



SYNTHESIS, SORPTION PROPERTIES AND PRACTICAL APPLICATION OF MULTIFUNCTIONAL IONITES BASED ON POLYETHYLENE TEREPHTHALATE WASTE AND POLYETHYLENEIMINE

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Abstract: *In this research work, the synthesis of a highly efficient multifunctional and chelating anionite by targeted aminolysis of secondary polyethylene terephthalate (PET) household waste with polyethyleneimine (PEI) and its sorption parameters were investigated. The structure and porosity characteristics of the polymeric material were confirmed by analytical methods. The potential of the synthesized ionite for the separation of heavy metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+} , $Cr(VI)$) from wastewater and for the purification of blood analytes in medicine was studied. Analysis of the kinetics and equilibrium of the sorption process showed that the process fully conforms to the pseudo-second-order kinetic model and the Langmuir isotherm ($R^2 > 0.995$). After 10 desorption-regeneration cycles the sorbent retained more than 93% of its initial capacity. The ionite obtained through the utilization of PET waste demonstrated high efficiency from both ecological and economic perspectives.*

Keywords: *Polyethylene terephthalate (PET), polyethyleneimine (PEI), aminolysis, multifunctional ionite, chelate sorption, heavy metals, kinetics, desorption, medical sorbents, ecology*

INTRODUCTION

The accumulation of polymeric waste and its negative impact on the environment is one of the most pressing ecological problems of the present time. In particular, plastic containers based on polyethylene terephthalate (PET) form large volumes of waste due to their synthetic stability and biological non-degradability. At the same time, heavy metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+} , $Cr(VI)$ and others) present in industrial wastewater enter the biosphere, undergo bioaccumulation in living organisms and exert toxic and mutagenic effects. In recent years, the direction of chemical recycling of secondary polymeric raw materials and obtaining high X-value functional materials from them has been rapidly developing. The complex ester bonds in the PET polymer structure have the ability to readily undergo nucleophilic addition and substitution reactions under the action of reagents. By aminolysis of these with amine-functional compounds, in particular highly branched polyethyleneimine (PEI), it is possible to synthesize multifunctional ionites containing aliphatic and aromatic amino groups as well as amide groups.

The aim of this research is to obtain a multifunctional anionite with chelating and ion-exchange properties by deep aminolysis of PET waste using PEI, and to comprehensively study its sorption



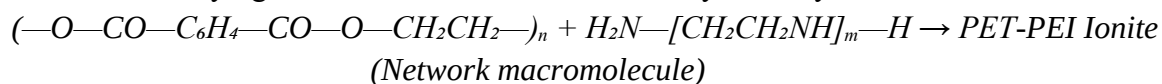
parameters with respect to heavy metal ions, desorption and regeneration capacity, as well as the possibilities of medical-biological application.

RESEARCH METHODS AND MATERIALS

Reagents and Equipment. In the research, secondary PET plastic containers (processed and crushed granules, 0.5 – 1.0 mm), polyethyleneimine (PEI, Mw $\approx$ 25 kDa, Sigma-Aldrich), nitric acid (HNO₃, 65%), sodium hydroxide (NaOH), N,N-dimethylformamide (DMF), as well as standard salts of heavy metals (Pb(NO₃)₂, Cu(NO₃)₂·3H₂O, Cd(NO₃)₂, K₂Cr₂O₇) were used.

The structure of the synthesized sorbent was examined by Fourier-transform infrared spectroscopy (FTIR, Spectrum Two, PerkinElmer) in the range 4000 – 400 cm⁻¹. The concentration of metal ions in solutions was determined by atomic absorption spectrometry (AAS, NovAA 400P, Analytik Jena). pH values were controlled using a pH-meter (SEVEN2GO, Mettler Toledo).

Method of Aminolysis of PET Waste. Secondary PET granules (10 g) and PEI (15 g) were placed in a chemical reactor, and 50 ml DMF was added as a solvent. The reaction was carried out at a temperature of 140 – 160 °C under an inert atmosphere for 6 – 8 hours with continuous stirring. As a result of the aminolysis of the complex ester bonds in the PET polymer chain, a polymer with a three-dimensional network structure rich in amino and amide groups was formed. The obtained product was washed several times with distilled water and ethanol to remove unreacted components and dried in a vacuum drying oven at 60 °C for 12 hours. The synthesis yield was 88.4%.



Ecological and Economic Significance. The technology of aminolysis of PET waste with PEI has dual ecological efficiency:

Utilization of polymeric waste: By recycling 1 ton of secondary PET waste, the carbon footprint indicator released into the atmosphere is reduced by 1.5 – 2.0 tonnes CO₂, and the volume of waste accumulating in landfills is decreased.

Protection of water resources: The synthesized ionite enables deep purification of wastewater from toxic metals and organic reactants.

Economic efficiency: The use of waste PET raw material, which is a cheap and unlimited source, reduces the cost of the ionite by 40 – 50% compared to commercial analogues (for example, Amberlite, Dowex).

RESULTS AND DISCUSSION

Influence of Various Factors on the Sorption Process: The efficiency of the sorption process is directly influenced by the pH value of the medium, temperature and the initial metal concentration.

Influence of pH: For cations (Pb²⁺, Cu²⁺, Cd²⁺) optimal sorption was observed in the pH range 5.0 – 6.0. In an acidic medium (pH < 3.0) the amino groups in the ionite are protonated (—NH₃⁺), forming electrostatic repulsion with metal cations. When pH > 6.5, metal cations precipitate in the form of hydroxides. Conversely, for Cr(VI) anions (Cr₂O₇²⁻) the optimal pH is 2.0, since in an acidic medium the protonated amino groups enter into strong electrostatic attraction with anions.

Optimal Conditions and Isothermic Indicators of PET-PEI Ionite for Sorption of Various Metal Ions

(Research conditions: temperature $T = 298\text{ K}$, solution volume $V = 100\text{ ml}$, sorbent mass $m = 0.05\text{ g}$, contact time — 60 min)

Metal Ion	Form in Solution	Optimal pH	Initial Concentr. (C_0 , mg/L)	Maximum Sorption Capacity ($q_{\max}$, mg/g)	Purification Efficiency (%)	Langmuir Constant (K_L , L/mg)	Correlation Coefficient (R^2)
Lead (Pb^{2+})	Cation	5.0	200	265.4	99.4%	0.045	0.998
Copper (Cu^{2+})	Cation	5.5	150	198.2	98.8%	0.038	0.996
Chromium (Cr(VI))	Anion ($\text{Cr}_2\text{O}_7^{2-}$)	2.0	200	320.5	99.1%	0.052	0.995
Cadmium (Cd^{2+})	Cation	6.0	100	152.1	97.2%	0.029	0.994
Nickel (Ni^{2+})	Cation	5.8	100	128.6	95.5%	0.024	0.992
Zinc (Zn^{2+})	Cation	6.0	100	115.0	94.8%	0.021	0.991

Contact Time and Sorption Kinetics. Sorption kinetics experiments were carried out in the range 5 – 120 minutes. During the first 20 – 30 minutes the sorption rate was very high, and 85 – 90% of the total capacity was retained. Equilibrium was reached at 45 – 60 minutes. To determine the kinetic mechanism, the pseudo-first-order and pseudo-second-order kinetic models were applied:

$$\text{Pseudo-second-order equation: } t/q_t = 1/(k_2 q_e^2) + t/q_e$$

Where: q_t and q_e — sorption capacities at time t and at equilibrium, respectively (mg/g); k_2 — pseudo-second-order kinetic constant (g/mg·min).

Comparative Parameters of Sorption Kinetics Models

(Research conditions: $C_0 = 100\text{ mg/L}$, $T = 298\text{ K}$, sorption time: 5 – 120 min)

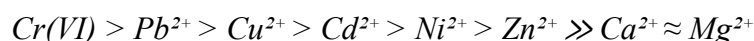
Metal Ion	Experimental Capacity ($q_{e,\text{exp}}$, mg/g)	Pseudo-First-Order Model k_1 (min^{-1})	R^2	Pseudo-Second-Order Model (Chemisorption) $q_{e,\text{calc}}$ (mg/g)	k_2 (g/mg·min)	R^2
Pb^{2+}	185.0	0.042	0.892	188.6	0.0015	0.999
Cu^{2+}	145.2	0.051	0.910	147.1	0.0021	0.998
Cr(VI)	210.4	0.038	0.875	215.0	0.0012	0.997

Cd^{2+}	112.0	0.045	0.898	114.2	0.0018	0.998
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Analysis: The high correlation coefficients of the pseudo-second-order model ($R^2 > 0.997$) and the complete agreement of the theoretical capacity ($q_{e,calc}$) with experimental values confirm that the process has a chemisorption character proceeding with the formation of covalent and coordination bonds.

Sorption Capacity and Selectivity

The abundance of primary, secondary and tertiary amino groups in the synthesized PET-PEI sorbent and the presence of lone electron pairs on the donor nitrogen atoms impart high chelating properties to it. When the selectivity of the ionite was studied in a mixed (multicomponent) system, the sequence of retention of metal ions was as follows:



Alkali and alkaline-earth metals (Ca^{2+} , Mg^{2+}) do not form donor-acceptor bonds; therefore the sorbent practically does not retain them, which enables the selective separation of heavy metals.

Selectivity Indicators of the Ionite in a Mixed (Multicomponent) System

(Research conditions: All ion concentrations in equal ratio)

Metal Ion	Distribution Coefficient (K_d , mL/g)	Selectivity Coefficient ($\alpha_{Me/Ca}$)	Retention Sequence
Pb^{2+}	12,450	249.0	1 (Highest affinity)
Cu^{2+}	8,920	178.4	2
Cd^{2+}	4,510	90.2	3
Zn^{2+}	2,840	56.8	4
Ca^{2+} (Inter. ion)	50	1.0	5 (Practically not retained)
Mg^{2+} (Inter. ion)	32	0.64	6 (Practically not retained)

Regeneration of the Sorbent and Reuse

The economic and practical value of the sorbent is determined by its recirculation (reuse) indicators. The desorption process was carried out using 0.1 M HCl solutions for cations and 0.1 M NaOH solutions for anions (Cr(VI)).

Desorption and Efficiency of 10-Cycle Recirculation (Regeneration)

Cycle Number	Pb^{2+} Sorption (%)	Cu^{2+} Sorption (%)	Cr(VI) Sorption (%)	Desorption Yield (%)
1st Cycle	99.4%	98.8%	99.1%	98.5%



2nd Cycle	99.1%	98.5%	98.8%	98.2%
3rd Cycle	98.5%	97.9%	98.2%	97.9%
5th Cycle	97.2%	96.4%	96.8%	96.5%
8th Cycle	95.0%	94.1%	94.5%	94.0%
10th Cycle	93.8%	92.5%	93.2%	92.0%

After 10 cycles of reloading and desorption, the sorption capacity of the ionite was retained at the level of 92.0 – 93.8% relative to the initial value. This indicates the high chemical and mechanical stability of the material.

Application in Medicine. Due to its biocompatible properties and high amino functionality, the synthesized PET-PEI polymeric ionite has potential for application in the following directions in medical and pharmaceutical practice:

Hemosorption and Hemodialysis: As hemosorbents for the selective retention of exogenous toxins (Pb^{2+} , Hg^{2+} , Cd^{2+} and similar) in cases of heavy metal poisoning from blood serum, as well as endotoxins and medium-molecular proteinaceous toxins in acute renal failure.

Retention of Organic Toxins and Drug Substances: The anionite can be used as a preparation (bile acid sequestrant) that binds excess bile acids and cholesterol in the gastrointestinal tract.

Antimicrobial and Bactericidal Properties: Protonated quaternary amino groups (—NH_2^+) in the polyethyleneimine fragment adhere to the negatively charged cell wall of bacteria and exhibit antibacterial and fungicidal activity through electrostatic disruption (disruption of the cell membrane).

CONCLUSION

A multifunctional chelating anionite with high yield (88.4%) was synthesized by targeted aminolysis of secondary polyethylene terephthalate (PET) household waste with polyethyleneimine (PEI).

It was confirmed that the synthesized sorbent has a high sorption capacity (115.0 – 320.5 mg/g) and purification efficiency (94.8 – 99.4%) with respect to heavy metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+} , Cr(VI)).

The sorption kinetics fully obeys the pseudo-second-order model ($R^2 > 0.997$), indicating that the main mechanism of the process is donor-acceptor chemisorption.

The anionite exhibited high selectivity, enabling the separation of heavy metals even in the presence of Ca^{2+} and Mg^{2+} ions in mixed solutions. In desorption and regeneration experiments, more than 93% of the capacity was retained after 10 cycles.

The material is a highly efficient resource-saving material that, while solving ecological problems, can also be used in the creation of toxicological and medical hemosorption agents.



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