Radiation-chemical synthesis of nanocomposite adsorbents based on polypropylene fibers for selective removal of heavy metals and radionuclides from contaminated waters

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Objective of the current research

Sources of radionuclides in Ukraine:
- Liquid radioactive wastes of Chernobyl origin;
- Liquid radioactive wastes of Nuclear power plants;
- Uranium ore processing waters

Typical concentration of radionuclides in liquid wastes of uranium ore processing plants and in waters of uranium mines

<table>
<thead>
<tr>
<th>RN</th>
<th>MPC*</th>
<th>Liquid wastes</th>
<th>Mining water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra-226</td>
<td>3 nCu/l</td>
<td>2000-10000 nCu/l</td>
<td>10-100 nCu/l</td>
</tr>
<tr>
<td>Th-230</td>
<td>600 nCu/l</td>
<td>500000-200000 nCu/l</td>
<td>Low</td>
</tr>
<tr>
<td>U-238</td>
<td>3-4 mg/l</td>
<td>1-10 mg/l</td>
<td>0-100 mg/l</td>
</tr>
</tbody>
</table>

*Maximum permissible concentration

Radionuclides activity in liquid and solid radioactive wastes produced at the South-Ukrainian NPP

Current project:
Development of novel nanocomposite adsorbents based on polymer fibers for selective removal of heavy metals and radionuclides from contaminated waters
Polypropylene (PP) 
Excellent physical–chemical properties:
• low density; • elasticity;
• chemical and thermal resistance;
• worker temperature till +80°C;
• nontoxicity

PP fibers
• good mechanical strength;
• highly developed specific surface;
• low hydraulic resistance; • low cost;
• easy modification by radiation methods;
• PP fibers are available as nonwoven fabric of different length and shape

Polymer adsorbents based on polypropylene fibers

Drawback:
PP is chemically inert material

Solution:
Modification of PP fibers’ surface by radiation-induced graft polymerization (RIGP)
Radiation synthesis of polymer adsorbent based on PP fibers

Polymer adsorbent consists of two main parts: chemically active functional group(s) of grafted chains on the surface of inert polymer matrix.

Irradiation of PP fibers to synthesize polymer adsorbents was performed at the Electron Beam Accelerator Center of Yeungnam University (S.Korea).

Conditions at which irradiation was carried out by electron beam accelerator:
- Accelerator voltage: 0.7 MeV
- Beam current: 4–7 mA
- Distance from window: 23 cm
- Conveyer speed: 2 m/min
- Dose range: 40–100 kGy
- Number of pass: 1 or 2 (for dose 100 kGy)
- Atmosphere: Air
- Ambient temperature: 15 °C

Electron beam accelerator ELV-05 with 0.7 MeV of accelerated energy
Some polymer adsorbents based on PP fibers synthesized by radiation-induced graft polymerization at the Institute of Environmental Geochemistry (Kiev, Ukraine)

<table>
<thead>
<tr>
<th>Base</th>
<th>Functional group</th>
<th>Type</th>
<th>Optimal ion-exch. capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP fiber</td>
<td>-COOH</td>
<td>Ion-exch. (weak acid)</td>
<td>5,0</td>
</tr>
<tr>
<td>PP fiber</td>
<td>-COOH -SO₃H</td>
<td>Ion-exch. (Strong acid, weak acid)</td>
<td>5,0 (COOH) 2,0 (SO₃H)</td>
</tr>
<tr>
<td>PP fiber</td>
<td>-SO₃H</td>
<td>Ion-exch. (Strong acid)</td>
<td>1,7</td>
</tr>
<tr>
<td>PP fiber</td>
<td>Iminodiacetic acid -N(COOH)₂</td>
<td>Chelating</td>
<td>2,5</td>
</tr>
<tr>
<td>PP fiber</td>
<td>Triethylamine [–N(CH₂CH₃)₃]</td>
<td>Strong base</td>
<td>1,8-2,3</td>
</tr>
<tr>
<td>PP fiber</td>
<td>Phosphoric acid (–PO₃ H₂)</td>
<td>Strong acid</td>
<td>1,8</td>
</tr>
<tr>
<td>PP fiber</td>
<td>Diethylene triamine (DETA)</td>
<td>Chelating</td>
<td>1,8</td>
</tr>
<tr>
<td>PP fiber</td>
<td>Triethylene tetraamine (TETA)</td>
<td>Chelating</td>
<td>1,5</td>
</tr>
</tbody>
</table>
Inorganic and organic adsorbents for selective removal of radionuclides

**Inorganic adsorbents**

- Acid salts (Zr, Ti, Th, Sn, Al, Cr...)
- Insoluble ferrocyanides, \( K_2[CoFe(CN)_6]_2 \ldots \)
- Hydrous oxides \( \text{(Fe(OH)}_3, \text{SnO}_2, \text{Sb}_2\text{O}_5 \ldots \) 
- Hydrous mixed metal oxides \( \text{(Na}_4\text{Ti}_9\text{O}_{20} \)
- Salts of heteropolyacids \( \text{(NH}_4\text{)}_3\text{PMo}_{12}\text{O}_{40} \)

**Positive:**
- selectivity for the specific ions,
- thermal and radiation stability

**Negative:**
- They are synthesized as ultrafine particles, which cannot be directly employed into adsorption due to their agglomeration, compaction and loss of chemical activity

**Organic adsorbents**

- Polymer adsorbents (resins, fibers, films ... with different functional groups)

**Positive:**
- durability, high adsorption capacity, low price

**Negative:**
- Low selectivity (if low price)

**Approach:** Synthesis of composite (hybrid) adsorbents which combine positive features of both inorganic and organic phases
Solid support matrix:
Inorganic - Porous silica gel, clay minerals, zeolites, metal oxides
Organic – Natural and synthetic polymers (in form of beads, films, fibers, fabric, etc.)

Synthesis of composite adsorbents

2 approaches:

- Incorporation of preformed inorganic grains into pores/voids, channels, cracks of solid support matrix
- In situ formation of inorganic grains within/on the solid support matrix

Our choice

Synthesis of composite adsorbents by in-situ formation of inorganic nanoparticles on the surface of polymer fibers

Polymer fibers: Polypropylene (PP) and Polyacrylonitrile (PAN)

Advantages:
- Physical-chemical link between inorganic phase and polymer matrix;
- Control of size and structure of inorganic crystals;
- High specific surface of nanoparticles allow to increase the rate of ion-exchange and adsorption;
- High rate of the effluent flow;
- No compacting of inorganic crystals;
- Use in adsorption and filtration processes;
- Reusing
- Variation in form and shape of adsorbing material
Nanocomposite adsorbents based on PP fibers:

**two-stage synthesis**

**1 stage:** Radiation-induced graft polymerization of a monomer with cationic-type functional groups on the polypropylene fiber surface

**2 Stage:** In-situ formation and stabilization of inorganic nanoparticles within the grafted chains on the fiber’s surface

We believe that the close position of the charged functional groups (ion-exchange, chelation) through the nano/micro-sized length of grafted chains as well as the close position of the neighboring chains can create the nucleation sites of Me (or MeO) nanoparticles; their subsequent reaction with corresponding chemicals can lead to the formation of more complex nano-sized compounds within the grafted chains.
SYNTHESIS OF COMPOSITE ADSORBENT BASED ON POLYPROPYLENE FIBERS COATED WITH HEXACYANOFERRATE NANOPARTICLES

Importance: The selective removal of 137Cs ions from liquid radioactive wastes and their quantitative determination in the environment has a great importance in recent years.

Hexacyanoferrates (HCFs) of transition metals (II) are very effective inorganic adsorbents for cesium.

Drawback: HCFs are usually synthesized as fine or ultrafine grains, which are not suitable for practical applications due to their low mechanical stability and tendency to become colloidal in aqueous solution.

Our approach:

Synthesis of composite adsorbents by in-situ formation of KNi HCF nanoparticles on the polypropylene fibers grafted with poly(acrylic acid)

Experimental

1. RIGP of acrylic acid monomer on the PP fibers’ surface (30 – 200 % degree of grafting)
2. In-situ formation of KNi HCFs nanoparticles on the PP fibers’ surface
3. SEM with EDS, IR, XRD analysis
4. Adsorption tests
Results and discussion: SEM analysis

Original PP fibers

Composite PP-KNiHCF fibers

\( DG (PP-g-PAA) = 30\% \)

\( DG (PP-g-PAA) = 178\% \)
Results and discussion: EDS, IR and XRD analyses

Results of the SEM-EDS analysis

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT %</th>
<th>ATOMIC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>34.23</td>
<td>46.01</td>
</tr>
<tr>
<td>N</td>
<td>28.90</td>
<td>33.31</td>
</tr>
<tr>
<td>O</td>
<td>12.10</td>
<td>12.22</td>
</tr>
<tr>
<td>K</td>
<td>11.29</td>
<td>4.66</td>
</tr>
<tr>
<td>Fe</td>
<td>6.60</td>
<td>1.91</td>
</tr>
<tr>
<td>Ni</td>
<td>6.88</td>
<td>1.89</td>
</tr>
<tr>
<td>TOTALS</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

$K_2Ni[Fe(CN)_6]$  

FT-IR-ATR spectra of PP, PP-g-PAA and composite PP-KNi HCF fibers

XRD pattern of $K_2Ni[Fe(CN)_6]$  
(JCPDS card No. 20-0915)

XRD of PP and nanocomposite PP-KNiHCF fibers
The exchange of K+ ions with Cs+ ions is quite fast. Only K+ ions which are closest to the crystal surface can participate in the exchange process. Therefore the rate of reaction and maximal value of adsorption also depend upon the crystal size (surface area) of the HCF particles.

Application of composite PP-KNiFCN fibers as selective adsorbent for Cs ions

$M^{I}_{2n}M^{II}_{2-n}[(Fe(CN)_{6})x mH_{2}O$

- K+, Na+, H+ or NH$_4^+$
- Cu, Ni, Co, Zn, Fe, etc.

Adsorption of Cs takes place by ion exchange with $M^{I}$ cation

Cs$^+$ $>$ Rb$^+$ $>$ K$^+$ $>$ NH$_4^+$ $>$ Na$^+$ $>$ H$^+$ $>$ Li$^+$

The exchange of K+ ions with Cs+ ions is quite fast. Only K+ ions which are closest to the crystal surface can participate in the exchange process. Therefore the rate of reaction and maximal value of adsorption also depend upon the crystal size (surface area) of the HCF particles.

Effect of contact time

pH 9;
Initial Cs concentration – 36 mg/l

Effect of competitive sodium ions

Na/Cs $\sim$ 3000

pH 9;
Initial Cs concentration – 780 mg/l

Cs$^+$ $>$ Rb$^+$ $>$ K$^+$ $>$ NH$_4^+$ $>$ Na$^+$ $>$ H$^+$ $>$ Li$^+$

The exchange of K+ ions with Cs+ ions is quite fast. Only K+ ions which are closest to the crystal surface can participate in the exchange process. Therefore the rate of reaction and maximal value of adsorption also depend upon the crystal size (surface area) of the HCF particles.
Application of composite PP-KNiFCN fibers as selective adsorbent for $^{137}$Cs

**Composition of brine from Liman Kuyalnik, Odessa**

<table>
<thead>
<tr>
<th>Content of the main ions, mg/l</th>
<th></th>
<th></th>
<th>Total mineralization, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$+K$^+$</td>
<td>Ca$^{2+}$</td>
<td>Mg$^{2+}$</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>22951-34644</td>
<td>1425-2012</td>
<td>4957-7470</td>
<td>60529-86550</td>
</tr>
</tbody>
</table>

**Adsorption of $^{137}$Cs on composite PP-KNi HCF fabric from multicomponent salt solution with mineralization of 80 g/l**

<table>
<thead>
<tr>
<th>Activity of the model solution, Bq</th>
<th>Activity of PP-KNiHCF fabric, Bq</th>
<th>$K_d$, cm$^3$/g</th>
<th>$\varepsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution*</td>
<td>Filtrate</td>
<td>$\Delta$</td>
<td>$1680 \pm 42$</td>
</tr>
<tr>
<td>2380</td>
<td>656</td>
<td>1724</td>
<td></td>
</tr>
</tbody>
</table>

*Ration $^{137}$Cs/(Na+K) = 1 : 2x10$^9$, pH=9, m=0.042 g, V=15cm$^3$
A novel composite adsorbent based on polypropylene fibers with chemically bound nanoparticles of potassium nickel hexacyanoferrate was successfully prepared by a two-stage experiment: radiation-induced graft polymerization of acrylic acid onto the surface of PP fibers followed by the in situ formation of KNiHCF nanoparticles and their stabilization on the fibers’ surface within the grafted chains.

SEM analyses revealed that KNiHCF forms a homogeneous layer on the fibers’ surface. This layer consists of the nanosized aggregates which are rather regular in shape and closely fit one to another forming a compact texture.

To prepare an effective composite adsorbent grafted PP fibers with a medium value of acrylic acid grafting degree (30-100 %) should be taken for the experimental work.

SEM, FT-IR-ATR, and XRD techniques confirmed the formation of KNiHCF as crystalline nanoparticles with a face-centered cubic structure.

The synthesized adsorbent demonstrated fast adsorption kinetics, high adsorption capacity over a wide pH range, and selectivity in removal of Cs ions from an alkaline solution with a high concentration of competitive sodium and potassium ions.

The synthesized composite fibers can be recommended for rapid determination of cesium radionuclides in natural and industrial waters, as well as for the purification of low level liquid radioactive waste with the high concentration of competing sodium and potassium ions.
The proposed strategy of the nanocomposite fibers synthesis opens ample opportunities for the fabrication of adsorbents, catalysts, biochemical and chemical sensors on the base of commercially available polymer fibers, fabrics, resins and membranes.
Ferrihydrite (Fh) is one of the distinct Fe oxide minerals $\left(5\text{Fe}_2\text{O}_3\times9\text{H}_2\text{O}\right)$. Unlike the other iron oxides Fh exists exclusively in nanocrystalline form (ranging from 2 to 6 nm in size); Ferrihydrite exhibits two different crystalline phases: low-crystalline 2-line (2L-Fh) and more crystalline 6-line ferrihydrite (6L-Fh). Ferrihydrite is widely distributed in surface and subsurface environments, and because of its small grain size and large surface area (hundreds of square meters per gram) it is well known as a scavenger for dissolved chemical species (Cd, As, Mo, V, Zn, Pb); Recent investigations have revealed an important role of Fh in adsorption and transportation of radionuclides (U, Pu, Am, Np and Tc) in natural waters; Ferrihydrite is also an important precursor of more stable crystalline iron oxides.

Aim of the work

Development of technology for synthesis of composite materials on the base of ferrihydrite nanoparticles for adsorption of uranium and transuranium species.
Results and discussion: SEM and EDS, XRD analysis

Composite fibers show two new broad reflections at 35 and 62 2θ degree, that identify the Fe oxide coating as 2-line ferrihydrite.
Results and discussion: IR analysis, chemical stability

Stability of composite PP-Fh fibers in aggressive solutions

<table>
<thead>
<tr>
<th>pH</th>
<th>Contact time, days</th>
<th>C (Fe), mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>42</td>
<td>9.0</td>
</tr>
<tr>
<td>2.8</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>5.1</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>8.3</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>10.2</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>10.2</td>
<td>42</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Less than 2 % of Fe deposited as Ferrihydrite was released into the contacting solution after 42 days at pH 2.

Composite PP fibers with surface coated ferrihydrite nanoparticles are stable in aggressive solutions and they release Fe negligibly.
Application of composite PP-Ferrihydrite fibers as selective adsorbent for uranium

Effect of contact time

![Graph showing U adsorption vs time](image)

**Effect of initial U concentration**

![Graph showing U adsorption vs initial U concentration](image)

**Adsorption of Uranium on composite PP-Fh fibers**

<table>
<thead>
<tr>
<th>№</th>
<th>Time</th>
<th>$C_{\text{final}}, \text{g/l}$</th>
<th>Amount of U adsorbing, mg/g</th>
<th>Sorption efficiency, %</th>
<th>$K_d$, l/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>30 min</td>
<td>$4.1 \times 10^{-2}$</td>
<td>8.1</td>
<td>57.7%</td>
<td>0.20</td>
</tr>
<tr>
<td>02</td>
<td>1 h</td>
<td>$1.6 \times 10^{-3}$</td>
<td>12.2</td>
<td>98.35%</td>
<td>7.64</td>
</tr>
<tr>
<td>03</td>
<td>2 h</td>
<td>$9.3 \times 10^{-4}$</td>
<td>13.84</td>
<td>99.4%</td>
<td>14.86</td>
</tr>
<tr>
<td>04</td>
<td>24 h</td>
<td>$2.0 \times 10^{-5}$</td>
<td>14.26</td>
<td>100%</td>
<td>714.0</td>
</tr>
<tr>
<td>05</td>
<td>12 days</td>
<td>$3.70 \times 10^{-6}$</td>
<td>14.26</td>
<td>100%</td>
<td>3955.0</td>
</tr>
</tbody>
</table>

High adsorption capacity due to nanostructure!!!

We suppose surface and inside (diffusion) adsorption mechanism

$pH$ 6-6.5; Initial U concentration – 0.097 g/l
Conclusions

- Polypropylene fibers with surface coated ferrihydrite nanoparticles were synthesized by two-stage experiment: radiation-induced graft polymerization of acrylic acid monomer followed by the in-situ formation and deposition of ferrihydrite nanoparticles on the fibers’ surface;
- Elemental analysis and XRD data confirm the formation of 2-line ferrihydrite coating on the PP fibers’ surface;
- SEM with EDS analyses revealed that ferrihydrite forms a homogeneous layer on the fibers’ surface. This layer consists of the nanosized aggregates (70-100 nm) which are rather regular in shape and closely fit one to another forming a compact texture;
- The synthesized composite fibers are stable in aggressive medium for long time;
- The composite fibers demonstrate excellent adsorption properties towards uranium ions: fast adsorption kinetics, high adsorption capacity and efficiency.
Sorption of U from multicomponent solution
PP-MnO$_2$ (birnessite)
Thanks for your attention