

## Synthesis of Nanocomposite Adsorbent on the Base of Polypropylene Fabric with Copper Ferrocyanide Grains

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Composite adsorbents based on polypropylene fibers with chemically bound nanoparticles of copper ferrocyanide were synthesized by two-stage experiment: radiation-induced graft polymerization of acrylic acid onto non-woven polypropylene fabric followed by in-situ formation of copper ferrocyanide nanoparticles and their stabilization on the fabric surface within the grafted layer. Scanning electron microscope investigations revealed a homogeneous compact layer of copper ferrocyanide nanosized aggregates (65-70 nm). The synthesized composite material was stable in the base solutions (pH ~ 10.5) and exhibited high efficiency for cesium adsorption.

**Keywords:** Composite adsorbent, Copper ferrocyanide, Nanoparticles, Polypropylene fabric, Radiation grafting, Selective adsorption, Cesium.

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### 1. INTRODUCTION

Current researches have shown that nanoparticles and nanocomposite materials represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems: pollution monitoring, industrial-, groundwater and soil remediation [1-3].

The selective removal of <sup>137</sup>Cs ions from liquid radioactive wastes and their quantitative determination in the environment has a great importance in recent years. Hexacyanoferrates or ferrocyanides (FCNs) of transition metals (II) (Cu, Co, Fe, Ni, etc.) are very effective inorganic adsorbents for <sup>137</sup>Cs. These compounds have low solubility, high radiation and chemical stability in wide range of pH, high capacity and selectivity for Cs in the presence of alkaline and alkaline earth metal ions [4]. However, FCNs 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. To overcome these drawbacks the preparation of composite adsorbent has been carried out by precipitation or implantation of FCNs on different solid supports as silica gel [5,6], zeolites [7], zirconium hydroxide [8], polyacrylonitrile [9], and others.

Fibrous polymers with ion-exchange groups are very perspective host solid support for synthesis composite adsorbent with FCNs grains. Such composite adsorbents will combine unique properties of nanoscaled FCNs (high specific surface, high speed of chemical reactions, selectivity) and technological properties of a fibrous polymers (flexibility, chemical stability, high specific surface of the fiber structure, low hydraulic permeability, and ease of manipulation both in dynamic and in static sorption regimes).

The present investigation has been undertaken for two reasons: (i) to develop two-stage synthesis involving radiation- chemical modification of polypropylene fibers followed by in-situ formation of copper ferrocyanide nanoparticles and their stabilization on the fiber

surface within the grafted layer; (ii) to examine the obtained composite adsorbent for enhanced removal of Cs ions from the model solutions in batch process.

### 2. EXPERIMENTAL SECTION

#### 2.1 Preparation of PP-CuFCN composite adsorbent

Nonwoven material made of polypropylene (PP) fibers with an average thickness of 0.5 mm was used for synthesis of hybrid adsorbent. All chemicals were of analytical grade.

The composite adsorbent on the base of PP nonwoven material was synthesized through the two-stage experiment. At the first stage the chemically inert polypropylene base was activated through radiation-induced graft polymerization of acrylic acid (AA) for introduction of chemically active carboxyl groups to the PP backbone.

The second stage consisted of the following three steps: Ion-exchange: The PP fibers with grafted polyacrylic acid (PAA) chains (PP-g-PAA fibers) were immersed in 0.1 M CuSO<sub>4</sub> solution for 12 h; In-situ formation of CuFCN nanoparticles: PP-g-PAA fibers with loaded Cu<sup>2+</sup> ions were put into 2.5% solution of K<sub>4</sub>Fe(CN)<sub>6</sub> for 24 h; Rinsing and thermal treatment: The resulting composite material was washed with deionized water till no coloration and precipitates appeared in the rinsing solution and then dried at 100 °C for 12 h.

#### 2.2 Characterization

The morphology of the PP fibers before and after CuFCN deposition was recorded by a Hitachi S-4100 field emission scanning electron microscope (SEM) at acceleration voltage of 15 keV. The samples were sputter coated with a thin Pt layer prior to examination.

The FT-IR measurements were carried out using a Nicolet NEXUS FTIR spectrometer in the reflectance mode.

XRD patterns of the powdered samples were recorded on an Dron -3 diffractometer using Cu-K $\alpha$  radiation.

### 2.3 Adsorption experiments

Adsorption experiments were carried out in batch mode at room temperature under shake by placing of dry samples (0.1 g) in a series of polypropylene flasks with 20 mL of CsCl solution. Once the required time elapsed the residual solution was filtered through Whatman filter paper and analyzed for Cs concentration by an atomic absorption spectrophotometer model AA-8500 (Nippon Jarrell-Ash Co. Ltd., Kyoto, Japan).

The amount of Cs adsorbed by the synthesized composite adsorbent at time  $t$   $Q_t$  (mg/g) was calculated as follows

$$Q_t = \frac{(C_i - C_f) \cdot V}{W},$$

where  $C_i$  and  $C_f$  are the initial and final concentrations of Cs at time  $t$  (mg/l) in the experimental solution,  $V$  is the volume of the solution (l) and  $W$  is the weight of the adsorbent (g).

## 3. RESULTS AND DISCUSSION

### 3.1 Preparation of PP-CuFCN fabric

The fibrous PP-CuFCN composite adsorbent was synthesized through two-stage experiment: radiation-induced graft polymerization of acrylic acid followed by the in-situ formation and stabilization of CuFCN nanoparticles within the grafted layer.

The first stage, which resulted in synthesis of PP fabric with grafted PAA chains containing functional carboxylic groups, was examined previously [10]. Grafted samples (PP-g-PAA) with a medium value of AA grafting degree (50-60%, and carboxylic group density of 3.0-3.5 mmol/g) were chosen for the experimental work.

The first stage is very important one due to the several reasons. First, it activates the chemically inert polypropylene base by immobilization of PAA chains with charged functional groups to the fiber backbone. As a result of grafting process the PP fabric surface became covered with cation exchange groups. Second, the grafted chains loaded with  $\text{Cu}^{2+}$  ions serve as precursors of CuFCN nanoparticles. The formation and precipitation of CuFCNs occur inside of the grafted chains and thus CuFCN nanoparticles become bound to the fiber backbone by both physical and chemical forces. Third, the characteristics of grafted chains (density, length, chemical nature of the functional group and others) make it possible to control the properties of a composite adsorbent, namely the formation, distribution and size of the precipitated inorganic particles.

The intent of the second stage consisted in formation of the stable CuFCN nanoparticles on the PP fabric surface.

### 3.2 Characterization of CuFCN-PP fabric

Figure 1 shows SEM images of the grafted PP fibers and fibers with CuFCN nanoparticles. The PP-g-PAA fibers have a smooth surface. CuFCNs formed a homogeneous layer on the grafted fibers. This layer consists of the nanosized CuFCN aggregates (65-70 nm) which are rather regular in shape and closely fit one to another forming a compact texture.

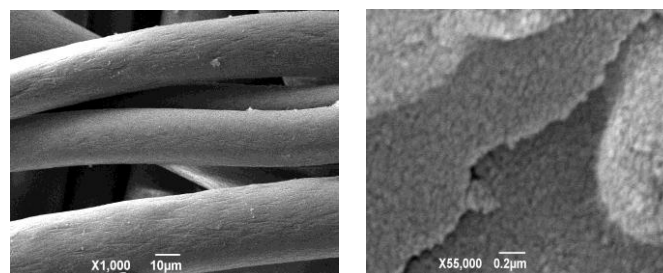


Fig. 1 – SEM images of the PP-g-PAA fibers (left); PP fibers coated with CuFCN, CuFCN aggregates (right) at high magnification.

Figure 2 shows the FTIR spectra of the PP-g-PAA (1) and PP-CuFCN fabric (2). The sharp and strong absorption peak at  $2095 \text{ cm}^{-1}$  corresponds to cyanide stretching region.

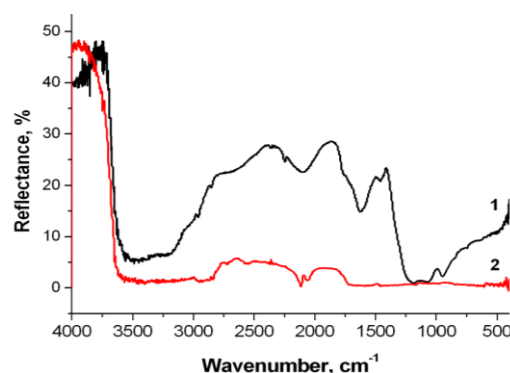


Fig. 2 – FTIR spectra of PP-g-PAA fabric (1) and PP - CuFCN fabric

Figure 3 shows the X-ray diffractograms of powdered PP (1) and PP-CuFCN (2) fibers. The sharp peaks appeared in spectra 2 reveal that synthesized CuFCN grains are highly crystalline.

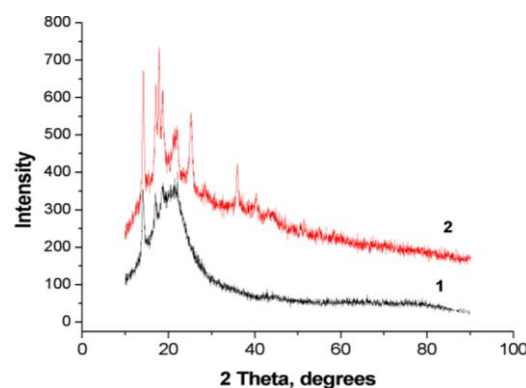
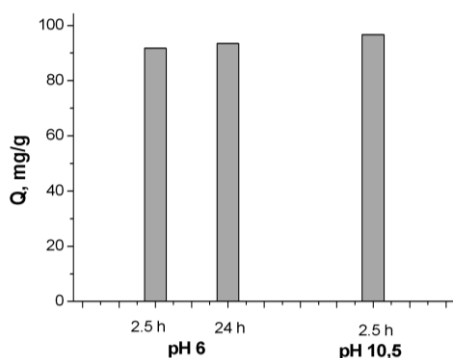


Fig. 3 – XRD pattern of PP (1) and PP-CuFCN fibers

### 3.3 Cesium adsorption studies

The cesium sorption from CsCl solutions with the same initial Cs concentration of 1170 mg/l but different pH (6 and 10.5) during the reaction time of 2.5 h was investigated. Also we compared the amount of Cs adsorbed during 2.5 and 24 h from the solutions with pH 6 (Fig.4). It follows from the obtained results that the cesium uptake does not strongly depend on pH; and over 90% Cs was adsorbed during the reaction time of 2.5 h.



**Fig. 4** – Amount of Cs adsorbed on PP-CuFCN fabric from the model solutions with pH 6 and 10.5. Adsorption time 2.5 and 24 h

Also we calculated the adsorption efficiency of Cs from alkaline solution (pH>10) at the presence of sodium ions (the solution with the initial Cs concentration of 36 mg/l contained 0.68 M NaNO<sub>3</sub>). In the above conditions, when the ratio Na/Cs = 2615 the synthesized PP-CuFCN fibers adsorbed about 93 % cesium. The obtained result testifies of high selectivity of the synthesized composite adsorbent to cesium ions.

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## 4. CONCLUSIONS

Composite adsorbents based on polypropylene fibers with chemically bound nanoparticles of copper ferrocyanide was synthesized by two-stage experiment: radiation-induced graft polymerisation of acrylic acid followed by the in-situ formation of CuFCN grains and stabilization of nanoparticles inside of the grafted layer.

SEM, FTIR, XRD analyses revealed that CuFCN form a homogeneous layer on the PP fibers. This layer consisted of the crystalline nanosized (65-70 nm) CuFCN aggregates which were rather regular in shape and closely fit one to another forming a compact texture.

The synthesized adsorbent demonstrated high adsorption capacity and selectivity in removal of Cs ions from alkaline solution with high concentration of Na competing cations.

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