STRUCTURE, THERMAL STABILITY, AND D-METAL ION SORPTION OF SORBENTS OBTAINED BY MODIFYING RECYCLED POLYMERS

Shoqulova Mahliyo To'lqin qizi
Safarov Azamat Rasul o'g'li
Bozorov Lutfulla Ubaydullayevich
Termez State Pedagogical Institute;
EMU University
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Abstract. This thesis describes the synthesis and structure of TX-1 and TX-2 ion-exchange and complex-forming sorbents obtained by modifying recycled polyethylene, polypropylene, and polyvinyl chloride with diethylamine, monoethanolamine, sodium diethyldithiocarbamate, and diphenylamine, as well as the thermodynamic behavior of the sorption of selected d-metal ions (Cu(II), Cd(II), Zn(II), and Ag(I)) by these sorbents. The results obtained from FTIR spectroscopy, differential thermal analysis (TGA-DTA-DSC), and sorption isotherms were analyzed, providing a scientific basis for the spontaneous nature of the sorption process.

Keywords. *recycled polymers, modification, ion-exchange sorbent, d-metals, sorption thermodynamics, Langmuir isotherm, complex-forming compounds.*

Introduction. Contamination of water bodies with ions of d-block metals such as copper, cadmium, zinc, and silver from industrial and domestic waste is one of today's pressing environmental problems. At the same time, post-consumer waste from widely used polymers such as polyethylene, polypropylene, and polyvinyl chloride also imposes a substantial environmental burden. The chemical modification of recycled polymer feedstocks into ion-exchange materials with high sorption capacity is considered a promising way to address both problems simultaneously. This study aimed to synthesize new TX-1 and TX-2 sorbents based on recycled PE, PP, and PVC and to investigate the thermodynamic behavior of the sorption of selected d-metal ions by these materials.

Materials and Methods. The TX-1 sorbent was synthesized by modifying polyvinyl chloride with diethylamine in a dimethylformamide solution at 80-90 °C, whereas the TX-2 sorbent was synthesized by modifying polyvinyl chloride with sodium diethyldithiocarbamate. Both sorbents were obtained as gel-like materials that partially swell in water and are insoluble in organic solvents; the reaction yields were 87-88%. The composition and structure of the sorbents were studied using an FTIR spectrometer (SHIMADZU, Japan; 400-4000 cm^{-1}), their thermal stability was evaluated by TGA-DTA-DSC using a Netzsch Simultaneous

Analyzer STA 409 PG (Germany), and their morphology and elemental composition were examined by scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). Metal-ion sorption was investigated spectrophotometrically (OPTIZEN III) at different pH values, temperatures (25-50 °C), and contact times.

Results and Discussion. In the FTIR spectrum of the TX-1 sorbent, the stretching vibrations of methyl and methylene groups were observed at 2978 and 2945 cm^{-1}, the deformation vibration of the N-CH_2 bond at 1425 cm^{-1}, and the C-O stretching vibration at 1024 cm^{-1}. In the spectrum of the TX-2 sorbent, the stretching vibration of the imino group was identified at 3392 cm^{-1}, while that of the sulfo group appeared at 1354 cm^{-1}. These results were confirmed by the appearance of new absorption bands that differed from those in the FTIR spectrum of the initial polyvinyl chloride, demonstrating the formation of the new sorbents.

According to the thermal analysis results, the TX-1 sorbent was thermally stable up to 120 °C. Endothermic effects were observed at 126, 275, 362, and 484 °C, whereas exothermic effects occurred at 162, 246, 284, 332, and 543 °C. For the TX-2 sorbent, endothermic effects were recorded at 84, 146, 205, 320, 426, and 562 °C, and exothermic effects at 292, 324, and 504 °C. The complexes formed upon metal-ion uptake by the sorbents exhibited substantially higher thermal stability than the sorbents themselves: the decomposition temperature shifted from 240-275 °C to 340-360 °C. This finding indicates that formation of metal-ligand coordination bonds increases the stability of the system.

The sorption study showed that the static ion-exchange capacities of the TX-1 sorbent under optimal pH conditions were as follows: Cu(II), 2.4 meq/g (pH 5); Cd(II), 2.3 meq/g (pH 5); Zn(II), 2.1 meq/g (pH 3); and Ag(I), 2.9 meq/g (pH 2). The corresponding values for the TX-2 sorbent were Cu(II), 4.6 meq/g (pH 5); Cd(II), 3.8 meq/g (pH 6); Zn(II), 2.8 meq/g (pH 6); and Ag(I), 4.7 meq/g (pH 4). For both sorbents, the degree of metal-ion sorption increased in the following order: Zn(II) < Cd(II) < Cu(II) < Ag(I). The decrease in sorption at pH > 6 indicates that metal ions are sorbed through the formation of ion associates with protonated active functional groups.

Analysis of the sorption isotherms showed that Cu(II) sorption on both sorbents followed the Langmuir model with greater accuracy than the Freundlich model, indicating sorption as a homogeneous monomolecular layer on the sorbent surface. The increase in the calculated maximum sorption capacity with temperature is explained by the temperature-dependent increase in swelling of

the polymer matrix, which allows the sorbed ions to penetrate more deeply into the sorbent.

Thermodynamic parameters calculated from the temperature dependence of the sorption equilibrium constant showed that Cu(II) sorption on both sorbents proceeded with negative free-energy ($\Delta G < 0$) and enthalpy ($\Delta H < 0$) values and an increase in entropy ($\Delta S > 0$). These findings indicate that the sorption process is exothermic and spontaneous; the increase in the entropy of the system can be attributed to disruption of the solvation shells surrounding the active functional groups of the sorbent. The thermodynamic favorability of the process further confirms that the synthesized sorbents can efficiently and stably sorb d-metal ions.

Conclusion. Highly efficient TX-1 and TX-2 ion-exchange and complex-forming sorbents were synthesized by modifying recycled polyethylene, polypropylene, and polyvinyl chloride with diethylamine and sodium diethyldithiocarbamate. The composition and structure of the sorbents were confirmed by FTIR spectroscopy and SEM-EDS, while TGA-DTA-DSC analysis demonstrated their sufficiently high thermal stability and showed that this stability increased further upon complex formation with metal ions. The sorption of Cu(II), Cd(II), Zn(II), and Ag(I) ions followed the Langmuir model and was thermodynamically spontaneous ($\Delta G < 0$, $\Delta H < 0$, and $\Delta S > 0$). The findings provide a scientific basis for developing inexpensive, environmentally safe, and highly efficient sorbents from recycled polymer feedstocks and demonstrate their potential for removing heavy-metal ions from industrial wastewater.

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