the synthesized resins are effective, thermally stable, and reusable materials suitable for industrial and municipal wastewater treatment applications. Further studies on regeneration cycles and real wastewater testing are recommended to assess long-term performance and environmental impact.

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